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# New organo-mineral materials based on silica gels modified *in situ* with nitrogen-containing polymers: synthesis and adsorption properties for Pb(II), Cu(II), Cd(II), and Fe(III) ions

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## ABSTRACT

Three new organo-mineral composite materials were obtained by *in situ* immobilization of polymers containing azo-, nitro-, and oxyquinoline groups in various combinations on the surface of silica gel. The fact of modification of the silica gel surface by nitrogen-containing polymers was confirmed by IR spectroscopy and thermogravimetric analysis combined with mass spectrometry. The SEM-photo analysis of the surface of the synthesized composites allows us to state that all *in situ* immobilized polymers are on the surface of silica gel in the form of individual convex formations that practically do not affect the structure of the original silica gel. Regarding Fe(III) cations, all composites showed an increase in sorption capacity by 4.5–6.4 times compared to the original silica gel and did not reveal additional sorption activity compared to the original silica gel for Cd(II) and Pb(II) ions. Regarding Cu(II) ions, an increase in the sorption capacity by more than five times compared to the original silica gel was observed for the composite *with in situ* immobilized poly-5-(4-nitro)-phenylazo-8-methacryloxyquinoline only.

## KEYWORDS

Adsorption; Cd(II); composite; Cu(II); Fe(III) ions; immobilization; *in situ*; Pb(II); poly [5-(p-nitrophenylazo)-8-methacryloxyquinoline]; silica gel

## Introduction

One of the promising ways to create organo-mineral composite materials with valuable adsorption properties for transition metal ions, but at the same time the least researched way of immobilizing polymers on solid surfaces, is *in situ* immobilization. *In situ* immobilization consists in the direct formation of an immobilized polymer layer in the presence of inorganic carrier particles [1–4]. Its advantages compared to the physical adsorption of pre-synthesized polymers on the surface of an inorganic carrier are:

- optimal (both energetically and geometrically) location of polymer macromolecules on a solid surface, which strengthens the fixation of the polymer on the

inorganic carrier and thereby creates additional opportunities for regeneration processes during repeated use of such a composite material as an adsorbent;

- the possibility of self-organization of polymer chains into supramolecular structures on the surface of an inorganic carrier, the presence of which increases the adsorption capacity of the composite;
- in the case of fixing copolymers - the possibility of synthesis on a solid surface of copolymers with such a ratio of components that cannot be achieved by synthesis in a homogeneous medium [5–8].

*In situ* polymerization includes two interconnected processes: the chemical process is the growth of macromolecules and the physical process is the self-assembly of growing chains into complex supramolecular structures. As a result, a certain ordered polymer layer is formed, which is strongly adsorbed on the surface of the carrier [9].

Compared to the chemical fixation of pre-synthesized polymers, *in situ* immobilization is characterized by the absence on the solid surface of the carrier of the remains of low-molecular compounds that were used as bridging groups between the inorganic carrier and the polymer. The possibility of varying the reaction parameters to obtain a product with given properties, the simplicity of synthesis and the ability to scale for industrial use are among the main advantages of this method [8].

Modification of the surface of silica gels with polymers with azo-, nitro-, and oxyquinoline groups in structural links made it possible to obtain sorbents with complexing properties that effectively remove cations of transition toxic metals from wastewater [9–13].

This work is devoted to the *in situ* modification of the silica gel surface with new polymers that simultaneously contain azo-, nitro-, and oxyquinoline groups in the structural units in various combinations: polymethacryl-[4-((E)-{4-[(E)-(4-nitrophenyl) diazenyl]phenyl} diazenyl)phenyl]-amine, polymethacryl-1-[4-((E)-{4-[(E)-(4-aminophenyl) diazenyl]phenyl} diazenyl)phenyl]ethanone and poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline, the investigation of changes in the surface structure of silica gel after the immobilization of selected polymers and the study of the adsorption properties of the synthesized materials with respect to Pb(II), Cu(II) and Fe(III) ions.

## Experimental

### Materials

#### Composite syntheses

Silica gel (fraction of 0.2–0.5 mm diameter particles, Merck) was used as the inorganic carrier of the composite. Characteristics of the silica gel surface are given in Table 1.

The synthesis of 5-(4-nitro)phenylazo-8-methacryloxyquinoline (AzoQN) was carried out by the reaction of acylation with methacrylic acid chloride in the presence of triethylamine as a hydrogen chloride acceptor in tetrahydrofuran according to the following procedure:

14.7 g (0.05 mol) of the dye was dissolved in 100 ml of dry tetrahydrofuran (THF), introduced into a flat-bottom flask with a volume of 250 ml, and 10.1 g (0.1 mol) (13.9 ml) of triethylamine (TEA) was added. The mixture was intensively stirred and

**Table 1.** Comparative characteristics of the surface parameters of the synthesized composites and the original silica gel.

Sample	$S_{sp}$ , m <sup>2</sup> /g			Average pore volume, cm <sup>3</sup> /g (BJH)	Average pore size, nm (BJH)
	According to the isotherm	BET	Langmuir		
Composite 1	131	141	217	0,24	6,70
Composite 2	113	123	188	0,22	7,01
Composite 3	335	349	522	0,61	7,03
Original silica gel [14]	447	463	687	0,69	5,90

cooled to 0 °C, gradually over 30 min, a solution of methacrylic acid chloride (9.7 ml in 10 ml of THF) was added dropwise. After that, the reaction mixture was stirred for another 3 h until the color changed from red to orange, and then left for a day. After a day, the synthesized monomer was thoroughly washed with water and left again for a day. Then it was filtered and dried. Monomer yield –12.52 g.

The fact of monomer formation was confirmed by NMR spectroscopy: <sup>1</sup>H NMR (DMSO):  $\delta$  7.483–7.593(t, 3H), 8.850–7.849 (s, 2H), 2.110(s, 3H), 3.136 – 2.490 (d, 2H), 5.85 (s, 1H), 6.4 (s, 1H).

The synthesis of methacryl-[4-((E)-{4-[(E)-(4-nitrophenyl)] diazenyl}phenyl)diazenyl]phenyl]-amine (BAZON), methacryl-1-[4-((E)-{4-[(E)-(4-aminophenyl) diazenyl]phenyl}diazenyl)phenyl]ethanone (BAZOM) was carried out according to the above similar procedure.

The fact of the formation of BAZON was confirmed by NMR spectroscopy: <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$  10.2 (s, 1H), 8.1 (d, 2H), 7.9 (d, 2H), 7.85 (m, 4H), 7.5 (m, 4H), 5.8 (s, 1H), 5.5 (s, 1H), 1.97 (s, 3H).

The fact of the formation of BAZOM was confirmed by NMR spectroscopy: <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$  9.9 (s, 1H), 7.8 (m, 6H), 7.5 (m, 6H), 7.4 (s, 1H), 5.8 (m, 1H), 5.6 (s, 1H), 5.5 (S, 1H), 2.2 (s, 3H).

*In situ* immobilization of the synthesized monomers 1–3 on the surface of silica gel was carried out by radical polymerization using azoisobutylnitrile (AIBN) as an initiator in tetrahydrofuran according to the following method:

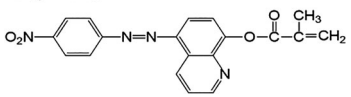
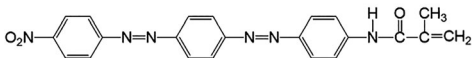
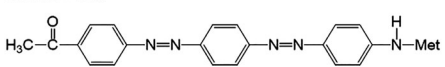
4.17 g of monomer, 12.52 g of silica gel (in the mass ratio of monomer to inorganic matrix as 1:3) and 0.209 g of AIBN (5% by weight of monomer) were added to a 250 ml flat-bottomed flask, 100 ml of pure dry THF was added and the reaction mixture was stirred using a magnetic stirrer, periodically passing argon through it. Next, the mixture was heated with intensive stirring to 60–65 °C for 6 h.

The abbreviated names of the synthesized composites are presented in Table 2.

## Methods

FTIR spectra of the samples of composite and the original silica gel were recorded using an IR spectrometer with Fourier transformation (Thermo Nicolet Nexus FT-IR, USA). For this purpose, the samples were ground in an agate mortar and pressed with KBr. The FTIR spectra were recorded in the spectral range of 500–4000 cm<sup>-1</sup> with 16 scans per spectrum at a resolution of 4 cm<sup>-1</sup>.

**Table 2.** The abbreviated names of the synthesized composites.

N monomer and composite	The structural formula of the monomer	Abbreviated name of the synthesized composite
1	<p>AzoQN + SiO<sub>2</sub></p> 	SiO <sub>2</sub> ] -AzoQN
2	<p>BAZON + SiO<sub>2</sub></p> 	SiO <sub>2</sub> ] -BAZON
3	<p>BAZOM + SiO<sub>2</sub></p> 	SiO <sub>2</sub> ] -BAZOM

### Thermal analysis

The amount of immobilized polymer on the surface of the silica gel was evaluated by thermogravimetric analysis, which were obtained on a 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 an instrument "STA 449 Jupiter F1" (Netzsch, Germany) with a mass spectroscopic attachment "QMS 403 C" (Germany).

### Low-temperature adsorption-desorption of nitrogen

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

### Surface morphology analysis

The surface morphology of composite was observed by using a scanning electron microscope (SEM, LEO 1430VP, Carl Zeiss, Germany).

### Description of adsorption processes

Properties of the obtained composite to adsorb Cu(II), Pb(II), Cd(II), Fe(III) were studied in static mode. Working solutions of nitrates of the corresponding metals were pre-prepared in volumetric flasks of 25 or 50 ml, diluting aliquots of the standard sample solutions with distilled water, and then pouring them into flat-bottomed flasks with 0.1 g of adsorbent.

The reaction was proceeding while the flasks were shaken mechanically. Equilibrium concentrations of ions were measured using atomic absorption methods.

Working nitrate solutions of Cu(II), Pb(II), Cd(II), Fe(III) are prepared with the sets of "standard sample solutions" of these salts on 1 M HNO<sub>3</sub> background (produced by A.V. Bogatsky FHI in Odesa) with concentrations of 1 and 10 mg/ml.

### Analysis of ion concentrations

Sorption capacity ( $A$ ) was calculated by formula (1):

$$A = (c_0 - [M])V/m \quad (1)$$

where  $c_0$  – is concentration of the metal in the starting solution,  $[M]$  – is concentration of the metal at equilibrium,  $V$  – is the volume of the starting solution,  $m$  – is mass of the composite.

Atomic Absorption Spectrophotometer "Saturn" (Ukraine) with air–propane– butane flame was used to measure equilibrium concentration of copper (II), cadmium (II), lead (II), iron (III). Equilibrium concentration in solutions were calculated comparing intensities of spectral lines with those for standard solutions. Maxima wavelengths were: 324.7 nm for Cu(II), 228.8 nm – for Cd(II), 283.3 nm – for Pb(II), 248.3 nm – for Fe(III), aperture being 0.5 cm wide.

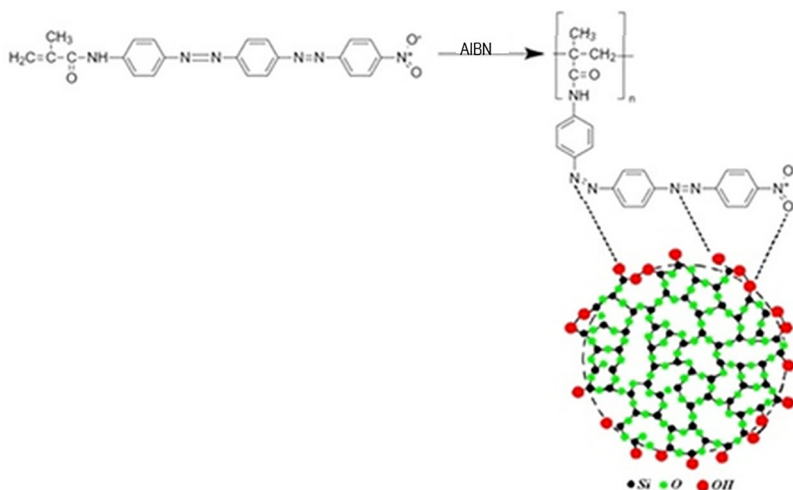
### Results and discussion

The chemical structure of *in situ* polymer immobilization methacrylic-[4-((E)-{4-[(E)-(4-nitrophenyl)diazenyl]phenyl}diazenyl)phenyl]amine on the silica surface could be presented as follows (Fig. 1) for example:

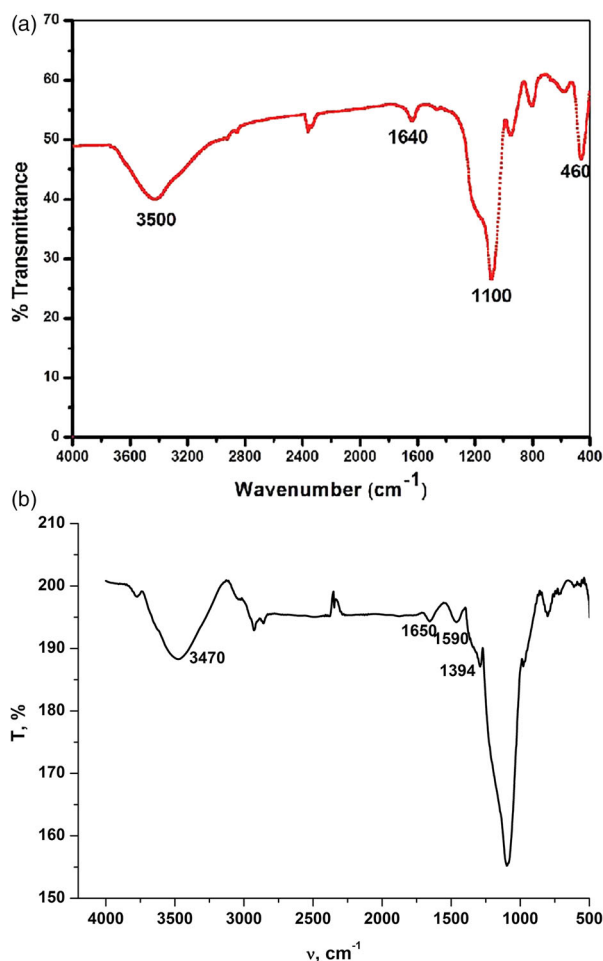
The fact of *in situ* immobilization of the selected polymers on the silica gel surface was confirmed by comparative analysis of the IR spectra of the original silica gel and the synthesized composites.

Examples of IR spectra of the original silica gel and the SiO<sub>2</sub>-AzoQN composite synthesized on its basis are shown in Fig. 2a,b. As can be seen from Figure 2b, the spectrum region from 1200 to 1800 cm<sup>-1</sup> is the most informative for confirming the presence of poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline in the surface layer of silica gel. The absorption bands ent in this region can be interpreted as follows:

- absorption bands at 1280 and 1300 cm<sup>-1</sup> correspond to valence and deformation vibrations of C-H bonds;



**Figure 1.** Scheme of *in situ* immobilization of polymethacrylic-[4-((E)-{4-[(E)-(4-nitrophenyl)diazenyl]phenyl}diazenyl)phenyl]amine (BAZON) on the silica gel surface.



**Figure 2.** IR spectra of the original silica gel (a) and the SiO<sub>2</sub>]-AzoQN composite (b) synthesized on its basis.

- absorption bands in the interval from 1394 to 1503 cm<sup>-1</sup> correspond to skeletal vibrations of C-C bonds, the valence vibrations of the C-H bonds in the aromatic ring with maxima at 3470, 3370, cm<sup>-1</sup> of the quinoline aromatic system;
- the vibrational absorption band at 1590 cm<sup>-1</sup> can be attributed to valence vibrations of C-N bonds;
- the absorption band at 1650 cm<sup>-1</sup> refers to asymmetric vibrations of NO<sub>2</sub> groups,
- the absorption band at 1760 cm<sup>-1</sup> belongs to valence vibrations of COO groups.

The presence of these absorption bands in the IR spectrum of the synthesized composite can be evidence of the presence of poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline in its composition.

Thermograms of the original silica gel and the composites synthesized on its basis are shown in Figs. 3–6, respectively. As can be seen from Figs. 4–6, the maximum thermal destruction of immobilized polymers occurs in the temperature range from 200 to 550 °C.

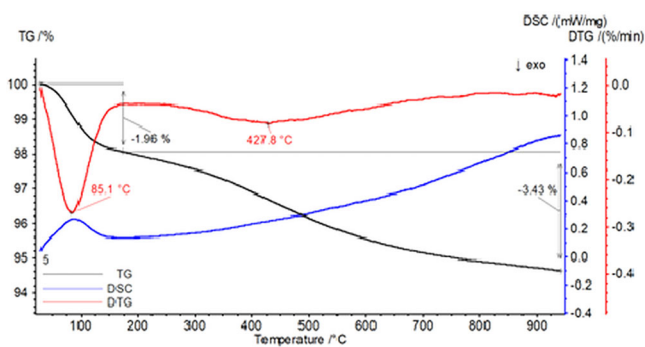


Figure 3. Thermogram of the original silica gel.

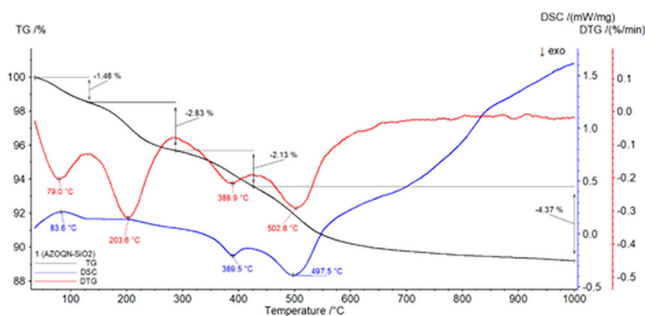


Figure 4. Thermogram of composite 1 (SiO<sub>2</sub>]-AzoQN).

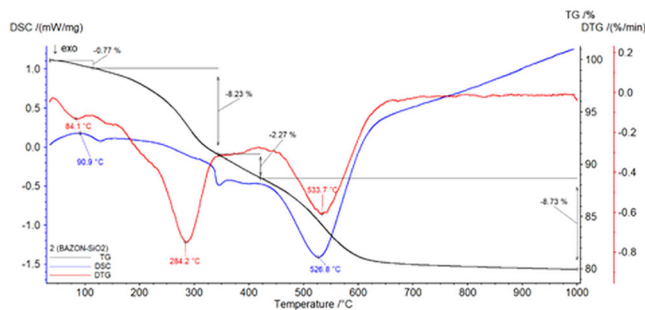


Figure 5. Thermogram of composite 2 (SiO<sub>2</sub>]-BAZON).

Fig. 3 shows that the mass loss of the original silica gel in this temperature range is 2.0%. Analysis of the thermogram of the SiO<sub>2</sub>]-AzoQN composite (Fig. 4) showed that the mass loss in the temperature range from 200 to 550 °C is 6.2%. Therefore, the mass fraction of *in situ* immobilized polymer in the synthesized composite 1 is 4.2%. Comparing the thermograms of composites 2 (Fig. 5) and 3 (Fig. 6) with the thermogram of the original silica gel makes it possible to state that the mass fraction of BAZON polymer in the composition of composite 2 is 13.6%, and composite 3 contains 3.0% in its composition polymer BAZOM.

In order to determine the products of thermal destruction of polymers immobilized on the surface of silica gel, thermograms of synthesized composites combined with



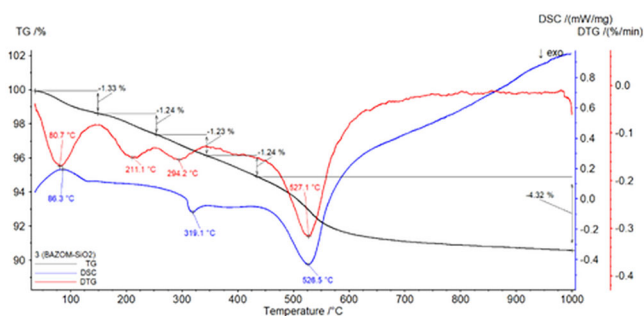


Figure 6. Thermogram of composite 3 (SiO<sub>2</sub>]-BAZOM).

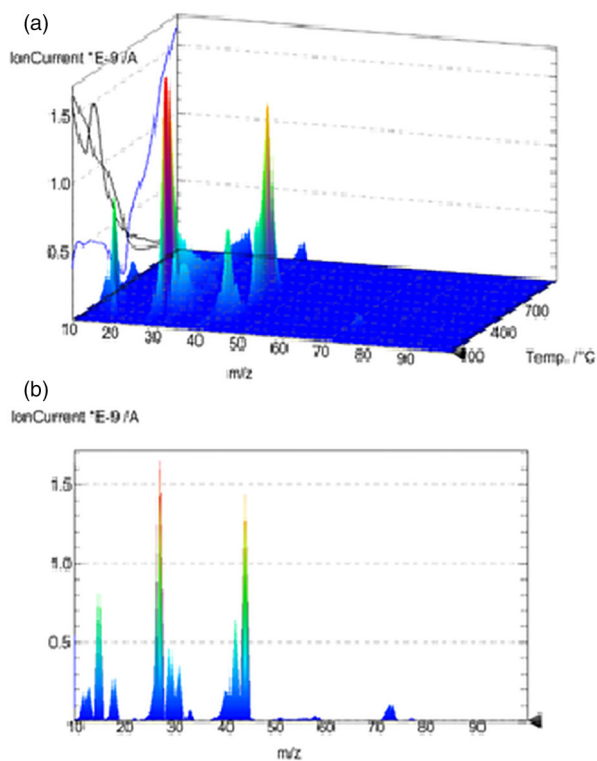
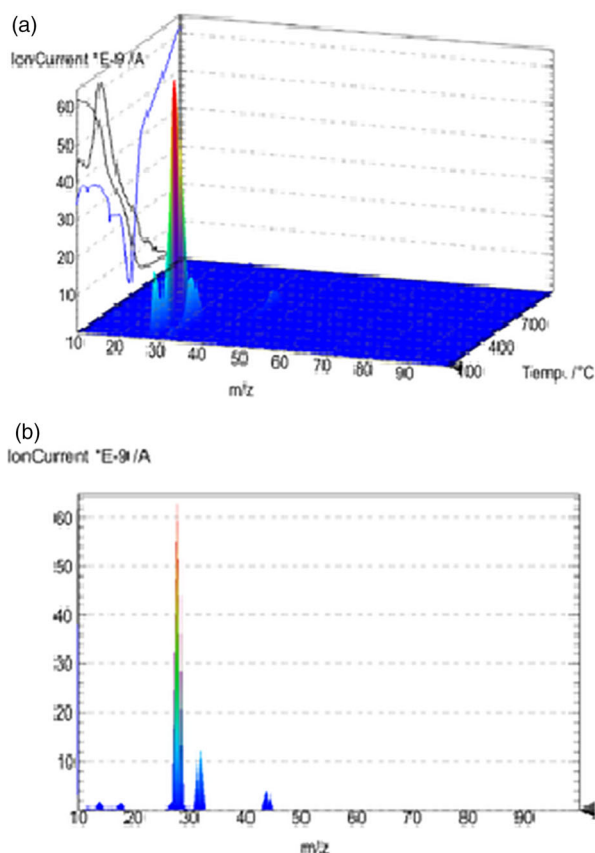


Figure 7. TG-MS-3D (a) and MS-2D (b) of synthesized composite 1.

mass spectra were obtained in 3D format (Figs. 7–9) and a number of their mass spectra at different temperatures in 2D format.

The thermogram, combined with the mass spectrum, of composite 1 (at a temperature of 498 °C) is presented in Fig. 7, has four main peaks corresponding to the masses 14, 18, 28, 44. They indicate the thermal destruction of the polymer with the splitting of the extreme CH<sub>2</sub>- groups, water molecules, the formation of CO and N<sub>2</sub> (its formation is indicated by a slight peak at 76, which corresponds to the cleavage of phenylene C<sub>6</sub>H<sub>4</sub>-) and the release of carbon dioxide.



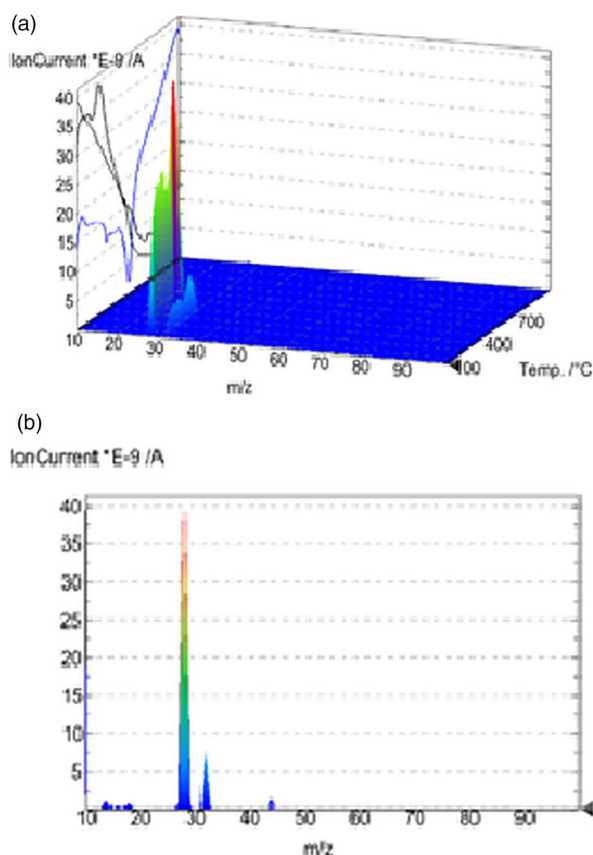
**Figure 8.** TG-MS-3D (a) and MS-2D (b) of synthesized composite 2.

As follows from Figs. 8, 9 and the analysis of the obtained mass spectra of composites 2 and 3, the composition of the products of thermal destruction of the BAZON and BAZOM polymers immobilized on the surface of silica gel is different from the thermal destruction of the AzoQN polymer in the composition of composite 1, and has three peaks: an intense peak at mass 28 – corresponds only to the formation of CO, the peak at 32 indicating the release of molecular oxygen and the minor peak at 44 indicating the release of carbon dioxide, respectively.

The surface parameters of the synthesized composites and the original silica gel [14] are shown in Table 1. The values of the specific surface area were obtained by computer processing of the data of low-temperature nitrogen adsorption-desorption isotherms by various methods. The average volume and pore size of the surfaces were calculated from the pore distribution diagrams.

After analyzing the data in Table 1, the following generalizations can be made:

- The specific surface area of silica gel after *in situ* modification with selected polymers decreases approximately 3.3 times for composite 1, 3.8 times – for composite 2 and 1.3 times – for composite 3. The logical result is the fact of the strongest decrease in specific area of the silica gel surface in composite 2, since



**Figure 9.** TG-MS-3D (a) and MS-2D (b) of synthesized composite 3.

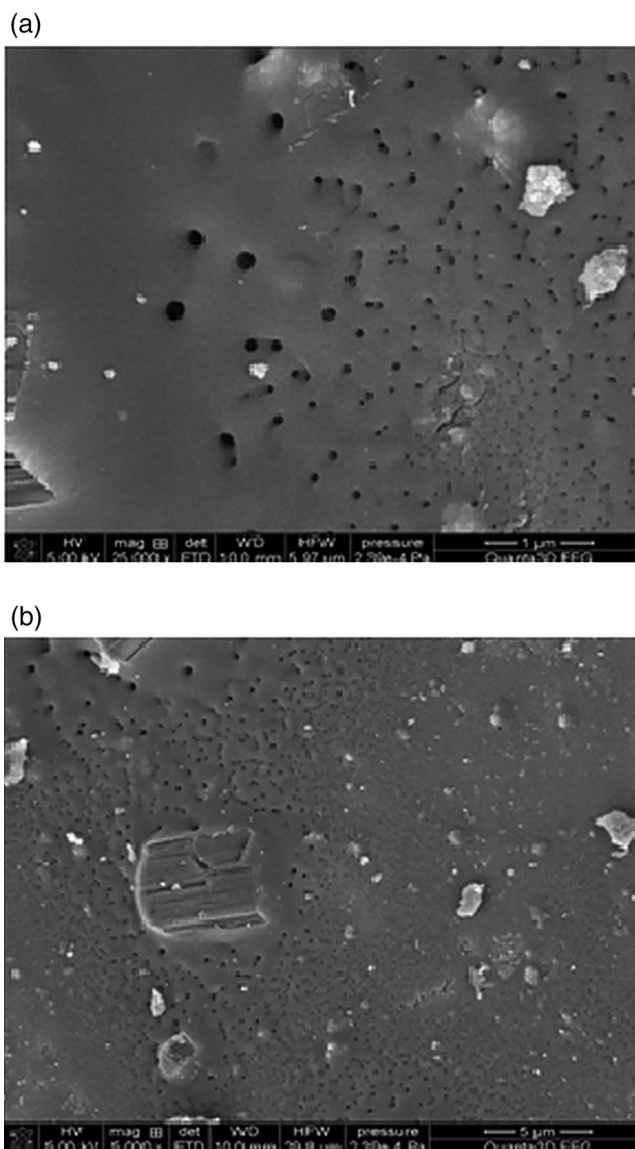
its composition contains the largest amount (14.6%) of non-porous polymer and, conversely, the smallest change in the value of the specific surface area for composite 3 with the smallest (4%) mass of immobilized polymer. Thus, the results of thermogravimetric analysis and the low-temperature nitrogen adsorption-desorption method correlate well with each other.

- The average pore volume of the synthesized composites decreases according to the same pattern as the specific surface area and, apparently, due to similar reasons: for composite 1 by 2.9 times, for composite 2 by 3.1 times, for composite 3 – only 1.13 times.

At the same time, there is a slight increase in the average pore size of all composites compared to the original silica gel: an average of 1.2 times for composites 2 and 3, and for composite one such an increase is only 1.13 times.

Recorded changes in the surface parameters of the original silica gel indicate that polymer modification only "smoothes out" its porosity, simultaneously reducing the depth of the pores and slightly expanding them.

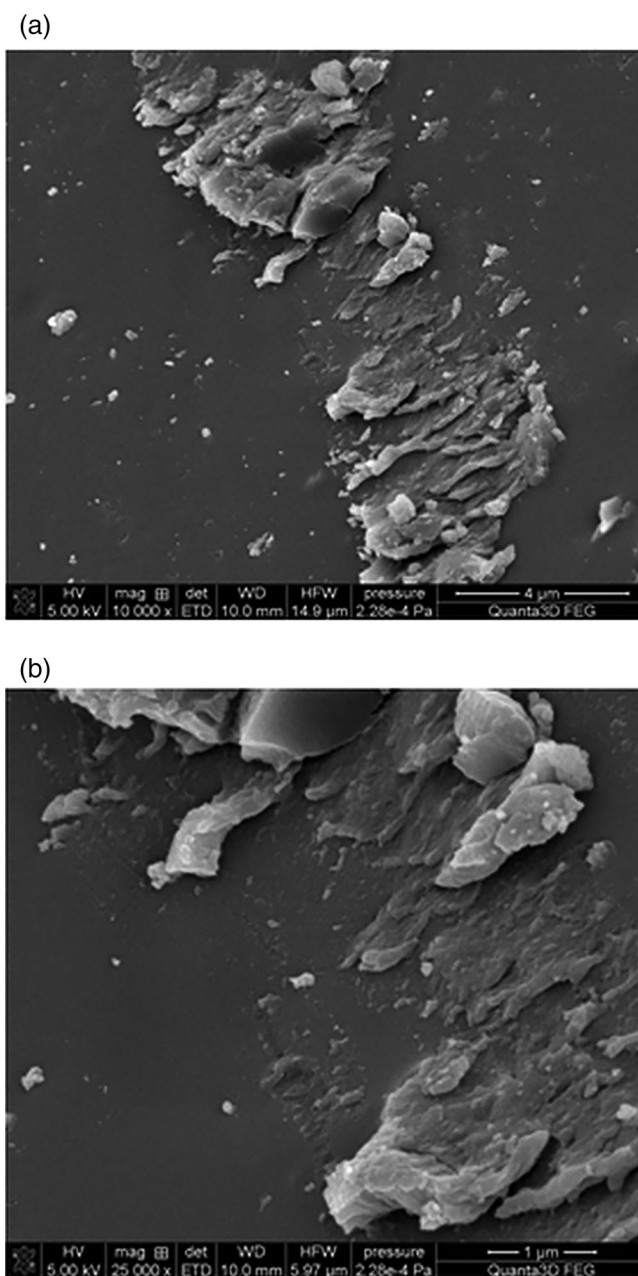
Changes in the surface morphology of composites 1–3 were investigated using scanning electron microscopy (SEM). SEM photo of the surface of composite one is shown in Fig. 10(a,b), of composite 2 – in Fig. 11(a, b), composite 3 – in Fig. 12(a, b).



**Figure 10.** SEM image of the SiO<sub>2</sub>-AzoQN surface (a - increase 25,000 $\times$ , b - increase 5,000 $\times$ ).

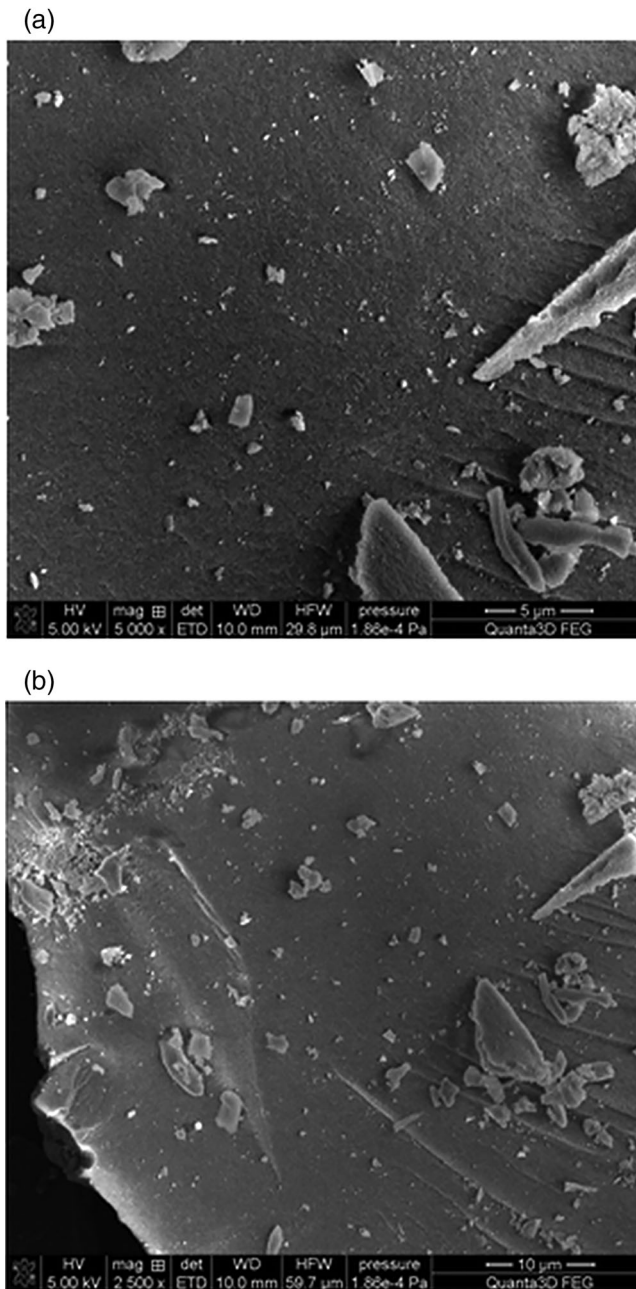
The analysis of SEM photographs (Figs. 10–12) of the surface of the synthesized composites allows us to state that all *in situ* immobilized polymers are on the surface of silica gel in the form of individual convex formations that were actively formed on the irregularities of the silica gel surface [15]. This form explains their insignificant influence on the surface structure of silica gel. A similar shape of polymers of different chemical nature is most likely the result of the chosen method of heterogeneous polymerization - *in situ* polymerization.

In the initial working solutions, Cu(II), Cd(II), Pb(II) and Fe(III) ions are mainly in the form of aqua complexes of the composition  $[\text{Cd}(\text{H}_2\text{O})_4]^{2+}$ ,  $[\text{Pb}(\text{H}_2\text{O})_4]^{2+}$ ,  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ . Since *in situ* immobilized polymers on the surface of



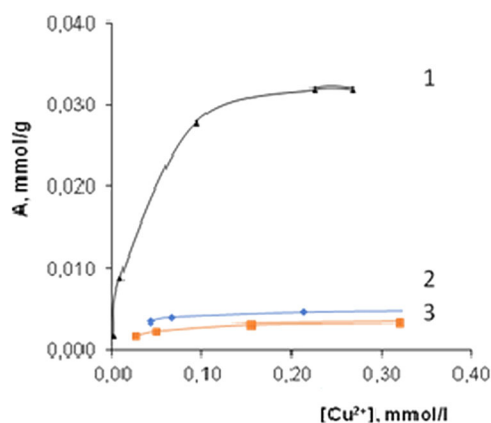
**Figure 11.** SEM image of the SiO<sub>2</sub>]-BAZON surface (a - increase 10,000×, b - increase 25,000×).

silica gel in their structural links contain active nitrogen-containing centers to participate in complex formation – azo group, quinoline or amino group, when in contact with aqua complexes of selected metals, processes of replacement of one aqua group in the aqua complex with a nitrogen atom of azo group, quinoline or amino groups can occur with the formation of various ligand complexes. The reason for this phenomenon is the greater affinity of the selected ions to nitrogen atoms compared to oxygen atoms in complexation processes.

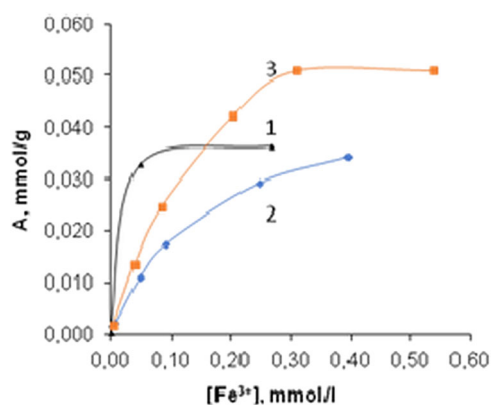


**Figure 12.** SEM image of the SiO<sub>2</sub>]-BAZOM surface (a - increase 5,000×, b - increase 2,500×).

Despite the similar shape and arrangement of polymers on the surface of silica gel, the adsorption properties of the synthesized composites with respect to the studied metal ions differ significantly. For example, in Figs. 13, 14 show isotherms of sorption of Cu(II) and Fe(III) ions from aqueous solutions of nitrates of these metals without the addition of buffers on the surface of all synthesized materials in the static mode of sorption.



**Figure 13.** Sorption isotherm of Cu(II) ions from aqueous nitrate solutions (without adding buffer solutions) on the surface of synthesized composites 1–3 in static mode, sorption time –1 day. The number of the curve coincides with the number of the composite.



**Figure 14.** Sorption isotherm of Fe(III) ions from aqueous nitrate solutions (without adding buffer solutions) on the surface of synthesized composites 1–3 in static mode, sorption time –1 day. The number of the curve coincides with the number of the composite.

**Table 3.** Comparison of the sorption capacity of the original silica gel and synthesized composites with respect to Cu(II), Cd(II), Pb(II) and Fe(III) ions.

Ion	Sorption capacity, mmol/g			
	Original silica gel	Composite 1 SiO <sub>2</sub> -AzoQN	Composite 2 SiO <sub>2</sub> -BAZON	Composite 3 SiO <sub>2</sub> -BAZOM
Cu(II)	0,006 [14]	0,032	0,005	0,003
Cd(II)	0,006 [14]	0,006	0,006	0,006
Pb(II)	0,002 [14]	0,002	0,002	0,003
Fe(III)	0,008 [14]	0,036	0,034	0,051

As follows from these figures, the given sorption isotherms belong to the 2L-type and allow us to unambiguously establish the value of the sorption capacity for each of the investigated ions. Table 3 shows the results of comparing the values of the sorption

capacity of the original silica gel [14] and the composites synthesized on its basis, which were established from the corresponding sorption isotherms.

The data in Table 3 allow us to assert that

- with regard to copper (II) cations, the synthesized composite 1 has the highest sorption capacity, and in situ immobilization of the AzoQN polymer on the surface of silica gel, which has azo and quinoline groups in its composition, increases the sorption capacity of the original silica gel by more than 5 times;
- in relation to lead (II) and cadmium (II) cations, the synthesized composites do not show additional sorption activity in comparison with the original silica gel. The obtained result can be explained by the fact that these metal ions more easily form complexes with "soft" oxygen-containing and chalcogen-containing ligands than with nitrogen-containing ones [16];
- with regard to Fe(III) cations, all composites showed an increase in sorption capacity: composites 1 and 2 – about 4.5 times, composite 3 – 6.4 times compared to the original silica gel.

The obtained results allow us to draw a preliminary conclusion that the increase in the sorption capacity of the synthesized composites in comparison with the original silica gel occurs as a result of complexation processes of the investigated metal ions with polymers immobilized on its surface mainly through nitrogen atoms in their composition, since the affinity of Cu(II) and Fe(III) ions for nitrogen atoms is greater than that of Cd(II) and Pb(II), the sorption capacity of the synthesized sorbents for Cu(II) and Fe(III) ions is also higher.

## Conclusions

In summary, silica gel was functionalized with polymers to improve the adsorption behavior toward Pb(II), Cu(II), Cd(II), and Fe(III) ions.

Three new organo-mineral composite materials were obtained by *in situ* immobilization of polymers containing azo-, nitro-, and oxyquinoline groups in various combinations on the surface of silica gel. The fact of modification of the silica gel surface by nitrogen-containing polymers was confirmed by IR spectroscopy and thermogravimetric analysis combined with mass spectrometry.

According to the results of thermogravimetric analysis, the mass fractions of *in situ* immobilized polymers in the synthesized composites were established, which are within 4–15 wt.%.

Changes in the values of specific surface area, average diameter, and pore volume obtained by computer processing of low-temperature nitrogen adsorption-desorption isotherm data by various methods indicate that in situ modification of the silica gel surface with selected polymers does not affect its surface structure but only "smoothes out" its porosity.

SEM-photo analysis of the surface of the synthesized composites allows us to state that all in situ immobilized polymers are on the surface of silica gel in the form of individual convex formations that were actively formed on the irregularities of the silica gel surface.



It was found that all the composites showed an increase in sorption capacity by 4.5–6.4 times compared to the original silica gel for Fe(III) cations and did not reveal additional sorption activity for Cd(II) and Pb(II) ions. Regarding Cu(II) ions, an increase in the sorption capacity by more than five times compared to the original silica gel was observed only for the composite with *in situ* immobilized poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline.

The present study revealed that new organo-mineral composite materials were obtained by *in situ* immobilization of polymers on the surface of silica gel are promising materials for the removal of Fe(III) and Cu(II) ions from wastewater.

## Disclosure statement

The authors report there are no competing interests to declare.

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## Data availability statement

The authors declare that the data supporting the findings of this study are available within the article.

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