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Synthesis and Adsorption Properties of 4 –Vinylpyridine, Styrene and Maleic Anhydride Copolymer *in Situ* Immobilized on Silica Surface

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ABSTRACT
A new mineral-organic composite by in situ immobilization of poly(4-vinylpyridine-co-styrene-co-maleic anhydride) on the silica gel surface was synthesized. According to TG-analysis, the composite contained 31.84 wt.% of immobilized copolymer. The highest sorption activity of a new composite was established towards microquantities of Cu (II) ions in neutral medium as well as towards Pb(II) and Fe(III) ions in a slightly acidic medium with the background of phthalate buffer and no sorption activity towards Cd(II) ions. The composite obtained exhibits a sorption capacity higher in 1.88, 5.00 and 3.35 times for Fe(III), Cu(II) and Pb(II) ions respectively in comparison with parent silica gel.

KEYWORDS
Adsorption; poly(4-vinylpyridine-co-styren-co-maleic anhydride); in situ immobilization; silica gel surface; heavy metals

Introduction

Pyridine and its derivatives are well-known ligands that form strong complexes with the ions of the most transition metals [1, 2]. Processes of complex formation are inherent to pyridine-containing polymers, too [3, 4]. Therefore, the modification of the surface of porous inorganic materials with pyridine-containing polymers is a perspective approach for preparation of composite complex-forming sorbents towards metal cations due to their interaction with Nitrogen moiety of pyridine fragment of immobilized polymer.

One of the promising ways of organo-mineral composite materials preparation with interesting and valuable sorption properties is the *in situ* polymer immobilization on the surface of a porous inorganic carrier - a formation of an immobilized polymer layer in the presence of inorganic carrier particles [5–7] during polymer syntheses.

This method of attaching polymers onto an inorganic surface has several advantages over simple mixing of pre-synthesized polymer with inorganic carrier or chemical bonding of polymer with inorganic surface.

In the case of *in situ* copolymerization, it is possible to create a polymeric layer on the surface of an inorganic carrier with the most optimal ratio of copolymer components.

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Table 1. Comparative characteristic of surface parameters of parent silica gel and poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride)/silica gel composite.

	Surface area, m^2/g				
	P/P_0	BET	Langmuir	Average pore volume, cm^3/g	Average pore diameter, nm
Silica gel	446.97	463.53 ± 0.89	686.91 ± 23.68	0.686 ± 0.003	5.92 ± 0.01
Composite	70.33	73.94 ± 0.14	110.76 ± 3.82	0.138 ± 0.003	7.47 ± 0.01

In [8], we describe the results of *in situ* immobilization of 4-vinylpyridine and styrene copolymer on silica gel surface. The synthesized composite material showed high sorption ability towards microquantitatives of Pb (II), Cd (II), Zn (II), Cu (II) and Fe (III) ions.

The presented paper deals with *in situ* immobilization on silica gel surface organic layer of poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride) as well as its adsorption characteristics with respect to Cu(II), Cd(II), Pb(II), Mn(II), Fe(III), and Ni(II) ions.

Experimental

Silica gel (fraction of 0.1–0.2-mm diameter particles, specific surface 428.61 m^2/g, Merck) was used as inorganic carrier of composite. Properties of the silica gel are given in Table 1.

Styrene (Merck) and 4-vinylpyridine (reagent grade, Ukraine) were distilled under vacuum and stored under argon at 3–5 °C. The reagent grade 2,2′-azobis(2- methylpropionitrile) (AIBN, Ukraine) served as an initiator of their radical polymerization. Maleic anhydride (Sigma-Aldrich Inc.) and other chemicals of p.a. quality (Sigma-Aldrich Inc.) were used as received.

Composite silica gel/poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride) was obtained by radical copolymerization of 4-vinylpyridine, styrene and maleic anhydride in the presence of silica gel.

Synthesis of composite was performed as follows: 0.36 g (3.46 mmol) of styrene, 0.65 g of maleic anhydride (3.46 mmol) and 2.68 g (25.5 mmol) of 4-vinylpyridine with 0.04 g of 2,2-azobis(2-methylpropionitrile) (AIBN) were dissolved in10 ml of CCl_4 and added into the reactor with 5 g of silica gel while stirring. An inert atmosphere was created by argon blowing during 20 min. After the interruption of argon blowing, the reaction mixture was heated to 75 °C. This temperature was maintained during 3 h. Then the reaction mixture was cooled, and the obtained suspension was filtered off. After filtration the suspension was washed with CCl_4, then washed with propanol-2 thrice to remove residual monomers and dried at room temperature during 24 h.

The scheme of *in situ* immobilization of 4-vinylpyridine-styrene-maleic anhydride copolymer on silica gel surface is presented in Fig. 1.

FT-IR spectra of the parent silica gel as well as silica gel with immobilized copolymer were recorded using an IR spectrometer with Fourier transformation (Perkin Elmer, Germany). The samples were pressed with KBr. The FT-IR spectra were recorded in a spectral range 500– 4000cm^{-1}.

The amount of immobilized copolymer on the silica gel surface was evaluated by thermo-gravimetric analysis. The data were obtained with TG/DTA analyzer "Shimadzu DTG-60 H" (Shimadzu, Japan) in the range 15-1000 °C with heating rate 10 °C min^{-1}.

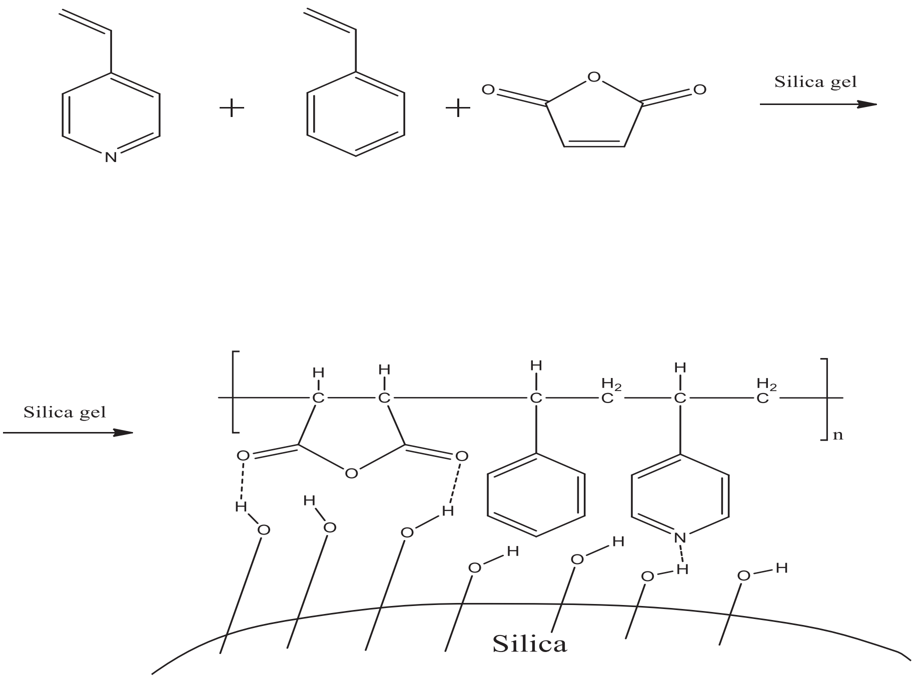


Figure 1. The scheme representation of *in situ* immobilization of copolymer poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride) on silica gel surface.

Thermal analysis was carried out on STA 449 Jupiter F1, Netzsch (Germany) under the following operational conditions: heating rate 10 °C min^{-1}, dynamic atmosphere of synthetic air (50 mL min^{-1}), temperature range 30–950 °C, samples masses 25-29 mg, sensor thermocouple type S TG-DSC. As a reference, empty Al_2O_3 crucible was used. The gaseous products emitted during decomposition of material were analyzed by QMS 403C Aeölos (Germany) coupling on-line to STA instrument. The QMS data were gathered in the range from 10 to 160 amu.

The *surface area* of the composite as well as pore diameter and their distribution was calculated using data of low-temperature adsorption-desorption of nitrogen obtained with ASAP 2420 V1.01 (Micromeritics, USA) sorptometer. Samples were degassed at 60°C during 24 hours before measuraments.

The surface morphology of composite as well as parent silica gel was observed by scanning electron microscope SEM, LEO 1430VP (Carl Zeiss, Germany).

The adsorption properties of the obtained composite with respect to Cu(II), Cd(II), Pb(II) and Fe(III) ions were measured in a static mode. For that, 0.1 g of each sample of the composite were put into an interaction with 25-100 mL of nitrate working solutions of corresponding metals. The interaction took place for 10, 30, 60, 90 minutes and 24 hours with mechanical shaking. The equilibrium concentration of metal ions was determined by atomic absorption method.

Nitrate working solutions of Cu(II), Cd(II), Pb(II) and Fe(III) were prepared using sets "standard sample solutions set" of these salts against the background of 1 M HNO_3 (manufactured by *A.V. Bogatsky* FHI Co, in Odesa) with 1 and 10 mg/ml concentrations.

Solution with pH 4 was prepared from the standard phthalate buffer ("standard sample solutions set" DSTU 8.135:2009, «RIAP», Kyiv, Ukraine). Solution with pH 1.2 ± 0.02 was prepared by addition of 0.1 M HCl, solution with pH 2.8 ± 0.02 was prepared by addition of 0.1 M of acetic acid. The exact pH values for all prepared solutions were controlled by pH-meter "HANNA TESTER WP" (Hanna instrument, China).

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

$$A = (c_o – [\mathrm{M}])\ V/m$$

where c_o – an initial molar concentration of metal, [M] – equilibrium molar concentration of metal, 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), $m_{\boldsymbol{ads}}$ – is mass of the metal adsorbed, $[m]$ – is mass of the metal at equilibrium after the adsorption, which was found $[m]$=C·V, where C – is concentration of the metal at equilibrium (mrg/ml) and V – is the volume of the solution at equilibrium (ml).

The equilibrium concentrations of the metals were determined by atomic absorption spectroscopy using a flame atomic absorption spectrophotometer "Saturn"(Ukraine) in "air-propane-butane flame mixture.

The characteristics wavelengths for measurements were used: 324.7 nm for Cu, 228.8 nm for Cd, 283.3 nm for Pb and 248.3 nm for Fe with 0.58 cm slit width. The calculations of the equilibrium concentrations in the solution were made by comparing the intensities of their lines in the spectrum with the intensity of the lines of standard solutions. For this purpose, standard solutions were prepared with concentration of metal 0.1-1.5 μg/ml, experimental error for Pb 0.01 μg/ml, for Cu and Cd 0.005 μg/ml.

Results and Discussion

The immobilization of copolymer poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride) on the silica gel surface could be recognized visually due dark yellow color of the obtained composite. The more detailed evidences were obtained by FT-IR spectroscopy. The corresponding spectra of the parent silica gel (1) and synthesized composite (2) are presented in Fig. 2.

Comparative analysis of FTIR spectra of the synthesized composite and original silica gel (Fig. 2) shows that absorption bands are present at 1605 cm^{-1} in the spectrum of the immobilized copolymer unlike the original carrier, which can be identified as ν (C-C) vibrations of the aromatic core in styrene and 4-vinylpyridine and ν (C-N) vibrations in 4-vinylpyridine. Signals what could be attributed to the aromatic systems are also present in the spectrum at 3070 cm^{-1} ν(CH) [9, 10].

Absorption bands in the region 1380-1480 cm^{-1} could be attributed to the stretching vibration of $\delta(CH_2)$ of the polymer chain. The main chain of copolymer also gives rise to ν(CH) vibrations at 2930 cm^{-1}.

Absorption band at 2340cm^{-1} was attributed to ν (Si-H) vibration and is an evidence of hydrogen bonding of copolymer with the silica gel surface.

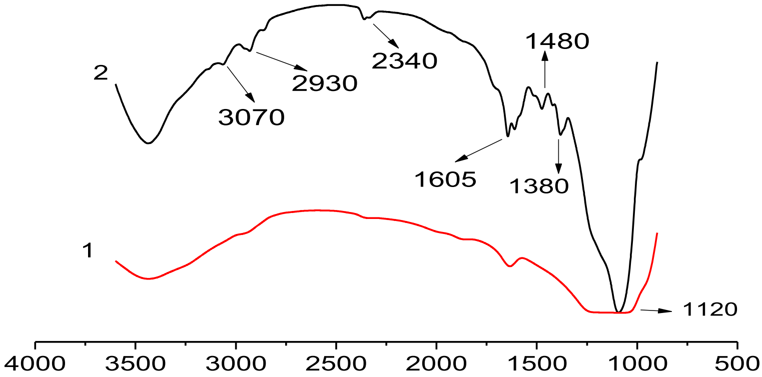


Figure 2. FTIR-spectra of the original silica gel (1) and composite poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride)/silica gel (2).

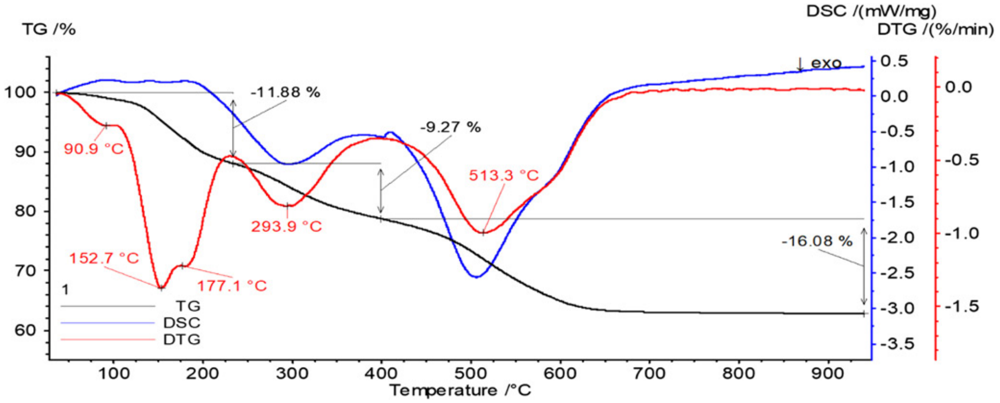


Figure 3. TG, DTG, DSC curves of composite poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride)/silica gel.

In the composite spectrum there is an absorption band at 1120 cm^{-1} due to ν (C-O-C) vibration of maleic anhydride fragment. Thus, FTIR spectroscopy data confirme an existance of poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride) on the silica gel surface.

A comparative analysis of TG and DSC-MS data for the parent silica gel and composite obtained was employed in order to estimate the mass ratio of copolymer in the composite. The obtained thermograms are shown in Figures 3 and 4. From Figure 3 it can be seen that the most active thermodestruction of the composite occurs in the temperature range 90-650 °C. The weight loss is about 37.23 wt.%. This loss is mainly due to the loss of residual water of the silica gel (about 5.39 wt.%, see Fig.4) and thermal degradation of polymer. Consequently, the mass of the immobilized polymer could be estimated as 31.84 ± 0.1 wt.%.

In order to detail the process of thermal destruction of the composite, its thermogram and 3D mass spectrum (Fig. 5) as well as series of 2D mass spectra at 92.4, 154.2, 174.9 (Fig. 6), 292 and 511.2° C were examined.

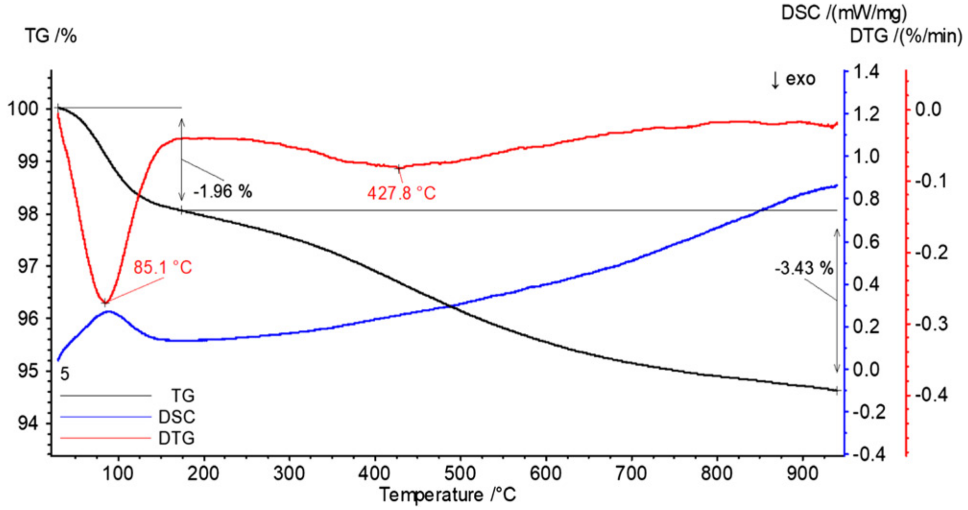


Figure 4. TG, DTG, DSC curves of parent silica gel.

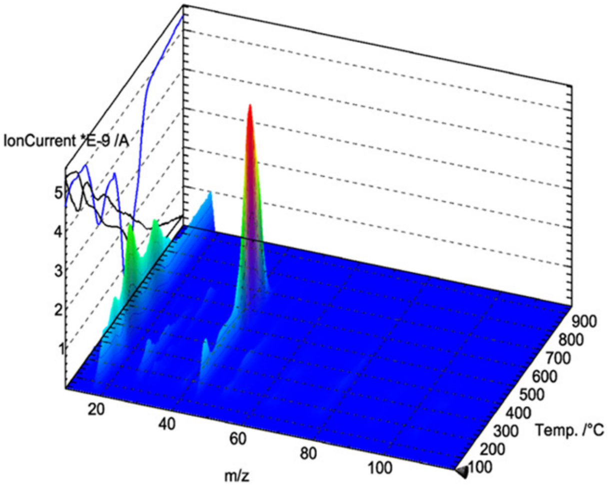


Figure 5. TG-MS-3D data for poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride)/silica gel composite.

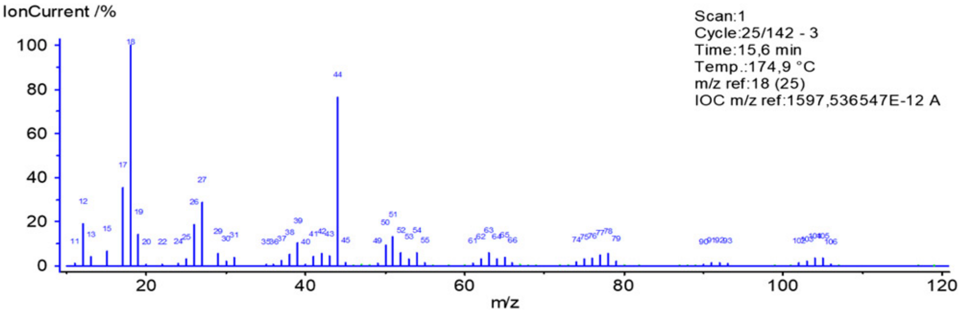


Figure 6. MS-2D of synthesized composite, T = 174,9 °C.

The first decomposition stage of the obtained composite was detected at 90–120 °C with weight loss ~1 wt.%. It is obvious that this loss is due to the evaporation of residual water in the silica gel, which is confirmed by the presence of intencive peak at 18 Da in the mass spectrum at 92.4 °C. The next significant mass loss occurring in the temperature range 154.2° C -174.9° C due to thermal degradation of the polymer. These considerations are confirmed with high intensity peaks in the mass spectra at 18 Da (H_2O) and 44 Da (CO_2) in the same temperature region (Fig. 6).

Low intensity signal at 26 Da can indicate the formation of CN radical, other peaks in the regions 49-55 Da, 61-66 Da and 74-79 Da could be attributed to the fragments of decomposed polymer chain.

In the temperature range 200-500 °C decomposition of the immobilized copolymer gives predominantly CO_2, N_2O (signal at 44 Da) and H_2O (18 Da).

The final polymer destruction was observed at the temperature above 500 °C. MS analysis confirmed the formation of organic carbon (12 Da), H_2O (18 Da) and N_2O (44 Da) at this stage.

To study the surface parameters of silica gel after immobilization of poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride) on the surface, a low-temperature nitrogen adsorption-desorption method was employed. Nitrogen adsorption-desorption isotherms obtained for silica gel and for the composite are similar and belong to type IV isotherms according to IUPAC classification [11]. The received data indicate that immobilized copolymer has virtually no effect on the structure of the silica gel surface. Calculated by computer processing of nitrogen adsorption-desorption isotherms data are shown in Table 1 for the composite and the parent silica gel.

It is evident that after immobilization of a large amount of copolymes (31.84 wt.%), the porosity of the silica gel surface is significantly reduced; the surface area decreases from 447 to 70.33 m^2/g, the average pore volume decreases from 0.686 to 0.138 cm^3/g, and the average pore diameter slightly increases from 5.92 to 7.47.

To clarify the geometry and location of poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride) on the silica gel surface SEM-microphotographs of synthesized composite at 500 × (A), 10 000 × (B) magnification (Fig. 7) were obtained. As one can see, the immobilized polymer located on the surface of silica gel irregularly.

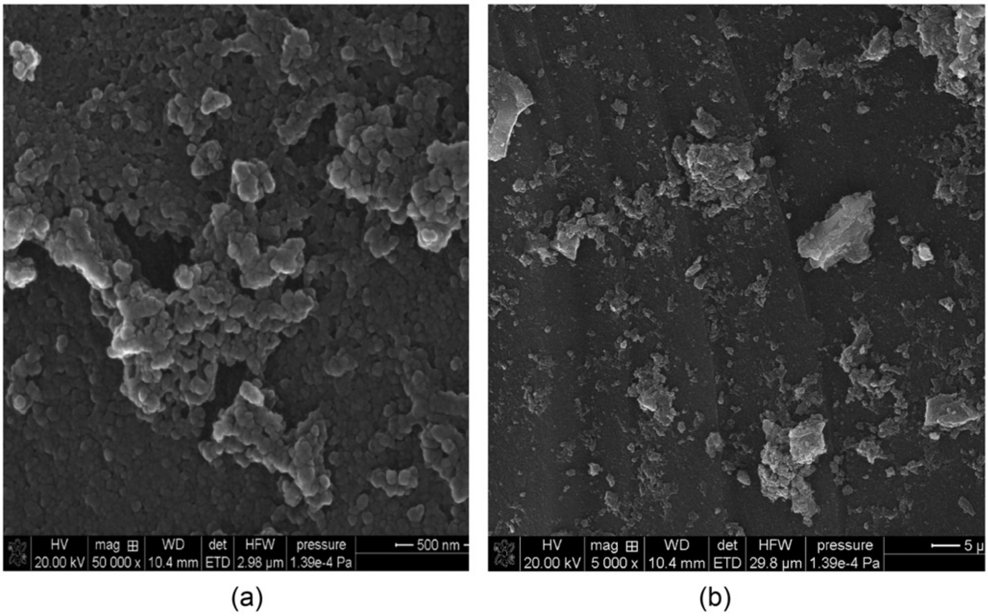
As one can see, the polymer on the inorganic carrier surface is located in the form of macrochain loops, coils and aggregates of coils.

In accordance with literature data, composite should exhibit an adsorption behaviour towards transition metals due to pyridine as well as maleic anhydride complexing properties of the immobilized copolymer units.

To confirm these considerations, sorption properties towards ions mentioned above with high affinity to such Nitrogen-containing ligands as Cu (II) and Fe (III) were investigated [12]. Also, good complexing of such metals as Cd (II) and Pb (II) with Oxygen should be taken into account [12].

Investigations of composite sorption properties included:

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



(a) (b)

Figure 7. SEM-microphotographs of synthesized composite at ×500 000 (a) and ×5 000 (b) magnification.

- plotting of sorption isotherms for each of the investigated metal ions on the composite surface;
- sorption capacity estimation for metal ions and comparison with the data obtained with the parent silica gel.

It should be noted that in a weakly-alkaline medium ($NaHCO_3$ solution, pH 8.1), partial flushing of the immobilized copolymer from silica gel surface was observed (the solution became yellow). Therefore, sorption properties of the synthesized composite were investigated in an acidic and neutral medium.

As we believe, aqua, chloride, acetate or phthalate coordination spheres of the investigated metals were formed in the initial solutions. Sorption occurs due to the complexes interaction with the macromolecules of immobilized copolymer leading to the formation on solid surface multi-ligand complexes.

The results of sorption activity studies of silica gel with immobilized poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride) towards Cu (II), Cd (II), Pb (II) and Fe (III) ions at different pH values and various chemical composition the medium are shown in Table 2.

The highest sorption activity was detected towards microquantities Cu (II) ions in a neutral medium and towards Pb (II) and Fe (III) ions in a slightly acidic medium (on the background of phthalate buffer). A sorption activity towards Cd (II) ions was not detected. It can be assumed that Cd complexes with a copolymer are less stable than Pb complexes. Assumption that the sorption of metal ions occurs due to their complexation with the polymer, may be the reason of low sorption ability of the composite toward Cd(II) ions.

Table 2. Dependence of Cu(II), Cd(II), Pb(II) and Fe(III) cations adsorption degree on the composite surface from pH and composition of initial solutions *(Experimental conditions: 0.1 g sorbent mass, volume of solutions -25 mL,* m^0_{Me} *-100 µg, interection time 24 h).*

	Degree of sorption, % ± 2 %			
pH	Cu^{2+}	Cd^{2+}	Pb^{2+}	Fe^{3+}
1.2 ± 0.02	1.12	13.12	4.40	6.74
2.8 ± 0.02	40.85	17.20	26.05	69.66
4.0 ± 0.02	69.46	14.58	98.97	96.35
5.5 (Distilled water)	82.89	15.45	66.15	79.49

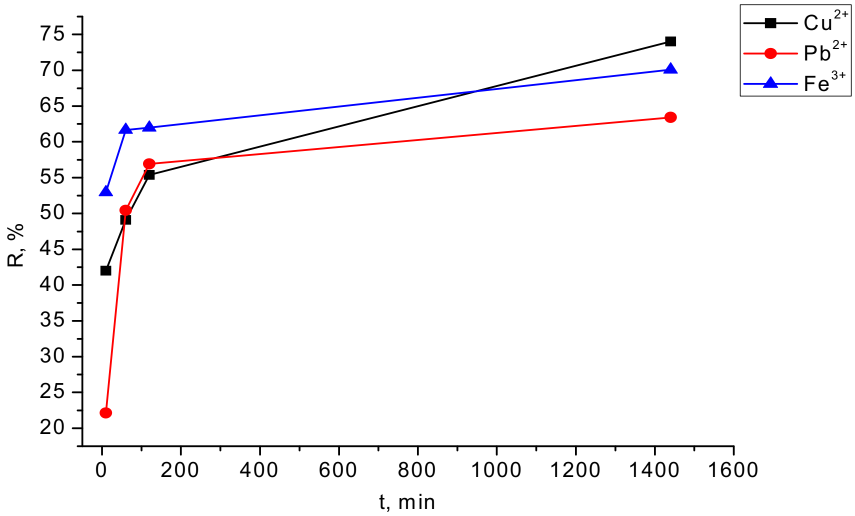


Figure 8. The dependence of Cu (II), Pb (II) and Fe (III) ions sorption degree (R, %) from the interaction time with the composite in the static mode.

Taking into account all of the foregoing, further investigations of sorption properties of the composite were carried out with the initial solutions of Cu (II) nitrate without adding buffers, and with Pb (II) and Fe (III) nitrates against the background of phthalate buffer.

The dependence of Cu (II), Pb (II) and Fe (III) ions sorption degree (R, %) on the silica gel surface with *in situ* immobilized poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride) from the interaction time in the static mode is shown in Figure 8.

The data obtained confirm that the maximum sorption takes place during the first day of the contact and sorption equilibrium is established after 24 hours. Such a small rate of sorption, according to the literature, is typical for the polymers or organo-mineral composites with more than 20 wt.% of the immobilized polymer.

In order to establish the values of silica gel with immobilized copolymer adsorption capacity towards Cu(II), Cd(II), Pb(II) and Fe(III) ions, adsorption isotherms were measured. The isotherms were obtained for aqueous solutions of nitrates of these metals (without adding any buffer solutions) in static mode and compared with the initial silica gel. The isotherms obtained for Cu(II) та Pb(II) are shown in Figure 9. All of the obtained adsorption isotherms are 2L-type in accordance with IUPAC [11] classification. The isotherms obtained were employed for adsorption capacity calculations.

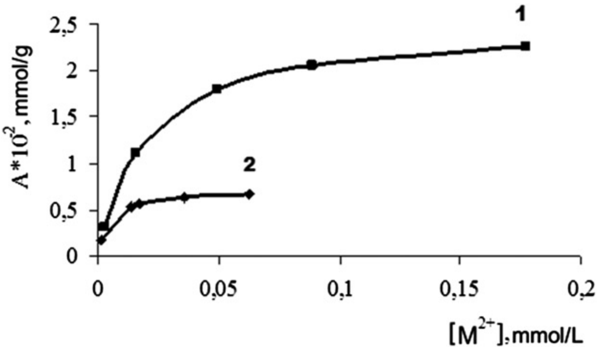


Figure 9. Sorption isotherms for Cu(II) (curve 1) and Pb(II) (curve 2) ions on the surface of poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride)/silica gel composite.

Table 3. Comparison of parent silica gel, poly(4-vinylpyridine-*co*-styrene)/silica gel composite [8] and poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride)/silica gel sorption capacities towards Cu(II), Cd(II), Pb(II) and Fe(III) ions.

	Sorption capacity, mmol/g ± 0.001		
Ion	Parent silica gel	Silica gel with immobilized poly (4-vinylpyridine-*co*-styrene)	Silica gel with immobilized poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride)
Fe(III)	0.008 [8]	0.027 [8]	0.015
Pb(II)	0.002 [8]	0.075 [8]	0.0067
Cu(II)	0.005 [8]	0.029 [8]	0.025

Sorption capacity values for Cu (II), Pb (II) and Fe (III) ions calculated using sorption isotherms for the synthesized composite poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride)/silica gel as well as literature data for the original silica gel and composite poly(4-vinylpyridine-*co*-styrene)/silica gel [8] are given in Table 3.

The data presented in Table 3 confirm that sorption capacity of silica gel after modification with poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride) is increased in1.88 times for Fe (III) ions, in 5.00 times for Cu (II) ions and in 3.35 times for Pb (II) ions.

However, the sorption capacity of poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride)/silica gel composite towards Pb (II), Cu (II) and Fe (III) ions is lower than sorption capacity of poly(4-vinylpyridine-*co*-styrene)/silica gel composite.

This result can be explained by two reasons. Firstly, the high mass of the immobilized copolymer (31.84 wt.%) reduces the silica gel matrix porosity. Secondly, non-uniform location of the copolymer on the silica gel surface (see Fig. 7, a.) leads to the sterical hindrance for incorporation of complexing copolymer centers into the coordination spheres of metal ions.

Conclusions

Precipitation polymerization was employed for the syntheses of a new mineral-organic composite by *in situ* immobilization of poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride) on the silica gel surface. The immobilization of copolymer on a silica gel surface was confirmed by FTIR spectroscopy.

A thermal decomposition of the immobilized copolymer was investigated by thermogravimetry and mass spectrometry and described in detail. According to TG-analysis, the composite contained 31.84 ± 0.1 wt.% of immobilized copolymer.

The highest sorption capacity of a new composite towards micro-quantities of Cu (II) ions was established in neutral medium as well as towards Pb (II) and Fe (III) ions in a slightly acidic medium with the background of phthalate buffer and no sorption activity towards Cd (II) ions.

Sorption process for Cu (II), Pb (II) and Fe (III) ions occurs gradually and equilibrium is established after 24 hours.

It was found that sorption capacity of silica gel increased in 1.88, 5.00 and 3.35 times for Fe (III), Cu (II) and Pb (II) ions respectively after immobilization of poly(4-vinylpyridine-*co*-styrene-*co*-maleic anhydride) on silica gel surface. However, the sorption capacity of a new composite towards Pb (II), Cu (II) and Fe (III) ions is lower than sorption capacity of early obtained poly(4-vinylpyridine-*co*-styrene)/silica gel composite [8].

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