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Silica based on inorganic–polymer hybrid materials for removing toxic ions from wastewater

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ABSTRACT

As a result of the adsorption of copolymer 5-(4-nitro)phenylazo-8-methacryloxyquinoline with methyl methacrylate on the surface of mesoporous silica gel, a new polymer-inorganic composite material was obtained. Based on the comparison of the sorption capacity of the synthesized composite and the composite based on silica gel with in situ immobilized poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline, it was concluded that the method of in situ immobilization of complex-forming polymers on the surface of silica gel is more effective compared to their physical adsorption.

KEYWORDS

Adsorption; Cd(II) ions; composite; Cu(II); Fe(III); Pb(II); silica gel; the copolymer of 5-(4'-nitro)-phenylazo-8-methacryloxyquinoline with methyl methacrylate

Introduction

Immobilization of polyfunctional polymers, which can exhibit complexing and ion-exchange properties, on the surface of porous inorganic matrices increases the efficiency of their use as sorbents for ions of transition toxic metals. Such polyfunctional polymers include polyelectrolytes with a quaternary nitrogen atom in the side chain (polycations) or in the main chain (polyionenes), in particular, such as polyhexamethyleneguanidine, its derivatives, polyaniline, polyacrylic acid [1–8]. But the ion-exchange properties of these polymers are significantly greater than the complex-forming ones, so sorbents based on them can remove mainly anionic forms of multivalent metals (molybdates, tungstates, chromates and dichromates, etc.) or acidic residues of mineral acids (in particular, nitrates, phosphates, arsenates) from wastewater and are characterized by a low sorption capacity for cations of transition metals. Therefore, the search for composite materials, which include polymers with purely complexing properties, which are capable of removing cationic forms of toxic metals by complexing them with active (amino-, azo-, oxoquinoline, pyridine, mercapto-, etc.) groups in the composition of immobilized polymers on hard surface of minerals [9–11].

The method of physical fixation of a polymer on the surface of an inorganic carrier consists in the precipitation (adsorption) of previously synthesized polymer macromolecules from a solution. As a result, the polymer is fixed on the solid surface of the carrier

due to the formation of hydrogen or π - π bonds, electrostatic forces, van der Waals forces, etc. With this method, it is advisable to fix negatively charged polymers on the positively charged surface of the silica matrix. At the same time, the polymer is held on a solid surface due to electrostatic forces.

Undoubtedly, it is best to use natural porous minerals from deposits that are currently being industrially developed as inorganic matrices for such composite materials from an economic and ecological point of view. However, in order to understand the effectiveness of their use as sorbents for cations of transition toxic metals, it is necessary to first establish correlations between the chemical nature of the immobilized polymer (chemical activity of the structural units of the polymer in relation to participation in complexation processes), the method of fixing the polymer, and the geometric form of its placement on a solid surface. These factors significantly affect the availability of complexes-active centers of the immobilized polymer and its adsorption capacity for certain cationic forms of metals. For this purpose, it is advisable to first fix polymers capable of complex formation on porous inorganic materials with well-studied (known) surface parameters and minimal sorption capacity for cations of transition metals. Such matrices include, in particular, mesoporous silica gels [12–17].

In work [18], we showed that in situ immobilization of poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline in silica gel (SiO₂)-AzoQN) leads to a 5-fold increase in the sorption capacity of the synthesized composite for Cu(II) ions and Fe(III) by 4.5 times compared to the original silica gel.

This work is devoted to the synthesis, investigation of the surface structure and sorption properties for Cu²⁺, Cd²⁺, Pb²⁺, Fe³⁺ ions of a polymer-inorganic composite based on silica gel with an adsorbed copolymer of 5-(4-nitro)phenylazo-8-methacryloxyquinoline and methyl methacrylate with the initial molar ratio of 1:3.

Experimental

The synthesis of 5-(4-nitro)phenylazo-8-methacryloxyquinoline was carried out in three stages, similarly to that described in [11]. The copolymerization reaction of 5-(4-nitro)phenylazo-8-methacryloxyquinoline and methyl methacrylate was carried out at an initial ratio of reagents of 1:3 in tetrahydrofuran in the presence of a reaction initiator (AIBN). The synthesis method was as follows: 18.40 g (0.05 mol) of 5-(4-nitro)phenylazo-8-methacryloxyquinoline, 15.0 g (0.015 mol, 16.02 ml) of methyl methacrylate, 0.668 g of AIBN (2% of the total weight of monomers) were added to a 250 ml flat-bottomed flask and 150 ml of dry distilled tetrahydrofuran (THF). After that, the mixture was stirred on a magnetic stirrer while heating to 62–65 °C for 5 h, passing argon through the mixture. The finished copolymer solution was left for a day and after that it was precipitated in water, filtered and dried for several days to a constant mass. The weight of the product was 27.98 g.

Merck silica gel with a particle diameter of 0.2–0.5 mm was used as a porous inorganic base for the synthesis of the composite, the surface characteristics of which are shown in Table 1.

Adsorption of the synthesized copolymer on the silica gel surface was carried out as follows: 3.05 g of the copolymer was added to a flat-bottomed flask with a volume of

Table 1. Comparison of surface parameters of silica gel and composite SiO₂]–AzoQN-MMA.

Sample	Surface area, m ² /g			Average pore volume cm ³ /g (BJH)	Average pore size, nm (BJH)
	By isotherm	BET	Langmuir		
Original silica gel	447	463	687	0.686	5.92
Composite SiO ₂]–AzoQN-MMA	233	242	354	0.451	6.48

250 ml and dissolved in 35 ml of THF. 9.15 g of silica gel was added to the resulting solution, the mixture was heated to a temperature of 60 °C, intensively stirring on a magnetic stirrer for 5 h, passing argon through the reaction mixture. After a day, the synthesized composite was decanted on a filter and dried at a temperature of 18–20 °C for several days to a constant mass. The synthesized composite based on silica gel will be abbreviated as SiO₂]–AzoQN-MMA.

The IR spectra of the original and copolymer-modified silica gel were recorded on an IR spectrometer “Spectrum BX” (Perkin Elmer, Germany) in the range of 500–4000 cm^{−1} in KBr tablets.

The mass fraction of the immobilized copolymer in the synthesized composite was calculated based on thermogravimetric analysis data obtained on a synchronous TG/DTA analyzer “Shimadzu DTG-60 H” (Shimadzu, Japan) in the temperature range of 15–1000 °C. The sample heating rate was 10 degrees/min.

The value of the specific surface area and the average diameter of the pores on the surface of the synthesized composite and the original mineral were calculated from the data of low-temperature nitrogen adsorption/desorption isotherms using the sorbometer software “ASAP 2420 V1.01” (Micromeritics, USA). Before measurement, samples were degassed at 60 °C for 24 h.

The surface morphology of the original silica gel and the synthesized composite was studied by scanning electron microscopy using an electron microscope “SEM LEO 1430 VP” (Carl Zeiss, Germany).

Sorption properties of SiO₂]–AzoQN-MMA with respect to Cd(II), Cu(II), Pb(II) and Fe(III) ions were studied in static mode. At the same time, 0.1 g of the composite during the day was in contact with 25 ml of working solutions of nitrates of the corresponding metals of various concentrations with constant mechanical shaking. The equilibrium concentrations of metal ions were recorded by the atomic absorption method. Working solutions of nitrates of selected metals for conducting research on the sorption properties of modified silica gel were prepared from the sets of “Standard sample solutions” of these salts (produced by A. V. Bogatskyi FCI, Odesa) against a background of 1 M HNO₃ with concentrations of 1 and 10 mg/ml. The sorption capacity of the synthesized composites (A) was calculated according to the formula (1):

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

where C_o is the initial molar concentration of the metal, [M] is the equilibrium molar concentration of the metal, V is the volume of the working solution, m is the mass of the sorbent (g).

The equilibrium concentration of ions of the corresponding 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 an air-propane-butane mixture. The measurement wavelengths were: for

copper – 324.7 nm, cadmium – 288.8 nm, lead – 283.3 nm, ferrum – 248.3 nm, and the slit width was equal to 0.5 cm. The equilibrium concentrations in the solution were calculated by comparing the intensities of their lines in the spectrum with the intensities of the lines of standard solutions. For this, standard solutions with metal concentrations of 0.1–1.5 $\mu\text{g/ml}$ were prepared.

Results and discussion

The scheme of adsorption of the copolymer 5-(4-nitro)phenylazo-8-methacryloxyquinoline with methyl methacrylate on the silica gel surface is shown in Fig. 1.

The fact of fixing the copolymer of 5-(4-nitro)phenylazo-8-methacryloxyquinoline with methyl methacrylate on the surface of silica gel was confirmed by comparative analysis of the IR spectra of the synthesized copolymer, the original silica gel, and the synthesized composite, which are shown in Figs. 2a and b, respectively.

As can be seen from Fig. 2b, the most informative for confirming the presence of a copolymer of 5-(4-nitro)phenylazo-8-methacryloxyquinoline with methyl methacrylate in the surface layer of silica gel is the region of the spectrum from 1200 to 1800 cm^{-1} , in which the absorption bands can be interpreted as follows:

- the absorption band at 1198 cm^{-1} can be attributed to valence vibrations of the C–O bond;
- the absorption band at 1242 cm^{-1} corresponds to valence vibrations of the C–N bond;
- the absorption band in the region of 1340 cm^{-1} belongs to the valence vibrations of the NO_2 group of the quinoline aromatic system;
- the absorption band at 1499 cm^{-1} refers to the N=N bond.
- the absorption band at 1740 cm^{-1} can be attributed to valence vibrations of the C=O bond.

The presence of these absorption bands in the IR spectrum of the synthesized composite can be evidence of the presence of the selected copolymer in its composition.

In order to establish the patterns of thermal destruction of the adsorbed copolymer and determine its mass fraction in the composition of the composite, a

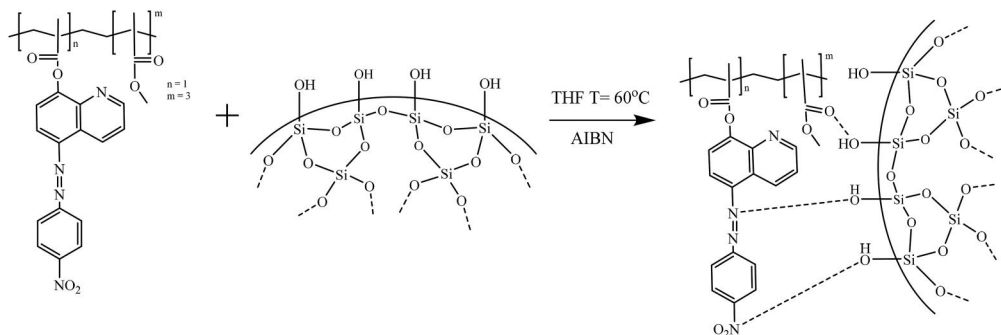


Figure 1. Scheme of the adsorption process of the copolymer 5-(4-nitro)phenylazo-8-methacryloxyquinoline with methyl methacrylate on the surface of silica gel.

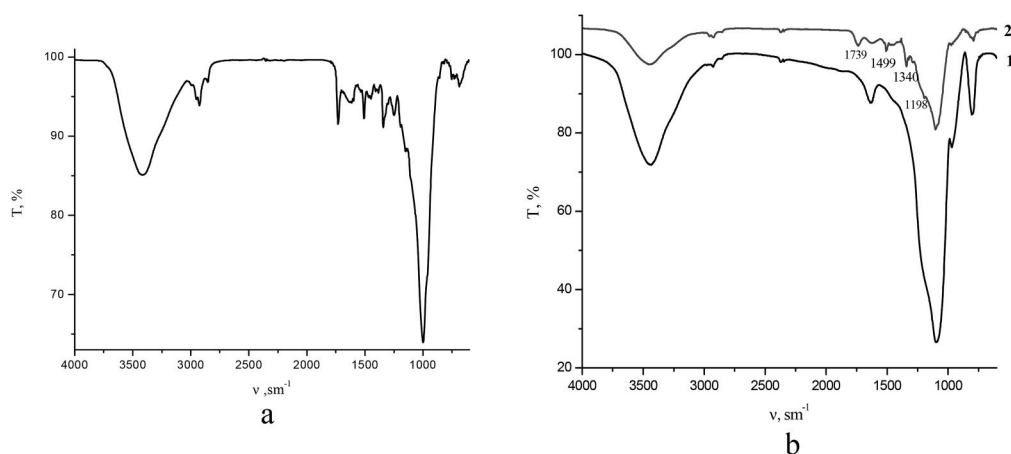


Figure 2. IR spectra of the copolymer 5-(4-nitro)phenylazo-8-methacryloxyquinoline with methyl methacrylate (2a), the original silica gel (curve 1) and the SiO₂]-AzoQN-MMA composite synthesized on its basis (curve 2) (2b).

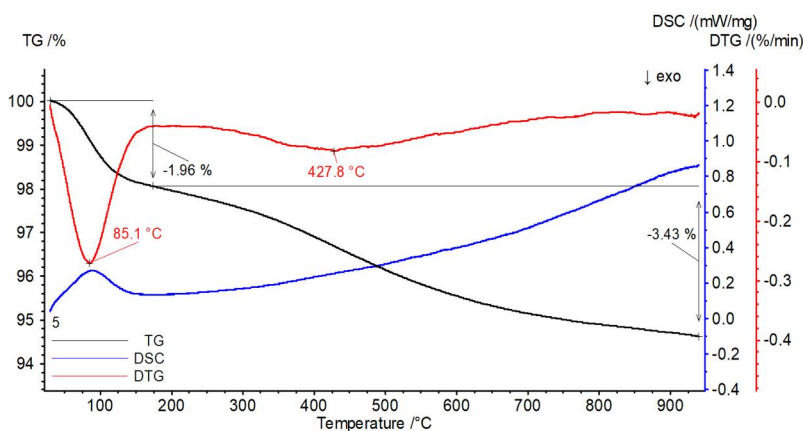


Figure 3. Thermogram of the original silica gel.

thermogravimetric analysis of the synthesized composite and the original silica gel was carried out. The resulting thermograms are shown in Figs. 3 and 4.

As can be seen from Fig. 4, thermal destruction of the fixed copolymer occurs in the temperature range from 190 to 550 °C. At the same time, the process of thermal destruction of the immobilized copolymer can be conditionally divided into three stages:

The 1st stage takes place in the temperature range of 190–320 °C, where the mass loss is 14.15%, most of which is lost at 349.6 °C;

The 2nd stage occurs in the temperature range of 320–470 °C, in which the mass loss is 4.78% with a maximum at a temperature of 350 °C.

The 3rd stage takes place in the temperature range of 470–520 °C, where the mass loss is 8.38% with a maximum at 349.6 °C.

As a result, the total mass loss of the SiO₂]-AzoQN-MMA composite is 30.5 ± 0.5 wt.%, while the total mass loss of the original silica gel can be estimated at

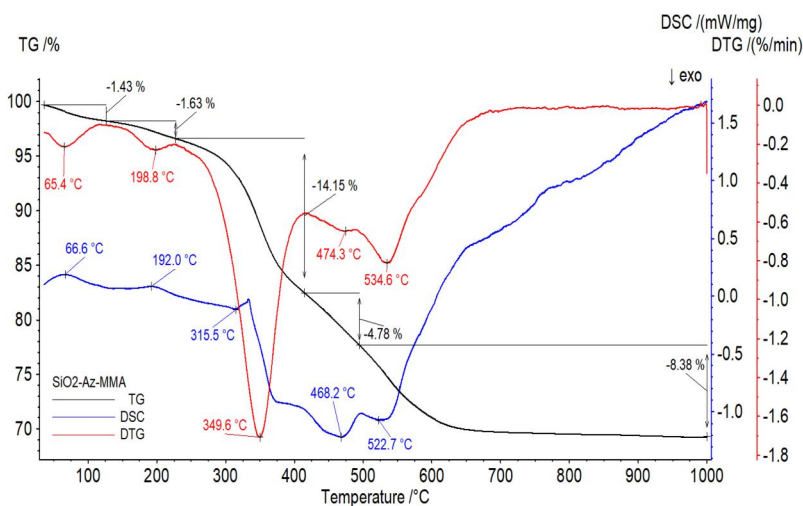


Figure 4. Thermogram of the composite $\text{SiO}_2\text{]-AzoQN-MMA}$.

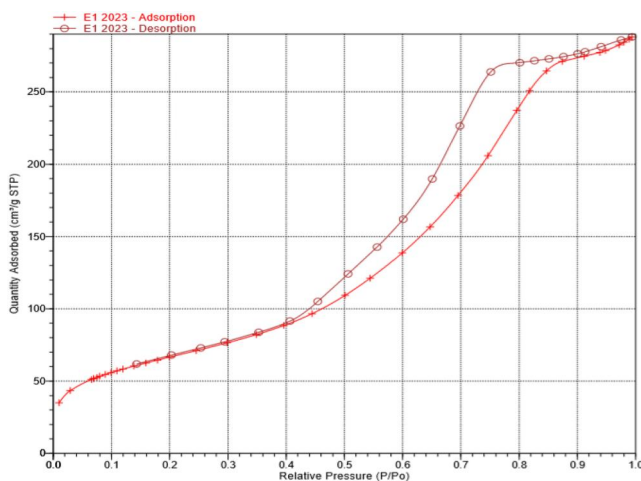


Figure 5. Low-temperature nitrogen adsorption-desorption isotherm of the synthesized composite $\text{SiO}_2\text{]-AzoQN-MMA}$.

5.5 ± 0.5 wt.% (Fig. 3). Therefore, the mass fraction of the copolymer in the composition of the composite is 25 ± 0.5 wt.%.

The low-temperature nitrogen adsorption-desorption method was used to study the parameters of the mineral surface after the adsorption of 5-(4-nitro)phenylazo-8-methacryloxyquinoline with methyl methacrylate. The obtained nitrogen adsorption-desorption isotherms for the synthesized composite are shown in Fig. 5. The similarity of the nitrogen adsorption-desorption isotherms for the synthesized composite and the original silica gel [19] allows us to claim that the adsorption of the selected copolymer did not affect the surface structure of the mineral in general.

By means of computer processing of the obtained nitrogen adsorption-desorption isotherms by various methods, the values of the specific surface area of silica gel and the

synthesized composite were obtained and compared. The mean diameter and pore volume values were found from the surface pore size distribution diagrams of the original silica gel and the synthesized SiO_2]-AzoQN-MMA composite calculated using the BJH method. The obtained values of the surface parameters of the original silica gel and the synthesized composite are shown in Table 1.

According to the data in Table 1, as a result of the adsorption of the copolymer on the silica gel surface, the specific surface area decreased by 1.9 times, the average pore volume decreased by 1.5 times, and the average pore diameter increased slightly. Thus, the obtained results confirm the modification of the silica gel surface with a non-porous copolymer.

The morphology of the silica gel surface after modification with the copolymer 5-(4-nitro)phenylazo-8-methacryloxyquinoline with methyl methacrylate was studied by scanning electron microscopy. SEM photographs of the surface of silica gel modified with the selected copolymer are shown in Fig. 6. From the given SEM photos, it follows that the copolymer does not completely cover the surface of the silica gel, but is in the form of individual convex formations, which do not change the structure of the surface in general, but only slightly reduce its porosity. Therefore, the results of scanning electron microscopy and low-temperature adsorption-desorption of nitrogen correlate well with each other.

As we have shown in [10], silica gel itself does not show sorption capacity for Cu^{2+} , Cd^{2+} , Pb^{2+} , Fe^{3+} ions. This fact allows it to be used as an inorganic porous matrix for fixing polymers, which by their chemical nature are prone to ion exchange or complexation, with the aim of establishing correlations "chemical nature of the immobilized polymer and the method of fixing the polymer on the surface of the porous inorganic matrix - sorption capacity of the composite". Since the selected copolymer contains oxyquinoline, azo, and nitro groups, in which nitrogen and oxygen atoms are potential ligands, the synthesized composite should exhibit complex-forming activity against transition metal ions that form stable complexes with nitrogen- and oxygen-containing

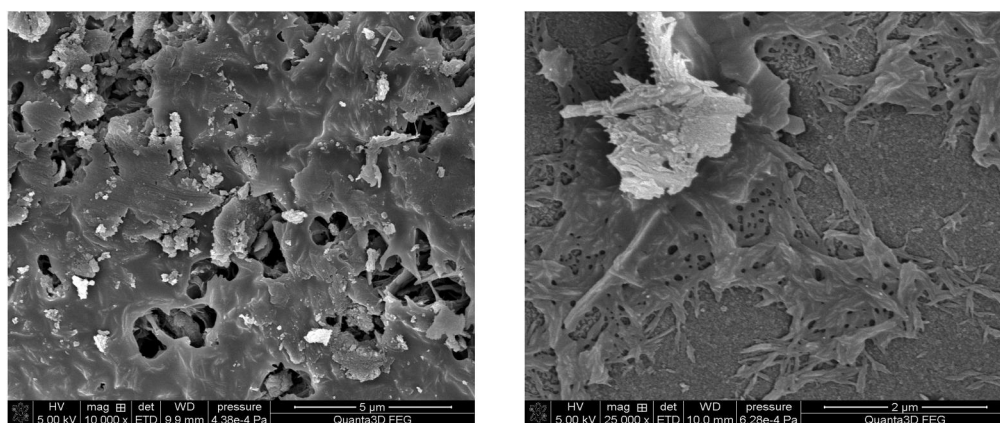


Figure 6. SEM photo of the silica gel surface after adsorption of the 5-(4-nitro)phenylazo-8-methacryloxyquinoline copolymer with methyl methacrylate: (a) (an increase of 10,000 \times); (b) (an increase of 25,000 \times).

substances, due to which its adsorption capacity for such ions should increase in comparison with the original silica gel.

The study of the sorption capacity of the synthesized SiO_2 –AzoQN–MMA composite with respect to Cu(II) , Cd(II) , Pb(II) and Fe(III) ions was carried out in a static mode similarly [18,19]. As a result, a sorption isotherm from aqueous solutions of nitrates was obtained for each of the ions (without additional addition of any buffers). Examples of isotherms of Cu(II) and Fe(III) ions are shown in Figs. 7 and 8, respectively.

As can be seen from these figures, the given sorption isotherms, like all the obtained ones, belong to the $2L$ type and make it possible to unambiguously establish the value of the sorption capacity for each of the investigated ions. Comparison of the sorption capacity values of the original silica gel and the SiO_2 –AzoQN–MMA composite synthesized on its basis, established from the corresponding sorption isotherms, and the composite based on the same silica gel modified in situ with poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline (SiO_2 –AzoQN), shown in Table 2.

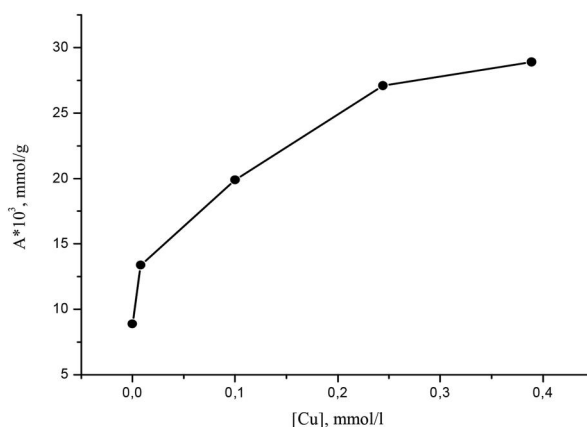


Figure 7. Sorption isotherm of Cu(II) ions on the surface of the SiO_2 –AzoQN–MMA composite from aqueous nitrate solutions (without adding buffer solutions) in static mode, sorption time – 1 day.

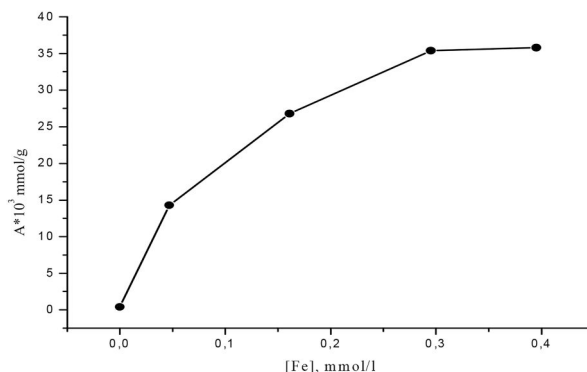


Figure 8. Sorption isotherm of Fe(III) ions on the surface of the SiO_2 –AzoQN–MMA composite from aqueous nitrate solutions (without adding buffer solutions) in static mode, sorption time – 1 day.

Table 2. Comparison of the sorption capacity for Cu(II), Cd(II), Pb(II) and Fe(III) ions of the original silica gel, composite based on silica gel, *in situ* modified poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline (SiO₂]-AzoQN) and silica gel with adsorbed copolymer 5-(4-nitro)phenylazo-8-methacryloxyquinoline with methyl methacrylate.

Ion	Sorption capacity, mmol/g		
	Original silica gel	Copposite SiO ₂]-AzoQN-MMA	Copposite SiO ₂]-AzoQN
Cu(II)	0.006 [19]	0.029	0.032 [18]
Cd(II)	0.006 [19]	0.007	0.006 [18]
Pb(II)	0.002 [19]	0.004	0.002 [18]
Fe(III)	0.008 [19]	0.036	0.036 [18]

The data in Table 2 allow us to state that both synthesized composites, which have azo-, nitro-, and quinoline groups as part of the structural links of immobilized polymers, show similar sorption properties with respect to the investigated ions. Namely:

- both composites do not show sorption capacity for Pb(II) and Cd(II) ions. For SiO₂]-AzoQN-MMA, a slight increase in the sorption capacity (by 2 times) was recorded for lead (II) cations and, within the margin of error, for cadmium (II) ions. This phenomenon can be explained by the fact that complex formation with “soft” oxygen-containing and chalcogen-containing ligands is more characteristic for these metal ions than with nitrogen-containing ones [20];
- both composites show an increased sorption capacity for copper (II) cations compared to the original silica gel. However, the composite with *in situ* immobilized poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline has a slightly higher sorption capacity for these ions compared to the adsorbed copolymer;
- with regard to Fe(III) cations, both composites have the same sorption capacity, which is 4.5 times higher than the value for the original silica gel.

Taking into account the fact that the mass fraction of the adsorbed copolymer 5-(4-nitro)phenylazo-8-methacryloxyquinoline with methyl methacrylate in the composition of the synthesized composite is 25.0 ± 0.5 wt.%, and the mass fraction of its *in situ* immobilized analogue (poly – 5-(4-nitro)phenylazo-8-methacryloxyquinoline) in the composition of the composite based on similar silica gel is only 6.2 ± 0.5 wt.% [18], it becomes obvious that the method of *in situ* immobilization of complexing polymers on the silica gels surface is much more effective in comparison with their physical adsorption.

Therefore, the obtained results allow us to draw a preliminary conclusion that the increase in the sorption capacity of the synthesized composite with respect to Cu(II), Pb(II) and Fe(III) ions in comparison with the original silica gel occurs as a result of complexation processes of these metal ions with immobilized macromolecules of the copolymer mainly through nitrogen atoms in the composition of 5-(4-nitro)phenylazo-8-methacryloxyquinoline.

Conclusions

This study presents a significant advancement in the development of a cost-effective composite comprising silica gels and polymers for efficient removal of Cu(II), Pb(II),

Fe(III) ions from aqueous solution. As a result of this study, effective sorbents were obtained for removal Cu(II), Pb(II), Fe(III) ions from wastewater by a new polymer-inorganic composite based on silica gel with copolymer 5-(4-nitro)phenylazo-8-methacryloxyquinoline:methyl methacrylate.

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 the modification of the silica gel surface with the selected polymer does not affect its surface structure, but only reduces its porosity.

The SEM-photo analysis of the surface of the synthesized composite allows us to state that the immobilized copolymer is located on the surface of silica gel in the form of separate formations of a convex shape, which were formed on the irregularities of the surface of silica gel.

It was established that the synthesized composite has 4.5 times higher sorption capacity for Fe(III) cations, almost five times higher for Cu(II) ions, two times higher for Pb(II) cations, but did not reveal additional sorption capacity regarding Cd(II) ions compared to the original silica gel.

It was found that in comparison with the composite based on silica gel, in situ modified with poly-5-(4-nitro)phenylazo-8-methacryloxyquinoline, the sorption capacity of the synthesized composite is similar for Fe(III) ions and slightly lower for Cu(II) ions.

Based on the obtained results, it can be asserted that the method of in situ immobilization of complex-forming polymers on the surface of silica gels is more effective in comparison with their physical adsorption. In conclusion, heavy metals can be removed by these composite materials with higher removal efficiencies.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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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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