Designed pendant chain covalently bonded to silica gel for cation removal

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Abstract

The precursor 1,4-bis(3-aminopropyl)piperazine organofunctionalized silica gel reacted with methylacrylate to yield a new inorganic–organic chelating material, by adopting a heterogeneous and divergent synthetic approach. The synthesized materials were characterized through elemental analyses and spectroscopic techniques such as infrared, nuclear magnetic nuclei of carbon-13 and silicon-29. Due to the increment of basic centers attached to the pendant chains the metal adsorption capability of the final chelating material, was found to be higher than its precursor. The adsorption of metal ions from aqueous solution followed the order $Cu^{2+} > Ni^{2+} > Co^{2+}$. Both Langmuir and Freundlich models were found to be applicable for the adsorption of copper, with the equilibrium parameter value within zero to one. The competitive sorption behavior, with variation of pH, was favorable for the separation of copper from binary mixtures with nickel and cobalt. When sodium, potassium and magnesium cations are present in the medium little effects on adsorption were observed, thus suggesting that the synthesized material can be useful for removal of toxic/heavy metal ions from natural and wastewater systems.
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1. Introduction

Functional groups attached to chemically organofunctionalized silica have ability in changing the original surface properties by giving valuable applications for such new materials [1,2]. A variety of organofunctional molecules anchored on various solid supports, such as crysotile fibers [3], natural talc [4] synthetic phyllosilicate [5], mesoporous silica [6], silicic acid [7] and hydroxyapatite [8] are successfully employed in trace metal separation and concentration methodologies. For such purpose, silica gel is mostly used not only due to the facility of immobilization process, but also to be relatively simple in comparison to organic polymers [9], with faster metal ion-exchange kinetics, good swelling resistance in different solvents, and chemical stability [10].

The advances in silica gel organofunctionalization field are closely associated with development of new silylating agents, which pendant organic chains can display non-hydrolyzable silicon–carbon bond, to prevent the leaching of the immobilized reagent to solution [11]. However, as the pendant chains incorporate donor basic atoms, an improvement on adsorption and exchange properties are normally increased [12,13]. For this purpose, the enlargement in organic chains through successive reactions, by including functional groups give well-defined conditions in determining ultimate properties [14], such as applications in various technological processes [15], and strong affinities for metals [16].

The present investigation reports the functionalization of silica gel with 1,4-bis(3-aminopropyl)piperazine and subsequent reaction with methylacrylate in a heterogeneous route, to yield a final product containing carboxylate moieties in the structure, with further potential to grow using a divergent synthetic approach. The present methodology offers a new initiative for silica having immobilized supramolecular chemistry and the characterized materials were explored for divalent copper, nickel and cobalt adsorption properties.
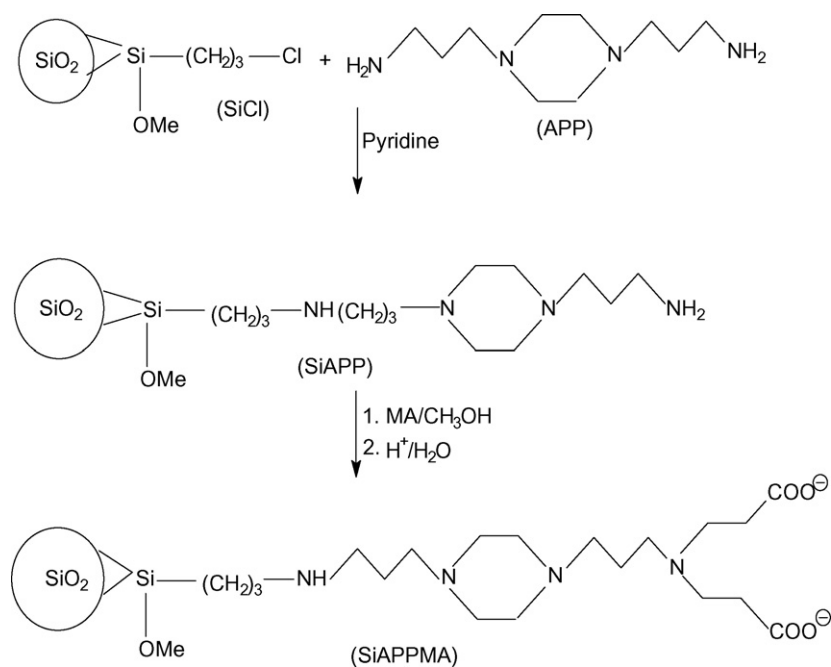
2. Experimental

2.1. Reagents

The reagents 3-chloropropyltrimethoxysilane (CPTS) and 1,4-bis(3-aminopropyl)piperazine (APP), Aldrich, were used as

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Scheme 1. Sequence of reactions for immobilization.

received. Methylacrylate (MA), Across, was washed with NaOH ($0.50 \, mol \, dm^{-3}$) and dried before use. Methanol, reagent grade, was distilled before use. Other solvents such as xylene, reagent grade, were used as received. The doubly distilled water (DDW) was obtained from an ultra-pure Milli-Q $18.2 \, M\Omega$ system. The methanol and ethanol were reagent grade. Solutions of M^{2+} (Cu, Ni, Co) were prepared from suitable reagent grade nitrate or chloride salts in DDW. Buffers such as KCl/HCl, Na_3PO_4/NaOH were used to control the pH of the medium.

2.2. Synthesis of chemically modified silica support

A heterogeneous route was adopted to chemically modify the surface silica with functional groups. A divergent synthetic approach was made for the preparation of amine-terminated wedge, and a subsequent carboxylate terminated wedge in the structure, as shown in Scheme 1.

In the first step, a sample of 15 g of silica gel, Fluka, with particle size 0.063–0.200 mm and with a mean pore of 6.0 nm was activated by refluxing with concentrated HCl for 4 h to remove any adsorbed metal ions, then filtered and repeatedly washed with water until the filtrate was neutral and dried in an oven at 370 K for 8 h to remove adsorbed surface water. Further, it was heated in a stream of dry nitrogen for 2 h and was immediately used. The organochloro functional agent was then immobilized by suspending a sample of 14 g of dry activated silica gel in $100 \, cm^3$ of dry xylene, followed by addition of $4.5 \, cm^3$ of 3-chloropropyltrimethoxysilane to the suspension. The mixture was allowed to react under continuous stirring and a dry nitrogen atmosphere at 340 K for 72 h. The suspension was filtered, washed with xylene, methanol and dried under vacuum [17], to give a product called SiCl. In the subsequent step a suspension of 12 g of SiCl in $50 \, cm^3$ of xylene was allowed to react with $15.0 \, cm^3$ of 1,4-bis(3-aminopropyl)piperazine (APP)

at 340 K under continuous stirring and a dry nitrogen atmosphere for 24 h. The product (SiAPP) was filtered, washed with xylene and an excess of ethanol and then dried under vacuum. In the subsequent step, a sample of 10 g of the preceding compound reacted with $10.0 \, cm^3$ of methylacrylate (MA) in $60 \, cm^3$ of methanol at a controlled temperature of 318–323 K and under a nitrogen atmosphere for 48 h to yield the final product, named SiAPPMA [18]. The white powder was washed with an excess of methanol, dried, and then treated with $50 \, cm^3$ of dilute hydrochloric acid $0.050 \, mol \, dm^{-3}$ for 2 h, and then again washed with methanol and further dried under vacuum.

2.3. Concentration of metal ions

The batch method was used to concentrate M^{2+} (Cu, Ni and Co) from aqueous solutions in order to obtain the adsorption isotherm [19,20]. For this procedure, samples of about 50 mg of each organofunctionalized silica were suspended in $20.0 \, cm^3$ of aqueous solutions of each cation with varying concentrations ranging from 0.010 to $1.0 \, mol \, dm^{-3}$. The samples were mechanically shaken at $298 \pm 1 \, K$ for 24 h, after which the solid was separated by centrifugation. The supernatant was analyzed using ICPOES. The amount of metallic cations adsorption was calculated using the expression: $N_f = (N_i - N_s)/m$, where N_f is the number of moles adsorbed on the pendant groups of the material, N_i and N_s are the number of moles in the initial solution and in the supernatant after equilibrium, and m is the mass of the solid adsorbent used in the adsorption process. The distribution coefficient (K_d, $cm^3 \, g^{-1}$) and the selectivity coefficient (α) were calculated according to the following equations:

$$K_d = \frac{C_1 (mmol \, g^{-1})}{C_2 (mmol \, cm^{-3})} \tag{1}$$

where C_1 and C_2 denote the metal concentration in the solid and solution phases, respectively.

$$\alpha = \frac{K_{d1}}{K_{d2}} \tag{2}$$

where 1 and 2 denote the metal ions 1 and 2, respectively.

2.4. Instrumentation

Elemental analysis was done on a PerkinElmer, model 2400, elemental analyzer. The infrared spectra of the samples in KBr pellets were performed by diffuse reflectance by accumulating 35 scan on a Bomem Spectrophotometer, MB-series, in the range of 4000–400 cm^{-1}, with 4 cm^{-1} of resolution. Nuclear magnetic resonance spectra of the samples were obtained on a Brucker AC 300/P spectrometer at room temperature. For each run, approximately one gram of each solid sample was compacted into a 7 mm zirconium oxide rotor. The measurements were obtained at frequencies of 59.63 and 75.47 MHz, for silicon and carbon atoms, respectively, with a magic angle spinning of 4 kHz. In order to increase the signal to noise ratio of the solid-state spectra, the CP/MAS technique was used. ^{29}Si and ^{13}C CP/MAS spectra were obtained with pulse repetitions of 3 s for both nuclei and contact times of 1 and 3 ms, respectively. The amount of cations adsorbed per gram of the support was determined by the difference between the initial concentration in aqueous solution and that found in the supernatant, by using an ICPOES PerkinElmer 3000 DV apparatus. For each experimental point, the reproducibility was checked by at least one duplicate run. The pH of the solution was measured using a pH/Ion Analyzer, model 450 M.

3. Results and discussion

3.1. Characterization

Considering three main stages as given for the reaction in Scheme 1 for the organofunctionalization of the surface, the final compound contains carboxylate moieties in the end of synthesized pendant chain bonded to the inorganic silica structure. The piperazine type compound anchored was chosen not only due to the incorporation of basic nitrogen atoms in the pendant structure, but also because the ring conformational structure, whose flexibility facilitates metal coordination. In principle, these basic centers can be useful to explore their potentiality to extract cations from an effluent solution. The percentage of carbon, hydrogen and nitrogen for SiAPP and SiAPPMA were found to be 19.9, 4.3, 8.3 and 20.5, 4.9, 7.7, respectively. Based on the nitrogen content, the pendant chains in the final compound, SiAPPMA, were calculated as 1.48 mmol g^{-1} of nitrogen atoms, which showed the incorporation of nitrogen donor atoms in the pendant chains of the synthesized materials.

The infrared spectra of the synthesized products are compared with pure silica gel in Fig. 1. The main features of the silica spectrum are: (a) the bands associated with the inorganic backbone such as the broad band between 3400 and 3200 cm^{-1},
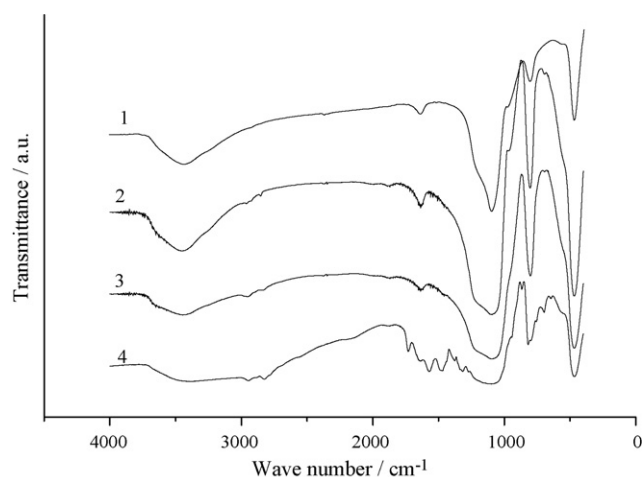

Fig. 1. FTIR spectra of silica gel (1), SiCl (2), SiAPP (3) and SiAPPMA (4).

which is attributed to the presence of the O—H stretching frequency of the surface silanol group and also to adsorbed water molecules, (b) the appearance of a peak related to the siloxane stretching frequency, ν(Si—O—Si), observed at 1100 cm^{-1}, (c) the band at 900 cm^{-1} assigned to Si—OH bending frequency and (d) the vibration at 1650 cm^{-1} attributed to the angular vibration of the water molecule. All the chemically modified silica gel materials, presented the same set of bands related to the inorganic backbone, however, an additional band at 2950 cm^{-1}, is assigned to the C—H stretching of the tetrahedral carbon, thus confirming the anchoring of the organic molecules onto the silica surface [21]. The spectrum of SiAPPMA indicated the incorporation of the methacrylate group by the appearance of carbonyl group vibration at 1720 cm^{-1}, in addition to the other characteristic features associated with the main pendant carbon chain. Some of the group vibrations were of lesser intensity, which could be due to the crowding of the molecules or groups of atoms on the surface.

Nuclear magnetic resonance in solid-state is a technique to give valuable information about the bonding of the pendant chains anchored on an inorganic backbone. For this purpose carbon and silicon nuclei were examined in order to better characterize the synthetic compounds. For silicon, the spectra shown in Fig. 2 provide information about the polysiloxane framework such as various local environments of the atoms involved and the attachment of pendant groups, and in the present case the assignments were based on a previously studied analogous system [22]. The organochloro-modified sample, SiCl, showed for the silicon nucleus four main peaks located at −58, −67, −99 and −110 ppm. The first peak at −58 ppm was assigned to silicon atom of the silylating agent bonded to one OH group and forming two siloxane bonds with silicon atom of silica structure, RSi(OSi)(OH)$_2$, assigned as a T^2 signal. The peak at −67 is attributed silicon atom in the RSi(OSi)$_3$ structure, with the signal named T^4. The result indicated the covalent-attachment of organic groups on the silica surface. The other two peaks, attributed to surface signals, are described as: (i) Si(OSi)$_4$, Q^4 at −110 ppm and (ii) surface signal, Si(OSi)$_3$OH, Q^3 at −99 ppm. A little shifting of the signals and broadening of the peaks were
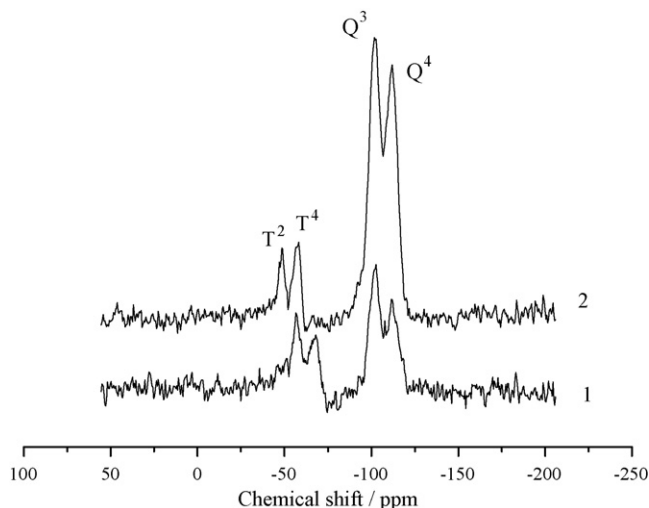
Fig. 2. ^{29}Si NMR of SiCl (1) and SiAPPMA (2).

noticed in case of SiAPPMA, however, the main features of all spectra are remained [23,24].

The spectra related to ^{13}CNMR in the solid-state are shown in Fig. 3. These data correlate the important information regarding the immobilization of pendant chains on the inorganic backbone of the silica structure. For SiCl the peaks at 10.2, 27.6 and 47.0 ppm were assigned to C_1, C_2 and C_3 atoms of the aliphatic propyl chain of the immobilized organochloro compound. The peak at 57.2 ppm denotes the carbon atoms from either unreacted alkoxy groups or surface anchored alkoxy groups [25]. The same set of peaks is also expected in the SiAPPMA spectra, representing the presence of the spacer aliphatic carbon atoms, however, with some shifting in signal positions and broader shapes attributed to the overlapping of group vibration frequencies upon the modification process [26]. The peak centered at 50 ppm, for SiAPPMA, is assigned to the methylene group vibrations in the compound. In addition, a weak peak is observed at 169 ppm in the insert part of Fig. 3, which is assigned to carbonyl carbon and confirms the presence of this group in the pendant chains. All these appearances in the spectrum are consistent with a more rigid micro-environment created upon the modification processes. Thus, correlating the data obtained from FTIR, ^{29}Si
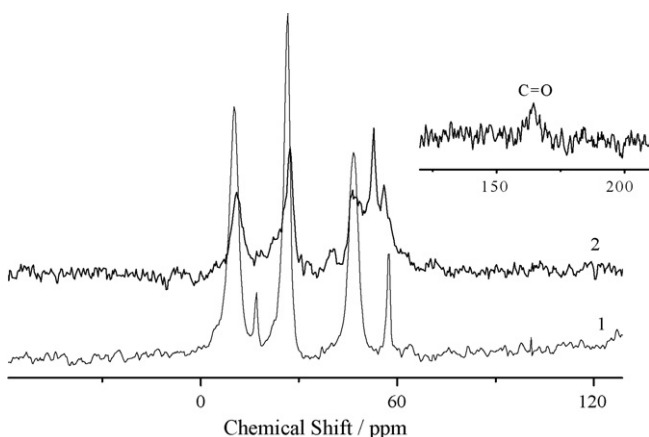

Fig. 3. ^{13}C NMR spectra of SiCl (1) and SiAPPMA (2).

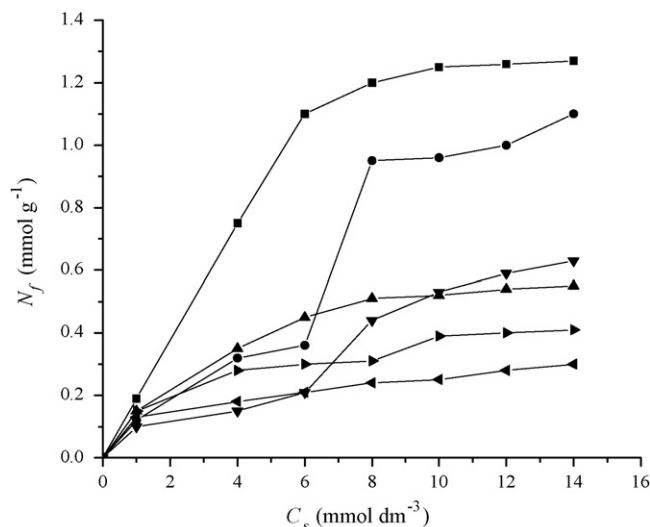Fig. 4. Adsorption of cations onto: (a) SiAPPMA: for Cu^{2+} (■); Ni^{2+} (●); Co^{2+} (▲) and (b) SiAPP for Cu^{2+} (▼); Ni^{2+} (►); Co^{2+} (◄).

and ^{13}C NMR techniques, it could be concluded that the organic group was covalently attached to the silica structure.

3.2. Analytical studies

The effect of metal ion concentration on the uptake behavior of the chelating materials was studied in the concentration range 0.010–1.0 mol dm^{-3}. A comparison of the adsorption behavior was made between the final chelating material SiAPPMA and its precursor SiAPP, which also contains sites for metal coordination. The profile of adsorption of metal ions is presented in Fig. 4. A leveling effect was noticed at the higher concentrations for both the materials because of saturation of the available coordination sites [27]. Metal sorption was found to follow the order Cu^{2+} > Ni^{2+} > Co^{2+}, which agrees well with the Irving-Williams series and the stability constants of the metal ions [28]. The SiAPPMA material showed a higher adsorption capacity for all the metal ions in comparison to its precursor SiAPP. This is attributed to the availability of more sites for coordination purposes. In contrast to the pure silica precursor, mixing the modified silicas with cation solutions gave a characteristic blue color to the solid for copper, and a light-pink color with the cobalt solution, which visually evidenced the complexation. These results suggest that the increase in coordination sites on the structure favored the metal coordination process. However, the metal chelating nature of the material also depends upon some other factors like the nature of the ligands present in the matrix, their mode of cation binding (stereochemistry), as well as their accessibility towards the metal ions in solution under various competitive and non-competitive conditions [29]. In a separate control the same procedure was applied with the original activated silica and no significance adsorption was observed.

The sorption isotherm for the Cu^{2+} was evaluated using the modified Langmuir equation [30]:

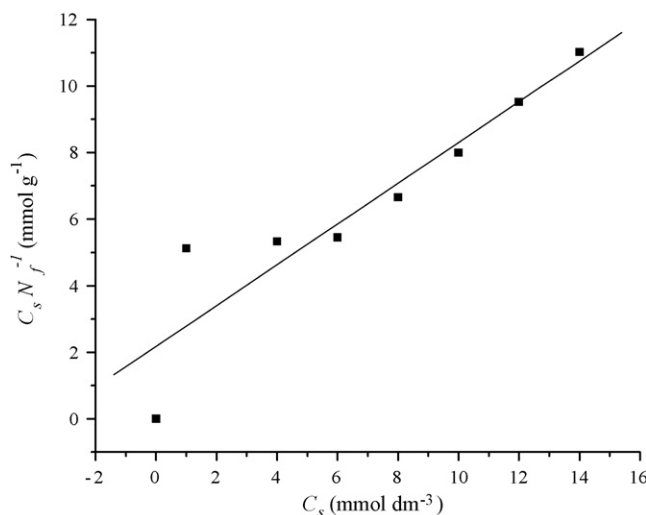$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s \cdot b} \tag{3}$$

Fig. 5. Langmuir adsorption isotherm for SiAPPMA: metal ion Cu^{2+} with time of contact of 24 h at temperature of 298 ± 1 K.

Fig. 6. Effect of adsorption pH for SiAPPMA: Cu^{2+}(■); Ni^{2+} (●); Co^{2+} (▲) and for SiAPP: Cu^{2+} (▼); Ni^{2+} (►); Co^{2+} (◄).

where C_s is the equilibrium concentration of adsorbate in solution (mol dm^{-3}), N_f is the amount of cations adsorbed on the adsorbent matrix per gram (mol g^{-1}), N_s is the maximum quantity of cations per gram necessary to form a monolayer on the modified surface (mol g^{-1}), and b is a proportionality factor that includes the equilibrium constant for the reaction. N_s and b values can be estimated from coefficients after linearization of the isotherm [5,31]. The linear plot of C_s/N_f versus C_s shows that the adsorption obeys the Langmuir adsorption model as shown in Fig. 5, from which, the values of N_s and b were determined for this adsorption. For SiAPPMA and SiAPP, the values were 1.63, 0.28 and 0.62, 0.52 mmol^{-1}, respectively. The equilibrium parameter is defined as $R_L = 1/(1 + bN_i)$, where b is the Langmuir constant and N_i is the initial concentration of metal ion. For SiAPPMA the values of R_L at two different concentrations, 1.0 and 10.0 mmol dm^{-3}, were 0.78 and 0.26, and for SiAPP the values were found to be 0.66 and 0.16, respectively. These values obtained at two different concentrations, lie between zero and one, which indicates a favorable adsorption of Cu^{2+} onto both chelating materials.

To test the applicability of the Freundlich adsorption isotherm (Eq. (4)), it was computed for the sorption of Cu^{2+} onto the chelating materials, as expressed by:

$$\log \frac{x}{m} = \log k_{ad} + \frac{1}{n} \log C_s, \tag{4}$$

where k_{ad} is the adsorption coefficient, C_s is the equilibrium concentration, x is the amount of metal ion sorbed by the chelating material and n is a constant. A plot of $\log (x/m)$ versus $\log C_s$ for adsorption of Cu^{2+} onto SiAPPMA shows a linear behavior and the constants k_{ad} and n were found to be 5.43 and 1.58, respectively. For SiAPP, the values of k_{ad} and n were 6.14 and 1.962, respectively. In all cases, the obtained values, $1 < n < 10$, indicate the favorable sorption of Cu^{2+} onto the chelating materials.

Changes in pH of the medium are one of the most important factors affecting the concentration and metal recovery procedure, which is related to the formation of soluble metal complexes and subsequently their stabilities in aqueous solution
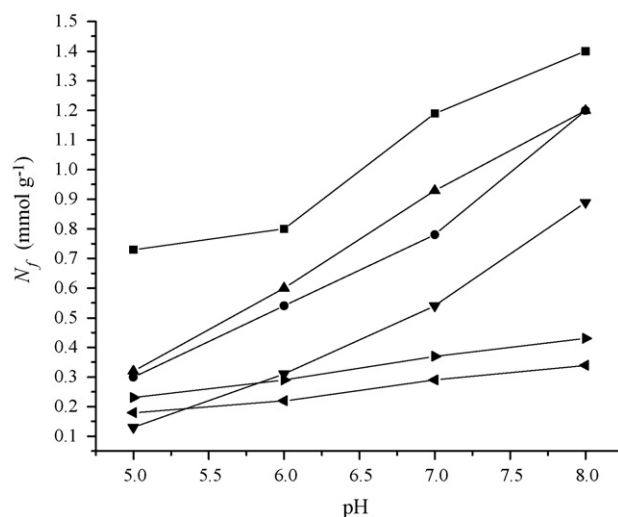
[32]. The metal ions were examined within a range of pH 5.0–8.0 as shown in Fig. 6. In acidic pH, the materials showed comparatively low metal ion uptake due to protonation of ligating sites that inhibit their binding to metal ions [33]. However, with the increase in pH of the medium, the metal sorption increased due to the availability of the basic centers and hence the coordination ability of the chelating material [34]. The order of metal sorption for both the chelating materials was found to be $Cu^{2+} > Ni^{2+} > Co^{2+}$. Investigation beyond pH 8.0 was discouraged due to the precipitation of some hydroxide species as well as the possibility of breaking of silica structure at higher pH.

3.3. Competitive sorption behavior

The competitive sorption behavior of the chelating material SiAPPMA was examined at different pH, by considering a mixture of M^{2+} (Cu, Ni, Co) to evaluate the preferential binding ability towards metal ions. It is known that the competitive sorption or separation of a given metal ion in the presence of other metal ions is controlled mainly by factors such as the nature of the donating sites, the nature of the metal ion and the pH [35]. However, other factors such as temperature and time of equilibration also play vital roles in a given separation process.

The distribution coefficient (K_d) can be taken as a representative value for the selective measurements, if all the tested metal ions and not only the individual ions compete with each other, in binding to the selective functional groups of the metal chelate-forming sorbent. From the plot of $\log K_d$ versus pH of the medium, as shown in Fig. 7, it could be seen that at low pH, the distribution coefficients were found to be low, which could be attributed to the protonation of the coordinating sites as well as incomplete ionization of the groups. In the present case, the $\log K_d$ value for Cu^{2+} was comparatively higher than that of Ni^{2+} and Co^{2+} even at lower pH. The selectivity coefficient α, often used as a measure of chromatographic separation processes determined as $\alpha = K_{d1}/K_{d2}$, where K_{d1} and K_{d2} are the distribution coefficients of two metal ions. The factor α was computed
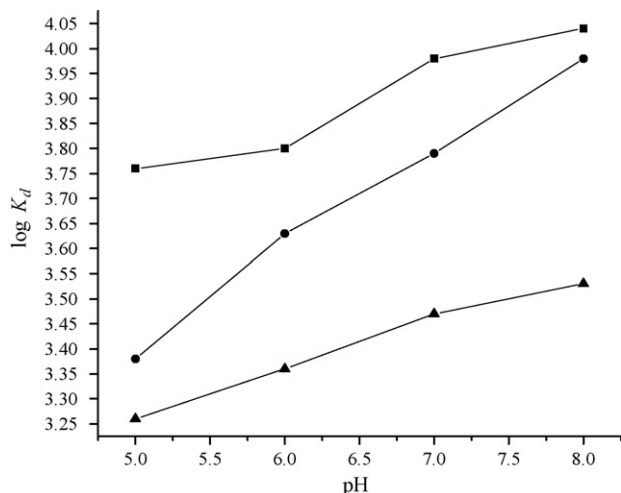
Fig. 7. Plot of pH *versus* log K_d for adsorption of Cu^{2+} (■), Ni^{2+} (●) and Co^{2+} (▲) onto chelating SiAPPMA material.

Table 1

The chelating ability of samples of about 50 mg of SiAPP and SiAPPMA adsorbents (AD) in 10.0 mg dm^{-3} of M^{2+} (Cu, Ni, Co), after 24 h of contact, to give the percentage of recovery (PR) and the recovery percentage (RP) in the presence of 20 mg dm^{-3} of each cation

AD	M^{2+}	PR (%)	RP (%)
SiAPP	Cu	98.9	96.3
	Ni	97.6	95.1
	Co	98.1	95.8
SiAPPMA	Cu	99.2	97.8
	Ni	98.5	96.3
	Co	97.3	95.0

Each value is an average of three independent determinations.

Table 2

Analysis of tap water samples using the chelating adsorbent SiAPPMA for M^{2+} (Cu, Ni), by considering cation added (CA) and found (CF) and the percentage recovery (PR)

M^{2+}	CA (mg dm^{-3})	CF (mg dm^{-3})	PR (%)
Cu^{2+}	0	0.32	–
	1.0	1.25	94.6
	2.0	2.21	95.2
Ni^{2+}	0	0.21	–
	1.0	1.10	90.9
	2.0	2.11	95.4

in the case of adsorption onto SiAPPMA only, for the separation of Cu^{2+} from binary mixtures at pH 5.0–8.0. The results for the binary mixture Cu^{2+}/Ni^{2+} at pH 5.0, 6.0, 7.0 and 8.0, gave the values 2.43, 1.48, 1.52 and 1.16, respectively. Identically, for the Cu^{2+}/Co^{2+} combination, the values were 3.17, 2.75, 3.20 and 3.25, respectively. Analysis of these results indicated that it could be possible to separate Cu^{2+} from the binary mixtures Cu^{2+}/Ni^{2+} and Cu^{2+}/Co^{2+} at appropriate pH of the medium. However, in the present case, the preferential extraction of Cu^{2+} was more favorable in the Cu^{2+}/Co^{2+} mixture than for Cu^{2+}/Ni^{2+}.

Further it may be noted that the higher affinity towards Cu^{2+} ions in a competitive environment may also be attributed to the preferential binding of the positionally active and non-sterically hindered donor atoms present in the final structure. This initial study highlights the positive aspect of carrying out detailed investigations with different metal ions for its future application in selective removal of metal ions by optimizing the parameters involved.

3.4. Effect of diverse foreign ions

Diverse foreign ions such as alkali and alkaline earth metal ions were examined for the concentration procedure using both chelating materials, SiAPPMA and SiAPP. These ions in matrix constituents are known to influence concentration procedure of heavy metal ions. In this case, the effect of matrix constituents was examined in the presence of salts of sodium, potassium and magnesium, which are common ionic species in natural waters. A high concentration of these diverse ions was chosen to magnify their interference effect. The results indicated that these matrix ions had little effect on the adsorption process, as indicated in Table 1. These data suggested the possibility to utilize such material for heavy metal ion removal from natural as well as sea water systems. These preliminary results were found to be encouraging, and some more studies regarding the effect of various common organic pollutants present in water bodies upon the metal uptake process by this new chelating material in progress.

3.5. Concentration of heavy metal ions from natural tap water samples

Tap water samples, spiked separately with Cu^{2+} and Ni^{2+}, 1.0–2.0 mg dm^{-3}, were prepared. Then 50 mg of the chelating material SiAPPMA was added. The mixture was kept under shaking for 24 h and centrifuged. The supernatant was analyzed by ICPOES and the results are listed in Table 2. This operation is in agreement with the recoveries of metal ions in all cases, with advantage to exceed 90%.

4. Conclusions

Chemical modification of silica gel was attempted using 1,4-bis(3-aminopropyl)piperazine and methylacrylate by a heterogeneous route to yield the chelating material SiAPPMA, which showed higher adsorption ability towards Cu^{2+} than for Ni^{2+} and Co^{2+} in both competitive and non-competitive conditions, in comparison to its precursor. The adsorption of Cu^{2+} onto the chelating material was found to obey both Langmuir and Freundlich adsorption models. The equilibrium parameter value was between zero and one. Evaluation of the distribution coefficient showed the effective Cu^{2+} removal from binary mixtures at appropriate pH of the medium. The effect of diverse ions like alkali and alkaline earth metal ions were found to be negligible on the chelating ability presented by the basic centers attached to the pendant chain ate the solid/liquid interface. The obtained data suggested the possible industrial utilization of such material in concentration and heavy element removal from natural as well as wastewater systems. The structural features

of the new synthesized material with long designed chain suggested that it could suitably be modified further by several other synthetic approaches, to yield higher stage pendant chains, for a wide variety of chemical applications.

Acknowledgements

References

[1] P.K. Jal, S. Patel, B.K. Mishra, Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions, Talanta 62 (2004) 1005–1028.

[2] I.M. El-Nahhal, N.M. El-Ashgar, A review on polysiloxane-immobilized ligand systems: synthesis, characterization and applications, J. Organomet. Chem. 692 (2007) 2861–2886.

[3] M.G. Fonseca, C. Airoldi, Thermodynamics data of interaction of copper nitrate with native and modified chrysotile fibers in aqueous solution, J. Colloid Interface Sci. 240 (2001) 229–236.

[4] M.G. da Fonseca, C. Airoldi, New amino-inorganic hybrids from talc silylation and copper adsorption properties, Mater. Res. Bull. 36 (2001) 277–287.

[5] J.A.A. Sales, G.C. Petrucelli, F.J.V.E. Oliveira, C. Airoldi, Some features associated with organosilane groups grafted by the sol–gel process onto synthetic talc-like phyllosilicate, J. Colloid Interface Sci. 297 (2006) 95–103.

[6] J.A.A. Sales, G.C. Petrucelli, F.J.V.E. Oliveira, C. Airoldi, Mesoporous silica originating from a gaseous ammonia epoxide ring opening and the thermodynamic data on some divalent cation adsorptions, J. Colloid Interface Sci. 315 (2007) 426–433.

[7] V.S.O. Ruiz, G.C. Petrucelli, C. Airoldi, Inorganic–organic hybrids derived from lamellar acidic kenyaite immobilizations for cation removal at the solid/liquid interface, J. Mater. Chem. 16 (2006) 2338–2346.

[8] O.G. da Silva, E.C. da Silva Filho, M.G. da Fonseca, L.N.H. Arakaki, C. Airoldi, Hydroxyapatite organofunctionalized with silylating agents to heavy cation removal, J. Colloid Interface Sci. 302 (2006) 485–491.

[9] M.R. Ganjali, F. Basiripour, M. Shamsipur, O.R. Hashemi, A. Moghimi, H. Aghabozorg, Ultratrace determination of lead, cadmium and copper in environmental and biological samples by atomic absorption spectrometry after their separation and preconcentration on octadecyl silica membrane disks modified with a new N–S Schiff base, Int. J. Environ. Anal. Chem. 83 (2003) 997–1008.

[10] O. Zaporozhets, N. Petruniock, O. Bessarabova, V. Sukhan, Determination of Cu(II) and Zn(II) using silica gel loaded with 1-(2-thiasolylazo)-2-naphthol, Talanta 49 (1999) 899–906.

[11] I.S. Khatib, R.V. Parish, Insoluble ligands and their applications. I. A comparison of silica-immobilized ligands and functionalized polysiloxanes, J. Organomet. Chem. 369 (1989) 9–16.

[12] J.A.A. Sales, C. Airoldi, Epoxide silylant agent ethylenediamine reaction product anchored on silica gel—thermodynamics of cation–nitrogen interaction at solid/liquid interface, J. Non-Cryst. Solids 330 (2003) 142–149.

[13] R.S.A. Machado Jr., M.G. da Fonseca, L.N.H. Arakaki, J.G.P. Espinola, S.F. Oliveira, Silica gel containing sulfur, nitrogen and oxygen as adsorbent centers on surface for removing copper from aqueous/ethanolic solutions, Talanta 63 (2004) 317–322.

[14] J.M. Fréchet, Functional polymers and dendrimers: reactivity, molecular architecture, and interfacial energy, Science 263 (1994) 1710–1715.

[15] C.R. Yates, W. Hayes, Synthesis and applications of hyperbranched polymers, Eur. Polym. J. 40 (2004) 1257–1281.

[16] A.W. Bosman, H.M. Janssen, E.W. Meijer, About dendrimers: structure, physical properties, and applications, Chem. Rev. 99 (1999) 1665–1688.

[17] A.G.S. Prado, C. Airoldi, A toxicity decrease on soil microbiota by applying the pesticide picloram anchored onto silica gel, Green Chem. 4 (2002) 288–291.

[18] L.J. Twyman, A.S.H. King, J. Burnett, I.K. Martin, Synthesis of aromatic hyperbranched PAMAM polymers, Tetrahedron Lett. 45 (2004) 433–435.

[19] J.A.A. Sales, C. Airoldi, Calorimetric investigation of metal ion adsorption on 3-glycidoxypropyltrimethylsiloxane + propane-1,3-diamine immobilized on silica gel, Thermochim. Acta 427 (2005) 77–83.

[20] J.A.A. Sales, F.P. Faria, A.G.S. Prado, C. Airoldi, Attachment of 2-aminomethylpyridine molecule onto grafted silica gel surface and its ability in chelating cations, Polyhedron 23 (2004) 719–725.

[21] A.G.S. Prado, C. Airoldi, The pesticide 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron) immobilized on silica gel surface, J. Colloid Interface Sci. 236 (2001) 161–165.

[22] A.G.S. Prado, C. Airoldi, Different neutral surfactant template extraction routes for synthetic hexagonal mesoporous silicas, J. Mater. Chem. 12 (2002) 3823–3826.

[23] K. Kosuge, P.S. Singh, Rapid synthesis of Al-containing mesoporous silica hard spheres of 30–50 μm diameter, Chem. Mater. 13 (2001) 2476–2482.

[24] K. Albert, E. Bayer, Characterization of bonded phases by solid-state NMR spectroscopy, J. Chromatogr. 544 (1991) 345–370.

[25] P. Sutra, F. Fajula, D. Brunel, P. Lentz, G. Daelen, J.B. Nagy, ^{29}Si and ^{13}C MAS-NMR characterization of surface modification of micelle-templated silicas during the grafting of organic moieties and end-capping, Colloids Surf. A 158 (1999) 21–27.

[26] M. Hughes, P. Miranda, D. Nielsen, E. Rosenberg, R. Gobetto, A. Viale, S. Burton, Silica polyamine composites: new supramolecular materials for cation and anion recovery and remediation, Macromol. Symp. 235 (2006) 161–178.

[27] T.I. Tikhomirova, V.I. Fadeeva, G.V. Kudryavtsev, P.N. Nesterenko, V.M. Ivanov, A.T. Savitchev, N.S. Smirnova, Sorption of noble-metal ions on silica with chemically bonded nitrogen-containing ligands, Talanta 38 (1991) 267–274.

[28] R.G. Anderson, G. Nickless, Heterocyclic azo dyestuffs in analytical chemistry: a review, Analyst 92 (1967) 207–238.

[29] R.K. Dey, U. Jha, A.C. Singh, S. Samal, A.R. Ray, Extraction of metal ions using chemically modified silica gel covalently bonded with 4,4′-diaminodiphenylether and 4,4′-diaminodiphenylsulfone-salicylaldehyde Schiff bases, Anal. Sci. 22 (2006) 1105–1110.

[30] I.S. Lima, C. Airoldi, A thermodynamic investigation on chitosan-divalent cation interactions, Thermochim. Acta 421 (2004) 133–139.

[31] T.R. Macedo, G.C. Petrucelli, C. Airoldi, Silicic acid magadiite as a host for *n*-alkyldiamine guest molecules and features related to the thermodynamics of intercalation, Clays Clay Miner. 55 (2007) 151–159.

[32] Ş. Tokalioğlu, T. Oymak, Ş. Kartal, Determination of palladium in various samples by atomic absorption spectrometry after preconcentration with dimethylglyoxime on silica gel, Anal. Chim. Acta 511 (2004) 255–260.

[33] E.M. Soliman, Synthesis, characterization and metal sorption studies of isatin and ninhydrin reagents immobilized on silica gel amine surface, Anal. Lett. 31 (1998) 299–311.

[34] S. Samal, S. Acharya, R.K. Dey, A.R. Ray, Synthesis and metal ion uptake studies of chelating resins derived from formaldehyde-furfuraldehyde condensed phenolic Schiff bases of 4,4′-diaminodiphenylether and *o*-hydroxyacetophenone, Talanta 57 (2002) 1075–1083.

[35] E.M. Soliman, M.E. Mahmoud, S.A. Ahmed, Synthesis, characterization and structure effects on selectivity properties of silica gel covalently bonded diethylenetriamine mono- and bis-salicylaldehyde and naphthaldehyde Schiff's bases towards some heavy metal ions, Talanta 54 (2001) 243–253.