CHAPTER 5

SYNTHESIS AND ADSORPTION PROPERTIES OF 4-AMINOSTYRENE AND METHACRYLIC ACID COPOLYMER, IMMOBILIZED IN SITU ON SILICA SURFACE

E. YANOVSKA,[1] L. VRETIK,[1] D. STERNIK,[2] O. KYCHKIRUK,[3]
O. NIKOLAEVA,[1] and M. MELNYK[1]

[1]Chemistry Faculty, Kyiv National Taras Shevchenko University, 12 L. Tolstogo Str., 01033 Kyiv, Ukraine, E-mail: lvretik@gmail.com

[2]Maria Curie-Skłodowska University, pl. Maria Curie-Skłodowskiej 3, 20-031 Lublin, Poland

[3]Department of Sciences, Ivan Franko Zhytomyr State University, 40 Velyka Berdychivska Str., 10008 Zhytomyr, Ukraine

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ABSTRACT

In situ immobilization of 4-aminostyrene and methacrylic acid copolymer has beenperformed on silica gel surface. ^{1}H NMR, IR and mass spectroscopy as well as TG analysis have been used to elucidate the structure of immobilized copolymer. An adsorption capacity of the synthesized composite towards Cu(II), Zn(II), Pb(II), Mn(II), Fe(III), Co(II), Ni(II) ions has been estimated. Adsorption activity to microquantity of Pb(II), Mn(II) and Fe(III) in a neutral aqueous medium has been observed.

5.1 INTRODUCTION

In the last two decades significant progress has been made in the study of complex formation processes on solid surfaces, in the compilation methods of purposeful synthesis of major groups of complex-forming adsorbents, including complex-forming chemically modified silica. To date, many examples of proven efficiency of complexes on solid carriers in catalytic processes have come to exist, these examples include the development of hybrid and combined methods in analytical chemistry that enhance the scope and accuracy of defining chemical elements, reduce the time of analysis, and are important for treatment technologies.

In particular, research efforts are aimed at finding methods of targeted one-step synthesis of adsorbents with monofunctional hard surface coating agents, capable of complex formation. To increase the adsorption capacity of adsorbents, adsorption or chemical attachment to inorganic surfaces and nitrogen–oxygen containing polymeric materials is increasingly used; the latter have inherent both complex-forming and ion exchange properties (polyions, *polyhexamethylene guanidine* and its derivatives, polyaniline and polyacrylic acid) [1–4]. To synthesize such materials it is appropriate to use in situ formation of immobilized polymer layer in the presence of inorganic carrier particles as a promising way of creating nanocomposites with new valuable properties.

The most universal method of polymer synthesis is radical polymerization. It allows you to implement sedimentary polymerization, for example, the process where polymer is formed in the polymerization solution as sediment precipitation. In the case of such polymerization polymerization rate of the polymer increases, moreover, the latter has a high purity [5]; the process conducted in the presence of particles of inorganic nature is a simple method to create polymer composites – inorganic carriers.

4-aminostyrene, as well as methacrylic acid, is polymerized in an inert atmosphere with radical initiators. However, in contrast with methacrylic acid, products with low molecular weight are formed under direct polymerization of 4-aminostyrene[6–10]. For high molecular weight polymer formation in conditions of radical polymerization, aminostyrene with blocked amino group is typically used (e.g., tert-butoxycarbonyl“protection”) [11]. Copolymerization of aminostyrenes with such active monomer as methacrylic acid, gives reason to expect the formation of sufficiently high molecular weight products.

This chapter deals with the in situ immobilization of 4-aminostyrene with methacrylic acid copolymer on the surface of silica gel, it concerns the research of the immobilized polymer structure and its absorption properties for ions of Cu (II), Zn (II), Pb(II), Mn(II), Fe (III), and Co (II).

5.2 EXPERIMENTAL PART

4-aminostyrene and methacrylic acid copolymerization in the presence of silica (fraction of particles with a diameter of 0.1–02 mm, specific surface 428.61 m^2/g, Merck) has been carried out under the argon atmosphere. A solution of 1.18 g (0. 0.006 mol) methacrylic acid, 0.82 g (0.006 mol) 4-aminostyrene and 0. 02 g of AIBN in 16 ml CCl4 (12.5 wt. %) were poured into a flask containing 10 g of silica gel. When argon blowing was finished after 25 min, the reaction mixture was heated to 70°C; polymerization continued for 5 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 isopropyl alcohol, filtered and air-dried for 24 hours at room temperature.

A model sample of 4-aminostyrene and methacrylic acid copolymer obtained under identical conditions in the absence of silica gel was used for the estimation of copolymer composition by ^{1}H NMR-spectroscopy.

^{1}H NMR: (400 MHz, DMSO-d$_6$, TMS) δ (ppm): 6.99 (2H, Ar); 6.5 (2H, Ar); 1.89 (3H, CH$_3$); 1.46–1.14 (5H, CH$_2$, CH).

The fact of a heterophase polymerization was additionally confirmed by infrared spectroscopy. IR spectra of the composite and silica output were recorded with an infrared spectrophotometer Thermo Nicolet Nexus FT-IR, USA.

The amount of copolymer on the surface of silica gel was evaluated by thermo gravimetric analysis with TG/DTA analyzer "Shimadzu DTG-60 H" (Japan) in the 15–1000°C temperature range. The heating rate of the samples was 10°/min.

To investigate composite surface, the BET method (low-temperature nitrogen adsorption-desorption) at the boiling point of liquid nitrogen was used with ASAP 2420 V1.01 (Micromeritics, USA) sorptometer. Before measurements, samples were degassed at 60°C. According to the computer processing results of the adsorption-desorption isotherms of nitrogen, the surface area of the composite and pore distribution with regard to diameter was determined.

Adsorption characteristics of synthesized composite as to ions of Cu(II), Zn(II), Pb(II), Mn(II), Fe(III), Ni(II) Co(II) were studied in static mode. Thus 0.1 g of the composite contacted 25–100 ml of nitrates solutions of corresponding metals under the permanent stirring with a mechanical vibrator at room temperature. Determination of the equilibrium concentration of the metals was performed by atomic absorption using a "Saturn" (Ukraine) atomic absorption spectrophotometer with flame atomizer in "air – propane – butane" flame mixture.

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

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

where m_o – mass of metal in the output solution, m_{ads} – mass of adsorbed metal, m – mass of metal in equilibrium solution after adsorption, which was calculated as

$$m = [\mathrm{M}]\cdot V,$$

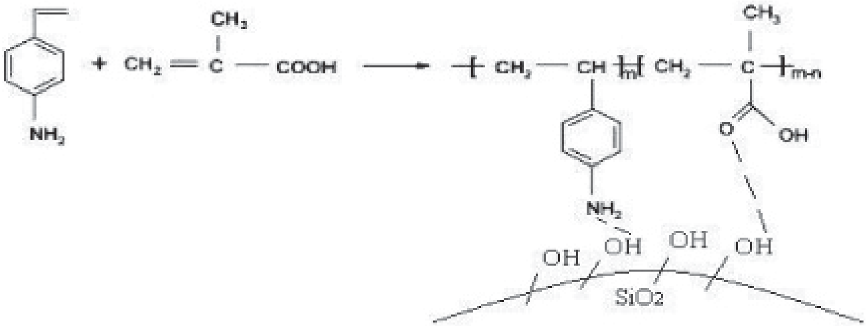
where [M]·– is equilibrium concentration of metal and Visvolumeof equilibrium solution.

Nitrate solutionsofCu (II), Zn (II), Pb (II), Mn (II), Fe (III), Ni (II) Co (II) were prepared using sets "standard sample solutions" of these salts against the background of1 M HNO_3 (manufacturedby*A. V. Bogatsky* FHI Co, in Odesa) with 1 and 10 mg/ml concentrations. To create the appropriate pH environment, standard buffer solutions (ISO 8.135:2009, manufacture red by RIAP JSC in Kyiv) were used.

Determination of the adsorption capacity of synthesized composite for the above mentioned transition metal ions included determining of the optimal range of pH environment, medium required phase contact time to achieve adsorption equilibrium in static mode and building sorption isotherms of the appropriate metal ions to establish the adsorption capacity.

5.3 RESULTS AND DISCUSSIONS

Intergel intensities of proton signals near 6.99 ppm (2H, Ar, styrene) and 1.89 ppm (3H, CH_3 methacrylic acid) were estimated as 3.8:1. This suggests that the ratio of 4-aminostyrene and methacrylic acid contained in the copolymer immobilized on the surface of silica is about 4:1. Then the *chemical structure* of *in situ* copolymer immobilization of 4-aminostyrene and methacrylic acid on the surface of silica could be presented as follows:



Chemical structure diagram of *in situ* immobilization of 4-aminostyrene-methacrylic acid copolymer on the silica surface ($m = 4$, $n = 3$).

Comparative analysis of IR spectra of synthesized composite and original silica gel (Figure 5.1) shows that absorption bands are present at 3460

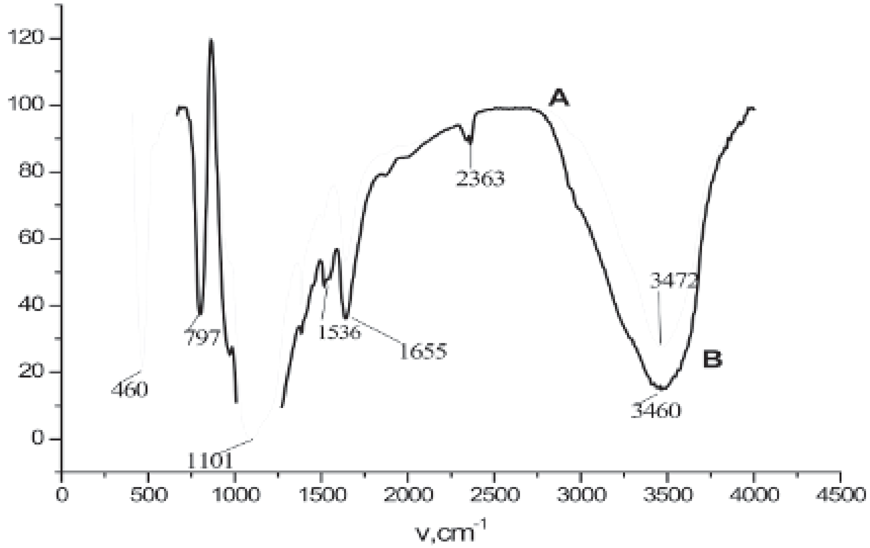


FIGURE 5.1 The FTIR-spectra of the original silica gel (A) and synthesized composite (B).

cm^{-1}in the spectrum of the immobilized copolymer unlike the original carrier, which can be identified as valence vibrations of υ (N-H) – aminostyrene bonds. Absorption bands which can be attributed to the stretching vibration of aminostyrene aromatic systems are also present in the spectrum of the composite in the range of 1500 to 1600 cm^{-1}, and so are bands of ca. 800 cm^{-1} deformation vibrations of CH-polymer bonds [12, 13].

To determine the mass of immobilized copolymer thermo gravimetric analysis was performed (Figure 5.2). It can be seen from the thermo gram presented that most of the copolymer decomposes in the temperature range from 300 to 600°C. Approximately, 10.5% of the composite weight is lost, which suggests that this is exactly the mass of copolymer to be found on the surface of silica gel.

Mass spectral analysis showed that thermal destruction of copolymer occurs in two stages. When temperatures are close to 100°C (118°C) carboxyl group water is produced, according to Ref. [14] accompanied by the formation of anhydride fragments. Further destruction occurs at temperatures above 300°C. The major products of the relative weight of 44 Da may be CO_2 and N_2O (Figure 5.3).

As seen in Figure 5.4, the forms adsorption-desorption isotherms of source silica gel nitrogen and composite are similar and belong to type IV

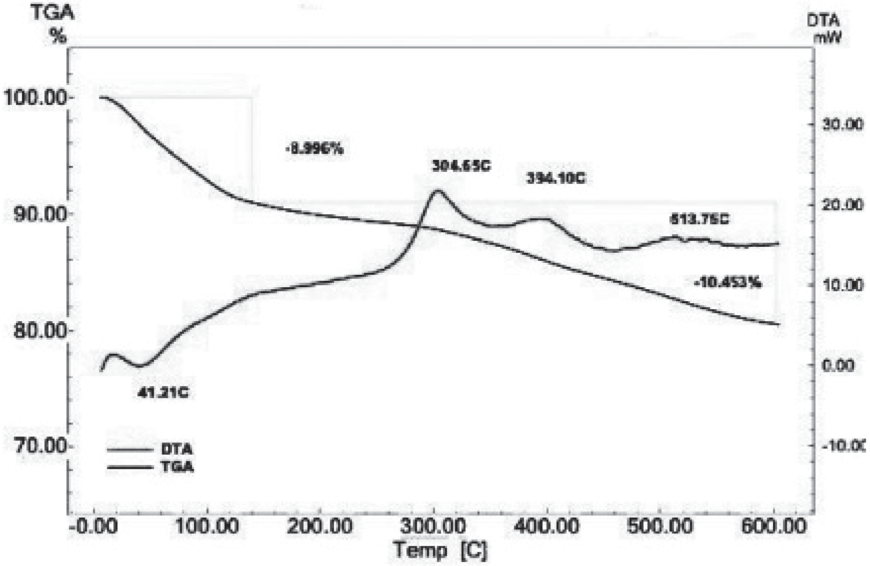


FIGURE 5.2 Thermogram of synthesized composite.

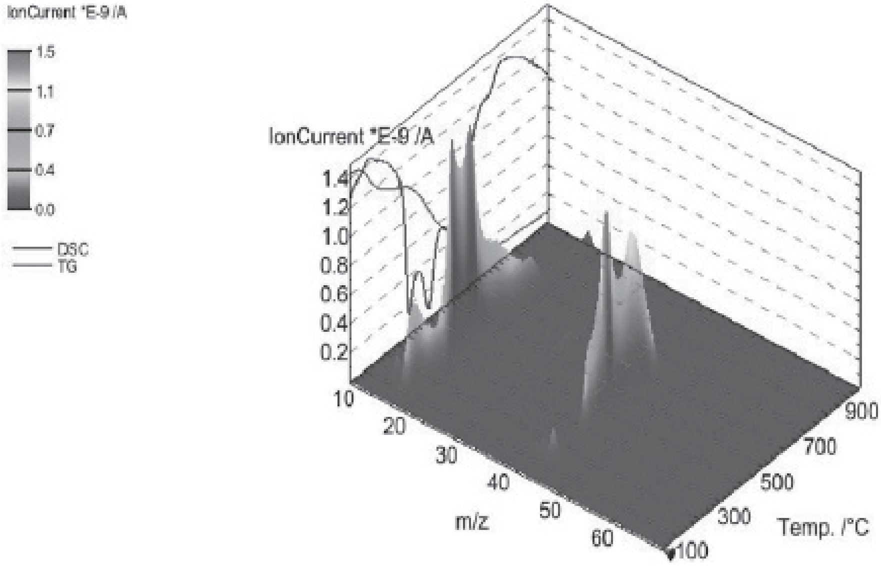


FIGURE 5.3 TG-MS-3D of synthesized composite.

isotherms according to IUPAC classification. The received data indicate that immobilized copolymer has virtually no effect on the structure of the surface layer of silica gel. The value of the specific surface area of silica gel following immobilization with polymer, calculated using the BET method, is 341.7 m^2/g. That is to say that the surface area decreases slightly after immobilization, which is a logical result of the consolidation on the surface of small pore polymer.

For a more detailed study of changes in the structure of the silica gel surface after modification with copolymer its surface pore size distribution diagrams were built, calculated using the BET method (Figure 5.5). As seen in Figure 5.5, modification virtually no effect on the silica gel pore size which is before and after the modification is predominantly of macro porous nature. Such pore distribution is usually characteristic of "islet" placement of the polymer on the surface of silica gel matrix, which was confirmed by the data of scanning electron microscopy.

The study of synthesized composite adsorption capacity for ions Cu (II), Zn (II), Pb(II), Mn(II), Fe(III), Ni(II) and Co(II) at different values of pH environments has shown in Table 5.1. Data presented have shown an adsorption activity of the synthesized composite against all studied trace metals in neutral and slightly alkaline environment (In the absence of initial hydrolysis

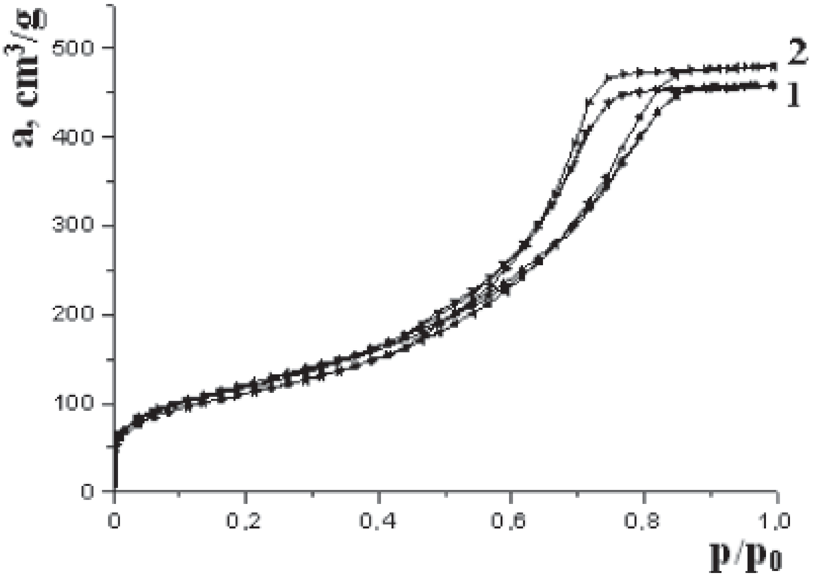


FIGURE 5.4 Adsorption–desorption isotherms of nitrogen of original silica (1) and composite (2).

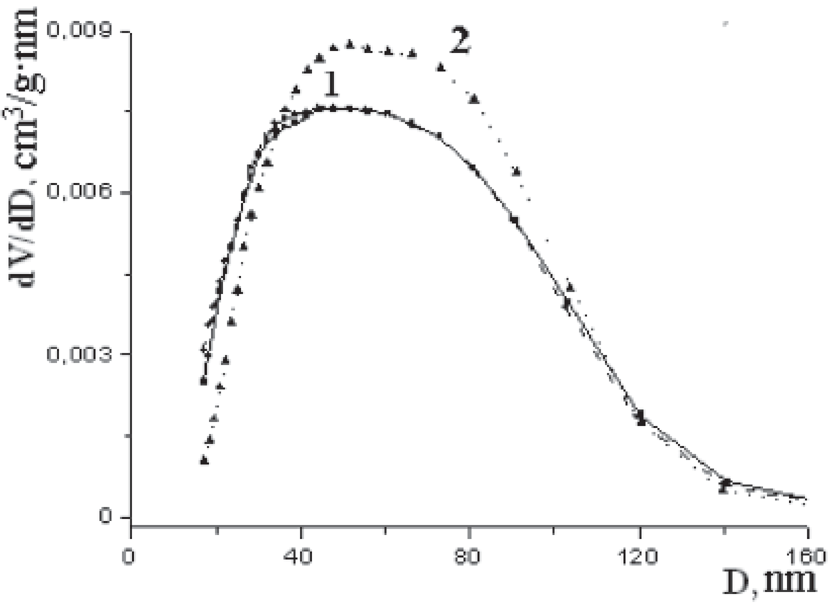


FIGURE 5.5 Pore size distribution curves of the original silica (1) and composite (2).

TABLE 5.1 Dependence of the Adsorption Degree of Metal Cations on Silica Gel with Immobilized Copolymer of 4-Aminostyrene and Methacrylic Acid

pH	**Degree of sorption, %**						
	Cu^{2+}	CO_2^+	Ni^{2+}	Mn^{2+}	Pb^{2+}	Fe^{3+}	Zn^{2+}
1	0.0	0.0	20.0	0.0	17.2	36.8	12.9
4.01	14.1	2.3	26.5	0.0	56.3	27.3	1.1
6.86	0	9.5	4.0	10.1	98.3	47.3	40.9
Distilled water	80.5	0.0	64.7	40.2	99.9	64.7	71.8
8.40	75.0	67.3	81.3	*	*	*	83.2

* – precipitation by hydrolysis of the salts of the corresponding metals was observed.

Experimental Conditions: 0.1 g Sorbent Mass, Volume of Solutions – 25 mL, m^0_{Me} – 100 mcg.

salts). But, as one can see, the quantitative adsorption recorded only for ions Pb(II) in neutral aqueous medium. In an acidic environment (0.1 M HCl) the synthesized composite was not stable and partial flushing of the immobilized polymer into solution was observed.

Adsorption isotherms of all metals studied have the same shape (Figure 5.6.), which is typical for chelating modified silica [15].One can make a preliminary conclusion that the adsorption capacityfor research synthesized composite transition metal ion complexation of due process aminostyrene nitrogen and oxygen atoms methacrylic acid.

An investigation of the degree dependence of adsorption of transition metals ions upon contact time in static mode (Figure 5.7) shows that all ions are adsorbed most instantly thus indirectly confirming the complexation mechanism of adsorption.

However, calculations of adsorption capacity of the synthesized composite made on the basis of adsorption isotherms, suggest (Table 5.2) that only for ions of Pb(II), Mn(II) and Fe(III) adsorption capacity of the synthesized composite is several times more than the adsorption capacity of source silica gel.

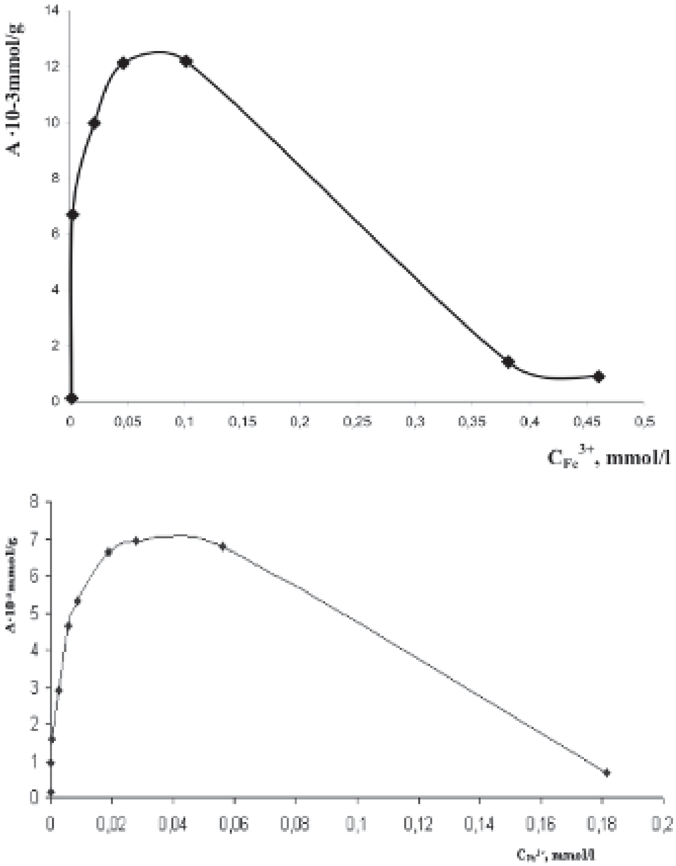


FIGURE 5.6 Adsorption isotherms of ions Fe(III) (a) and Pb(II) (b) on silica gel immobilized with copolymer of 4-aminostyrene and methacrylic acid from aqueous solutions of their nitrates (without addition of buffer solutions).

TABLE 5.2 Adsorption Capacity of the Synthesized Composite

Cation	**Sorption capacity**			
	Source silica gel		**Composite**	
	mmol/g	**mg/g**	**mmol/g**	**mg/g**
Mn(II)	0.010	0.55	0.020	1.10
Fe(III)	0.008	0.45	0.012	0.70
Pb(II)	0.002	0.41	0.007	1.45
Ni(II)	0.008	0.47	0.008	0.47

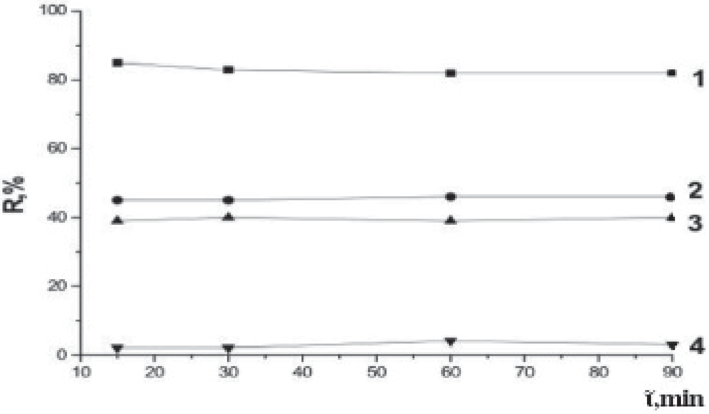


FIGURE 5.7 Dependence degree of adsorption of aqueous complexes Pb^{2+}(1), Cd^{2+}(2), Mn^{2+}(3), CO_2^{+}(4) (Terms of experiment: sorbent mass, 0.1 g volume of solutions, −20 mL, m^0Me – 80 mg).

5.4 CONCLUSIONS

A new organic composite material has been synthesized by *in situ* immobilization of 4 aminostyrene and methacrylic acid copolymer on the surface of silica. The fact of heterophase polymerization has been confirmed by H^1NMR, IR and mass spectrometry. According to H^1 NMR it has been found that the ratio of 4-aminostyrene and methacrylic acid containedin the copolymer immobilized on the surface of silica is about 4:1. It has been found due to the results of thermo graphic analysis that in the synthesized composite is 10.5wt.% of copolymer. A comparison of the adsorption-desorption isotherms of nitrogen and source silica gel and composite shows that immobilized copolymer has virtually no effect on the structure of the surface layer of silica gel. Adsorption activity of the synthesized composite for micro-ions of Pb(II), Mn(II) and Fe (III) in a neutral aqueous medium has been observed.

KEYWORDS

- **4-aminostyrene and methacrylic acid copolymer**
- **adsorption properties**
- **in situ immobilization**
- **metal complexes**
- **modified silica**

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