



Adsorption capacity of poly[4-methacroyloxy-(4'-carboxy-3-chloro)-azobenzene], *in situ* immobilized on the silica gel surface to toxic metals ions

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ABSTRACT

By mean of heterophase polimerization on the silica gel surface has been made *in situ* immobilization of poly[4-methacroyloxy-(4'-carboxy-3-Chloro)-azobenzene] and has been received new organic-mineral composit material. The fact of polymer immobilization has been confirmed by IR spectroscopic method and thermogravimetric analysis combined with mass spectrometry. According to the results of thermogravimetric analysis, has been found the mass of the immobilized polymer is 13.33%.

The synthesized composite revealed sorption activity to the ions of Cu (II), Pb (II) and Fe (III) micro quantities in a neutral water environment. Maximum sorption ions Cu (II), Pb (II) and Fe (III) degree is reached during first contact hour in static sorption condition. According to the results of isotherms sorption treatment has been determined the silica gel surface poly [4-methacroyloxy- (4'-carboxy-3-chloro)-azobenzene] modification led to the sorbtion volum Cu (II) ions more than 1.5 times, for ions Pb (II) - 3.6 times, but for Fe (III) ions - almost 2 times.

KEYWORDS

adsorption; poly[(4-methacroyloxy-(4'-carboxy-3-chloro)-azobenzene)]; composite; *in situ* immobilization; heavy metals; silica

1. Introduction

Porous inorganic materials surface modification by nitrogen-containing polymers allows to get organo-mineral composite materials which can be used as sorbents for getting toxic metals ions from the waste water by means of their complex formation with immobilized polymer [1–4] nitrogen atoms. Azo-containing polymers belong to the nitrogen-containing ones which are capable to the complex formation [5].

One of the promising ways of the organic-mineral composites minerals with important sorption properties formation is polymerization or *in situ* immobilization, which is laid down in direct formation of the immobilized polymeric layer formation with the inorganic carrier [6].

Table 1. Comparative parameter characteristic of the original silica gel surface and synthesized composite

	Surface area, m ² /g			Average pore volume, cm ³ / g	Average pore size, nm
	P/P ₀	BET	Langmuir		
Silica gel	446.9	463.5	686.9	0.686	5.92
Synthesized composite	309.3	326.5	493.5	0.505	6.19

We have described silica gel sorption properties [7] with the [4 methacryloxy - (4'-carboxy) -azobenzene] immobilized molecules and it is determined that composite material shows sorption capability to the ions of Cu (II), Pb (II) and Fe (III) micro quantities in a neutral water medium. It is fixed the quantitative sorption Pb (II) and Fe (III) ions micro quantities. It is discovered the surface silica gel immobilization leads to its sorption volume increasing according to the Fe (III) ions – threefold and Cu (II) and Pb (II) twofold.

This work is devoted to the poly[4 methacryloxy - (4'-carboxy-3-chloro) -azobenzene] in situ immobilization on the silica gel surface and its sorption properties researching according to the Pb (II), Cd (II), Cu (II) and Fe (III) ions. The aim is arecerching of the chlor atom inputting into the azobenzene influence the complex formed nitrogen groups as to selected metals ions.

2. Experimental

As the inorganic matrix composite was used the Merck silica gel (fraction with pasts diametes of 0.1-0.2 mm), the characteristics of which are given in Table 1.

In situ polymerization 4-methacryloxy- (4'-carboxy-3-chloro) -azobenzene on the silica gel surface was made in accordanCe with the next method:

11.5 g 4- methacroyloxy (4'-carboxy-3-chloro)-azobenzene and 0.4025 g 2,2'-azobisisobutyronitrile, which was used as polymerization reaction initiator of, soluted in 60 ml of tetrahydrofuran, placed in the reactor and, while stirring added 16.2 g of silica gel. Thus, the initial mass ratio of monomer and silica gel was 1: 2. Gomopolymerization was made in inert atmosphere, which made by means of 10 minutes argon blowing. After argon overlapping, reaction mixture was heated to 65° C. Next, the synthesized composite was removed from the reactor, filtered from the solution, washed out of the excess monomer and the initiator by propanol-2 and dried up in the air.

The scheme of polymerization reaction during *in situ* immobilization of 4-methacryloxy- (4'-carboxy-3-chloro) -azobenzene on the surface silica gel is shown on the Figure 1.

IR spectra of original and modified silica gel were registered on the IR spectrometer "Spectrum BX" (Perkin Elmer, Germany) is about 500-4000 cm⁻¹ in tablets KBr.

The number of immobilized polymer on the modified silica gel surface was marked by the thermogravimetric analysis, the data of which were obtained on the 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 the device "STA 449 Jupiter F1" (Netzsch, Germany) with a mass spectrometer prefix "QMS 403C" (Germany).

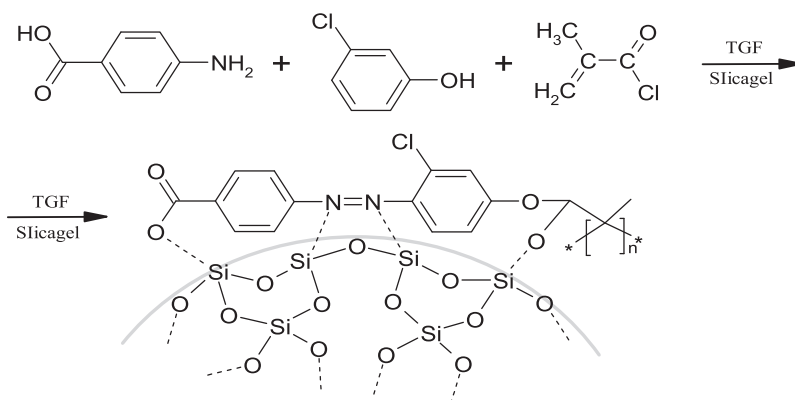


Figure 1. The scheme of *in situ* polymerization of 4-methacryloxy- (4'-carboxy-3-chloro) -azobenzene on the surface silica gel

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 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).

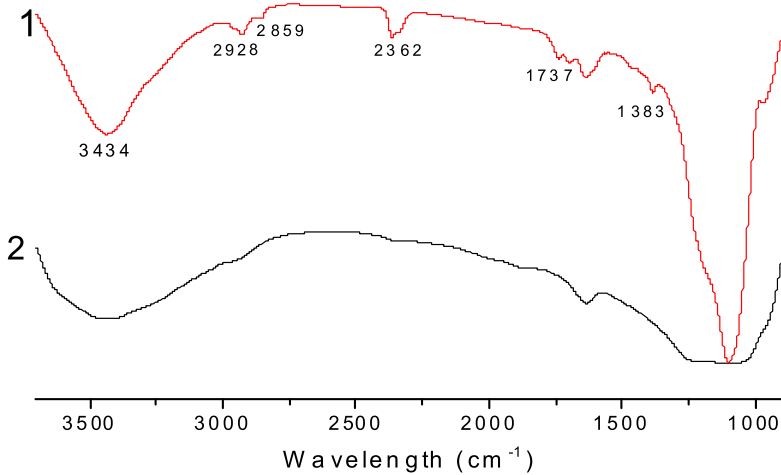


Figure 2. IR- spectra of the original (2) and modified (1) silica gel

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 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, plume - 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 $\mu\text{g}/\text{ml}$.

3. Results and Discussion

IR- spectrums of the original (1) and modified (2) silica gel are shown on the [Figure 2](#).

Syntesized composite silica gel and monomer IR spectra comparing analyse testifies there are absorption bands from 3500 to 1200 cm^{-1} , unlike the output of the matrix, which can be interpreted as follows:

- at 1383 cm^{-1} , there is ν (N=N) stretching vibrations, which are typical for nitrogen compounds;
- absorption bands at 2362 cm^{-1} , which can be refered to the ν (Si-H) stretching vibrations indicates the existence of wates linke between polymer and silica gel;
- absorption bands from 2859 to 2928 cm^{-1} can be refered the ν (C-H) to stretching vibrations of the polymer hybridized carbon link. Their presence at the

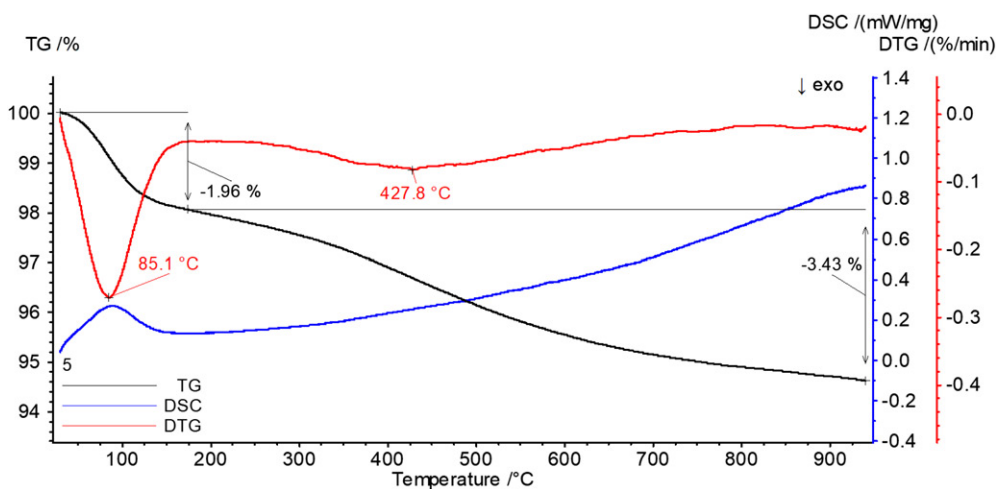


Figure 3. Thermogram of original silica gel

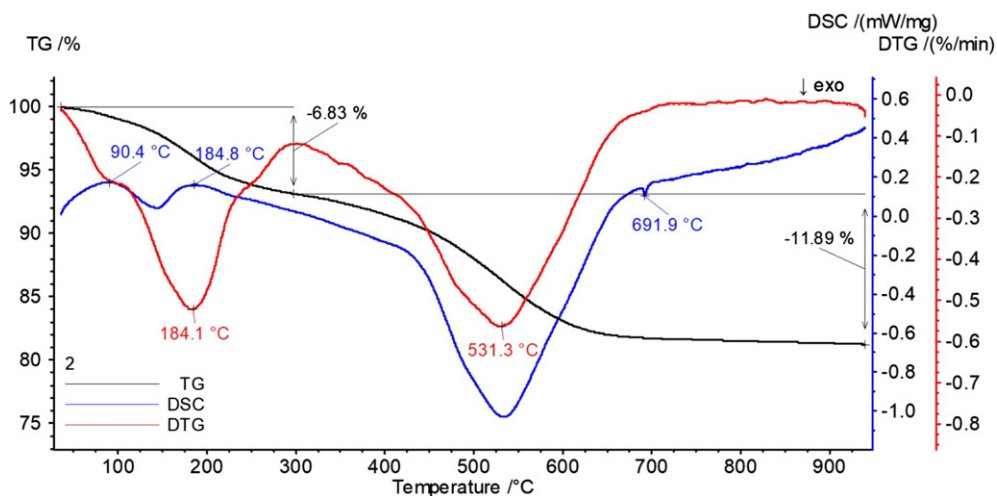


Figure 4. Thermogram of modified silica gel

composite spectra assures the fact of the polymerization reaction passing on the inorganic surface of the matrix.

- absorption bands at 3434 cm^{-1} suits to the ν (O-H) stretching vibrations of the carboxyl group [8, 9].

This, IR spectroscopy results confirm the fact of the polymer presence on the silica gel surface. Besides, the change of silica affirms polymer immobilization.

To determine the immobilized silica gel mass it was done the synthesized composite and original silica gel termogravimetric analyse (Figures 3 and 4). From Figure 4 we can see composite destruction take place from 90 to 650° C. This leads to 18.72% weight lost. This loss is caused by polymer destruction and water rest loss in silica gel

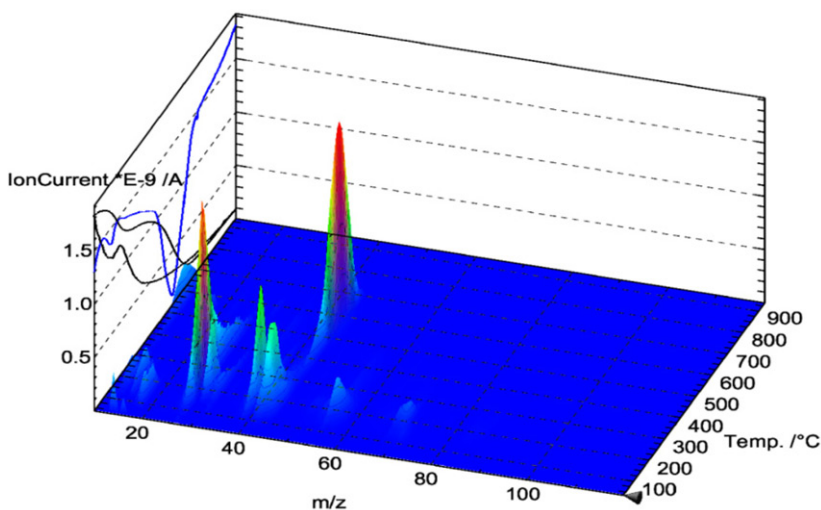


Figure 5. TG-MS-3D synthesized composite under another angle

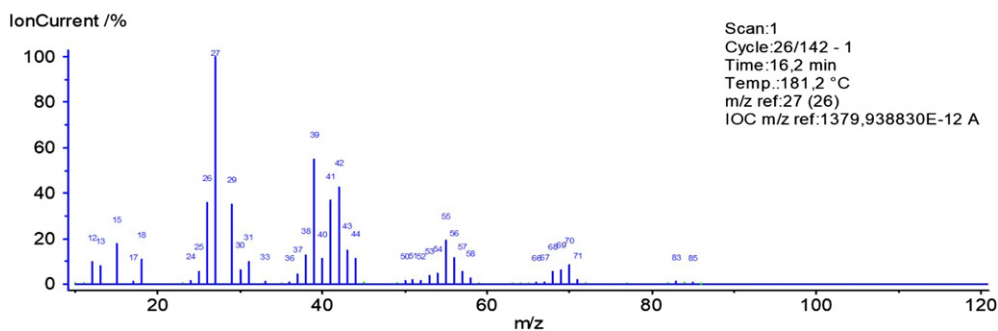


Figure 6. Synthesized composite mass-spectra in 2D format at T 181.2° C.

composition, the mass of which according to Figure 3, is 5.39%. Thus, the immobilized polymer mass is 13.33%.

To detailize the composite thermal destruction process was taken its termogram, combined with mass-spectra at 3D-format (Fig. 5) and a series of mass-spectra at 2D-format and temperatures of 92° C, 181.2° C (Fig. 6), 529.8 and 690.3° C.

Thermogravimetric data interpretation affirms the main mass composite loss between 90 and 300° C is caused by rest water taking-of silica gel composition, it is confirmed by high intensity peak at 18 in mass spectra at 92, 4° C and 181.2° C, and immobilized polymer destruction, the passing, of which is confirmed by mass-spectra peaks at 181.2° C (see Figure 6):

- 15 mass peak is explained by the methyl radical formation;
- 26-27 mass peaks are linked with the CN-groups formation;

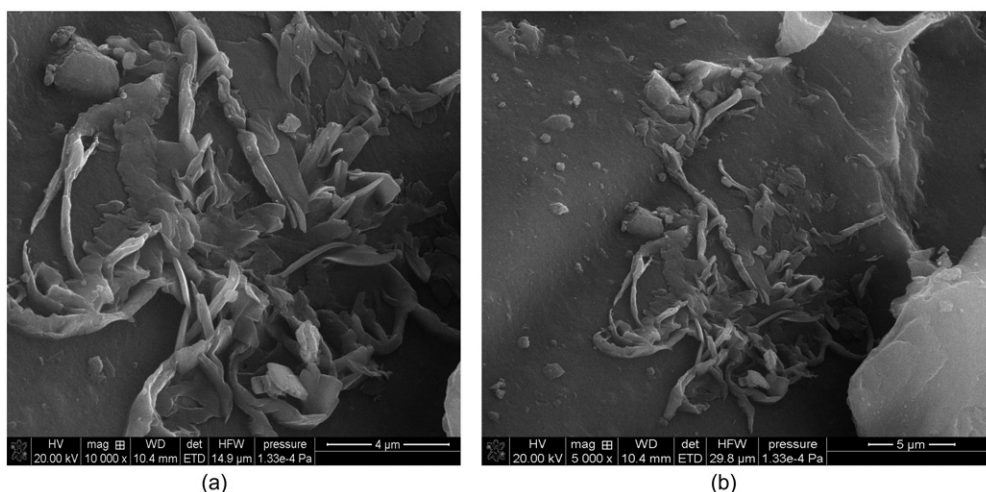


Figure 7. The SEM photo surface of the polymer modified silica gel at 10,000 (a) and 5,000 (b) increasing.

- 36-39 and 71 mass peaks can be referred to the chlor atoms and molecules formation;
- 39-43, 50-58 and 66-71 mass peaks can be referred to the carbon chain polymer.

Thus, immobilized polymer destruction begins from azobenzene thermodestruction. At higher temperatures (from 500 to 700° C), immobilized polymer thermodestruction is taken place with its pieces burning to carbonic dioxide (and possibly N_2O), water, with soot formation, it is explained by composite mass-spectra only peaks at 44, 18 and 12 at temperature of 529.8° C.

For silica gel surface parameters researching after poly [4-methacryloxy- (4'-carboxy-2'-nitro) -azobenzene] was applied low the temperature nitrogen adsorption-desorption (BET) method. Taken nitrogen adsorption-desorption isotherms for original silica gel and the synthesized composite are similar and belong to the IV type isotherms according IUPAC classification [10]. Thus, silica gel surface structure in the result of selected polymer immobilizations practically does not change.

Calculated by means of isotherms computer treatment nitrogen adsorption-desorption parameters of the synthesized composite surface, are shown at the [Table 1](#). Taken data affirms the fact of small silica gel surface porosity decreasing: the surface area is decreased from 447 to 309 m^2/g , middle pores volume is decreased from 0.67 to 0.5 cm^3/g , and middle pores diameter increases from 5.92 up to 6.19 nm.

Morphology of silica gel surface changes in the result poly [4-methacryloxy- (4'-carboxy-3-chloro) -azobenzene] modification were researched by means of scanner electron microscopy. The SEM photo surface of the polymer modified silica gel at 10,000 (a) and 5,000 (b) increasing are given on the [Figure 7](#).

As we see on the photos, polymers on the inorganic matrix surface is located mainly in the manner of microcircuit loops, that, immobilized polymer on the solid surface is in the open condition and its azo groups are sterically maximum approachable for participation in the complex formation.

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 poly [4-methacryloxy- (4'-carboxy-3-chloro) - azobenzene], from the pH and the chemical composition of the medium of the initial solutions. Conditions of the experiment: mosb = 0.1 g, Vrots. = 25 ml, m0M = 100 µg, contact time 24 hours

pH	Degree of sorption, %			
	Cu ²⁺	Cd ²⁺	Pb ²⁺	Fe ³⁺
2.8	0.00	8.14	31.05	73.31
4.0	0.00	0.00	10.36	16.57
5.5 (диСТ Н ₂ О)	69.33	35.20	81.03	73.88

Synthesized composite has to exhibit sorption capability to the transitional metals ions by means of atoms complex formation activity of the nitrogen azo groups and immobilized polymer. To confirm this opinions, we reserched Cu (II) and Fe (III) ions sorption, which have high relationship to the nitrogen-containing ligands [11]. Also, researched Cd (II) and Pb (II) toxic ions sorption, which make complexes with oxygen atoms [11].

Synthesized composite sorption capability researches as to the recalculated meals ions included:

- optimal pH range sorption medium definition;
- sorption isotherms building of every reserched metal ions on the synthesized composite surface;
- necessary contact fase time determination for balance reaching in static condition;
- sorption volume determination as to the researched metal ions and comparing with such for the original silica gel and modified by poly [4-methacryloxy- (4'-carboxy) azobenzene] silica gel.

Puring previous experimental researches was revealed in the alkaline medium, this immobilized polymer particle is washed from the silica gel surface, this for synthesized composite sorption properties researching were realized only in acid and neutral medium. In the researching metals output solutions were formed aqua acetate coordination spheres. In the sorption process such complexes interacted with immobilized polymer molecules with multi-ligand complex formation on the solid surfaces, due to it the sorption is taken place.

The silica gel sorption activity researching results, *in situ* modified poly [4-methacryloxy- (4'-carboxy-3-chloro) -azobenzene] as to the Cu (II), Cd (II), Pb (II) and Fe (III) ions at different acid data and chemical medium composition are given in Table 2.

Table 2 analysis allows to affirm synthesized composite reveals the best sorption properties to the selected ions microquantities in water medium (without the addition of any buffer solutions). Unfortunately, as it follows from this table, quantitative sorption is not observed for any of the investigated ions.

The stability constants of multi-alloy complexes, which are formed on the solid surface, depending on the chemical composition of the initial coordination spheres, can be deffored and it effects on its sorption degree at different pH meanings. For example, as we see from the Table 2, Fe (III) (at pH 2.8) acetate complexes are sorbed by the

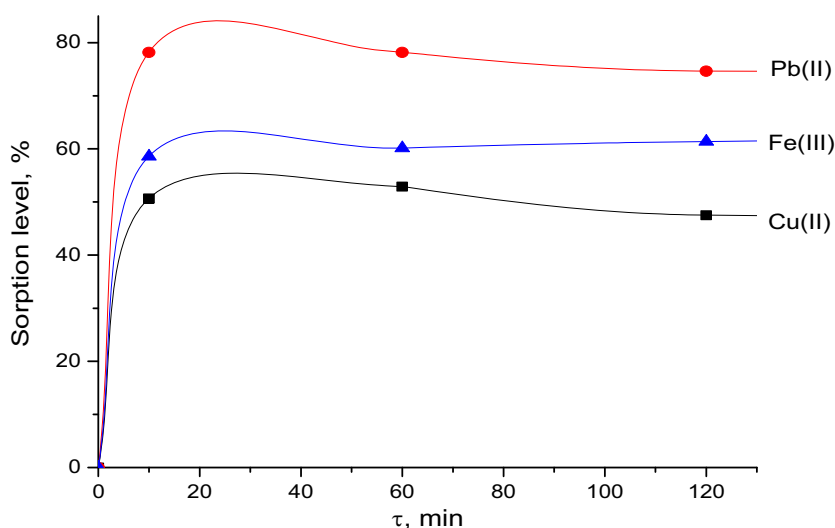


Figure 8. Dependences of the Cu (II), Pb (II) and Fe (III) ions sorption degree from the contact time with synthesized composite in the static state

synthesized composite surface on the same level with aqua complexes (on the 73%), while phthalate complexes (pH 4) are removed at another the similar experimental conditions – only on the 16.6%.

Taking into consideration all above - mentioned, further modified silica gel sorption properties researching was carried with nitrates Cu (II), Cd (II), Pb (II) and Fe (III) output solutions in the neutral medium without buffers adding. Dependences of the Cu (II), Pb (II) and Fe (III) ions sorption degree on the silica gel surface, *in situ* modified poly [4-methacryloxy- (4'-carboxy-3-chloro) -azobenzene] are shown on the [Figure 8](#).

As can be seen from [Figure 8](#), all researched ions are maximum sorbed during the first contact hour with the composite surface and during the further contact, their sorption degree is decreased. The reason can be in low stability of the Cu (II), Pb (II) and Fe (III) various copper complexes with the immobilized polymer ions participation.

To determine modified silica gel sorption volume meaning according to the elected transition metal was build their sorption isotherms. Cu (II) and Fe (III) sorption ions isotherms on the silica gel surface, *in situ* modified poly [4-methacryloxy- (4'-carboxy-3-chloro) -azobenzene] are shown on [Figures 9](#) and [10](#).

All taken isotherms belong to the 2L-species. This isotherm type are typical for silica matrices, modified by complexing substances [12]. All take isotherms allows calculate the synthesized composite sorption volume. The comparison sorption volume meaning comparing according to the Cu (II), Pb (II) and Fe (III) ions which were found in the process of sorption isotherms data working up and output silica gel are given in [Table 3](#).

As it affirms from the [Table 3](#), silica gel surface poly [4-methacryloxy- (4'-carboxy-3-chloro) -azobenzene] modification reduce to increasing sorption volumes of Cu (II)

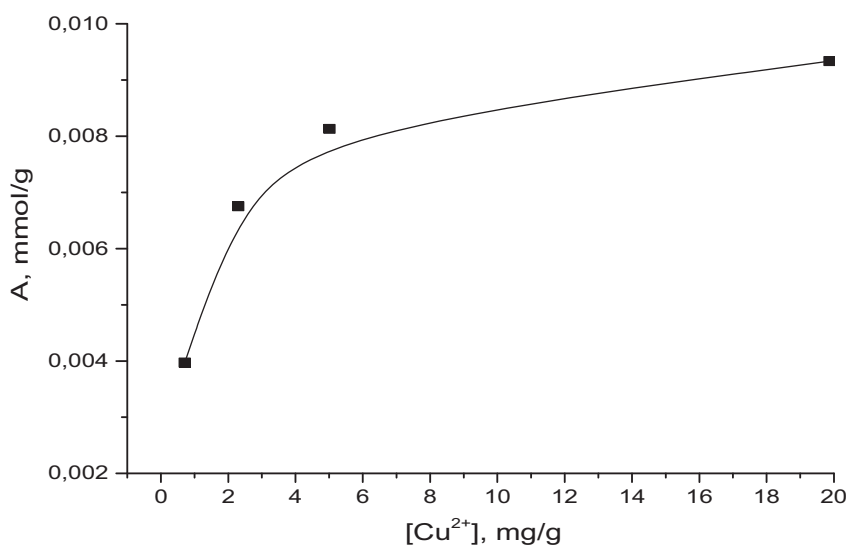


Figure 9. Cu(II) sorption isotherm on the *in situ* modified silica gel

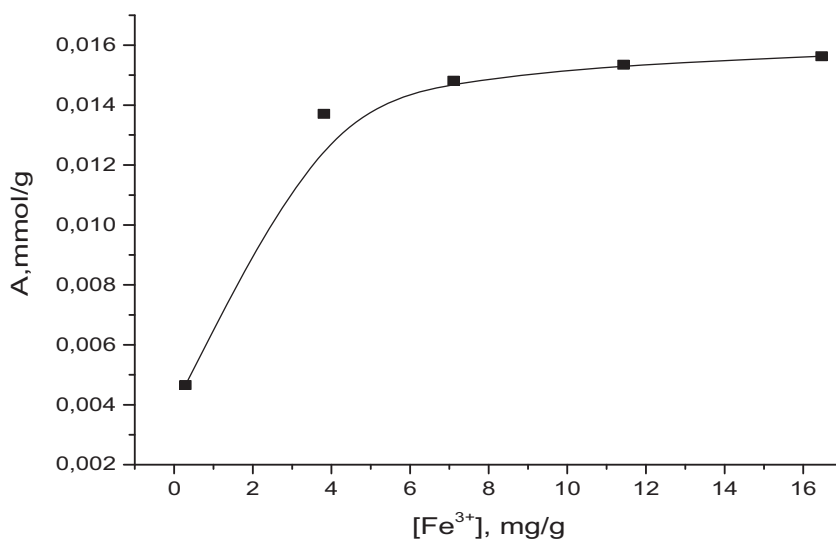


Figure 10. Fe(III) sorption isotherm on the *in situ* modified silica gel

Table 3. Comparison of the sorption capacitance for the Cu (II), Pb (II) and Fe (III) ions of the synthesized composite, the initial silica gel and silica gel, modified poly [4-methacryloxy- (4'-carboxy) azobenzene]

Ion	Sorption capacity, mmol / g		
	Output silica gel	silica gel, modified poly [4-methacryloxy- (4'-carboxy) -azobenzene]	silica gel, modified poly [4-methacryloxy- (4'-carboxy-3-chloro) -azobenzene]
Fe(III)	0.008 [7]	0.016 [7]	0.016
Pb(II)	0.002 [7]	0.0048 [7]	0.0072
Cu(II)	0.006 [7]	0.012 [7]	0.009

ions more than 1.5 times, Pb (II) - 3.6 times, Fe (III) - almost 2 times. Comparing with silica gel sorption capacity of, modified poly [4-methacryloxy- (4'-carboxy) -azobenzene], Fe (III) ions sorption capacity is remaine on the same level acording Pb (II) ions - increases 1.5, Cu (II) ions - decreases in 1,3 times.

Thus, chlor atom introduction into azobenzene makes better immobilized polymer characteristics of the Pb (II), and makes worse to Cu (II) ions.

4. Conclusions

By means of 4-methacryloxy- (4'-carboxy-3-chloro) -azobenzene polymerization on the silica gel surface with 2,2'-azobisisobutyronitrile presence as polymerization initiator, was accomplished *in situ* immobilization poly [4-methacryloxy- (4'-carboxy-3-chloro) azobenzene] and new organo-mineral composite material was obtained.

Polymer immobilization fact is confirmed by IR spectroscopy and thermogravimetric analyse method. By the thermogravimetric analysis results was found the mass of immobilized polymer was 13.33%.

Analysis of the CEM photo of the synthesized composite showed that the immobilized polymer on the surface of the silica gel is placed in the form of polymeric macros.

It was fixed the synthesized composite reveals sorption activity relative to the Cu (II), Pb (II) and Fe (III) ions micro quantities in a neutral water medium (without any buffer solutions adding).

Maximum Cu (II), Pb (II) and Fe (III) ions sorption degree is reaced during first contact hour in a static sorption state. According to the data isotherms sorption results it is defined the silicagel poly [4-methacryloxy- (4'-carboxy-3-chloro) -azobenzene] surface modification reduced to increasing sorption capacity of Cu (II) ions more than 1.5 times, for ions Pb (II) - 3.6 times, but for Fe (III) ions - almost 2 times. That is, chlor atom introduction into azobenzene makes immobilized polymer characteristics of the Pb (II) ions and makes worse Cu (II) ions.

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