

Research Article

Preparation and Heavy Metal Ions Chelating Properties of Multifunctional Polymer-Grafted Silica Hybrid Materials

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In this research work, novel hybrid materials based on multifunctional polymers and silica were developed and investigated in view of possible employment as sorbents for removal of heavy metal ions from water in presence of various ions. Organic-inorganic hybrid materials were prepared by covalent bonding of vinyl-terminated polyamidoamine (PAA) onto aminated silica particles. Two series of polyamidoamine-grafted silica, differing in the PAA chemical structure, were synthesized, and their heavy metal ions chelating properties were investigated. Column adsorption procedure for Cu, Zn, and Ni in aqueous solution was successfully established. Moreover, the adsorption behaviour of the materials was evaluated in different ionic strength solutions as well as in distilled and natural water. Organic-inorganic hybrid materials exhibited excellent chelating properties and selectivity for different metal ions. The hybrid columns showed exceptional eluting and regenerating property using diluted hydrochloric acid solution as eluent. In particular, the hybrid materials containing more carboxy groups possessed superior adsorption ability, reusability, and stability. The consecutive adsorption-desorption experiments exhibited that this material could be reused more than 20 cycles without almost any loss of adsorption capability. These new organic-inorganic sorbents appear very promising as an effective solid-phase extraction material for the selective preconcentration or removing of heavy metal ions from the environment.

1. Introduction

Heavy metal pollution is one of the most widespread environmental concerns threatening human health and ecosystems because of their recalcitrance and persistent nature in the environment and high water solubility, facilitating environmental mobilization or even bioaccumulation [1]. Moreover, ever-increasing industrial development and the use of several pesticides in agriculture have been worsening this environmental pollution scenario over time. The discharged heavy metal ions that are difficult to be degraded into cleaning products, being as a part of the food chain, accumulate into living organisms and eventually cause serious health issues even at extremely low concentrations. Therefore, efficient removal of heavy metal ions from the environment still holds a great significance and attracts considerable research to maintain ecological stability and public safety. A variety of methods or technologies including

chemical precipitation, reverse osmosis, electrodialysis, ultrafiltration, solvent extraction, coagulation, ion exchange, and adsorption have been applied to separate heavy metal ions from contaminated waste water [2]. Although all technologies appear with individual merits and demerits, the adsorption method can be considered as a simple and effective technique for removing heavy metal ions from the environment because of its wide adaptability, low cost, and reusability [2, 3]. However, adsorbents such as activated carbons, zeolites, clays, nanomagnetic particles, nanosized metal oxides, and low-cost biosorbents investigated so far for adsorbing heavy metal ions from aqueous solutions suffer from low adsorption capacities, selectivities, and inabilities or high degree of difficulties to be recycled [4, 5]. Hence, specific sorbents consisting of a ligand (e.g., ion-exchange material or chelating agents), which interacts with the metal ions specifically, and a carrier matrix, which may be an inorganic material (e.g., aluminium oxide, silica, or glass)

capable of immobilizing ligands, are currently considered as one of the most promising techniques [6–8]. In this context, there is a need to design organic-inorganic hybrid materials accompanied by good adsorption capability, particularly tendency to form metal complexes with various metal ions in solution, high selectivity, and chemical and mechanical stability, under experimental conditions to combat water pollution [9, 10]. Recently, organically-modified silica is considered as a promising adsorbent for waste water treatment [11]. Numerous studies focused on developing novel functionalized silica-based sorbents is stimulated by the need to meet the stringent criteria of real environments such as high adsorption capacity, superb selectivity, prolonged service-life, easier and faster regeneration with minimal capacity loss, excellent mechanical stability, low toxicity, and low cost [12–17]. However, there are only few reports on silica-based adsorbents which are capable of selectively adsorbing a wide range of heavy metal ions in the presence other ions such as Na^+ and Ca^{++} with long-term stability upon adsorption-desorption cycling and convenient regeneration ability under mild conditions [18–20]. Therefore, there is need to develop a novel single material fulfilling all these aforementioned requirements.

Herein, we investigated new procedures to obtain silica-based organic-inorganic hybrid materials for sequestering heavy metal ions from water with excellent features such as high adsorption capability, stability, and effective recyclability. Silica is a widely investigated sorbent because of its attractive physical and chemical properties such as water stability, thermal stability, and good mechanical strength along with convenient surface functionalization for the immobilization of organic groups [3, 5]. In our preliminary studies, grafting of vinyl-terminated macromonomers, namely, polyamidoamines (PAAs), onto pre-aminated silica gel through covalent bonding was described to obtain new modified silica having improved chelating properties and thermal stability [21]. PAAs, synthetic water-soluble polymers, are characterized by the presence of amido and tertiary amino groups regularly arranged along their macromolecular chain. These polymers have been extensively studied because the versatility of their chemical structures has allowed for a variety of applications ranging from drug delivery [22] to metal ions complexation [23] and gas sensing [24]. Moreover, PAAs were used to obtain surface-modified gold electrodes [25] to prepare chemical sensors that can be tailored to produce increased sensitivity and selectivity toward heavy metals. They were applied for the real-time detection of heavy metal ions in water [26]. Generally, the grafted PAAs maintained their chelating properties, and the complexing capacity of the resulting mixed organic-inorganic products was in the same order from a quantitative point of view, as that in their free counterparts in aqueous media (1 metal ion per grafted polymer repeating unit).

In this study, the chemical structure of the adsorbents was well designed, and the adsorption ability of the new organic-inorganic hybrid materials for heavy metal ions (i.e., Cu^{2+} , Co^{2+} , Zn^{2+} , and Ni^{2+}) was investigated using both single and mixed ion solutions. Moreover, the reusability of

materials was examined using 20 consecutive adsorption-desorption cycles.

2. Experimental Section

2.1. Materials and Instruments. All starting reagents were purchased from Fluka and used without further purification with the exception of 2,2-bis(acrylamido)acetic acid (BAC) which was synthesized as previously described [21].

Calcination data: the products were burned after drying under vacuum at 80°C . Intrinsic viscosities were measured at 32°C in 0.1 M NaCl by using Ubbelohde viscometers. Gel permeation chromatograms were obtained using TSK-GEL G 3000 PW and TSK-GEL G 4000 PW columns connected in series, with 0.1 M Tris buffer, 0.2 M NaCl, pH 8, as the mobile phase and a flow rate of 1 mL/min (Knauer model HPLC Pump 64), and the samples were checked by a Knauer UV detector operating at 230 nm. Fourier transform infrared (FTIR) spectra were obtained on dry samples using a Thermo Scientific Nicolet iS50 FTIR spectrophotometer equipped with a PIKE MIRacle attenuated total reflectance attachment and recorded over a range of 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} . The thermal decomposition of the materials was investigated by means of thermogravimetric analysis using a TA instrument (TGA Q500, TA Instruments). The weight losses were recorded at a heating rate of $20^\circ\text{C}/\text{min}$ under nitrogen as a function of temperature.

2.2. Methods

2.2.1. Synthesis of Aminated Silica. Particles-size fractionation of silica gel was obtained by sieving using standard sieves in dry conditions, and the fraction was collected between 125 and $200\ \mu\text{m}$. γ -Aminopropyltriethoxysilane (10.8 ml 23 mM) was added to a suspension of silica gel (10 g; 125 – $200\ \mu\text{m}$) in toluene (50 ml). The reaction mixture was allowed to react at 60°C for 48 h. Then, silica was collected by filtration and purified by solvent extraction with toluene followed by washing with HCl 3 N ($3 \times 30\text{ ml}$) and water ($3 \times 50\text{ ml}$). The product was finally dried to a constant weight, and the chloride content, assumed correspond to the NH_2 content, was determined by titration and was found to be 1 mM/g.

2.2.2. Preparation of (BAC-DMEDA)_x-Grafted Silica (Siγ-[BAC-DMEDA]). 2,2-Bis(acrylamido)acetic acid (BAC) (36.46 g, 0.184 mol) was dissolved in an equimolecular quantity of 2 M NaOH followed by addition of *N,N'*-dimethylethylenediamine (DMEDA) (18.49 ml, 0.16 mol). The reaction was carried out at 20°C for 8 h under nitrogen atmosphere to avoid discolorations. After that, the solution was added to aminated silica (30 g) under vacuum condition. The reaction mixture was carefully degassed and purged with nitrogen and then was allowed to react while stirring in the dark at room temperature for three days. The product was collected by filtration, washed with water ($3 \times 30\text{ ml}$), methanol ($2 \times 30\text{ ml}$), HCl 1 M ($2 \times 50\text{ ml}$), and water

(3 × 50 ml), and finally dried in a desiccator at reduced pressure.

2.2.3. Preparation of (BAC-EDDA)_x-Grafted Silica (Si_y[BAC-EDDA]). BAC (27.74 g, 0.14 mol) was dissolved in an equimolecular quantity of 2 M NaOH followed by addition of *N,N'*-ethylethylenediamino diacetic acid (EDDA) (21.57 g, 0.12 mol) and triethylene amine (TEA) (50.43 ml, 0.36 mol). The reaction was carried out at 20°C for 8 h under nitrogen atmosphere to avoid discolorations. After that, the solution was added to aminated silica (30 g) following the same procedure as mentioned above. The final product was isolated and purified as described before.

2.2.4. Column Operations. The heavy metal ion adsorbing abilities of the products were tested in a column in the following way. A fixed amount of appropriate material (200 mg) was packed in a glass column, which was supported between glass wool beds. A column with a diameter of 5 mm and a length of 100 mm was employed. The wall effect can be ignored since the column diameter is about 20 times larger than that of the resin beads. The dried resin was weighed and equilibrated with water before filling the column. In the sorption runs, a metal acetate or metal sulphate solution was fed into the upper part of the column (flow down) by a pump (Knauer model HPLC Pump 64).

Fresh materials were used for the determination of metal ion adsorption. All experiments were performed at 25°C, and the elution rate was 2 ml·min⁻¹. At appropriate time intervals (based on the experiments performed with copper as model ion), the effluent samples were collected (3 × 100 ml) and the concentrations of metal ions were determined with an atomic absorption spectrophotometer.

The resins were then eluted with 0.6 M HCl (25 ml) so that the adsorbed ions were completely released. This procedure was repeated several times in cyclic operations. Figure 1(a) shows the assembled column during ion adsorption, and Figure 1(b) shows the attained colored dry resins after chelation of ions.

3. Results and Discussion

3.1. Preparation of the Hybrid Materials. Polymer surface-grafting reaction was enabled through the amino-groups of the inorganic substrate capable of covalent bonding with functional end groups of the PAA. In particular, pre-synthesized end-functionalized macromonomers were prepared in water and directly grafted onto the aminated silica particles without any polymers fractionation, thus obtaining the final product in a single step. In this way, the product is suitable for industrial development and, as demonstrated by GPC traces where low molecular weight species disappeared, the possibility to graft monomers and low oligomers was avoided.

Two structurally related PAAs, which in linear form have been shown to possess excellent complexing ability, were selected for this study [23]. Besides, the first structure of BAC-DMEDA showed excellent uptake properties after

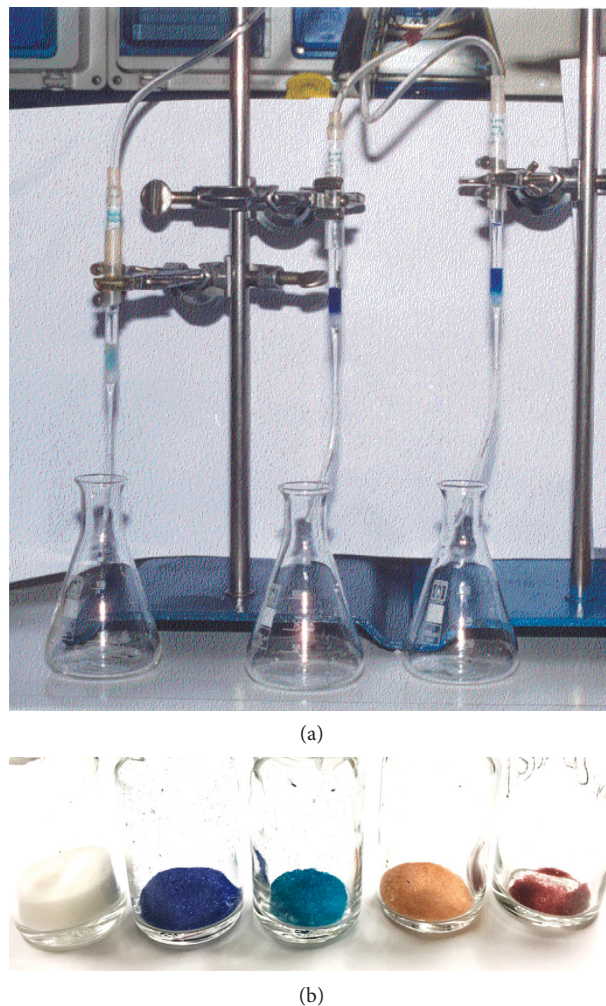


FIGURE 1: Assembled columns for ion adsorption/desorption experiments (a) and coloured dry hybrid materials isolated after Cu²⁺ and Co²⁺ chelation (b).

grafting onto silica particles as compared with the aminated silica [21]. This fact was ascribed to the presence in Si_y[BAC-DMEDA] of carboxyl groups which could participate to ion chelation increasing the stability of the complexes thus formed. Inspired by previous assessment, a second PAA structure, namely, BAC-EDDA carrying 3 carboxy groups per repeating unit instead of 1, was selected to show the effectiveness of such assessment and to select the best polymer structure for preparing heavy metal ions complexing systems. The two polymers were characterized in terms of molecular weights and molecular weight distributions by analytical GPC (Table 1), making use of PAAs purposely prepared and analysed by NMR techniques [27].

Silica gel was functionalized by treatment with γ -aminopropyl triethoxysilane. The nonbonded silane was removed by extraction with toluene, and the residual organic content was found to be 1 mM per gram of inorganic material as determined by amino group analysis. In order to use the amino groups attached to the silica surface as binding points, vinyl-terminated polyamidoamines macromonomers were obtained by employing an

TABLE 1: Polymer structure, viscosity, molecular weights, and glass transition temperature.

| Structure | η_{sp}/C^a (dl/g) | M_w (g/mol) | M_n (g/mol) | T_g ($^{\circ}\text{C}$) | T_g^b ($^{\circ}\text{C}$) |
|--|------------------------|---------------|---------------|------------------------------|--------------------------------|
| $\left[\text{CH}_2\text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{NH} - \underset{\text{COOH}}{\text{CH}} - \text{NH} - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_2\text{CH}_2 - \underset{\text{CH}_3}{\text{N}} - \text{CH}_2\text{CH}_2 - \underset{\text{CH}_3}{\text{N}} \right]^n$ <p style="text-align: center;">BAC-DMEDA</p> | 0.12 | 6050 | 4820 | 99 | 115.9 |
| $\left[\text{CH}_2\text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{NH} - \underset{\text{COOH}}{\text{CH}} - \text{NH} - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_2\text{CH}_2 - \underset{\text{CH}_2}{\text{N}} - \text{CH}_2\text{CH}_2 - \underset{\text{COOH}}{\text{N}} \right]^n$ <p style="text-align: center;">BAC-EDDA</p> | 0.10 | 6900 | 5900 | 122 | 133 |

^aC = 0.2% in 0.1 M NaCl; ^bsilica-grafted polymers.

excess of bisacrylamide (15 mol%) through a stepwise mechanism. After few hours, the reaction was continued in a suspension of the functionalized silica gel to obtain hybrid organic-inorganic product. The grafting reaction was carried out in water at 25 $^{\circ}\text{C}$, where the polymerisation of linear PAAs is known to yield the highest molecular weight products.

FTIR analysis was performed on the samples after washing out the eventually unreacted and soluble components to confirm the chemical structure. FTIR spectra of unmodified silica, aminated silica, linear polymers, and polymer-grafted materials obtained from the above procedure are shown in Figure 2. As shown in the spectra, all characteristic peaks of the individual components were observed in the hybrid materials. Aminated silica showed the appearance of the band due to amino N-H bending in the 1525 cm^{-1} region. Grafted silica showed the appearance of the typical bands of the corresponding linear products which appear after PAA grafting especially in the 1620–1655, 1527, and 1400 cm^{-1} regions. The first one is ascribed to CO amidic and CO carboxylic stretching, the second is ascribed to N-H amidic bending, and the third one is attributed to CH_2 bending. The absorption in the 1000–1200 cm^{-1} region is ascribed to Si-O stretching.

As far as the degree of grafting is concerned, the PAA content was determined by calcinations and confirmed by elemental analyses. The values were found to be 10.00% and 15.60%, respectively, for Si_y -[BAC-DMEDA] and Si_y -[BAC-EDDA] grafting, as indicated in Table 2.

To investigate the thermal stability of hybrid materials and further confirm grafting reactions, TGA measurements were carried out under nitrogen. For comparison purposes, thermogravimetric measurements were performed for aminated silica, starting PAAs, and metal complexes. Figure 3 shows the traces relative to the BAC-DMEDA system, because the results obtained for BAC-EDDA are quite similar. The silica particles were observed to slightly influence the decomposition temperatures of linear PAA increasing their thermal stability (Figure 3(a)). Two degradation processes, which can be ascribed to the presence of both aminopropyl silica gel and PAAs, could be noticed (Figure 3(b)). The polymer weight loss determined by TGA was observed in good agreement with the degree of grafting evaluated by elemental analyses and calcinations. The

presence of metal complexes, such as Cu and Co, reduced the total weight loss and decreased the thermal stability of hybrid materials by about 20 $^{\circ}\text{C}$, encouraging decomposition. All the hybrid materials showed slow and gradual weight loss. On the other hand, the thermal decomposition in a solid medium is a complex process associated with different processes. Chemical and diffusion processes of solid polymers are markedly influenced by segmental mobility, and the situation becomes even more complicated in composites in which the presence of an inorganic phase may influence the kinetics of product transfer.

Furthermore, X-ray photoelectron spectroscopy (XPS) was performed to probe the surface chemical composition of the particles after polymer grafting as well as metal ion chelation. In the past, we had analysed a series of PAA cast films by this technique, and the results were in excellent agreement with those expected from the bulk polymeric structure [28]. Survey spectra revealed the presence of four elements: carbon, nitrogen, oxygen, and silicon. In addition, ion-chelated hybrid materials revealed the presence of copper or cobalt. Atomic compositions for each material were calculated using the narrow-scan peak areas and the appropriate sensitivity factors for each element. XPS measurements showed a marked increase in C and N elements and a neat decrease of O and Si as a result of PAA grafting (Table 3). The carbon content of hybrid [BAC-DMEDA] and hybrid [BAC-EDDA] was 50.8 and 46.6, respectively, which was coming from a total organic content of 22.5 and 24.1, as evaluated by calcination. This suggested that polymer chains were grafted on the surface of the particles incorporating the silica, and consequently, the silicon content was very low. On the other hand, lower amounts of metal ions were detected than expected on the basis of that calculated by atomic absorption probably because the complex formation occurring through a cyclic structure around the metal atoms [23] highly masked the latter, and the scanning depth of XPS is just about 5–10 nm.

SEM observations of the uncoated and coated silica particles are shown in Figure 4. The morphological analysis performed on the uncoated silica particles clearly showed a regular and compact surface (Figures 4(a) and 4(b)). Polymer-coated particles (Figures 4(c) and 4(d)) showed a homogeneous layer all over the surface with pores of 20–

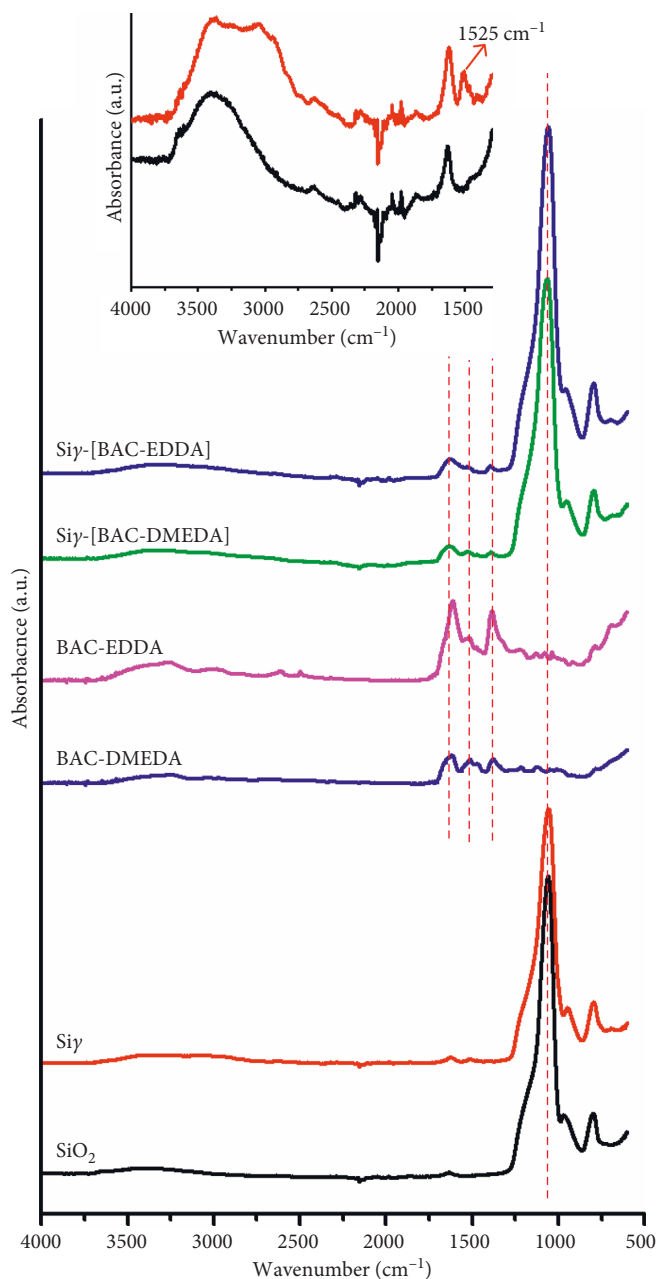


FIGURE 2: FTIR spectra of silica (SiO_2), aminated silica (Si_γ), linear polymers ([BAC-DMEDA], [BAC-EDDA]), and polymer-grafted materials (Si_γ -[BAC-DMEDA], Si_γ -[BAC-EDDA]). Inset shows the amplified spectra of silica (SiO_2) and aminated silica (Si_γ) within the wavenumber region of 4000 and 1700 cm^{-1} .

40 nm in addition to the characteristic spherical agglomerates of dimensions close to 100 nm typical of polymer coating. Observation of the edge after tilting the specimen (Figure 4(e)) highlighted more precisely the presence of the polymeric coating.

3.2. Adsorption/Desorption and Reusability. Adsorption is now recognized as an effective and economic method for

heavy metal wastewater treatment as it offers flexibility in design and operation and sometimes reversibility. The heavy metal ions, particularly, Hg^{2+} , Co^{2+} , Zn^{2+} , Ni^{2+} , Cr^{3+} , Mn^{2+} , Cd^{2+} , and Pb^{2+} should be removed from wastewater to protect the people and the environment owing to their toxicity.

In our preliminary studies, this type of organic-inorganic hybrid materials has been shown to possess good complexing ability towards Cu^{2+} and Co^{2+} ions [21]. The sorption capacity of Cu^{2+} was determined by agitating the resin in excess CuSO_4 solution. Here, we present further studies in which the hybrid resin was packed in a column and eluted with a metal ion solution. Firstly, Cu^{2+} has been used as a model ion in our investigations because the adsorption/desorption of Cu^{2+} can be easily estimated from the color intensity of the solid phase (Figure 1). The crucial point addressed was the possibility of regeneration/recycling capability of these materials from the practical point of view. It is well known that the stability of the PAA complexes with heavy metal ions is largely affected by the pH of the solution and is observed to drop down drastically at pH levels below 3 which indicate that the sorbed metal ions could be easily stripped by dilute acid. When a sample containing metal ions is passed over the resin at a proper pH range, the ions are chelated by the polymer chains grafted onto silica, and thus retained by the resin. The metal ions can be removed from the resin and eluted by properly selecting the pH, generally by using acids. This also helps in regeneration of the resin, and thus chelating resins can be reused. Such a type of separation avoids the use of carcinogenic organic solvents and is eco-friendly.

For this reason, the materials were tested to assess the possibility of regeneration and reusability after treatment with 0.6 M HCl. Firstly, a column packed with the organic-inorganic resin was eluted with a CuCl_2 solution. Quickly, the white hybrid material at the top of the column became blue, and then, more and more intense blue band was progressively extended over the entire length of the column. The concentration of Cu^{2+} in the starting solution and after elution was evaluated, and the percentage of ions adsorbed on the resin was determined by the difference. To better evaluate the efficiency of the resin during time, three consecutive eluate fractions of 100 ml were collected and analysed separately. The material was finally eluted with 0.6 M HCl (25 ml), immediately obtaining the whitening of the resin. The metal ion recovery on the hydrochloric acid fraction was greater than 95% for all the tested materials. When HCl solution was used as the eluting agent, the coordinate bond interaction between Cu^{2+} and the resin was disrupted, and Cu^{2+} was released into the solution. Noteworthy, the metal solution was concentrated into a 12 times smaller volume. To evaluate possible damage of the adsorbing materials induced by acid treatment, further adsorption/desorption cycles were performed using the same procedure. The adsorption/desorption cycle was repeated 20 times using the same sorbent. The experimental results are shown in Figure 5. It was noticed that the absorbing capacity increased from 55% to a plateau of 95% for the starting material after two adsorption/desorption cycles.

TABLE 2: Degree of grafting evaluated by calcinations and confirmed by elemental analyses.

| Product | Degree of grafting (%) | Organic content (%) | HCl (%) | Si γ (%) |
|--------------------------|------------------------|---------------------|---------|-----------------|
| Si γ -[BAC-DMEDA] | 10.00 | 22.50 | 4.70 | 86.34 |
| Si γ -[BAC-EDDA] | 15.60 | 24.10 | 1.60 | 82.80 |

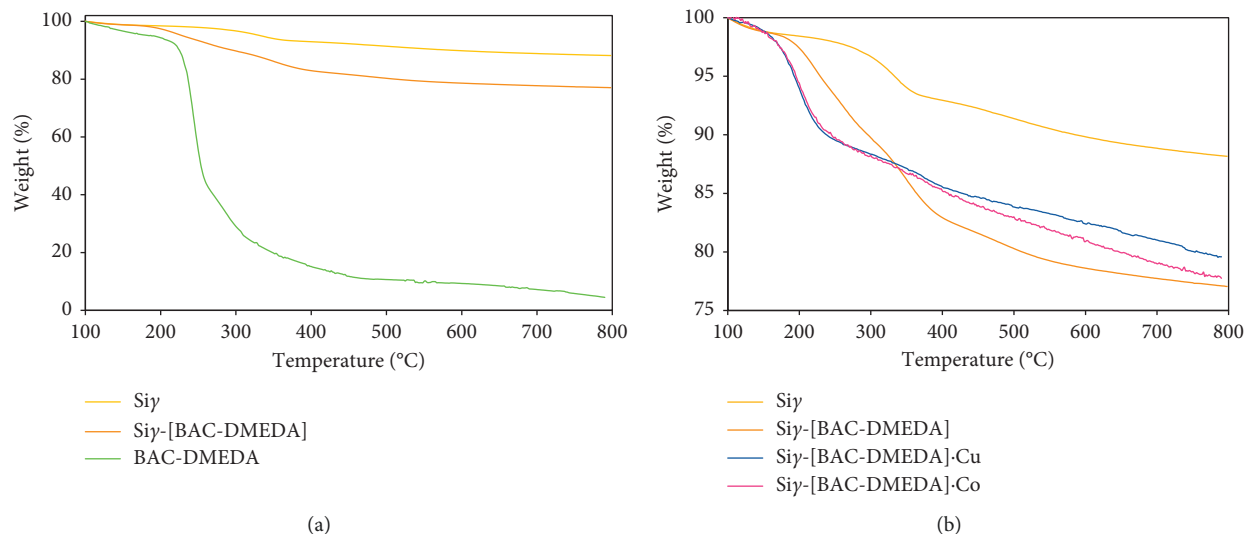
FIGURE 3: TGA traces of aminated silica, Si γ -[BAC-DMEDA], and linear [BAC-DMEDA] polymer (a) and of aminated silica, Si γ -[BAC-DMEDA], Si γ -[BAC-DMEDA]Cu, and Si γ -[BAC-DMEDA]Co (b) obtained at a heating rate of 20°C/min under nitrogen atmosphere.

TABLE 3: Surface atomic composition of aminated silica, PAA-grafted silica, and ion-chelated hybrid silica.

| Sample | Surface atomic composition (%) | | | | | Metal ion |
|----------------------------|--------------------------------|------|------|------|--|-----------|
| | C | N | O | Si | | |
| Si γ | 16.2 | 4.2 | 50.0 | 29.6 | | — |
| Si γ -[BAC-DMEDA] | 50.8 | 8.7 | 27.5 | 13.0 | | — |
| Si γ -[BAC-EDDA] | 46.6 | 11.2 | 29.1 | 13.1 | | — |
| Si γ -[BAC-DMEDA]Cu | 39.5 | 10.8 | 34.4 | 14.4 | | 0.9 |
| Si γ -[BAC-EDDA]Cu | 47.5 | 11.1 | 27.0 | 13.3 | | 1.1 |
| Si γ -[BAC-DMEDA]Co | 44.3 | 9.2 | 31.6 | 14.0 | | 0.9 |
| Si γ -[BAC-EDDA]Co | 44.9 | 11.1 | 29.3 | 13.9 | | 0.8 |

This increase might be a consequence of the fact that not all amino groups in the synthesized material were protonated, and the presence of salt decreased the absorption efficiency. Furthermore, it was observed that the material did not undergo appreciable damage due to the regeneration treatment. The hybrid Si γ -[BAC-EDDA] showed superb sorption capacity during 20 consecutive cycles and nearly remained stabilized on the whole.

3.3. Effect of Salts on Adsorption Capacity. From our preliminary investigation on Cu²⁺ uptake, it was deduced that the resins need to be preconditioned with 0.6M HCl to remove the eventually chemisorbed salts remaining after preparation and execute the best performance.

Therefore, an acid pretreatment was adopted in all subsequent studies on the adsorption of heavy metal ions. The adsorption of Cu²⁺, Zn²⁺, and Ni²⁺ in different media

ranging from drinking water to different salt solutions (CaCl₂, MgSO₄, and Na₂SO₄) is shown in Figure 6.

The presence of ions can compete with heavy metal ions complexation and may also affect the sorption process by contributing to the ionic strength of the solution and/or by complexing the metal cations. For example, chloride in sufficiently high concentrations can lead to complexation of the metal. Moreover, there are many different substances of natural and/or industrial origin in water together with metal ions. The presence of complexing agents in solutions has an influence on the adsorption equilibrium, and such systems can lead to both decreasing and increasing metal ion adsorptions. Ligands can compete by forming metal complexes in the aqueous phase and thereby limit the sorption efficiency, and they can also contribute to the sorption process by ternary surface complex formation. The effect depends on the concentration of the ligand, its specificity, or ability to form strong complexes.

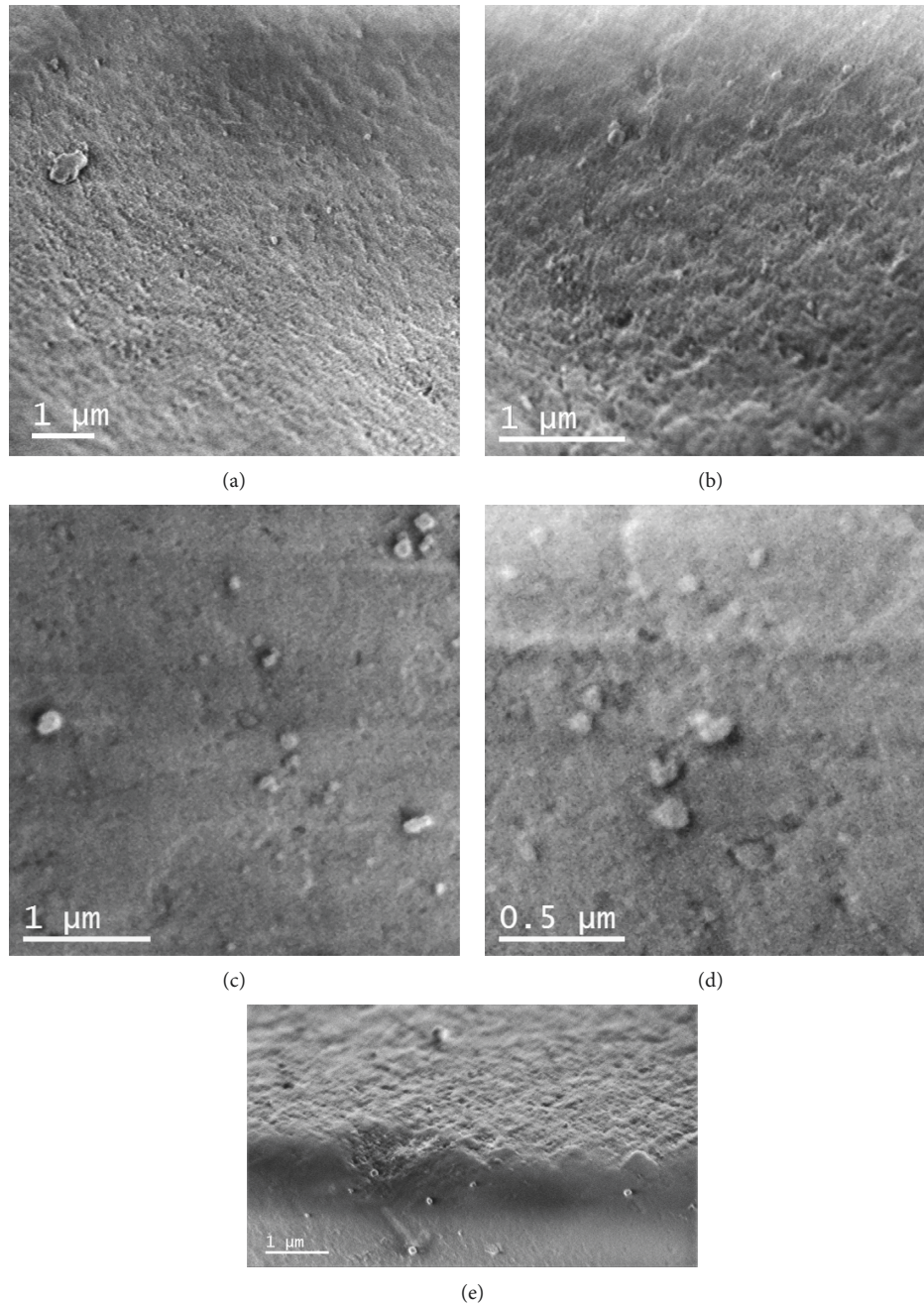


FIGURE 4: Scanning electron microscopy (SEM) images of (a, b) uncoated silica at different magnifications, (c, d) coated silica at different magnifications, and (e) polymer-coated silica, observation at crazing angle.

Useful information regarding the salt effects can be obtained by measuring sorption capacity in the presence of salts, which in principle may interfere with the uptake of heavy metal ions. To this purpose, the adsorption of Cu^{2+} , Zn^{2+} , and Ni^{2+} was evaluated in a series of experiments under the same ratio reaction in distilled water and in salt solutions with high ionic strengths (0.1 M CaCl_2 , 0.1 M MgSO_4 , and 0.1 M Na_2SO_4) (Table 4).

From the inspection of Figure 6, it was evident that polymer-grafted silica (Figures 6(b) and 6(c)) showed improved adsorption ability compared with aminated silica

(Figure 6(a)). $\text{Si}\gamma$ -[BAC-EDDA] was able to remove more than 90% of all ions tested in the drinking water, whereas $\text{Si}\gamma$ -[BAC-DMEDA] was less effective, particularly in the case of Zn^{2+} and Ni^{2+} . This result confirmed the complexation capacity of the PAA chains in the grafted form. The execution of better uptake by $\text{Si}\gamma$ -[BAC-DMEDA] is because of the presence of one carboxy group per repeating unit which can participate in the ion chelation process. As expected, $\text{Si}\gamma$ -[BAC-EDDA] displayed the best performance because of possessing three carboxy groups per repeating unit, resulting in maximum metal ion

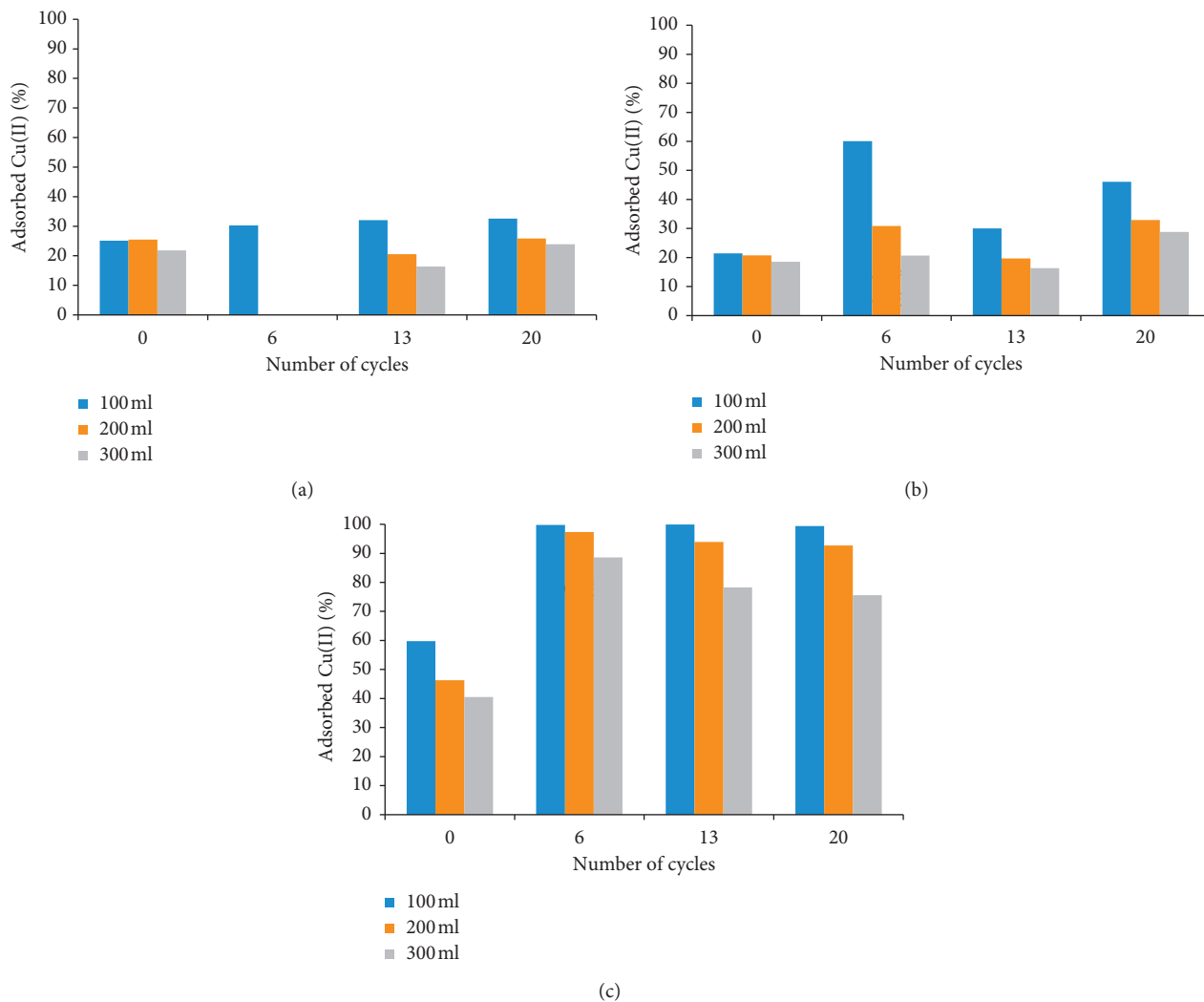


FIGURE 5: Adsorption (%) of Cu^{2+} on Si γ (a), Si γ -[BAC-DMEDA] (b), and Si γ -[BAC-EDDA] (c) at increasing adsorption-desorption cycles.

complexation. The complexing capacity of the Si γ -[BAC-DMEDA] resin towards three metal ions was found to be $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$, whereas the complexing capacity of Si γ -[BAC-EDDA] resin was higher and of the same order for the three metal ions.

Literally, there was no effect of ionic strength on the sorption capacity of Si γ . However, an increasing trend of sorption ability was observed for Si γ -[BAC-DMEDA] resins, particularly a pronounced effect for Cu^{2+} and Ni^{2+} . The presence of a high ionic strength equally increased the adsorption of Cu^{2+} , Zn^{2+} , and Ni^{2+} on Si γ -[BAC-EDDA], and it was the best adsorbent in our system.

3.4. Adsorption from Mixtures of Metal Ions. The need for more specific metal ion recovery processes in both hydrometallurgical and environmental applications has led to a growing in selective ion exchange. In order to study the selectivity towards different metal ions of our materials, competitive adsorption was investigated using Cu^{2+} , Co^{2+} , Zn^{2+} , and Ni^{2+} . It is known that in hydrometallurgy, the

separation of copper from cobalt and nickel is of considerable importance. To this purpose, a column packed with the appropriate material (100 mg) was eluted with a solution containing about 0.4 mg/L of each metal ion except for Zn^{2+} which was 0.9 mg/L. Figure 7 and Table 5 show the percent of adsorption for each metal ion evaluated after elution on Si γ , Si γ -[BAC-DMEDA], and Si γ -[BAC-EDDA].

The results demonstrated that the starting Si γ could take up very low amounts of metal ions, particularly Co^{2+} and Ni^{2+} , whereas the hybrid Si γ -[BAC-DMEDA] adsorbed significant quantities of Cu^{2+} , Zn^{2+} , and Ni^{2+} but relatively lower amounts of Co^{2+} .

Surprising results was obtained with the hybrid Si γ -[BAC-EDDA] that was able to adsorb very high quantities of all ions tested ($\geq 95\%$), with the amount of nonadsorbed ions remaining negligible. So, the hybrid Si γ -[BAC-EDDA] exhibited a strong adsorption ability for Cu^{2+} , Co^{2+} , Zn^{2+} , and Ni^{2+} ions and could be potentially used as the solid-phase extraction material for the selective adsorption of trace metal ions in real water samples.

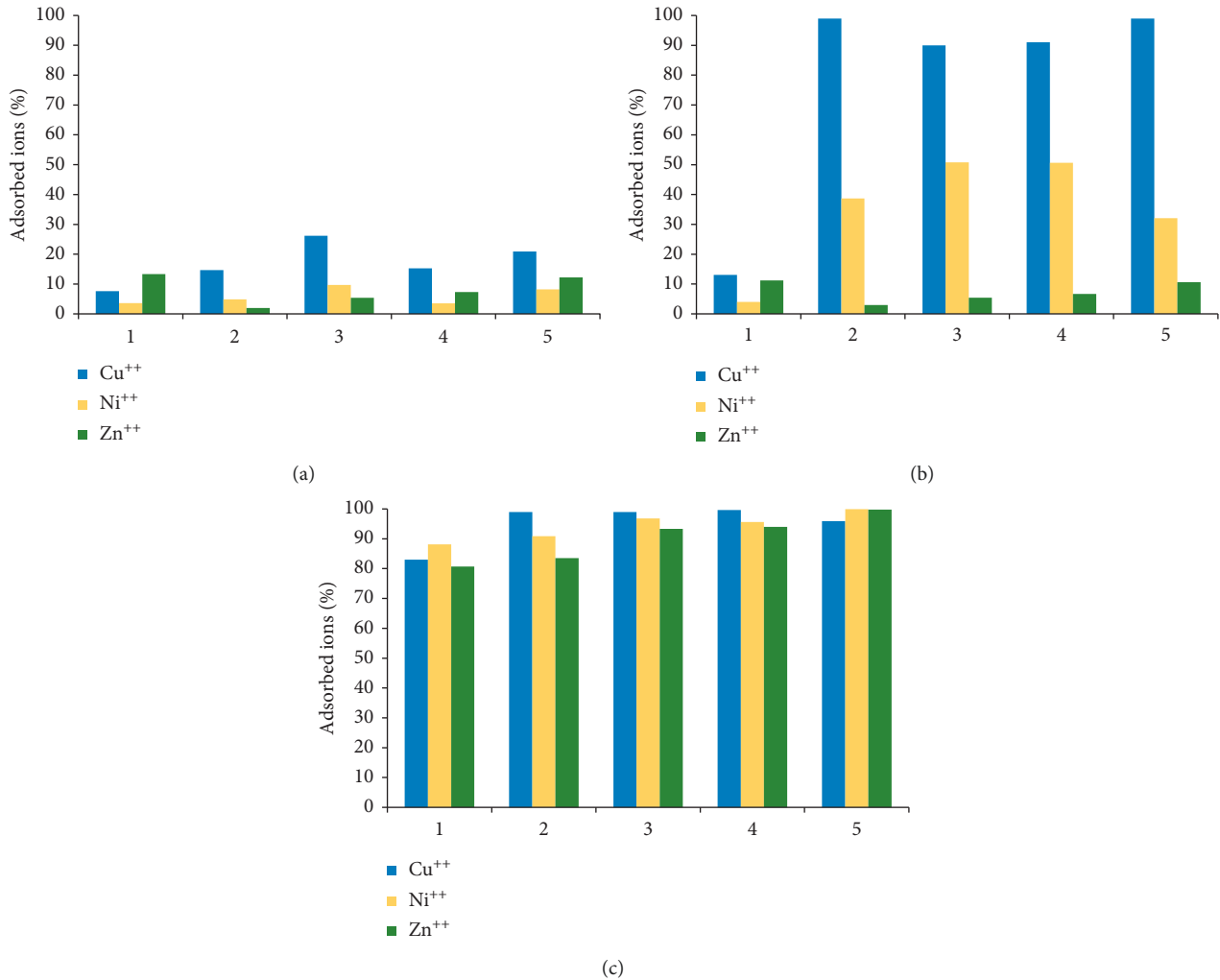


FIGURE 6: Adsorption (%) on Siγ (a), Siγ-[BAC-DMEDA] (b), and Siγ-[BAC-EDDA] (c) of heavy metal ions dissolved in (1) distilled water, (2) 0.1 M CaCl₂, (3) 0.1 M MgSO₄, (4) 0.1 M Na₂SO₄, and (5) drinking water.

TABLE 4: Initial heavy metal concentration and ion removal after elution on Siγ, Siγ-[BAC-DMEDA], and Siγ-[BAC-EDDA].

| Solvent | Initial [Cu ²⁺] (mg/l) | (% Cu ²⁺ removal) | | |
|---------------------------------------|------------------------------------|------------------------------|-----------------|----------------|
| | | Siγ | Siγ-[BAC-DMEDA] | Siγ-[BAC-EDDA] |
| Distilled water | 13.2 | 7.6 | 13.1 | 82.9 |
| 0.1 M CaCl ₂ | 0.8 | 14.7 | >98.7 | >98.7 |
| 0.1 M MgSO ₄ | 13.8 | 26.2 | 89.9 | 98.7 |
| 0.1 M Na ₂ SO ₄ | 13.4 | 15.3 | 90.4 | 99.6 |
| Drinking water | 3.4 | 20.9 | 98.8 | 95.9 |
| Solvent | Initial [Ni ²⁺] (mg/l) | (% Ni ²⁺ removal) | | |
| | | Siγ | Siγ-[BAC-DMEDA] | Siγ-[BAC-EDDA] |
| Distilled water | 15.3 | 3.6 | 4.0 | 88.11 |
| 0.1 M CaCl ₂ | 14.4 | 4.9 | 38.7 | 90.9 |
| 0.1 M MgSO ₄ | 15.8 | 9.7 | 50.8 | 96.8 |
| 0.1 M Na ₂ SO ₄ | 11.8 | 3.5 | 50.6 | 95.6 |
| Drinking water | 14.8 | 8.2 | 32.1 | 99.9 |
| Solvent | Initial [Zn ²⁺] (mg/l) | (% Zn ²⁺ removal) | | |
| | | Siγ | Siγ-[BAC-DMEDA] | Siγ-[BAC-EDDA] |
| Distilled water | 9.0 | 13.3 | 11.2 | 80.7 |
| 0.1 M CaCl ₂ | 9.4 | 2.0 | 3.0 | 83.5 |
| 0.1 M MgSO ₄ | 9.2 | 5.4 | 5.4 | 93.3 |
| 0.1 M Na ₂ SO ₄ | 9.2 | 7.3 | 6.7 | 94.0 |
| Drinking water | 8.5 | 12.2 | 10.6 | 99.8 |

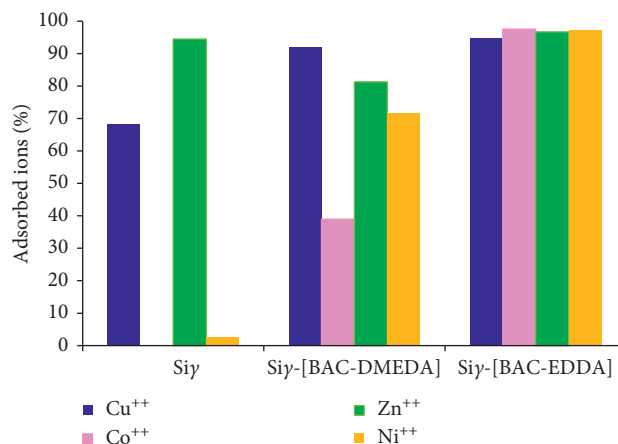


FIGURE 7: Adsorption (%) on Siγ, Siγ-[BAC-DMEDA], and Siγ-[BAC-EDDA] from a solution of mixed metal ions.

TABLE 5: Starting mixture concentration, residual concentration, and percent adsorption of heavy metal ions after elution on Siγ, Siγ-[BAC-DMEDA], and Siγ-[BAC-EDDA].

| Heavy metal ions | Initial conc. (mg/l) | Siγ | | Si-[BAC-DMEDA] | | Si-[BAC-EDDA] | |
|---------------------|----------------------|-----------------------|----------------|-----------------------|----------------|-----------------------|----------------|
| | | Residual conc. (mg/l) | Adsorption (%) | Residual conc. (mg/l) | Adsorption (%) | Residual conc. (mg/l) | Adsorption (%) |
| [Cu ²⁺] | 0.38 | 0.12 | 68.4 | 0.03 | 92.1 | 0.02 | 94.8 |
| [Co ²⁺] | 0.41 | 0.41 | 0 | 0.25 | 39.0 | 0.01 | 97.6 |
| [Zn ²⁺] | 0.91 | 0.05 | 94.5 | 0.17 | 81.3 | 0.03 | 96.7 |
| [Ni ²⁺] | 0.39 | 0.38 | 2.6 | 0.11 | 71.8 | 0.01 | 97.4 |

4. Conclusions

In this work, two organic-inorganic hybrid materials of PAAs-grafted aminated silica, namely, Siγ-[BAC-DMEDA] and Siγ-[BAC-EDDA], were synthesized through covalent bonding to assess the execution level of performance towards heavy metal ions chelating properties, both in single and mixed metal ion solutions. In both cases, Siγ-[BAC-EDDA] resin showed excellent adsorption ability for all metal ions tested. In addition, the regeneration study showed that this resin was stable after repeated use. According to the obtained results, the novel Siγ-[BAC-EDDA] ions chelating resin could be a promising solid-phase extraction material for the removal of heavy metals, blessed with several unique characteristics, such as facile synthesis, low price, obvious mechanical strength, fast and high adsorption capacity, convenient recovery from waste water under mild reactive conditions, and proper selectivity.

Data Availability

The data used to support the findings of this study are included within the article.

Disclosure

An earlier version of this paper has been presented as a conference abstract in "Organic-inorganic hybrid composites for removal of heavy metal ions from water" in the following link: <https://aip.scitation.org/doi/abs/10.1063/1.5046003>.

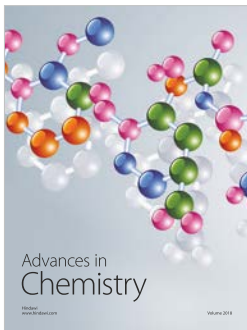
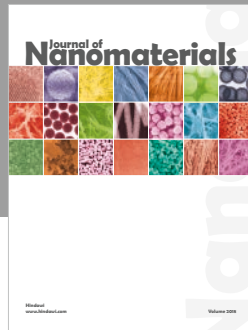
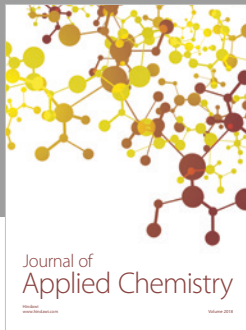
Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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