

Diethyl sulfide modified silica and calix[4]pyrrole chelating resin: Synthesis and mercury(II) cation retention properties

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Diethyl sulfide was chemically immobilized on the surface of silica gel (0.2–0.5 and 0.06 mm) for the formation of two newly synthesized silica gel phases (S₁ and S₂). A new chelating resin containing *meso*-tetramethyl-tetrakis-(thiophene)calix[4]pyrrole, CP(I), was also synthesized *via* the condensation of CP(I) with formaldehyde. The selection of this receptor is based on fundamental studies. Among the cations and anions considered, CP(I) interacts only with mercury(II). The functionalized silicas and the calixpyrrole resin were characterized by elemental analysis and mass spectrometry. The batch removal of metal cations (Hg²⁺, Pb²⁺ and Cd²⁺) by these materials from aqueous solutions was investigated. The uptake capacities of the silica based materials (S₁ and S₂) and calixpyrrole polymers (R₁) for the Hg²⁺ cation were determined. The Hg(II) cation uptake data have been found to fit both, the Langmuir and Freundlich isotherms, and the coefficients indicated favorable uptake of this cation by these materials. Parameters such as the kinetics of the uptake process, pH, temperature, silica particle size and metal-ion concentration effects were evaluated. The data obtained clearly indicate that S₁ has the higher uptake capability and faster retention rate for Hg(II) ions relative to S₂ and R₁. In a column operation, it was observed that the Hg²⁺ cation was effectively removed from aqueous solution by the calixpyrrole resin, R₁. The percentage of recovery of this resin for the Hg²⁺ cation was found to be higher than 95%. The results obtained are compared with previously reported materials for mercury removal from aqueous solutions.

Introduction

Heavy metals have been considered as human health hazards. They may cause kidney toxicity, neurological damage, paralysis, chromosome breakage, and birth defects.¹ Water contamination with heavy metals is a problem of worldwide concern.^{2,3} For instance, mercury and mercury compounds are considered as priority pollutants and various regulations and guidelines have been developed limiting their levels in water and sediments.⁴ However, mercury plays an important role in Science and Technology and, inevitably, is found in the environment.^{5,6} The detection of mercury has long called the attention of analytical chemists and, as such, a large number of protocols have arisen.^{7–10}

A number of methods for the removal of mercury(II) from aqueous solutions are available, including reduction process treatments involving sulfide, ferrous chloride and magnetic ferrites as well as the use of ion exchangers and chelating resins.¹¹ It is known that adsorption is one of the most efficient methods for the removal of heavy metals from wastewater. Activated carbon is the most widely used material due to its excellent adsorption capability for heavy metals. However, the use of these methods is often limited due to the high cost particularly for Developing Countries.

Many techniques for metal pre-concentration such as liquid–liquid extraction (LLE)¹² and solid phase extraction (SPE)^{13–18} are available. Among the many types of solid phases used in SPE, the immobilization of silica gel with various organic compounds as metal chelating agents has received considerable attention. Within this context, silyl mixed-ligands have been investigated for their reactivity with metal cations.^{19–21} The major objective of this process is to improve selectivity by the incorporation of certain functional groups in the newly synthesized phases to extend their use and applications. There are several recent reports on the use of functionalized silica gel for metal enrichment. Silica gel functionalized with dithizone,²² acid red-88,²³ acid alizarin violet-N,²⁴ didecylaminoethyl-b-tridecylammonium,²⁵ 3-methyl-1-phenyl-4-stearoyl-5-pyrazolone,²⁶ formylsalicylic acid,²⁷ thiourea,²⁸ 2-mercaptobenzo-thiazole,²⁹ dithiocarbamate,³⁰ salicylaldehyde,³¹ o-vanillin³² and 2-hydroxy-5-nonylaceto-phenoxime^{33,1} is reported as a chelating collector for metal ions, Zn(II), Mg(II), Ca(II), Fe(II), V(IV), Fe(III), Cu(II), Cd(II), Co(II), Ni(II), Pb(II), Hg(II), Ag(I), Au(III) and Pt(II). Sulfur containing compounds are considered as soft bases and therefore they are able to interact strongly and selectively with metal ions such as mercury(II), and silver(I) which are classified as soft acids. This characteristic behavior have prompted many researchers to immobilize the silica gel surface with sulfur containing chelate compounds for pre-concentration, selective extraction and separation of these metal ions.^{34–36} The preferential binding of sulfur containing compounds for mercury(II) through the sulfur donor atoms have been reported.^{37,38}

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Calixpyrroles, a class of hetero-calixarenes, are a topic of considerable current interest in Supramolecular Chemistry because of their ability to act as receptors for anions^{39–43} cations^{44,45} and neutral molecules.⁴⁶ Although they are well known for their high selectivity for anions, a few reports⁴⁷ have been published in the field of polymer based calixpyrrole macrocycles. Andrzej *et al.*⁴⁸ have demonstrated the synthesis of calixpyrrole polymer matrices and their analytical performance towards anions as well as cations. Recently, Sessler *et al.*⁴⁹ have developed the first bonafide polymeric systems containing a calixpyrrole anion receptor directly appended to a polymeric backbone which could be readily optimized for use in a range of ion-binding and extraction applications.

So far no data concerning the pre-concentration of mercury(II) cation salts by the calix[4]pyrrole polymers have been published. In the light of the results reported for CP(I) which shows its unique interaction with the Hg(II) cation, this receptor is now polymerized and its ability to uptake Hg(II) cation salts from aqueous media has been studied. Therefore, this paper reports the synthesis, the characterization and the mercury(II) extraction properties of:

- i- an oligomeric resin containing a hybrid calixpyrrole as anchor group.
- ii- two newly silica gel materials containing diethyl sulfide derivatives.

The removal capacities of these materials to extract Hg²⁺ from aqueous solutions are compared with those previously reported in the literature. Final conclusions are given.

Experimental

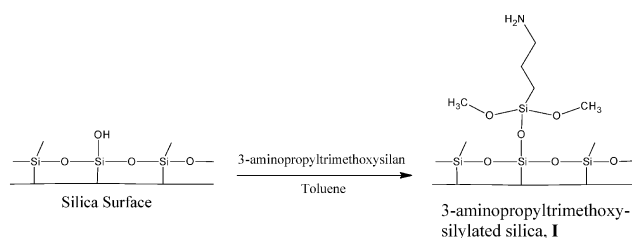
Chemicals

Thiophene, 2-acetylthiophene (98%), pyrrole (98%), methanesulfonic acid (99.5+ %), boron trifluoride etherate, potassium carbonate (K₂CO₃), sodium hydrogen carbonate (NaHCO₃), (3-aminopropyl)trimethoxysilan (97%) and 18-crown-6 (18-C-6) were all purchased from Aldrich and used as received. Silica gels (0.2–0.5 mm and 0.06 mm) were heated at 400 °C for 12 h and then kept in the desiccator over P₄O₁₀ to maintain their dryness. Metal cation (Hg(II), Pb(II), Cd(II)) salts (nitrate as counter ion) were all purchased from Aldrich Chemical Company.

Methanol, hexane, ethanol and acetone (HPLC grade, Fisher) were used without further purification. Acetonitrile (Aldrich) and dimethyl sulfoxide (Aldrich) were first refluxed in a nitrogen atmosphere with calcium hydride for several hours and then distilled.⁵⁰ The deuterated acetonitrile (CD₃CN) and tetramethylsilane (TMS) were purchased from Aldrich.

Preparation and characterization of modified silica

Synthesis of 3-aminopropyltrimethoxysilylated silica, I. In a typical immobilization process (Scheme 1), dried silica (60 µm) (10 g) was dispersed in anhydrous toluene (200 ml). To this slurry, (3-aminopropyl)trimethoxysilan (6 g) was added. The resulting mixture was refluxed for 6 h and then cooled down. The final product was filtered, washed with toluene and methanol, dried in vacuum at 120 °C for a further period of 12 h and kept in a desiccator for further use. Microanalysis was carried out at the University of Surrey. Experimental percentages of C, H and N



Scheme 1 Synthetic procedure used for the preparation of 3-aminopropyltrimethoxy-silylated silica, I.

were 4.68, 1.32 and 1.13, respectively. It is worth mentioning that the experimental percentages of C, H and N of silica alone are zero.

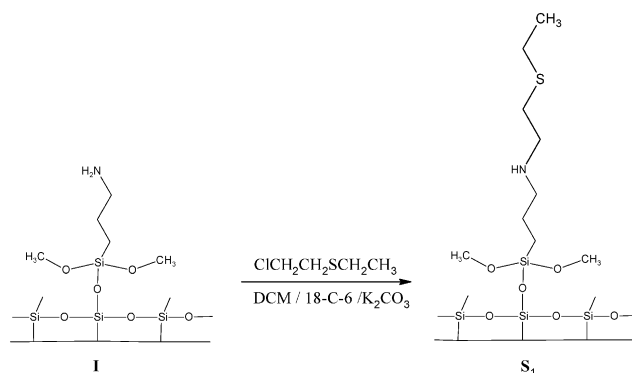
Synthesis of modified Silica, S₁. The synthetic procedure used for the preparation of S₁ is shown in Scheme 2. A mixture of I (7 g), K₂CO₃ (3 g) and 18-crown-6 (0.5 g) in dichloromethane (200 ml) was refluxed for 2 h and then 2-chloroethyl ethyl sulfide (5 ml) was added gradually over a period of 5 min. The reaction mixture was refluxed for 12 h, left to cool, filtered off, and washed with various solvents according to the following order: dichloromethane, methanol, NaHCO₃ aqueous solution, methanol and dichloromethane. It was then dried in vacuum at 120 °C for 12 h. Microanalysis carried out for S₁ gave the following %: C, 5.86; H, 1.38 and N, 1.48.

Synthesis of 3-aminopropyltrimethoxysilylated silica, II. The same procedure applied for the preparation of I was used for the synthesis of II using a 0.2–0.5 mm silica particle size. Microanalysis carried out for II gave the following %: C, 6.84; H, 1.76 and N, 2.06.

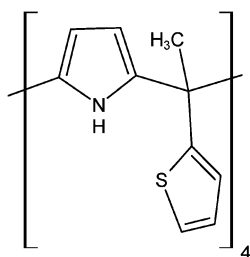
Synthesis of modified silica, S₂. The same procedure applied for I in the preparation of S₁ was used for the synthesis of S₂ using a 0.2–0.5 mm silica particles size. Microanalysis carried out at the University of Surrey gave the following %: C, 7.84; H, 1.81 and N, 2.12.

Preparation and characterization of a calix[4]pyrrole based resin

Synthesis of meso-tetramethyl-tetrakis-(thiophene)calix[4]-pyrrole, CP(I). CP(I) was prepared by following a previously



Scheme 2 Synthetic procedure used for the preparation of S₁.



CP(I)

Scheme 3 CP(I)

reported procedure.⁴⁵ Microanalysis carried out for $C_{40}H_{36}N_4S_4$ (Calc. C, 68.53; H, 5.18; N, 7.99%; found: C, 68.53; H, 5.18; N, 8.04%). 1H NMR, (CD_3CN), δ (ppm): 8.27 (bs, 4H, NH), 7.13 (s, 4H, thiophene), 6.76 (s, 4H, thiophene), 6.58 (s, 4H, thiophene), 5.64 (s, 8H, pyrrole), 1.47 (s, 12H, CH_3) (Scheme 3).

Polymerization of *meso*-tetramethyl-tetrakis-(thiophene)-calix[4]pyrrole, R_1 . R_1 was obtained by the condensation of the calix[4]pyrrole derivative, CP(I), with formaldehyde in the presence of H_2SO_4 (Scheme 4).⁵¹ Calixpyrrole, CP(I), (0.5 g, 0.7 mmol), and 65 ml of 37% formaldehyde (2.14 mmol) were dissolved in acetonitrile (50 ml). Sulfuric acid (0.5 ml) was then gradually added to the mixture. The polymerization was completed after 90 min yielding a solid, insoluble chelating resin which was collected, filtered-off, washed with acetonitrile followed by water and finally with acetonitrile. The sample was dried and its molecular mass was determined. The molecular weight of the calixpyrrole derivative, CP(I), was found to be $701.005\text{ g mol}^{-1}$.⁴⁵ From the mass spectrum of this material, the residual peak observed at 1401.7 indicated the formation of a dimer.

Metal ions uptake from aqueous solutions by silica materials (S_1 and S_2) and chelating resin (R_1) at 298.15 K

Analytical determination of metal cations in aqueous solution. Stock solutions of mercury, lead and cadmium were prepared

separately by dissolving accurate amounts of $Hg(NO_3)_2$, $Pb(NO_3)_2$ and $Cd(NO_3)_2$ (analytical grade), respectively, in de-ionized water (500 ml). The analysis of metal ions in the aqueous phase was performed by a Perkin-Elmer Model AAnalyst 400 Atomic Absorption Flame Spectrometer (AAS) and by complexometric EDTA titrations. The instrument (AAS) was calibrated using appropriate standards of metal ions salts.

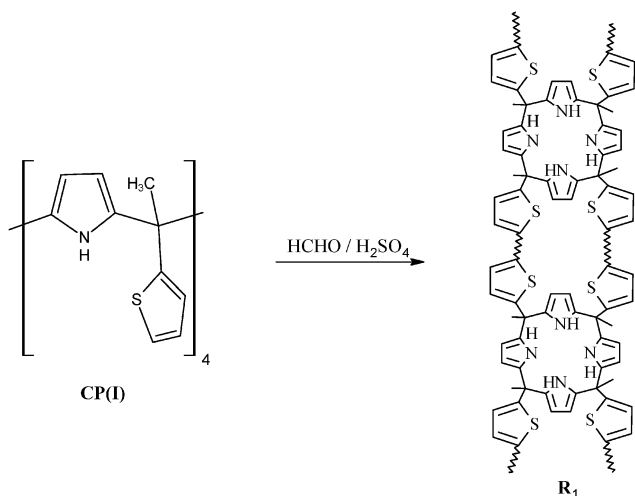
Optimum mass of silica materials (S_1 and S_2) and calixpyrrole polymer (R_1) for the removal of $Hg(II)$ ions from aqueous solutions at 298.15 K. For these experiments, different quantities (0.01–0.25 g) of silica based materials (S_1 or S_2) and the calixpyrrole polymer (R_1) were weighed and added to a set of ten test tubes, each one containing a volume (10 ml) of the same concentration ($1 \times 10^{-3}\text{ mol/dm}^3$) of a given aqueous solution of the metal cation salt prepared in de-ionized water. The tubes were then shaken on a rotamixer for 5 min to ensure homogenous mixing, sealed and then left overnight in a thermostated water bath at 298.15 K. After equilibrium was attained, the solutions were filtered through $0.45\text{ }\mu\text{m}$ Millipore filters (Type HA) and filtrates were analyzed to determine the metal cation salt concentrations.

Uptake capacity of silica materials (S_1 and S_2) and calixpyrrole polymer (R_1) for metal cations at 298.15 K. The metal cation salt uptake capacities of the calixpyrrole polymer and the silica based materials were determined under static conditions by the batch equilibrium technique. An optimum mass of the solid phase (0.035, 0.125 and 0.1 g of S_1 , S_2 and R_1 , respectively) was added to a volume (10 ml) of metal cation salt solutions of different concentrations ($1.00 \times 10^{-5} - 1.00 \times 10^{-2}\text{ mol dm}^{-3}$) and the mixtures were mechanically shaken for 5 min to attain equilibrium. Then the tubes were placed in a water bath and the temperature was maintained at 298.15 K. After the equilibrium was attained, aliquots of metal cation salt solutions were withdrawn with a syringe and filtered through $0.45\text{ }\mu\text{m}$ Millipore filters (Type HA). Metal ions were then analyzed by atomic absorption spectrometry and/or complexometric EDTA titration using a buffer solution (hexamine) and Xylenol Orange as indicator. The amount of metal ions retained by the materials was calculated from the difference in their initial and final concentrations in the aqueous solution.

The kinetics of the extraction process as well as the effect of pH, salt concentration and temperature on the extraction process were determined as described below.

Effect of the solution pH on the uptake of metal cations from aqueous solutions by modified silica (S_1 and S_2) and the calixpyrrole polymer (R_1) at 298.15 K. The efficiency of the calixpyrrole polymer (R_1) and the modified silica materials (S_1 and S_2) to retain metal ions was investigated in the 2–10 pH range under static conditions, keeping constant the concentrations of the initial ion salt ($10^{-3}\text{ mol dm}^{-3}$) in aqueous solution.

Kinetics of mercury(II) extraction processes of cation from aqueous solutions by the calixpyrrole resin and the silica materials at 298.15 K. The kinetics of the extraction process involving these materials was determined under the same batch conditions, but at different periods (5, 10, 20, 40 60, 80, 100, 120 min) keeping the



Scheme 4 Synthetic procedure used for the preparation of R_1 .

solution at the pH at which the highest metal-ion uptake by these materials was found.

Effect of temperature on the uptake of metal cations from aqueous solutions by modified silica (S_1 and S_2) and calixpyrrole oligomer (R_1) at 298.15 K. To investigate the temperature effects on the extraction ability of these materials, a fixed amount of the solid phase material was equilibrated with a volume (10 ml) of the metal ion salt solution ($1 \times 10^{-3} \text{ mol dm}^{-3}$) at different temperatures (15, 20, 25 and 35 °C). The phases were separated and the concentrations of metal ion salts in the aqueous phase were determined.

Column operations with the calixpyrrole oligomer. An accurate amount of the calixpyrrole resin (R_1) (0.6 g) was packed in a stainless steel micro-column (0.5 cm \times 5 cm) with a porous frit. Then, the column was coupled to an air vacuum pump. Before running the samples, the column was washed with de-ionized water (100 ml). Then, an aqueous solution containing the Hg(II) salt ($1 \times 10^{-4} \text{ mol dm}^{-3}$) was passed through the column at a flow rate of 2 ml min $^{-1}$. The Hg(II) cation concentration in the eluate was measured and the percentage of mercury retained in the column was calculated. Recycling of the material was carried out sequentially by using an EDTA solution (0.1 mol dm $^{-3}$). The assay and analytical measurements were carried out by triplicate.

Results and discussion

Characterization of the modified silica and calixpyrrole resin

The amounts of attached diethyl sulfide to silylated silica (**I** and **II**) were calculated by determining the carbon, hydrogen and nitrogen contents using microanalysis (Table 1). Thus, based on the % composition of carbon atoms in S_1 and S_2 , the concentration of diethyl sulfide immobilized into the silylated silica was 0.25 and 0.20 mmol g $^{-1}$ for S_1 and S_2 , respectively. As far as the calixpyrrole polymer (R_1) is concerned, mass spectrometry was used to gain information about the number of monomers forming the chelating resin. Thus, the residual peak observed at 1411.3 for R_1 indicates the formation of a dimer.

Effect of the solid/solution ratio on the extraction of metal cations (nitrate as counter-ion) from aqueous solution at 298.15 K

The effect of the amount of material (R_1 , S_1 or S_2) used to explore the retention properties of these extracting agents has been studied by varying the amount of material and keeping other parameters [pH, temperature, contact time, and the initial

Table 1 The percentage of metal cations uptake by calixpyrrole polymer (R_1) and silica based materials (S_1 and S_2) from aqueous solution at 298.15 K

% Metal Uptake				
Metal cation	$[M^{2+}]_{\text{initial}} \text{ (mol/dm}^{-3}\text{)}$	R_1	S_1	S_2
Hg(II)	1×10^{-3}	71	90	60
Cd(II)	1×10^{-3}	0	38	28
Pb(II)	1×10^{-3}	0	60	3

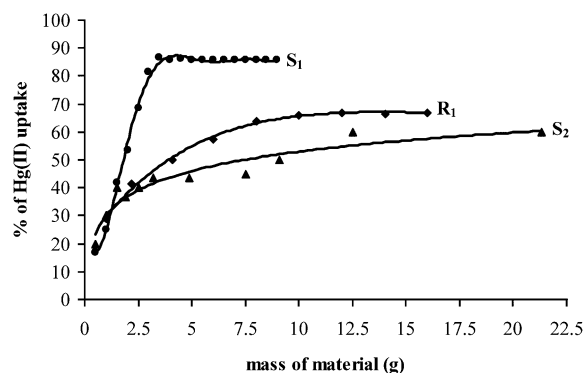


Fig. 1 Effect of the amount of R_1 , S_1 and S_2 on the percentage extraction of Hg(II) cations from aqueous media at 298.15 K.

concentration of metal cations ($1 \times 10^{-3} \text{ mol dm}^{-3}$) constant. It can be observed that the uptake capability of the active materials generally improve with increasing their amounts in Hg(II) solution (Fig. 1). This is expected due to the fact that the higher the amount of material in contact with the solution, the greater is the availability of binding sites for the ions.

In all cases, at a given solid/solution ratio no further uptake of Hg(II) from aqueous solution was observed. Maximum percentage of metal cation removed and solid/solution ratios were as follows: S_1 , 86%, 3.5 g l $^{-1}$; S_2 , 60%, 12.5 g l $^{-1}$ and R_1 , 67%, 10 g l $^{-1}$.

It is interesting to note that the maximum removal capacity of the three types of materials differs from one another. Therefore, the difference observed in the extraction percentage of S_1 and S_2 is attributed to the difference in the silica particle size, where the particles of smaller size (S_1) show a higher capability than S_2 to extract the Hg(II) ions from aqueous solutions. On the other hand, the calix[4]pyrrole based material (R_1) shows a higher extracting ability toward the mercury ions (67% at 10 g l $^{-1}$) than that of large particle size silica (S_2). However, the higher removal efficiency of S_1 (86%) for the Hg(II) cation relative to the sulfur containing calixpyrrole polymer may be attributed to the smaller size particles of the former material and, hence, the higher concentration of diethyl sulfide (0.25 mmol g $^{-1}$) anchored to its surface.

It should be mentioned that the capacity of the modified silica and calixpyrrole materials is an important factor to consider,

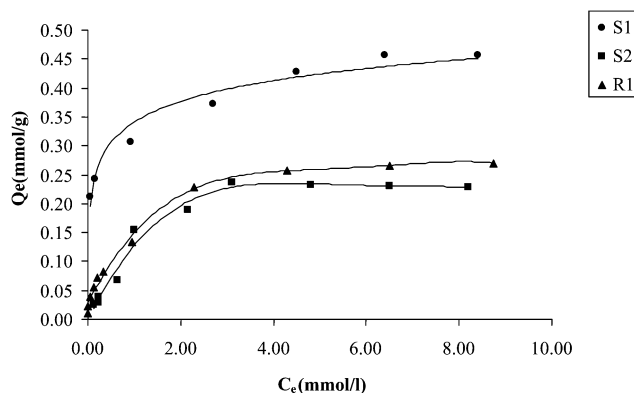


Fig. 2 Uptake isotherm for the Hg(II) cation from aqueous solution by R_1 , S_1 and S_2 at 298.15 K.

since it determines the amount of sorbent is required to quantitatively remove a specific concentration of metal ion salt from solution (Fig. 2). Thus the capacity was tested following the batch procedure. In order to reach the saturation, the initial metal ion salts' concentrations were increased till plateau values (capacity values) were obtained. The results showed that the capacity of various metal ions probably differ due to their size, degree of hydration likely to be reflected in the transfer process of the salt (dependent of the counter-ion) and the value of their interaction with the active sites of the sorbent.

The higher affinity of Pb(II) relative to Cd(II) in S_1 may be attributed to the stronger interaction of the N and S donor atoms with Pb(II) relative to Cd(II).⁵²

Using the same optimum mass for the maximum extraction of Hg(II) cations from aqueous solutions at 298.15 K, the ability of silica materials to uptake metal cations such as Pb(II) and Cd(II) from aqueous solutions was tested and the results are included in Table 1.

Metal cations uptake isotherms at 298.15 K

The equilibrium experimental data were correlated with Langmuir (eqn (1)) and Freundlich (eqn (2)) isotherm models.

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (\text{eqn. 1})$$

In eqn (1), C_e is the equilibrium concentration (mmol l⁻¹), q_e is the amount of metal cations uptake at equilibrium time (mmol g⁻¹), and q_m and b are Langmuir constants related to the uptake capacity and energy, respectively.

The Freundlich adsorption isotherm is represented by the following equation:

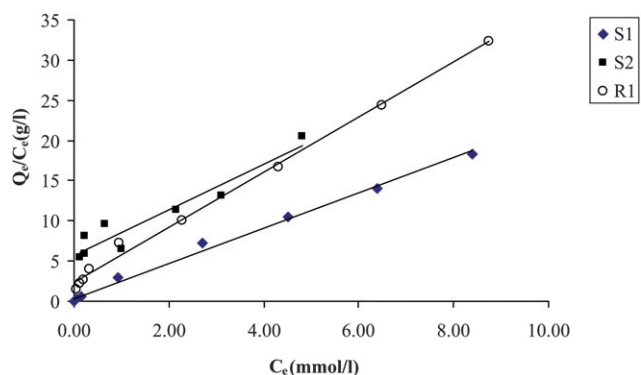


Fig. 3 Linearized Langmuir isotherms for Hg(II) uptake by R_1 , S_1 and S_2 at 298.15 K.

Table 2 Langmuir and Freundlich Hg(II) ion uptake parameters at 298.15 K for R_1 , S_1 and S_2

Material	Langmuir				Freundlich		
	$q_m/\text{mmol g}^{-1}$	$b/l \text{ mmol}^{-1}$	R^2	R_L	$k/\text{mmol g}^{-1}$	n	R^2
R_1	0.29 ± 0.01	15.12	0.99	0.99	0.34 ± 0.01	2.48	0.98
S_1	0.46 ± 0.02	6.16	0.99	0.99	0.33 ± 0.01	6.25	0.98
S_2	0.35 ± 0.01	0.50	0.91	1.00	0.10 ± 0.01	1.42	0.95

$$\log q_e = \log k + \frac{1}{n} \log C_e \quad (\text{eqn. 2})$$

In eqn (2), k and n are Freundlich constants. An indication of the favourability is given by n and k denotes the capacity of the material.

i- Langmuir isotherm. Fig. 3 shows the linear plots of C_e/q_e vs. C_e , which is an indication of the applicability of the Langmuir isotherm for the systems under consideration. The uptake of Hg(II) ions by these materials follows the Langmuir isotherm model. The q_m and b values represented in Table 2 are calculated from the slopes and intercepts of the plots.

Generally, the high binding constants, b , listed in Table 2 support the uptake of Hg(II) cation from the aqueous solution by the solid phase *via* strong binding with the sulfur donor sites.^{53,54} These values are larger for R_1 , indicating a high thermodynamic stability.

The Langmuir monolayer capacity is quite large with values of 0.29, 0.46 and 0.35 mmol g⁻¹ for R_1 , S_1 and S_2 , respectively (Fig. 2). The separation factor, R_L , also supports the favorable uptake of Hg(II) cations by the calixpyrrole polymer and the modified silica, S_1 . On the other hand, the metal uptake by S_2 is linear ($R_L = 1$).

ii- Freundlich isotherm. The Hg(II) retention by R_1 , S_1 and S_2 follows the Freundlich relationship (Fig. 4). The plots show reasonable linearity ($R^2 = 0.95\text{--}0.98$). The values of uptake coefficients, computed from these plots are given in Table 2. As far as R_1 and S_1 are concerned, the correlation coefficients show that, in general, the Langmuir model fitted the results slightly better than the Freundlich model. However, the Freundlich isotherm equation ($R^2 = 0.95$) seems to describe better the uptake of the Hg(II) cation by S_2 than the Langmuir equation ($R^2 = 0.91$). The values of coefficients indicate the favourable nature of the retention of the Hg(II) cation by the calixpyrrole oligomer and modified silicas. The $1/n$ values obtained in this study (Table 2) ($0.1 < 1/n < 1.0$) indicate that these materials can be used effectively for the removal of the Hg(II) cation from aqueous solutions.

The effect of solution pH on the uptake of metal cations from aqueous solutions by modified silica (S_1 and S_2) and the calixpyrrole oligomer (R_1) at 298.15 K

The effect of pH on the uptake of the Hg(II) cation salt from aqueous solution by R_1 , S_1 and S_2 was investigated. For this purpose, the amount of material used and the concentration of solution ($1 \times 10^{-3} \text{ mol dm}^{-3}$) was kept constant. The outcome of

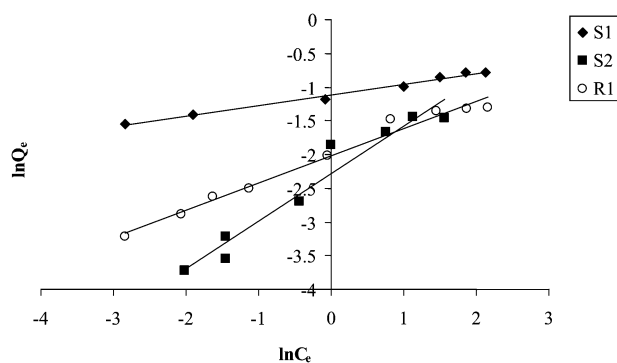


Fig. 4 Linearized Freundlich isotherms for Hg(II) uptake by R₁, S₁ and S₂ at 298.15 K.

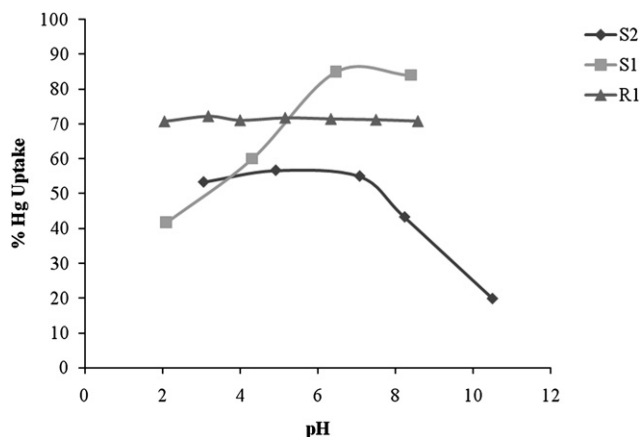


Fig. 5 Effect of pH on the uptake of Hg(II) cations from aqueous solution at 298.15 K by R₁, S₁ and S₂ at 298.15 K.

these experiments is shown in Fig. 5 in which percentages of extraction (% E) are plotted against the initial pH of the solution. The mercury(II) uptake by the calixpyrrole based polymer (R₁) shows no changes by altering the pH of the solution.

The most significant changes in the extraction percentages as a function of the pH are observed for S₁, which shows the maximum Hg(II) uptake at a pH close to 7 and remain almost constant until pH 8. The poor degree of extraction at low pH must be attributed to the protonation of the NH group in the pendent arm of the modified silica. As observed for S₂, it is expected that at pH higher than 8, there is a decrease in the extraction ability of the material due to the formation of hydroxo species and these are unable to interact with the binding sites on the surface of the material.

Kinetics of extraction processes of mercury(II) cation from aqueous solution by calixpyrrole resin and modified silica at 298.15 K

The kinetics of the uptake of Hg(II) from aqueous solution by R₁, S₁ and S₂ was investigated by determining the percentage of extraction of the Hg(II) cation salt at different time intervals (10–160 min). Other parameters such as amount of the material, pH of the Hg(II) aqueous solution were kept optimum, while the temperature was 298.15 K. The outcome of these experiments is

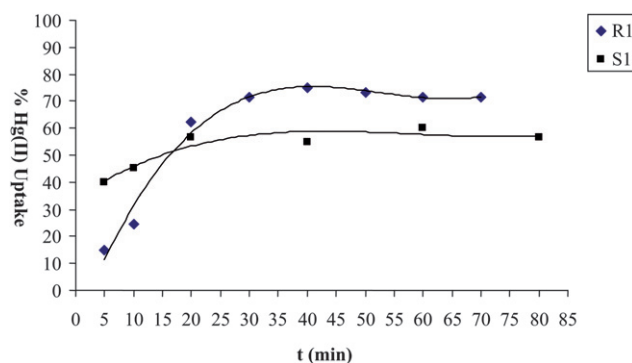


Fig. 6 Optimum time for the uptake of Hg(II) cations from aqueous solution by R₁, S₁ and S₂ at 298.15 K.

shown in Fig. 6 in which percentages of extraction (% E) are plotted against the contact time. The results indicate that the % E increases with an increase in the contact time before equilibrium is reached. It can be seen that the uptake of the Hg(II) cation by R₁ from aqueous solution increases from 25% to 70% when the contact time was increased from 10 to 30 min. Optimum contact time for S₁ was found to be less than 5 min as compared to that of S₂ which was 20 min. Therefore, the kinetics of the extraction process of Hg(II) by the modified silica with smaller size particles (S₁) is faster relative to S₂ (large size particles) and calixpyrrole polymer (R₁). The availability of various functional groups on the surface of silylated silica, required for interaction with the Hg cations, significantly improved the binding capacity and the kinetics of the extraction process. This result is an important aspect to consider in wastewater treatments.

Effect of temperature on the uptake of metal cations from aqueous solutions by modified silica (S₁ and S₂) and calixpyrrole oligomer (R₁)

The uptake of Hg(II) ions by S₁, S₂ and R₁ was studied as a function of temperature. While the initial concentration of Hg(II) in the aqueous solution was kept constant (1×10^{-3} mol dm⁻³), the percentages extraction of Hg(II) from aqueous solution by the active materials as a function of $T/^{\circ}\text{C}$ are shown in Fig. 7. As far as silica based materials are concerned, insignificant changes in the extracting ability of S₂ were observed by increasing the temperature while it seems that there is an increase in the % E for S₁. On the other hand, it is evident from Fig. 7 that the removal of Hg(II) from aqueous solution by R₁ increases significantly with the temperature. In the extraction of metal cation salts by solid materials there are a number of factors to be considered such as the transfer of metal-ion salt (dependant on the counter-ion) from aqueous to solid phase as well as the affinity of the active sites of the material for the particular ion. Therefore the increase in extraction with temperature must be attributed to either or both processes. However, the fact that this is an endothermic process may indicate that the transfer of the metal-ion salt from water to the solid phase may be predominant relative to that involving the interaction of the active site of the calixpyrrole with the cation given that the latter is expected to be an exothermic process.⁵⁵

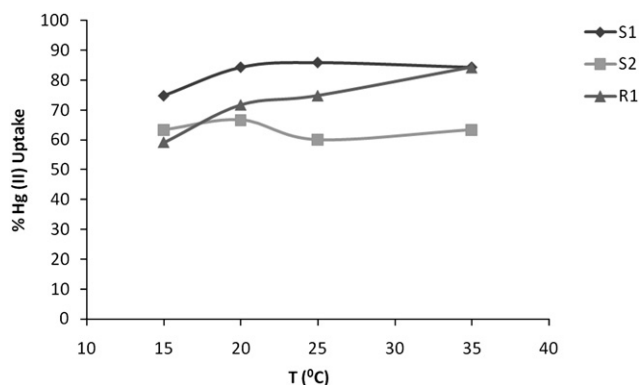


Fig. 7 Effect of temperature on the uptake of Hg(II) cations from aqueous solution by R₁, S₁ and S₂.

Effect of the silica particle size on the removal of mercury(II) from aqueous solutions at 298.15 K

Uptake experiments were carried out for the determination of the capacity of silica based materials, q_e , for the removal of the Hg(II) cation from aqueous solutions using two different sizes of silica particles (0.06 mm and 0.2–0.5 mm for S₁ and S₂, respectively). The results presented in previous sections show that the capacity of S₁ (small particle size) for the Hg(II) cations is higher than that of S₂ (large particle size). This is because the smaller particles size offered comparatively larger surface area and hence higher uptake occurs. Silica based materials of small particle size also improves the kinetics of the extraction process given that a shorter period is required to achieve equilibrium with S₁ than with S₂. However, it may be noted that the main advantage of using silica materials of large particle sizes (S₂) is that the building up pressure inside the extracting systems is lower for this material relative to that involving small particles (S₁).

Column operation

Uptake and elution processes are governed by different factors (pH, flow rate, sample volume, analyte concentration, elution volume and sample matrix). The uptake of Hg(II) ions was carried out by passing an aqueous solution of the salt (1×10^{-4} mol dm⁻³) through a stainless column (0.5 cm inner diameter and 5 cm length) packed with R₁ (0.58 g) at a flow rate of 2 ml min⁻¹. The amount of mercury retained in the column remains constant up to 520 ml (Fig. 8). However, the ability of the calixpyrrole polymer to uptake Hg(II) cations starts to decrease after the flow of 520 ml of Hg(II) solution. Saturation point was reached after 1 litre of Hg(II) solution passed through the column. The capacity of the functionalized silica gel column for mercury was found to be 0.089 mmol g⁻¹. The lower capacity of extraction of Hg(II) ion salts by column technique is consistent with previously reported data.⁵⁶ This must be attributed to the fact that the extraction of metal cations by column technique is mainly dependent on several well known factors, such as the type and amount of packing stationary and mobile phases and the flow rate of the mobile phase.⁵⁷

An extracting agent is considered to be highly efficient if the release of retained metal ions is fast and quantitative. In this context, it was found that 0.1 M EDTA was effective in recycling

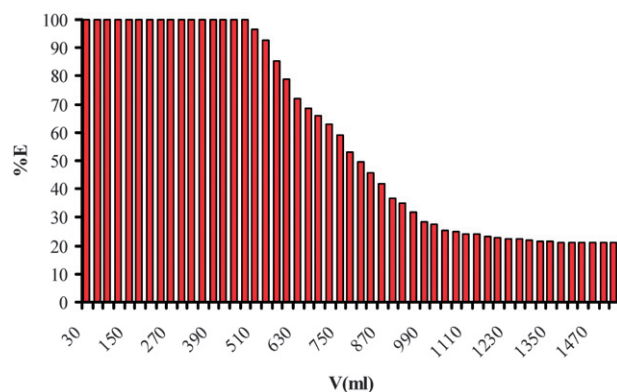


Fig. 8 Percentage uptake of Hg(II) cations by R₁ as a function of volume of Hg(II) ion solution.

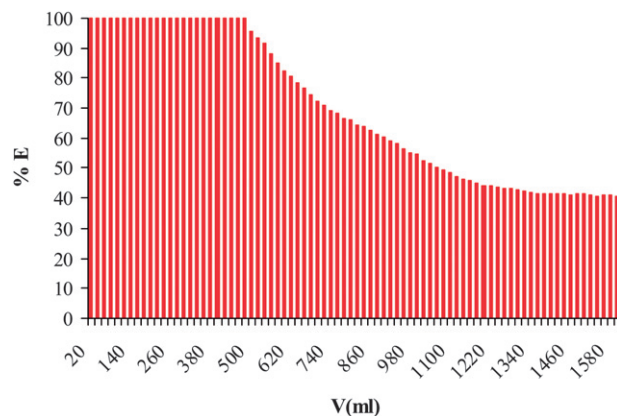


Fig. 9 Percentage uptake of Hg(II) cations by recycled calixpyrrole polymer (R₁) as a function of volume of Hg(II) ion solution.

the calixpyrrole oligomeric material. After mercury ions were recovered from the resin, the resin was washed by passing through the column distilled water for 1 h at a flow rate of 2 ml min⁻¹. This regenerated material was used again for the extraction of mercury.

The cycle of extraction-recovery-regeneration was repeated several times through a column containing the calixpyrrole oligomer (Fig. 9). The uptake capacity of the regenerated material was found to be very close to that of the freshly prepared resin which indicates that this material can be regenerated and reused repeatedly for several times.

Effect of the counter-ion

The experimental work was carried out using the nitrate anion as a counter-ion mainly because as mercury(II), nitrate is a contaminant in drinking water and high concentrations lead to health problems in humans.^{58,59} Given that these materials contain neutral active sites, anions and cations are taken up simultaneously. We have previously shown⁶⁰ that the effect of the counter-ion on the uptake of cations by a resin containing 18-crown-6 as anchor groups follows the same pattern as the single-ion transfer Gibbs energies of anions from water to a non-aqueous solvent (data based on the Ph₄AsPh₄B convention).⁶¹ These data although available in the literature^{61–63} are hardly

Table 3 Comparison of calixpyrrole polymer and silica based materials with some reported sorbents for mercury cation

Adsorbent	Capacity/mmol g ⁻¹
Dithiocarbamate grafted on silica gel	0.30 ^a
1,5 Diphenylcarbazide functionalized sol-gel material	0.028 ^a
Dithiocarbamate-incorporated monosize polystyrene microspheres	0.16 ^b
Dithioacetal graft immobilized on silica-gel	0.70 ^c
S ₁	0.45 ^d
S ₂	0.35 ^d
R ₁	0.29 ^d

^a Ref. 57. ^b Ref. 58. ^c Ref. 59. ^d This work.

used to predict counter-ion effects in the case of anion or cation extraction processes. Therefore, we strongly recommend their use instead of carrying out unnecessary experimental work.

Comparison with alternative materials

It is worth mentioning that the comparison is limited to certain materials found in the literature^{64–66} due to the usage of different counter-ions during the process of extraction of metal cations from aqueous media. Therefore the capacity of any material for ion extraction may change significantly by changing the counter-ion.^{67,68} Therefore, for a valid comparative assessment on the extraction properties of materials, the same counter-ion must be present in the aqueous phase.

Although materials reported in the literature for the uptake of mercury, shown in Table 3, can effectively achieve mercury concentration reduction in water, there is scope for improvement. The modified silica (S₁ and S₂) show fast mercury uptake, recycling and reasonable selectivity. In addition, R₁ has many distinctive features over modified silica and other materials reported in the literature. Firstly, it interacts selectively with the Hg(II) cation⁴⁴ and, as such, the interference from other metal cations during the extraction process will be negligible. Secondly, it is of low cost, easily prepared and shows comparable capacity levels. It is a safe, simple, rapid and inexpensive method for the extraction of Hg(II) cations from aqueous media.

Conclusions

The results of this study indicate that these materials (R₁, S₁ and S₂) are suitable for the development of efficient systems for the removal and recovery of Hg(II) ions from aqueous media. The uptake of Hg(II) cation by these materials was influenced by experimental parameters such as initial metal ion salt concentrations, the amount of resin, the pH and the temperature. The optimum time for Hg(II) ions removal was determined as 20 min, less than 5 and 30 min for R₁, S₁ and S₂, respectively. The observed capacities for R₁, S₁ and S₂ were 0.29, 0.45 and 0.35 mmol g⁻¹, respectively. These are comparable with other types of immobilized silica reported in literature. However, the advantage of the calix[4]pyrrole polymer (R₁) is the ease of

preparation, the low cost involved and the effectiveness in its recycling. This material can be regenerated and reused after EDTA treatment. The uptake capacity of the recycled polymer hardly changes. The Hg(II) ions uptake maximum capacity was strongly influenced by silica particles size. Thus, the immobilized silica material, S₁, (0.06 mm) shows a higher capacity for Hg(II) ions than that of S₂ (0.2–0.5 mm).

The results of extraction studies also indicate that the calixpyrrole oligomer is very selective in the removal and recovery of Hg(II) from aqueous media. This is an interesting property of the calixpyrrole oligomer over other materials for which the interference from other metal cations is significant.

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