Adsorption Properties of Silica Gels, In Situ, Modified with Nitrogen-Containing Polymers with Complexing Properties for Ions Cu(II), Fe(III), Pb(II)

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ABSTRACT

This review article introduces the latest achievements in the research of new polymer-inorganic composites based on silica gel and polymers of different chemical structures for the extraction of toxic metal ions from wastewater. This paper presents an overview of polymer-modified silica gels and reviews several of our recent studies using these composites as pollutant adsorbents, outlining the main characteristics of the various adsorption systems, demonstrating the specifics of each process, and identifying patterns to inform future research. Data are given on the possible practical use of the obtained hybrid materials as adsorbents of toxic metal ions.

4.1 INTRODUCTION

Immobilization of multifunctional polymers with complexing and ionexchange properties on the porous surface of inorganic matrices increases the efficiency of such matrices as sorbents for ions of transition toxic metals.

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Such multifunctional polymers include polyelectrolytes with a quaternary nitrogen atom in a side chain (polycations) or the main chain (polyionenes), e.g., polyhexamethylene guanidine, its derivatives, or polyaniline [1–9]. However, the ion-exchange properties of such polymers are significantly greater than the complexing ones. Sorbents based on them can remove mainly anionic forms of multivalent metals (molybdates, tungstates, chromates, dichromates, arsenates, etc.) or acidic remnants of mineral acids (in particular, nitrates, phosphates, arsenates) and have low sorption capacity toward cations of transition metals. Therefore, the search for organo-mineral composite materials bearing polymers with only complexing properties due to active (amino-, azo-, oxoquinoline, pyridine, mercapto-, etc.) groups which are able to remove cationic forms of toxic metals by their complexation is still relevant.

Undoubtedly, from an economic and ecological point of view, the best inorganic matrices for such composite materials are natural porous minerals currently being industrially developed from deposits [10–16]. However, it is necessary to establish a correlation between the chemical nature of the immobilized polymer and its adsorption capacity towards certain cationic forms of metals in terms of the complex process. It is also important to establish correlations between the method of polymer immobilization on a mineral carrier and the geometric shape of its placement on the inorganic surface. The shape of the macromolecule (coil, globule, aggregates of coils, etc.) significantly affects the accessibility of its complexing centers. All of the mentioned studies are important for clarifying the effectiveness of such sorbents for separating cations of transition toxic metals. That is why in the initial stages, it is necessary to use as mineral carriers for polymers with complexing properties porous inorganic materials with well-defined surface parameters, and minimal sorption capacity towards cations of transition metals. Such matrices include, in particular, mesoporous silica gels [17-21].

The main methods of polymer immobilization on the inorganic carrier are physical and chemical immobilization, sol-gel method, and *in situ* immobilization. Each of these methods has advantages and drawbacks.

Precipitation and further adsorption of previously synthesized polymer from a solution onto the inorganic carrier leads to the physical fixation of macromolecules on the mineral surface. Polymer immobilization on the solid surface of the carrier occurs due to the formation of hydrogen or π - π bonds, electrostatic forces, van der Waals forces, etc. It is advisable to use such a method to fix positively charged polymers on the negatively charged surface, e.g., silica matrix. In such a case, the polymer is held on a solid surface due to electrostatic forces.

The formation of covalent bonds between macromolecules and the inorganic carrier surface leads to a chemical fixation of the polymer. Synthesis of organo-mineral composites by the sol-gel method accompanies the formation of the inorganic component of the sol-gel composite around the polymer particles. As a result, areas of different nano-sized phases are formed, which can affect the desired properties of the composite. The method of *in situ* polymer immobilization on the surface realizes the direct formation of a polymer layer during the polymerization process in the presence of an inorganic matrix. This immobilization method is well-studied for polyaniline. A polymerization of aniline on the silica gel surface carried out with ammonium peroxodisulfate is described in [22]. It has been proven that the *in situ* polymerization of aniline allows the formation of a chemically and physically stable layer of polymer on a solid surface. It is a result of the simultaneous passage of interconnected processes: chemical - growth of macromolecules and physical-self-assembly of chains into supramolecular structures. Therefore, during the in situ polymerization, a special spatial structure of the polymer is irreversibly formed, which is firmly immobilized on the carrier surface [23]. It is noted that in situ polymerization of aniline is the only way to obtain polyaniline layers on porous and powdery nano-sized carriers. In situ polymerization of aniline is a versatile method concerning the chemical nature of the carrier. The only limitation is the acidity of the reaction medium, which must be in the interval pH=1-5.

The presented paper is devoted to the sorption properties of Cu (II), Fe(III), and Pb(II) ions with polymer-inorganic composites based on mesoporous silica gels with nitrogen-containing polymers of different chemical nature immobilized on the surface by *in situ* polymerization. The paper describes composites containing organic polymers bearing such groups as:

- NH₂: poly[2-amino-5-hydroxy-1,4-phenylene-bis(2-dimethacrylate)];
- NH-C=O: poly[N-(4-carboxyphenyl)methacrylamide];
- N=N-: poly[(4-methacryloyloxy-(4'-carboxy)azobenzene], poly[(4methacryloyloxy-2-chloro-(4'-carboxy)azobenzene]; poly[4methacryloyloxy-(4'-carboxy-2'-nitro)azobenzene]; and
- Oxyqiunoline: poly[8-oxyqiunoline methacrylate].

4.2 EXPERIMENTAL METHODS AND MATERIALS

4.2.1 METHODS

FTIR spectra of the samples of composite and the original mineral 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⁻¹ with 16 scans per spectrum at a resolution of 4 cm⁻¹.

- Thermal Analysis: The amount of immobilized polymer on the surface of the modified saponite was evaluated by thermogravimetric analysis, which was 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 403C" (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 sorbometer software "ASAP 2420 V1.01" (Micromeritics, USA). Before measurement, the samples were degassed at 100°C for 24 hours.
- Surface Morphology Analysis: The surface morphology of the composite was observed by using a scanning electron microscope (SEM, LEO 1430VP, Carl Zeiss, Germany).

4.2.1.1 DESCRIPTION OF ADSORPTION PROCESSES

Properties of the obtained composite to adsorb Cu (II), Pb (II), Cd(II), and Fe(III) were studied in static mode. Working solutions of nitrates of the corresponding metals were prepared in volumetric flasks of 25 ml, 50 ml, or 100 ml, diluting the solutions to the mark with water, and then adding the required volume to flat-bottomed flasks containing 0.1 g of adsorbent. The reaction proceeded while the flasks were shaken mechanically. Equilibrium concentrations of ions were measured using atomic absorption methods.

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Working nitrate solutions of Cu(II), Pb(II), and Fe(III) are prepared with the sets of "standard sample solutions" of these salts on 1 M HNO₃ background (produced by A.V. Bogatsky FHI in Odesa) with concentrations of 1 and 10 mg/ml.

4.2.1.2 ANALYSIS OF ION CONCENTRATIONS

Absorption capacity (A) was calculated by formula (1):

$$A = (c_0 - [M]) V/m \tag{1}$$

Where; c_0 is the concentration of the metal in the starting solution; [M] is the concentration of the metal at equilibrium; V is the volume of the starting solution; and m is the mass of the composite.

Atomic Absorption Spectrophotometer "C115-M" (Ukraine) in the flame of a mixture of "acetylene–air" was used to measure equilibrium concentrations of copper (II), cadmium (II), lead (II), and iron (III). Equilibrium concentrations in solutions were calculated by comparing the intensities of spectral lines with those for standard solutions. The maximum wavelengths were: 324.7 nm for Cu (II), 228.8 nm for Cd (II), 283.3 nm for Pb (II), and 248.3 nm for Fe (III), with an aperture width of 0.5 cm.

Silica gel manufactured by Merck (fraction with a particle diameter of 0.1–0.2 mm) was used as an inorganic carrier of composites. The surface parameters of this original SiO₂ are given in Table 4.3. Synthesis of polymers was carried out in the presence of original silica particles by initiated radical polymerization of the corresponding monomers using $\alpha, \alpha, '$ azoisobutyronitrile (AIBN) as a radical initiator. Methods of composite synthesis are described in papers [24–30]. Table 4.1 shows the full and abbreviated names of the synthesized composites and the chemical structures of the immobilized polymers.

4.3 RESULTS AND DISCUSSION

Polymers *in situ* immobilization on the silica gel surface were confirmed by IR spectra comparative analysis of the composites and original silica gel. Examples of IR spectra of Composite 1 and Composite 2 are shown in Figures 4.1 and 4.2, respectively.

TABLE 4.1 Full and Abbreviated Names of Synthesized Composites and Structures of

 Nitrogen-Containing Composites

Full Name of Composite	Abbreviated Name of Composite	Schematic Representation of Composite Structure		
Silica gel <i>in situ</i> modified with poly[2-amino-5-hydroxy- 1,4-phenylene-bis(2- dimethacrylate)]	Composite 1	H ₂ N of o		
Silica gel <i>in situ</i> modified with	Composite 2	P O O O O O O O O O O O O O		
meth-acrylamide]				
Silica gel <i>in situ</i> modified with	Composite 3			
poly[(4-methacryloyloxy- (4`-carboxy) azobenzene]				
Silica gel <i>in situ</i> modified with	Composite 4			
poly[(4-methacryloyloxy- 2-chloro-(4'-carboxy) azobenzene]				
Silica gel <i>in situ</i> modified with	Composite 5			
poly[4-methacryloyl- oxy-(4`-carboxy-2`-nitro) azobenzene]				
Silica gel <i>in situ</i> modified with	Composite 6	il. D		
poly[8-oxyqiunoline methacrylate]				



FIGURE 4.1 IR spectra of original silica gel (curveA) and composite 1 (curve B).



FIGURE 4.2 IR spectra of original silica gel (1), composite 2 (2), and starting monomer (3).

The obtained IR spectra of all synthesized composites contain an absorption band at 2,930 cm⁻¹ and a number of bands in the region 1,700–1,200 cm⁻¹. The first band is attributed to the v(C-H) vibration of sp³-hybridized carbon. This band confirms the fact that polymerization has taken place on the surface of silica gel.

Thermogravimetric analysis of the synthesized composites was carried out to determine the weight fraction of immobilized polymers in the composites and to establish the temperature range of thermal decomposition of immobilized polymers. The results of the thermogravimetric analysis of the synthesized composites carried out under the same conditions are shown in Table 4.2.

Composite	Temperature Range of Exothermic Effect	Weight Fraction of the Immobilized Polymer (± 0.1), wt.%
Composite 1	300–600°C	22.1
Composite 2	420–700°C	9.3
Composite 3	400–650°C	10.6
Composite 4	400–650°C	13.3
Composite 5	400–650°C	10.1
Composite 6	390–700°С	3.9

TABLE 4.2Thermogravimetric Analysis Data of the Synthesized Composites [24–30]

As one can see from the data in Table 4.2, the weight fractions of immobilized polymers in the composites are approximately the same and are ~ 10 wt.%. The exceptions are 22 wt.% for poly[2-amino-5-hydroxy-1,4-phenylene-bis(2-dimethacrylate)] in composite 1 and 4 wt.% for poly[8-oxyquinoline methacrylate] in composite 6. The temperature range of their final thermal decomposition with an exothermic effect is 400–650°C.

Thermograms combined with mass spectra in 3D format were obtained for all synthesized composites as well as mass spectra in 2D format at different temperatures. Examples of TG-MS-3D data of composites 2 and 4 are shown in Figures 4.3 and 4.4.



FIGURE 4.3 TG-MS-3D data of composite 2.



FIGURE 4.4 TG-MS-3D data of composite 4.

The products of thermal destruction of polymers immobilized on the silica gel surface were analyzed using mass spectra data. As could be expected, the final products of the thermal decomposition of all immobilized polymers are water and CO_2 , and nitrogen is released in the form of N_2 or N_2O . Thermal destruction of the chlorine-containing polymer in composite 4 also resulted in Cl_2 formation.

Changes in the silica gel surface morphology after modification with polymers were recognized with the method of low-temperature adsorption-desorption of nitrogen. The obtained nitrogen adsorption-desorption isotherms of the synthesized composites and the original silica gel are similar. This observation indicates that the structure of the silica gel surface does not change after *in situ* immobilization of the polymers.

The values of the specific surface area of the composites and original silica gel were obtained by computer processing of the obtained nitrogen adsorption-desorption isotherms using the BET and Langmuir methods (*see* Table 4.3).

It was found that after surface modification by *in situ* immobilization of polymers, the specific surface area decreases by about 33%. The average diameter of silica gel pores calculated using the BJH method increases insignificantly.

By means of computer processing of the obtained nitrogen adsorptiondesorption isotherms using the BET and Langmuir methods, the values of the specific surface area of the synthesized composites and the original silica gel were obtained and compared (Table 4.3). It was found that after surface modification by *in situ* immobilization of the corresponding polymers, the specific surface area decreases by about a third. At the same time, the average diameter of silica gel pores, calculated using the BJH method, increases insignificantly as a result of the *in situ* immobilization of polymers.

A comparison of the data in Tables 4.2 and 4.3 allows us to trace a clear correlation between the mass fraction of the immobilized polymer in the composition of the composite and the amount of reduction in the specific surface area and the average pore size of the original silica gel, namely: the greater the mass fraction of the polymer in the composition of the composite, the greater the reduction in the specific surface area of silica gel and the average volume of its pores.

Sample	S _{nu}	т (m²/g)		Average	Average Pore
	Calculated from Isotherm	BJH	Langmuir	Pore Volume (cm ³ /g)	Size (nm)
Original silica gel	447	464	687	0.68	5.9
Composite 1	345	363	593	0.41	5.5
Composite 2	252	264	396	0.42	6.3
Composite 3	386	402	600	0.61	6.1
Composite 4	309	327	494	0.51	6.2
Composite 5	341	358	539	0.57	6.4
Composite 6	390	407	610	0.62	6.1

TABLE 4.3 Comparison of Surface Parameters of Original and *in situ* Polymer-ModifiedSilica Gel [24–30]

The geometric shapes of the arrangement of polymers on the surface of silica gel were established using scanning electron microscopy. SEM photos of the surfaces of all composites are shown in Figures 4.5–4.10. As follows from the given photos, for polymers in the composites Composite 1, Composite 2, Composite 5, and Composite 6, an "island" or "globular" arrangement of the polymer on the silica gel surface is observed, and in the composites Composite 3 and Composite 4, the characteristic arrangement of polymers is mainly in the form of linear fibers.

Summarizing the obtained results, it can be stated that *in situ* immobilization of uncharged polymers on the surface of silica gels leads mainly to their "island" or "globular" form of placement on the surface. This leads to less availability of the active centers of the polymer for complex formation. This factor significantly reduces the potential sorption capacity of composites based on silica gel for cationic forms of transition metals and thus prevents the realization of the main advantage of polymers compared to immobilized low molecular weight compounds.

However, sometimes the chemical nature of the polymer makes it possible to form horizontal thread-like forms of the polymer on the surface of silica gel during *in situ* immobilization, which makes it available for participation in the complex formation of a much larger number of potentially active centers of polymer macromolecules. An example of this phenomenon is azopolymers in the composition of Composites 3 and 4. Most likely, their chemical structure made it possible to obtain similar chain forms of these polymers on the surface of silica gel (*see* Figures 4.7 and 4.8).



FIGURE 4.5 SEM photo of the surface of the composite 1 (x50000).



FIGURE 4.6 SEM photo of the surface of the composite 2 (x5000).



FIGURE 4.7 SEM photo of the surface of the composite 3 (x50000).

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FIGURE 4.8 SEM photo of the surface of the composite 4 (x50000).



FIGURE 4.9 SEM photo of the surface of the composite 5 (x10000).



FIGURE 4.10 SEM photo of the surface of the composite 6 (x10000).

Since the immobilized polymer on the silica gel surface contains nitrogencontaining (amino-, azo-, oxyquinoline) groups, the synthesized composites should show sorption activity for those metal ions that have a high affinity for nitrogen-containing ligands. To confirm these considerations, we investigated the sorption of ions Cu (II), Fe (III), and Pb (II).

Studies of the sorption capacity of synthesized composites for Cu (II), Pb (II), and Fe (III) ions are described in detail in works [24–30]. These studies included the following: determination of the optimal pH range of the sorption medium; establishing the necessary contact time of phases to achieve sorption equilibrium in static mode; construction of sorption isotherms of the corresponding metal ions on the surface of the synthesized composites; establishing the sorption capacity for the listed metal ions and comparing it for the original silica gel and each of the synthesized composites. In particular, it was found that all synthesized composites show the maximum sorption capacity for selected ions in an aqueous environment without the additional addition of any buffer solutions to the initial solutions of these metal salts.

Therefore, the best sorption occurs with the original aqua complexes. And, in our opinion, it effectively occurs due to the formation of various ligand complexes on the surface of silica gel due to the replacement of oxygen atoms in the original aqua complexes with nitrogen atoms in the composition of immobilized polymers. Examples of schemes of such reactions are shown in Figures 4.11 and 4.12.



FIGURE 4.11 Scheme of complex formation of Cu (II) ions with composite 1 through the nitrogen atom of the amino group.



FIGURE 4.12 Scheme of complexation of Cu (II) ions with composite 2 through the nitrogen atom of the amide group.

Comparative characteristics of the sorption capacity of the synthesized composites and the original silica gel with respect to Cu (II), Pb (II), and Fe (III) ions are shown in Table 4.4.

Sample	Sorption Capacity, mmol/g			
	Cu (II)	Fe (III)	Pb (II)	
Original silica gel	0.006	0.007	0.002	
Composite 1	0.021	0.010	0.010	
Composite 2	0.010	_	0.004	
Composite 3	0.012	0.016	0.005	
Composite 4	0.009	0.016	0.007	
Composite 5	0.086	0.016	0.010	
Composite 6	0.009	0.012	0.002	

TABLE 4.4Comparison of The Sorption Capacity of the Original Silica Gel and SynthesizedComposites with Respect to Cu (II), Pb (II) and Fe (III) Ions

From the data in Table 4.4, it follows that the greatest sorption capacity for all studied ions is characteristic of silica gel *in situ* modified with poly[4methacryloyloxy-(4'-carboxy-2'-nitro) azobenzene]. This polymer has two nitrogen atoms as part of its structural links, which increases the probability of complexation processes with selected transition metal ions. In favor of the fact that the chemical nature of this polymer plays a decisive role in this case, the fact that this polymer does not have a large (compared to other synthesized composites) concentration on the surface, because its mass fraction in the composition of the composite is 10%, nor the best (linear) geometric arrangement of macromolecules of the immobilized polymer on the surface of silica gel.

It also follows from the data of Table 4.4 that;

• The sorption capacity of composites with immobilized azopolymers is higher than that of composites with immobilized amino-, amido-, and oxyquinoline groups for Fe(III) ions.

The sorption capacity of the composite with immobilized poly[2-amino-5-hydroxy-1,4-phenylene-bis(2-dimethacrylate)] is equal to the composite with immobilized poly[4-methacryloyloxy-(4'-carboxy-2'-nitro) azobenzene] relative to Pb(II) ions and the second largest relative to Cu(II) ions.

These facts can be explained by the high concentration of this immobilized polymer compared to other synthesized composites (the mass fraction of poly[2-amino-5-hydroxy-1,4-phenylene-bis(2-dimethacrylate)] in the composition of the composite is 22%, which is twice the mass fractions of other polymers).

4.4 CONCLUSION

- 1. By *in situ* immobilization of poly[2-amino-5-hydroxy-1,4-phenylene-bis(2-dimethacrylate)], poly[N-(4-carboxyphenyl) methacrylamide], poly[(4-methacryloyloxy-(4'-carboxy)-azobenzene], poly[4-methacryloyloxy-2-chloro-(4'-carboxy)azobenzene], poly[4-methacryloyloxy-(4'-carboxy-2'-nitro)azobenzene] and poly[8-oxyquinoline methacrylate] on the surface of silica gel, 6 new composite materials were obtained.
- 2. The fact of the *in situ* immobilization of polymers on the surface of silica gel was confirmed by the methods of IR spectroscopy and thermogravimetric analysis combined with mass spectrometry. Thus, the possibility of using this method of surface modification with selected nitrogen-containing polymers was proven for the first time.
- 3. It was found that the mass fractions of *in situ* immobilized polymers in the composition of composites are in the range of 4–22%. The final thermal destruction of all immobilized polymers on the surface of silica gel occurs in the temperature range of 400–650°C with the predominant formation of carbon dioxide, water, and N₂ or N₂O.
- 4. It was established that *in situ* immobilized nitrogen-containing polymers have different locations on the silica gel surface: in the form of loops of macrochains, adsorbed tangles, or linear fibers. This modification almost does not affect the structure of its surface; the surface area is slightly reduced only.
- 5. It was found that all the synthesized composites show better sorption properties for Cu(II), Pb(II), and Fe(III) ions in a neutral aqueous environment compared to the original silica gel, with the exception of *in situ* immobilized poly[8-oxyquinoline methacrylate] for Pb ions (II).
- 6. The effect of the chemical nature of the immobilized polymer on the sorption properties of the obtained materials is shown: the composite with *in situ* immobilized poly[4-methacryloyloxy-(4'carboxy-2'-nitro) azobenzene] was the best sorbent for Cu (II) and Pb (II) ions. Azopolymers fixed on the surface of silica gel are superior to polymers that contain nitrogen in the composition of amino-, oxyquinoline, and amide groups in terms of the sorption capacity for Fe (III) ions.

KEYWORDS

- adsorption
- *in situ* immobilization
- polymer
- silica gel
- α,α,'-azoisobutyronitrile

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