

Adsorption properties of silica gel *in situ* modified with copolymers of 4-vinylpyridine and styrene towards ions of toxic metals

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In situ modification of silica gel surface was carried out with immobilization of organic copolymers synthesized by radical copolymerization of 4-vinylpyridine and styrene at different starting molar ratios. Immobilization of organic polymers on the silica gel surface was proved by IR-spectroscopy, thermogravimetric analysis coupled with mass spectrometry. All of the composites have adsorption activity towards microquantities of Cu(II), Pb(II) and Fe(III) ions in a neutral water medium. Composites based on the copolymer with an initial molar ratio 4-vinylpyridine:styrene 3:1 exhibited the best adsorption properties in accordance with the data of adsorption isotherms.

Keywords: adsorption, *in situ* modification, poly(4-vinylpyridine-co-styrene), organo-mineral composite.

На поверхності силікагелей здійснена *in situ* іммобілізація сополімерів 4-вінілпіридину та стиролу з різними співвідношеннями мономерів, отримано ряд нових органо-мінеральних композитів. Факт іммобілізації полімерів на поверхності силікагелей підтверджено методами ІК-спектроскопії та термогравіметричного аналізу, об'єднаного з мас-спектрометрією. Зафіксовано, що всі синтезовані композити проявляють сорбційну активність по відношенню до мікроколіцтв іонів Cu(II), Pb(II) і Fe(III) в нейтральній водній середі. Установлено, що серед усіх синтезованих композитів кращими сорбційними властивостями по відношенню до цих іонів володіє силікагель, *in situ* модифікований сополімером стиролу і 4-вінілпіридину з вихідним співвідношенням 1:3.

Сорбційні властивості щодо йонів токсичних металів силікагелів, *in situ* модифікованих кополімерами 4-вінілпіридину та стиролу. *Е.С.Яновська, Л.О.Вретік, О.У.Кондратенко, О.А.Ніколаєва, Д.Стернік.*

На поверхні силікагелів здійснено *in situ* іммобілізацію кополімерів 4-вінілпіридину та стиролу з різними співвідношеннями мономерів, отримано ряд нових органо-мінеральних композитів. Факт іммобілізації полімерів на поверхні силікагелів підтверджено методами ІЧ-спектроскопії та термогравіметричного аналізу, об'єднаного з мас-спектрометрією. Зафіксовано, що синтезовані композити виявляють сорбційну активність щодо мікроколіцтв йонів Cu(II), Pb(II) і Fe(III) у нейтральному водному середовищі. Встановлено, що серед синтезованих композитів найкращі сорбційні властивості щодо цих йонів притаманні силікагелю, *in situ* модифікованому кополімером стиролу та 4-вінілпіридину з початковим співвідношенням 1:3.

1. Introduction

Pyridine and its derivatives are well-known ligands which form stable complexes with most transition metals ions. Processes of complex formation are also typical for pyridine-containing polymers [1, 2]. Therefore, the modification of the surface of porous inorganic materials by pyridine-based polymers is a perspective approach to produce new composite materials that can be used as effective adsorbents of metal cations due to their complexation with nitrogen atoms of pyridine function in immobilized polymer [3, 4].

One of the promising ways of creating such organo-mineral composite materials with interesting and valuable adsorption properties is polymer immobilization *in situ* on the surface of a porous inorganic carrier [5, 6]. The advantage of this method of polymer immobilization is its versatility with respect to the chemical nature of the carrier. The *in situ* method can be successfully applied to carriers of different shapes and rigidity. Moreover, such a method is the only way to obtain a polymer layer on

porous and powdered nanoscale carriers [7, 8]. And in the case of immobilization of copolymers, it is possible to create a polymeric layer on the surface of an inorganic carrier with the most optimal ratio of copolymer components.

In [3] we have shown that *in situ* immobilization of copolymer of 4-vinylpyridine and styrene with molar ratio 4:1 on the silica gel surface allowed us to obtain a material with good adsorption activity towards Pb(II), Mn(II), Ni(II) and Fe(III) ions.

This work is devoted to *in situ* modification of silica gel (Merck) with immobilized copolymers of poly(4-vinylpyridine-co-styrene) with different molar ratios of co-monomers (see Table 1) and to the study of the adsorption properties of the obtained composites towards Cu(II), Cd(II), Pb(II), Mn(II) and Fe(III) ions.

2. Experimental

As a mineral carrier of the composites was used silica gel (fraction of 0.1–0.2 mm diameter particles, specific surface 428.61 m²/g, Merck), properties of the silica gel surface are given in a Table 2.

Table 1. Results of thermogravimetric analysis of synthesized composites

Sample No.	Molar ratio St:4VPy	Temperature range of decomposition, °C	Polymer content in the composite, wt. %
1	1:2	98–523	30.6
2	1:3	82–517	30.0
3	1:4	83–521	30.8
4	1:6	91–515	29.6
5	2:1	102–532	22.5
6	3:1	84–540	19.1
7	4:1	100–541	18.4
8	5:1	100–542	18.4
9	6:1	100–541	15.7

Table 2. Comparative characteristic of surface parameters of parent silica gel and composites

Sample	Surface area, m ² /g			Average pore volume, cm ³ /g	Average pore diameter, nm
	p/p^0	BET	Langmuir		
Silica gel	447.00	463.53	686.91	0.68	5.92
Composites					
St:4VPy = 1:2	84.82	87.77	139.64	0.14	6.24
St:4VPy = 1:3	89.06	95.73	135.33	0.24	9.89
St:4VPy = 1:4	213.21	221.38	354.61	0.59	10.71
St:4VPy = 1:6	61.89	65.22	86.35	0.23	14.02
St:4VPy = 2:1	141.88	149.95	208.91	0.24	6.43
St:4VPy = 3:1	85.64	88.22	139.47	0.13	6.08
St:4VPy = 4:1	208.90	215.18	342.22	0.34	6.36

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

Copolymerization of 4-vinylpyridine and styrene was carried out by heterogeneous radical copolymerization in CCl_4 in the presence of silica gel by the following procedure:

Solutions with 1–6 moles of styrene, 1–6 moles of 4-vinylpyridine (see Table 1) and 0.04 g of azobisisobutyronitrile (AIBN) in 16 ml of CCl_4 were mixed in reaction flasks containing 20 g of silica gel. Synthesis was carried out in an inert atmosphere, which was created by argon purging for 30 min. After stop of the argon flow, the reaction mixture was heated to 76°C; polymerization lasted for another 5 h at continuous stirring. The reaction was stopped by cooling the reaction mixtures. The resulting suspensions were left overnight. The synthesized composites were washed several times to remove the excess of unreacted starting materials with isopropyl alcohol, filtered off and dried on air at room temperature for a day.

The scheme of composites syntheses is the same as described in [3].

FT-IR spectra of parent and modified silica gel for samples with identical weight were recorded on a "Spectrum BX" IR spectrometer with Fourier transformation (Perkin Elmer, Germany) in the spectral range of 500–4000 cm^{-1} in KBr pellets.

The amount of immobilized copolymer on the surface of the modified silica gel was evaluated by thermogravimetry using TG/DTA analyzer "Shimadzu DTG-60 H" (Shimadzu, Japan) in the temperature range of 15–1000°C. The rate of the samples heating was 10°C·min⁻¹.

Thermal analysis of the composite was performed in a differential scanning calorimeter "STA 449 Jupiter F1" (Netzsch, Germany) coupled with a mass spectrometer "QMS 403C" (Germany).

The values of the specific surface and the average pore diameter were calculated from the isotherms of low temperature nitrogen adsorption/desorption using the "ASAP 2420 V1.01" software (Micromeritics, USA). Samples were degassed at 60°C for 24 h before measurements.

The morphology of the silica gel surface before and after modification by poly(4-vinylpyridine-co-styrene) copolymers was

explored by scanning electron microscopy using an electron microscope "SEM LEO 1430 VP" (Carl Zeiss, Germany).

The study of the adsorption capacity of the synthesized composite towards Pb(II), Cu(II) and Fe(II) ions included:

- establishing the optimal pH region of adsorption medium;

- establishing the time of the phase contact that required to achieve the adsorption equilibrium in the static sorption mode;

- plotting of adsorption isotherm for each metal ion on the synthesized composites surface;

- estimation of their adsorption capacity towards mentioned above metal ions and comparison with the parent silica gel.

The adsorption characteristics of the synthesized material with respect to the selected ions were studied in the static mode. The composite (0.1 g) was contacted with 25–100 ml of working nitrate solutions of the corresponding metals. The interaction took place for 10, 20, 40, 60, 120 minutes and 24 h with continuous mechanical shaking. The equilibrium concentrations of the metal ions were measured by the atomic absorption method.

Working nitrate solutions of the selected metals were prepared using sets of "standard sample solutions set" of these salts with the background of 1 M HNO_3 (manufactured by A.V.Bogatsky FHI Co, Odesa, Ukraine) with 1 and 10 mg/ml concentrations without addition of any buffer solutions.

The degree of adsorption (R) was calculated by the formula:

$$R = \frac{m_{ads}}{m_o} \cdot 100\% = \frac{m_o - [m]}{m_o} \cdot 100\%, \quad (1)$$

where m_o is the mass of the metal in the output solution, m_{ads} is the mass of adsorbed metal, $[m]$ is the mass of the metal in the equilibrium solution after adsorption, which was calculated as $[m] = [M] \cdot V$, where $[M]$ is the equilibrium concentration of the metal and V is the volume of the equilibrium solution.

The equilibrium concentration of ions of the 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 the "air-propane-butane-mixture". The measured wavelengths were 324.7 nm for Cu, 228.8 nm for Cd, 283.3 nm for Pb, and 248.3 nm for Fe; and the slit width was 0.5 cm. Calculations of the equilibrium

concentrations in the solution were made by comparing the intensities of their spectral lines with the intensities of the lines for standard solutions. For this purpose, the standard solutions were prepared with metal concentrations in the range of 0.1 to 1.5 $\mu\text{g}/\text{ml}$.

3. Results and discussion

3.1. Evidences of *in situ* immobilization of poly(4-vinylpyridine-co-styrene) copolymers on the silica gel surface

As a result of precipitation polymerization, the silica gel surface acquires the dark-red color. Thus, the fact of *in situ* immobilization of 4-vinylpyridine — styrene copolymers on the silica gel surface is visually confirmed.

The immobilization of 4-vinylpyridine-co-styrene polymers on the silica gel surface was established by comparison of FT-IR spectra for the parent (see Fig. 2) and modified silica gel samples. Some samples of silica gel modified with copolymers of 4-vinylpyridine with styrene in different molar ratios (St:4VPy=1:2, St:4VPy=1:3, St:4VPy=1:4) are presented in Fig. 1.

A comparative analysis of the FT-IR spectra of the parent silica gel and modified silica gel samples proves the following characteristic absorption bands of the immobilized copolymers presented in the composites:

- bands in the region of 1557–1662 cm^{-1} , which can be attributed to the C=C and C=N vibrations in the aromatic system of 4-vinylpyridine;

- bands in the region of 1420–1453 cm^{-1} , which can be attributed to the $\nu(\text{C}-\text{C})$ C=C vibrations in the aromatic system of styrene (however, the absorption band at 1453 cm^{-1} can be also attributed to the $\delta(\text{CH}_2)$ deformation vibrations);

- bands in the region of 2860–2930 cm^{-1} ($\nu(\text{C}-\text{H})$ of CH and CH_2 groups of the main polymer chain) that confirm the copolymer formation on the inorganic carrier surface [9].

Comparative analysis of the FT-IR spectra for the synthesized composites indicates that the absorption intensity of the bands in the region of 1420–1622 cm^{-1} decreases with an increase of the amount of styrene co-monomer in the starting reaction mixture.

3.2. Thermogravimetry analysis of thermo-destruction of immobilized copolymers

Concentration of immobilized copolymers was estimated by comparison of thermogravimetry data for the synthesized composites and parent silica gel.

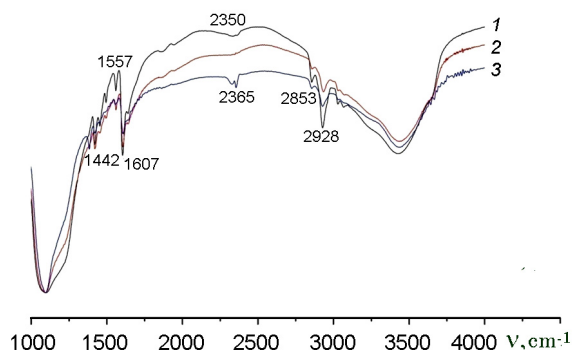


Fig. 1. FT-IR spectra of the composites with starting molar ratios of styrene (St) and 4-vinylpyridine (4VPy): 1 — St:4VPy = 1:2; 2 — St:4VPy = 1:3; 3 — St:4VPy = 1:4.

The analysis of thermograms proved that the most of the immobilized copolymers decomposes at the temperature range of 100–600°C. Taking into account that in this temperature range, the weight loss of parent silica gel is about 5.39 wt % [3], weight fractions of the immobilized polymers in the composites were calculated (see Table 1). As it is seen, the weight fraction of the immobilized copolymer decreases with an increase of the styrene content in the starting monomer mixture. Thus, the thermo-gravimetric results are in a good agreement with the FT-IR spectra analysis data.

3.3. Analyzing thermo-destruction of immobilized copolymers by thermogravimetry coupled with mass-spectrometry

To study in detail the process of thermal destruction of copolymers immobilized on the silica gel surface, their mass spectra in TG-MS-3D and MS-2D and 3D formats were obtained.

An example of the spectra for the composite with the starting molar ratio of St:4VPy = 1:3 of the co-monomers is presented in Fig. 2.

Mass-spectrometry analysis showed that the products of thermo-destruction of the immobilized copolymers are not identical for all the samples. The mass spectra of the decomposition products looks similar to each other for the composites obtained at the starting co-monomers' molar ratios of St:4VPy = 1:3, St:4VPy = 1:6, St:4VPy = 4:1 and St:4VPy = 5:1. All the spectra have an intensive peak at the relative weight 28 which could be attributed to the release of CO and N_2 ; also low intensity signals at 18, 30 and 44 Da due to water, C_2H_6 and CO_2 formation are presented. In contrast, for

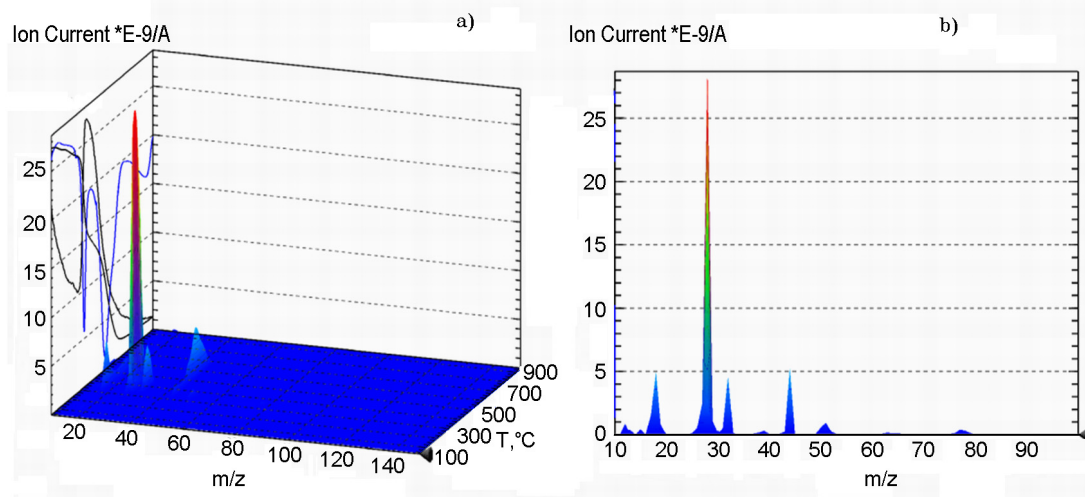


Fig. 2. TG-MS-3D (a) and MS-2D (b) data for the composite obtained with the starting molar ratio of co-monomers of St:4VPy = 1:3.

the immobilized copolymer obtained at the molar ratio of St:4VPy = 1:4, in the mass-spectrum of the decomposition products, two intensive picks at 18 and 44 Da are presented (CO_2 , N_2O and water release). Other signals at 50, 65 and 77 Da could be explained as a result of the main polymer chain as well as destruction products of aromatic groups.

Thus, the mass-spectrometry data give us an evidence that the regularities of thermal destruction of the composite obtained at the starting molar ratios of St:4VPy = 1:4 of the co-monomers are rather different in comparison with the composites formed at the other molar ratios of co-monomers.

3.4. A comparison of silica gel surface morphology before and after modification with styrene-4-vinylpyridine copolymers

The surface parameters of the parent silica gel and composites: specific surface area calculated with the methods of computer processing the nitrogen sorption-desorption isotherms, an average pore volume and an average pore diameter estimated from the curves of pore distribution in the samples — are presented in Table 2. From the detailed analysis of Table 2 data, the following conclusions can be made about the changes in the silica gel surface morphology as a result of modification with styrene-4-vinylpyridine copolymers:

— at the increase of the prevailing amount of 4-vinylpyridine in an immobilized copolymer from 2 to 6, the specific surface area sharply diminishes from $447 \text{ m}^2/\text{g}$ for parent silica gel to $62 \text{ m}^2/\text{g}$. The average pore volume diminishes from

$0.68 \text{ cm}^3/\text{g}$ to $0.24 \text{ cm}^3/\text{g}$, and average pore size grows from 5.92 nm to 14 nm ;

— surface parameters of the composite obtained with the starting molar ratio of St:4VPy = 1:4 is outside this tendency; namely, the decrease of the specific surface area and average pore volume is not sufficient and folds $213 \text{ m}^2/\text{g}$ and $0.59 \text{ cm}^3/\text{g}$, respectively;

— in contrast, at the further increase of prevailing styrene amount in the immobilized copolymer from 2 to 6, the pore specific surface area increases from 142 to $231 \text{ m}^2/\text{g}$, gradually approaching the value for parent silica gel ($447 \text{ m}^2/\text{g}$); the average pore volume and average pore size increase insignificantly from 0.24 to $0.38 \text{ cm}^3/\text{g}$ and from 6.43 to 6.49 nm , respectively;

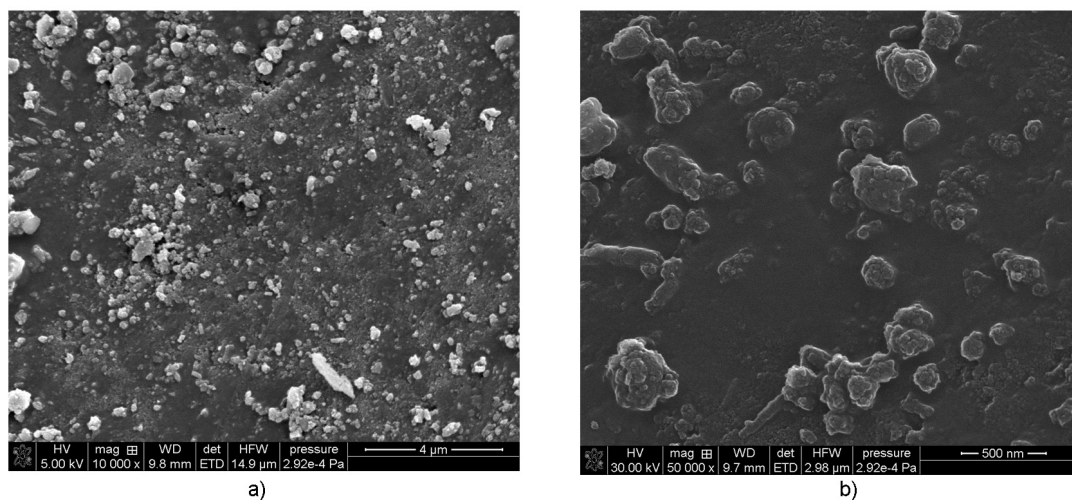
— surface parameters of the composite obtained with the starting molar ratio of 4VPy:St = 3:1 are outside of this tendency; namely, the decrease of the specific surface area and average pore volume is more significant and folds $85.64 \text{ m}^2/\text{g}$ and $0.13 \text{ cm}^3/\text{g}$ respectively; this testifies the differences in the surface structure of this composite in comparison to others composites with predominant styrene content.

The obtained results testify that the structure of silica gel surface with immobilized composite with the starting molar ratio of co-monomers styrene to 4-vinylpyridine, St:4VPy = 1:4 some differs in comparison to the composites with other prevailing contents of 4-vinylpyridine. These data well correlate with the described above results on thermo-destruction.

To clarify the question about the shape and location geometry of the copolymers im-

Table 3. Adsorption capacity of silica gels *in situ* modified with copolymers of styrene (St) and 4-vinylpyridine towards of Cu(II), Pb(II) and Fe(III) ions in a static mode

No.	Sample	Adsorption capacity					
		Pb(II)		Cu(II)		Fe(III)	
		mmol/g	mg/g	mmol/g	mg/g	mmol/g	mg/g
1	Parent silica gel	0.002	0.41	0.005	0.32	0.008	0.45
2	Composite St:4VPy = 1:2	0.011	2.27	0.023	1.47	0.032	1.79
3	Composite St:4VPy = 1:3	0.014	2.89	0.036	2.30	0.036	2.02
4	Composite St:4VPy = 1:4	0.006	1.24	–	–	0.013	0.73
5	Composite St:4VPy = 1:6	0.008	1.65	0.027	1.73	0.025	1.40
6	Composite St:4VPy = 2:1	0.013	2.69	0.023	1.47	0.024	1.34
7	Composite St:4VPy = 3:1	0.014	2.89	0.036	2.30	0.010	0.56
8	Composite St:4VPy = 4:1	0.006	1.24	0.027	1.73	0.011	0.62
9	Composite St:4VPy = 5:1	–	–	0.019	1.22	0.013	0.73
10	Composite St:4VPy = 6:1	–	–	0.019	1.22	0.014	0.78

Fig. 3. SEM surface images of the composite synthesized with starting molar ratio of co-monomers of St:4VPy = 1:6 at $\times 10\,000$ (a) and $\times 50\,000$ (b) magnifications.

mobilized on the silica gel surface, SEM-photos of the synthesized composites were made with a magnification in 10000, 50000 and 100000 times. The SEM-photos of the surface of samples with starting molar ratios of St:4VPy = 1:6 with a magnification in 10000 and 50000 times are presented on Fig. 3.

As one can see, the copolymers are unevenly located on the inorganic carrier surface in the shape of loops of macro-chains, adsorbed rings and ring aggregates. In the case of a predominant styrene content of in the copolymer, the hydrophobicity increases and, as a result, the adhesion to the silica gel surface gets worse. With the increase of the 4-vinylpyridine content in the copolymers, the hydrophilicity grows up resulting in the better adhesion. The surface structure of the composite changes more suffi-

ciently that leads to more substantial changes in the surface parameters.

3.3. Comparison of adsorption ability of synthesized composites towards Pb(II), Cu(II) and Fe(III) ions

In our previous studies, all obtained composites were found to exhibit negligible adsorption activity towards the ions Cd(II) and Mn(II). Therefore, a more detailed study of adsorption properties was carried out only for Pb(II), Cu(II) and Fe(III) ions. The adsorption properties of the composites were studied both in acidic and in neutral media; in an alkaline medium, immobilized copolymers were washed away from the silica gel surface. In the initial solutions of the investigated metals, the aqua, chloride, acetate or phthalate coordination spheres are

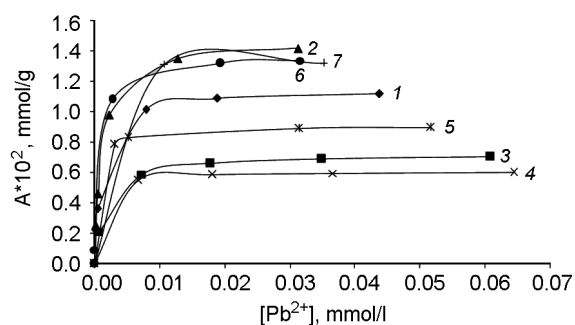


Fig. 4. Isotherms for Pb(II) ions adsorption on the silica gel surface *in situ* modified with copolymers of 4-vinylpyridine and styrene in a static mode from water nitrate solutions of Pb(II) without addition of buffer solution. 1 — St:4VPy = 1:2; 2 — St:4VPy = 1:3; 3 — St:4VPy = 1:4, 4 — St:4VPy = 4:1; 5 — St:4VPy = 1:6; 6 — St:4VPy = 2:1; 7 — St:4VPy = 3:1; (Experimental conditions: weight of adsorbent — 0.1 g, time of interaction — 24 h).

formed. Adsorption occurs due to interaction of such complexes with molecules of the immobilized polymer resulting in formation of multi-ligand complexes on the solid surface [10, 11].

In accordance with the obtained results, micro-quantities of Pb(II), Cu(II) and Fe(III) ions are best adsorbed in an water medium on the surface of silica gel modified *in situ* with copolymers of 4-vinylpyridine and styrene without addition of buffers, so, in the form of aqua complexes. It was found that as the styrene content in the composition of the immobilized copolymer increased, its adsorption ability towards Pb(II) and Cu(II) ions increased as well. For starting molar ratios of St:4VPy = 2:1 and higher, the significant adsorption of micro-quantities of both these ions is observed. In contrast, the adsorption of Fe(III) ions is higher on the surface of the composites with a predominance of 4-vinylpyridine in the immobilized copolymers in the aqueous medium. The adsorption degree of 100 μg of this ion on the surface of 0.1 g of each composite with a predominant content of 4-vinylpyridine exceeds 90% under the chosen adsorption conditions. Wherein the composite with the starting molar ratio of St:4VPy = 1:3 showed the maximum adsorption capacity at the level of 97 % towards Fe(III) ions.

The Pb(II) and Cu(II) ions are negligibly adsorbed on the modified silica gel surface in the presence of various acids in the initial solutions (chloride, acetic and phthalic

acid). The exception is a composite with an initial ratio of St:4VPy = 4:1, which effectively removes Cu(II) ions in the presence of chloride and acetic acids due to formation of chloride and acetate complexes. In the acidic medium, Fe(III) ions are removed better than Pb(II) and Cu(II) ions. For the synthesized adsorbents, the adsorption degree of 100 μg Fe(III) varies at the level of 65–82 % in the presence of acetic acid (pH 2.8) and at the level of 40–70 % in the presence of phthalic acid (pH 4.0).

The obtained correlation between the adsorption degree of Pb(II), Cu(II) and Fe(III) ions on the surface of the synthesized composites and the contact time in a static mode allow us to make the following conclusions:

- the prevailing part (more than 90 %) of Pb(II) ions is adsorbed during the first 10 min of the contact with the surface of all synthesized composites. However, the fastest adsorption equilibrium for these ions is attained for the composites based on the copolymers of 4-vinylpyridine and styrene with starting molar ratios of St:4VPy = 1:2 and St:4VPy = 3:1.

- Cu(II) and Fe(III) ions are adsorbed on the surface of all the synthesized composites more slowly than the Pb(II) ions. Although the predominant part of Cu(II) ions is removed during the first minutes of the contact, maximum adsorption is observed only after one contact day in the static mode.

Isotherms of adsorption of Pb(II) ions on the surface of silica gel modified *in situ* with copolymers of 4-vinylpyridine and styrene from aqueous solutions of nitrates are shown in Fig. 4 in the static mode. The isotherms of Cu(II) and Fe(III) ions adsorption have a similar shape. As one can see from the Fig. 4, all the isotherms obtained allow for unambiguous establishing the adsorption capacity for these ions. The values of the adsorption capacity found from the adsorption isotherms of all synthesized composites towards Cu(II), Pb(II) and Fe(III) ions are summarized in Table 3.

As follows from Fig. 4 and Table 3, the highest adsorption capacity towards Cu(II), Pb(II) and Fe(III) ions is demonstrated by silica gel *in situ* modified by copolymer with an initial molar ratio St:4VPy = 1:3. Its adsorption capacity for Cu(II) and Fe(III) ions is 0.036 mmol/g and 0.014 mmol/g for Pb(II) ions. The results obtained can be explained by the formation of complexes of these ions with nitrogen atoms of the immobilized copolymer.

4. Conclusions

In situ immobilization of 4-vinylpyridine and styrene copolymers on the silica gel surface was carried out by polymerization of precipitated radicals of these monomers in the presence of silica gel, and a number of new organo-mineral composite materials were obtained. FT-IR spectroscopy and thermogravimetry coupled with mass-spectrometry analysis proved polymers immobilization on the silica gel surface. In accordance with thermogravimetry data, the mass fraction of the immobilized copolymer in the composites obtained decreases from 30.6 to 15.7 wt % with an increase of styrene content in the starting reaction mixture of the monomers.

SEM images of the synthesized composites proved that the immobilized polymers on the silica gel surface are placed in the shape of loops of macro-chains and adsorbed balls. It was established that all the synthesized composites exhibit adsorption activity towards micro-quantities of Cu(II), Pb(II) and Fe(III) ions in a neutral aqueous medium (without the addition of any buffer solutions).

According to the results of adsorption isotherms processing, the highest adsorption capacity towards Cu(II), Pb(II) and Fe(III) ions is demonstrated by silica gel modified *in situ* by copolymers with an initial molar ratio of St:4VPy = 1:3.

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