



Methylene crosslinked calix[6]arene hexacaarboxylic acid resin: A highly efficient solid phase extractant for decontamination of lead bearing effluents

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ABSTRACT

Calixarene-based cation exchange resin has been developed by methylene crosslinking of calix[6]arene hexacaarboxylic acid derivative and the resin has been exploited for solid phase extraction of some toxic heavy metal ions. The selectivity order of the resin towards some metal ions follows the order $Pb(II) > Cu(II) > Zn(II), Ni(II), Co(II)$. The maximum lead ion binding capacity of the resin was found to be 1.30 mmol g^{-1} resin. The loaded lead was quantitatively eluted with dilute acid solution regenerating the resin. Mutual separation of $Pb(II), Cu(II)$ and $Zn(II)$ was achieved by using the column packed with the resin.

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1. Introduction

Increased industrial activity raises the question of waste water treatment, particularly concerning heavy metal ions. In recent years, decontamination of heavy metal bearing industrial effluents has become the topic of great interest. Among heavy metals, lead is the most abundant and certainly the most toxic metal ion causing adverse environmental and health problems. When absorbed into the body, it is highly toxic to many organs and systems and seriously hinders the body's neurological development. At low levels, biochemical processes are affected with impaired psychological and neurobehavioral functions. At high levels of human exposure, there is damage to almost all organs and organ systems, most importantly the central nervous system, kidneys and blood, culminating in death at excessive levels [1]. However, lead ions are commonly encountered in industrial wastewaters because of their wide application in many industrial technologies such as lead mining, battery manufacturing, smelttries and printed circuit board factories, etc. Accordingly, exposure to environmental lead is clearly a major public health hazard of global dimensions. Consequently, for global environmental remediation concerning with the development of sustainable environment, there is the need of renewed interest in processing of industrial effluents containing such toxic metal ions.

Recently, there have been some examples of calixarene-based chromogenic [2] and fluorogenic [3] sensors reported for the early

recognition of $Pb(II)$ ions with high sensitivity. Selective removal of lead in presence of other metal ions is, however, not well addressed by such analytical techniques and there is still a significant need to provide real time applicable reagents for the separation of trace amount of $Pb(II)$ in polluted streams and industrial effluents. Previously, we had reported the solvent extraction behaviour of carboxylic acid derivative of *p-tert-octylcalix[4]arene* towards lead ion [4]. The efficiency of calixarene carboxylic acid derivatives for the selective removal of lead by solvent extraction has also been well addressed by some other groups [5–8]. However, the conventional solvent extraction processes using macrocyclic extractants are subjected to several limitations such as tedious operation, emulsion formation which sometimes breakup very slowly or incompletely leading to low efficiency, exposure to toxic solvent and their disposal cost, etc. [9–11]. Hence, because of environmental and economic concerns, many common liquid/liquid processes have been modified to either utilize benign solvents, or move to more frugal processes such as solid phase extraction (SPE). SPE is one of the important techniques for the separation of heavy metals from metal bearing effluents with various advantages including its easy handling with more flexible working conditions together with good stability and selectivity, rapidity, high efficiency in a wide range of metal ion concentration and easier recovery of analyte and extractant [12–16]. SPE is an extremely efficient method for isolating and concentrating the solutes from large volumes of liquids. In addition, SPE offers a number of important benefits over solvent extraction such as reduction in solvent use and minimal cost due to low consumption of reagents, safety with respect to hazardous solvents, ease of automation, etc. [17,18]. Consequently, apart from

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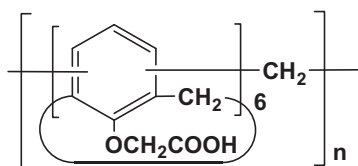


Fig. 1. Ideal structure of the resin employed in present study.

the considerable interest in recent years in the use of calixarene monomers as supramolecular receptors for solvent extraction, the growing interest has shifted towards the fabrication of calixarene-based polymers/resins as solid phase extractants [19–25].

Some solid phase extractants that have been exploited for the removal of lead include impregnated and chelating resins [26,27], imprinted polymer [28], chemically modified silica [29–31], modified cellulose [32] and peanut shell [33], carbon nanotubes [34,35], activated carbon [36] and modified activated carbon [37–39], various low cost extractants/adsorbents such as clinoptilolite and sepiolite [40] activated sludge [41], sawdust [42,43], etc. Most do not lead to satisfactory decontamination with respect to their operational costs and binding capacities. Though they are easily available and inexpensive, the agricultural by-products also have poor binding capacities. Consequently, the development of real time applicable and cost effective reagent for effective and quantitative removal of lead from aqueous environment is of particular concern. The calixarene-based solid phase extractants developed either by covalently linking [19–22] or blending [23,24] calixarene derivatives to the existing polymer have also proved their worth as solid phase extractants for lead ion. However, relatively low metal uptake capacity probably due to the ineffective polymer matrix is one of the biggest stumbling blocks to the widespread application of such reagents.

According to Dung and Ludwig, removing two of four carboxyl groups of calix[4]arene host results in a significant drop in lead extractability inferring that the aggregating effect of large number of proton ionizable functional groups enhances the lead ion extractability [5]. It has been proposed by Kubota et al. that the dehydration ability of cyclic ligand towards a hydrated metal ion is greater than that of acyclic ligand due to chelating effect of multifunctional groups [44]. Due to the higher degree of aggregating and coordinating effect, the calix[6]arene hexacarboxylic acid derivative is expected to show stronger dehydration ability towards a hydrated metal cation. The pieces of reports made by Dung and Ludwig and Kubota et al. led us to anticipate that binding capacity of calixarene carboxylate derivatives towards lead ion could be enhanced by increasing the number of proton ionizable groups possessed by the host molecule. Consequently, in a continuation of our interest to develop the solid-phase extractant that can be used advantageously for scavenging lead ion, in present paper, we report the synthesis of methylene crosslinked calix[6]arene hexacarboxylic acid resin **4** (ideal chemdraw structure of which is shown in Fig. 1) and its lead extraction behaviour. The extractant contains carboxylic acid groups appended at lower rim of calix[6]arene skeleton which act in cooperative manner to facilitate the extraction of cations by ion exchange.

2. Experimental

2.1. Instrumentation

^1H NMR spectra of the synthesized compounds were recorded by Jeol JNM-AL300 spectrophotometer in CDCl_3 with TMS as an internal standard. IR spectra were recorded by JASCO FT-IR 410 spectrophotometer. Scanning electron microscope (SEM) images were taken by Jeol JSM-5510 scanning electron microscope. Metal

ion concentration of aqueous solutions was measured by atomic absorption spectrophotometer (AAS, Shimadzu AA 6800) and/or inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Shimadzu 8100). pH of the aqueous solution was measured by TOA DKK HM-30R pH meter.

2.2. Reagents and materials

All chemical reagents were of reagent grade and used without further purification unless mentioned otherwise. Analytical TLC was performed on pre-coated silica gel plates (SiO_2 , 60 F_{254}). Analytical grade metal nitrate salts were used to prepare the stock solutions (10.0 mM in 0.1 M HNO_3). The stock solutions were diluted to the desired concentration either with 0.1 M HNO_3 or with 0.1 M HEPES [2-{4-(2-hydroxyethyl)-1-piperazinyl} ethanesulphonic acid] buffer.

2.3. Synthesis of the resin

For the synthesis of resin **4**, the starting compound 5,11,17,23,29,35-hexa-*tert*-butylcalix[6]arene-37,38,39,40,41,42-hexol (*p-tert*-butylcalix[6]arene) was synthesized according to the literature procedure [45] and analyzed for its purity by TLC and ^1H NMR. *De-tert*-butylation of *p-tert*-butylcalix[6]arene to get calix[6]arene (**1**) was also based on the procedure reported for its tetrameric analogue [46]. Chemical modification of calix[6]arene to its carboxylic acid derivative and its resinification was carried out according to Scheme 1.

2.4. Synthesis of 37,38,39,40,41,42-hexakis(ethoxycarbonyl)methoxy]calix[6]arene (2)

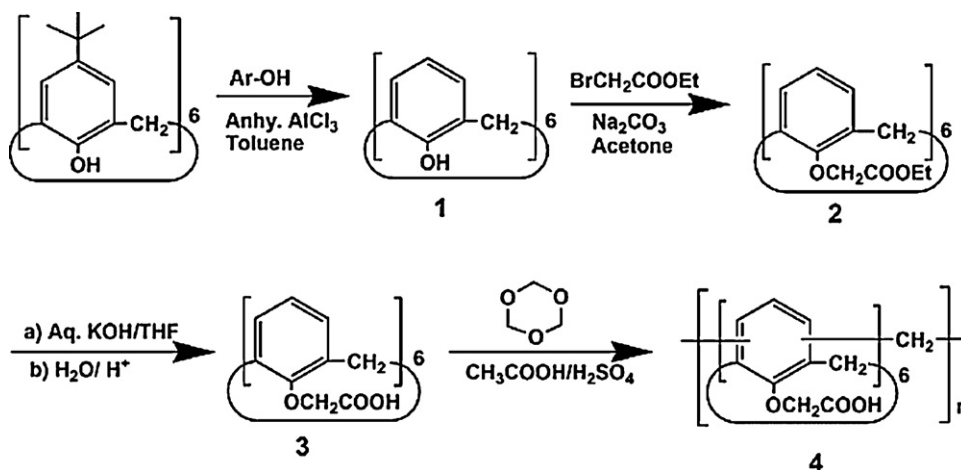
Etherification at phenolic group of **1** in a manner similar to Williamson's synthesis of ether as reported previously [4] afforded the compound **2** in 70% yield. Purity of the compound was checked with IR and ^1H NMR spectra. IR (KBr) disappearance of $\nu_{\text{O-H}}$ band of starting compound **1** centred at 3176 cm^{-1} and appearance of a sharp band for $\nu_{\text{C=O}}$ at 1751 cm^{-1} , $\nu_{\text{C-H}}$ at 2983 cm^{-1} , $\nu_{\text{C=C}}$ at 1462 cm^{-1} , $\nu_{\text{(C=O)-O}}$ at 1213 cm^{-1} , $\nu_{\text{C=C-O}}$ at 1187 cm^{-1} , $\nu_{\text{ArC-H}}$ (out of plane bending) at 769 cm^{-1} . ^1H NMR (300 MHz, CDCl_3 , TMS) δ 1.24 (t, $J=8\text{ Hz}$, 18H, CH_3 of ethyl), 4.04 (s, 12H, O-CH_2), 4.12 (q, $J=6.5\text{ Hz}$, CH_2 of ethyl), 4.19 (s(b), buried inside the quartet peak, $\text{Ar-CH}_2\text{-Ar}$), 6.6 (t, $J=7.5\text{ Hz}$, 6H, Ar-H , *para*), 6.75 (d, $J=8.4\text{ Hz}$) 12H, Ar-H , *meta*).

2.5. Synthesis of calix[6]arene-37,38,39,40,41,42-hexaacetic acid (3)

Compound **3** was also synthesized by adopting the previously published procedure for tetrameric analogue [4]. Saponification of ester group followed by acidification afforded the compound **3** in almost quantitative yield. Purity of the compound was checked with IR and ^1H NMR spectra. IR(KBr) $\nu_{\text{O-H}}$ (broad) centred at 3062 cm^{-1} , $\nu_{\text{C-H}}$ 2920 cm^{-1} (superimposed upon O-H stretching), $\nu_{\text{C=O}}$ 1741 cm^{-1} , $\nu_{\text{C=C}}$, $\nu_{\text{C-O-H}}$ and $\nu_{\text{C-O-C}}$ vibrations $1462\text{--}1057\text{ cm}^{-1}$, $\nu_{\text{ArC-H}}$ 847 and 766 cm^{-1} . ^1H NMR (300 MHz, CDCl_3 , TMS) δ 3.41 (s(b) 6H, ArCH_2Ar , *exo*), 4.26 (s(b) 12H, ArOCH_2), 4.54 (s(b) 6H, ArCH_2Ar , *endo*), 6.6 (s(b) 6H, Ar-H , *para*), 6.93 (s(b), 12H, Ar-H , *meta*).

2.6. Synthesis of methylene crosslinked calix[6]arene-37,38,39,40,41,42-hexaacetic acid (4)

Under nitrogen atmosphere, the mixture of **3** (2.0 g, 2.03 mmol) and *s*-trioxane (1.08 g, 6.09 mmol, 3 equivalents) in acetic acid (20 cm^3) was stirred at $80\text{ }^\circ\text{C}$ for 30 min. This was followed by the



Scheme 1.

drop wise addition of mixture of 20 cm³ acetic acid and 3 cm³ conc. H₂SO₄ for 30 min. After addition of acid mixture, temperature was increased to 110 °C and the mixture was stirred at that temperature for 8 h. During heating at 110 °C, a clear solution was first obtained by the dissolution of reactants which later changed to a suspension and finally to a resinous product. Then, the cooled reaction mixture was poured in small aliquots in NaHCO₃ solution (5%, w/v) for neutralization. The solid was collected by filtration and washed with hot water, 1 M HCl followed by distilled water. The crude resin was heated overnight at 80 °C in a convection oven and stirred with 0.05 M NaOH solution for several hours to remove the unreacted feed materials, if any. After several washings with above operations and drying at 80 °C for 12 h, 2.6 g resin was obtained which was pulverized into fine powder (particle size upto 150 μm). IR(KBr) ν_{O-H} 3286 cm⁻¹, ν_{C-H} 2920 cm⁻¹, $\nu_{C=O}$ 1732 cm⁻¹, $\nu_{C=C}$, ν_{C-O-H} and ν_{C-O-C} vibrations 1433–1051 cm⁻¹, ν_{ArC-H} 893 cm⁻¹, disappearance of ν_{ArC-H} at 847 and 766 cm⁻¹.

2.7. The extraction experiments

2.7.1. General extraction

The percentage extraction of metal ions at different pH values was determined by conventional batch method. The metal ion solutions prepared in 0.1 M HNO₃ and 0.1 M HEPES buffer were arbitrarily mixed to adjust the pH and 10 cm³ solutions were added to 0.01 g resin. The heterogeneous mixture was agitated for 10 h. The metal ion concentrations of the aqueous solutions before and after equilibrium in single species extraction were measured by AAS and in extraction from the mixture were measured by ICP-AES. From the measured initial and equilibrium concentrations of metal ions, percentage of each metal ion extracted in solid phase extractant was calculated.

2.8. Elution of loaded lead

In order to carry out the elution test of the loaded Pb(II) on the resin, the resin was first loaded with Pb(II) ions by carrying out sorption experiment in batchwise method. In a typical experiment, 0.06 g resin was equilibrated with 50 cm³ of 2.0 mM Pb(II) solution at pH 4.1 for 24 h. After filtration of the resin, the Pb(II) concentration in the filtrate was measured and the amount of Pb(II) loaded on the resin was calculated, which was found to be 213.4 mg Pb(II) per gram resin. The metal loaded resin was washed with distilled water and dried. Then, the elution test of the loaded Pb(II) was carried out by shaking the lead loaded resin with hydrochloric acid solution. For this, 0.01 g Pb(II)-loaded resin was shaken with 10 cm³ of

hydrochloric acid solution of different concentrations for 6 h. After filtration of the resin, amount of Pb(II) eluted was measured by AAS and elution percentage was calculated from the difference.

2.9. Column experiment

The performance of the resin under dynamic condition was assessed by column breakthrough experiment using glass column of 24.5 cm height and 0.8 cm internal diameter. In this experiment, 0.150 g resin, which was immersed in de-ionized water for few hours, was loaded into the glass column. The resin was tightly packed and was supported by glass beads on both ends of the column to prevent the resin from floating and also to allow the uniform distribution of the influent. The aqueous feed solution was prepared by dissolving lead, copper and zinc nitrates into 0.1 M HEPES buffer solution. The pH of synthetic solution was adjusted to 4.1 with 1 M HNO₃ and the concentrations of lead and copper were 12 ppm each and that of zinc was 120 ppm. The synthetic feed solution was passed through the column at a constant flow rate of 6 cm³ h⁻¹ using a peristaltic pump (Iwaki PST-100N). Under such experimental condition, the extractant volume was 0.3769 cm³ and liquid hourly space velocity (LHSV) was 15.91. The effluent solution was collected at hourly intervals using a Biorad 2110 fraction collector in an 8 ml tube and was analyzed periodically to determine the residual concentration of metal ions in the effluent by using ICP-AES. Once the saturation of metal loading was achieved, the loaded resin was washed with distilled water and adsorbed metal was eluted with 2 mol dm⁻³ hydrochloric acid, also with the feed rate of 6.0 cm³ h⁻¹. The metal concentration in eluted solution was analyzed as before.

3. Results and discussion

3.1. Synthesis of resin and its characterization

Synthesis of **4** is a five-step reaction. Synthesis of *p*-*tert*-butylcalix[6]arene as the starting compound followed by AlCl₃ catalyzed debutylation yielded calix[6]arene. Treatment of calix[6]arene with ethyl bromoacetate in a manner similar to Williamson's synthesis of ether as reported elsewhere in literature afforded the calix[6]arene ester in 70% yield. Saponification of calix[6]arene ester followed by acidification of corresponding carboxylate salt yielded the calix[6]arene carboxylic acid derivative in almost quantitative yield. Crosslinking of calixarene units with methylene group was accomplished using *s*-trioxane as crosslink-

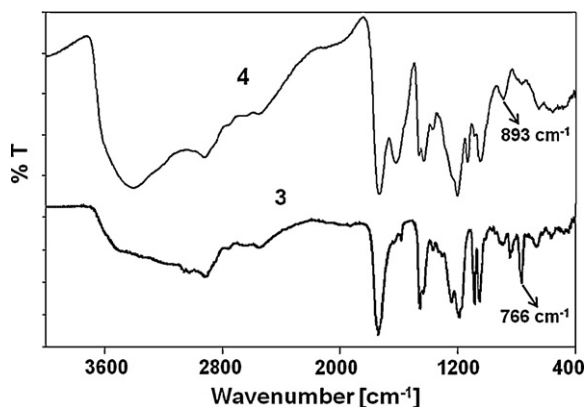


Fig. 2. FT-IR spectra of **3** and **4**.

ing agent in acetic acid in presence of catalytic amount of conc. H_2SO_4 (Scheme 1).

The synthesized compounds were characterized with FT-IR and ^1H NMR spectra. The ^1H NMR spectrum of **2** exhibited a triplet at 1.24 ppm and a quartet at 4.12 ppm, respectively for CH_3 and CH_2 protons of ester group and a singlet at 4.04 ppm for ArOCH_2 protons. The broad singlet at 4.19 ppm for bridged methylene (ArCH_2Ar) protons in the ^1H NMR spectrum of **2** indicates that the compound is conformationally flexible at NMR time scale. The ^1H NMR spectrum of **3**, however, displayed two broad singlets at 3.41 and 4.26 ppm for ArCH_2Ar protons inferring the cone-like conformation. According to Shimajo et al., the calix[6]arene acetic acid favourably adopts a cone conformation because of stabilization by intramolecular hydrogen bond interactions among six carboxylic acid groups [47]. In the present case also, the rotational freedom of compound **3** is restricted due to intramolecular hydrogen bonding interactions among the carboxylic acid groups and **3** tends to adopt the cone conformation. Since the resin precursor exists in cone-like conformation, it is not unreasonable to propose that the calix[6]arene maintains the cone-like conformation in the resin **4**.

The IR spectrum of **1** exhibited a broad band centred at 3176 cm^{-1} for O–H stretching frequencies of phenolic groups. Upon etherification at phenolic oxygen, the band at 3176 cm^{-1} was disappeared and compound **2** displayed a sharp band at 1751 cm^{-1} for C=O stretching vibrations of ester group. The IR spectrum of **3** revealed a broad band centred at 3062 cm^{-1} for O–H stretching and a sharp band at 1741 cm^{-1} for C=O stretching vibrations of carboxyl group. In addition, the compounds **1**, **2** and **3** all exhibited a sharp band at around 760 cm^{-1} due to Ar–H out of plane bending vibrations of phenyl units of calixarene backbone. The Ar–H bending frequency which appears in $910\text{--}665\text{ cm}^{-1}$ region is most important in determining the group positions of substituted benzene derivatives. The three adjacent hydrogens of aryl group absorb between 800 and 765 cm^{-1} , two adjacent hydrogens of aryl group absorb between 855 and 800 cm^{-1} and the single hydrogen of aryl group absorbs between 910 and 835 cm^{-1} regions of the IR spectrum [48]. The intense band at 766 cm^{-1} in the IR spectrum of **3** is therefore attributed to the C–H bending vibrations of three adjacent Ar–Hs of compound **3**. Upon resinification, the band at 766 cm^{-1} was vanished (Fig. 2) which is strong indication of crosslinking. The disappearance of sharp band at 766 cm^{-1} and absence of absorption band in $855\text{--}800\text{ cm}^{-1}$ region for two adjacent hydrogens of aryl group supports the fact that crosslinking occurred from 4-position of aryl group and all the C–H bonds of 4-position disappeared after crosslinking. In addition, the absorption band due to single hydrogen at 893 cm^{-1} was quite small inferring that crosslinking also took place partially from 3- and 5-positions of aryl group. The hydroxymethyl group introduced at the more reac-

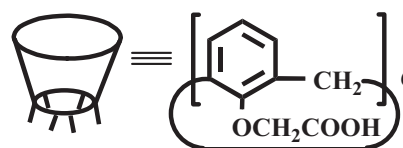
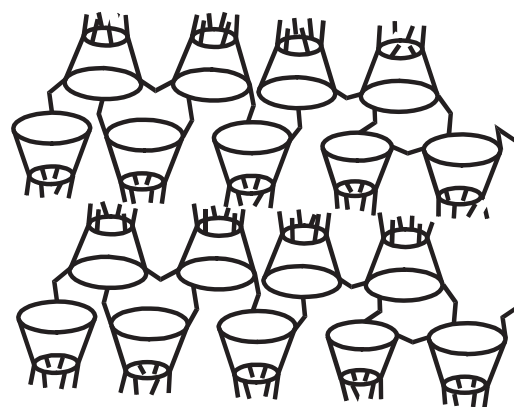


Fig. 3. Hypothetical structure of the resin.

tive 4-position of phenyl unit of calix[6]arene is capable of reacting with another free aryl hydrogen at 3 and 5-positions by condensation reaction giving methylene bridges. This fact is also evident from the molar ratio of formaldehyde: phenol residues used in synthesis of the resin. In the synthesis of resin **4**, the molar ratio of formaldehyde: phenolic unit reaches 3:2 so that it is apparent that every phenolic unit is linked together via methylene bridges and the system is entirely crosslinked. This resulted into the formation of highly rigid resin with irregular, three-dimensional network of bowl-shaped macromolecular calix[6]arene units having pre-defined cavity and carboxylic acid groups to facilitate the cation recognition by ion-exchange.

Based on the aforementioned evidences, hypothetical structure of the resin is proposed as shown in Fig. 3 in which the wider rim of calixarene bowls in cone-like conformation are facing each other and are crosslinked by methylene bridges in a random fashion.

Further, the resin **4** was insoluble in any organic diluent in which **3** was soluble (data not shown). Such insolubility behaviour of **4** in organic diluents also supports the formation of resin. Introduction of methylene crosslinks interconnects the various calixarene units in a random fashion and renders the resin insoluble in water as well as in organic diluents. In addition, the resin was insoluble in moderately acidic as well as mild basic solutions (data not shown). Since the resin dissolution requires the rupture of carbon–carbon bonds of irregular three-dimensional network, the resin was found to be insoluble in all solvents by which the carbon–carbon bonds are not disrupted. This property of the resin is immensely useful particularly for adsorptive systems in which the metal ion is separated from various aqueous environments.

Since the resin **4** is insoluble in ordinary diluents, the molecular weight of the resin could not be determined by common methods such as osmometry [49], viscometry [50], NMR spectroscopy [51], size exclusion [52] and gel permeation [53] chromatography, etc. and the degree of crosslinking could not be assessed. However, the surface morphology of the resin was analyzed by scanning electron microscopy (SEM) image of the resin shown in Fig. 4. The surface morphology of **4** exhibits somewhat flesh and lumpish structure with agglomerated particles of irregular shape probably due to random crosslinking.

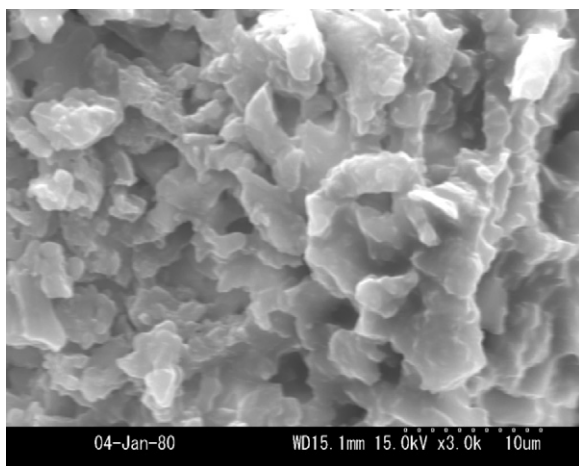


Fig. 4. SEM image of 4.

3.2. Effect of pH on solid phase extraction of metal ions with resin 4

The experimental results of pH dependency on single species extraction of Pb(II), Cu(II), Zn(II), Co(II) and Ni(II) and extraction of metal ions from the mixture with the resin 4 are shown in Fig. 5(a) and (b), respectively, where the percentage of extraction, %E is defined by equation (1).

$$\%E = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where C_i and C_e are initial and equilibrium concentrations of metal ions in aqueous solution respectively.

The selectivity order of 4 for extraction of metal ions is $Pb > Cu > Zn, Co, Ni$, which resembles to that of other carboxylic acid type of resins as in our previous results [21,23,24]. Since the availability of carboxylate anion increases with increasing pH facilitating the cation exchange, the percentage extraction of metal ions also increases with pH. All the metal ions studied fall under intermediate hardness in Pearson's classification of hard and soft acids and bases (HSAB) principle. Although our extractant contains O-donor atoms, these cations are extracted in the different position on the spectrum of pH indicating that 4 is more selective for Pb(II) over other metal ions. As it is obvious from Fig. 5, lead is quantitatively extracted with the resin 4 after pH 3.6 at which extraction of copper is moderate and that of zinc, cobalt and nickel ions is insignificant. In fact, the extraction of copper with the present resin is quantitative after pH 4.2 and extraction of other metal ions quantitative only after pH 4.8 indicating that the resin is applicable for selective scavenging of lead ion from aqueous environment by adjusting the pH. The logarithms of formation constant ($\log \beta_1$) for metal carboxylate (acetate) complexes of Cu(II) are higher than those of Pb(II) [54] which invokes that the extractants containing acetic acid group should form stable complex with Cu(II) rather than with Pb(II) and must be selective for Cu(II). In contrary to this generalization, the present resin is more selective for Pb(II) than Cu(II). Thus, it can be inferred that the macrocyclic ring plays a critical role for the transport of Pb(II) from aqueous phase into the solid phase. Though the role of macrocyclic ring is not clearly understood, it is attributable to the calix[6]arene cavity dimension being the governing factor for cation selectivity under the investigated system coupled with cooperativity effect of multifunctional groups. Among the metal ions studied, lead ion has larger size which matches the calixarene cavity dimension defined by coordinating atoms and the complexes of lead ion are in relatively lower strain energy situation than that of the smaller ions and it is selectively extracted by the resin 4.

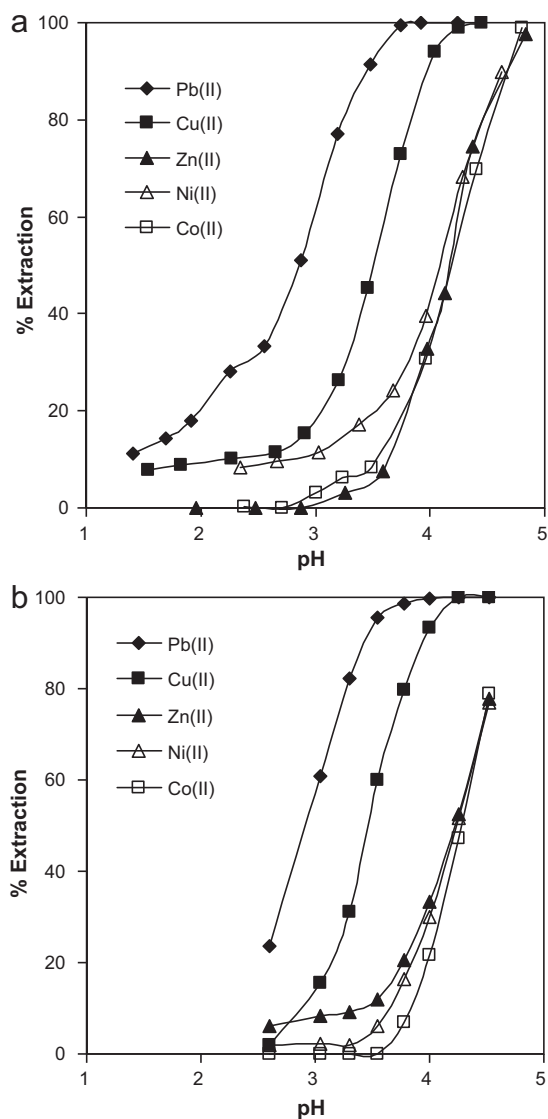


Fig. 5. Effect of equilibrium pH on percentage extraction of metal ions by 4. (a) Single species extraction, and (b) extraction from the mixture of cations. [metal ion]=0.1 mM ($M = \text{mol dm}^{-3}$), volume of aq. solution = 10 cm^3 , weight of resin = 0.01 g, shaking time = 10 h, adjustment of pH 0.1 M HNO_3 and 0.1 M HEPES buffer.

3.3. Maximum binding capacity of 4 towards lead and complexation stoichiometry

As the resin 4 has significant lead selectivity, the maximum lead uptake capacity of 4 was examined by equilibrating the resin with varying initial concentration of metal ion at constant initial pH. The quantity of lead loaded on the resin, q (mmol g^{-1}), was evaluated by the Eq. (2) and the results are presented in Fig. 6

$$q = \frac{C_i - C_e}{W} \times V \quad (2)$$

where C_i and C_e are initial and equilibrium concentrations of metal ions in aqueous solutions respectively, W (mg) and V (cm^3) are weight of the resin and volume of aqueous solution respectively.

As it is obvious from the results of Fig. 6, the amount of lead loaded on the resin (q) increases with increasing lead concentration of the reacting fluid and reaches a constant value at higher concentration region. The maximum binding capacity of the resin 4 towards lead, as evaluated from the plateau region of Fig. 6, was 1.3 mmol g^{-1} , which is reasonably high as compared to some solid

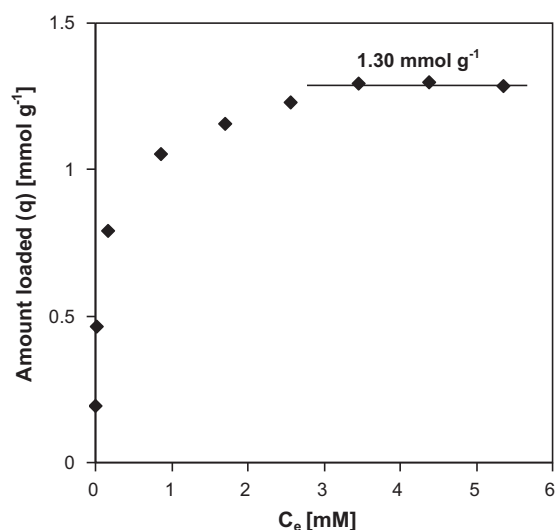


Fig. 6. Maximum Pb(II) binding capacity of **4**. Initial pH 4.0, weight of the resin = 0.01 g, volume of the test solution = 10 cm³, shaking time = 24 h at 303 K.

Table 1

Binding capacities of different adsorbents/extractants towards lead ion.

Solid phase extractant/adsorbent	$q/\text{mg g}^{-1}$	Reference
Calix[4]CH ₂ COOH polymer supported resin	128.46	[21]
Calix[4]CH ₂ COOEt polymer supported resin	21.09	[22]
<i>t</i> -Oct calix[4]CH ₂ COOH impregnated resin	58.01	[23]
<i>t</i> -Oct calix[6]CH ₂ COOH impregnated resin	31.08	[23]
<i>t</i> -Bu calix[4]CH ₂ COOH impregnated resin	68.37	[24]
Imprinted polymer	19.66	[28]
Ofloxacin modified silica gel	48.69	[31]
Iminodiacetate-type cellulose	178.19	[32]
Phosphonic acid modified peanut shell	116.70	[33]
Carbon nanotubes	10.30	[34]
Carbon nanotubes	12.41	[35]
Methylene crosslinked calix[6]CH ₂ COOH	269.36	Present work

phase extractants used so far for the removal of such toxic metal ion. For comparison, the binding capacities of different extractants/adsorbents exploited for scavenging of lead are summarized in Table 1 along with that of the present extractant. The relatively higher adsorption capacity of **4** is attributable to the cyclic structure of calix[6]arene with predefined cavity and aggregating effect of larger number of carboxyl functional groups which are responsible for uptake of lead ion.

The stoichiometry of complex formation between **4** and lead ion was determined from the number of millimoles of calix[6]arene units per gram resin and the maximum amount of lead loaded on the resin. The number of mmoles of **4** per gram resin, determined by pH titration¹ and neutralization titration² was found to be 1.35.

¹ In typical method for pH titration, 0.1 g resin was immersed in 25 ml distilled water and agitated for 4 h at 300 rpm in order to allow the wetting of the resin to facilitate the release of H⁺ ions. Then, the slurry was titrated by stepwise addition of titrant (0.1 N NaOH). After each addition of the titrant (200 μl), the system was allowed to equilibrate until a stable pH reading was obtained. The end point was determined by the sharp increase in pH of the system upon the addition of base. From the known volume of base consumed by the known weight of the resin until the end point, the number of milliequivalents of NaOH required for complete neutralization was estimated and the number of millimoles of calix[6]arene units per gram resin was calculated.

² For neutralization titration, 0.1 g resin was immersed in 25 ml of 0.1 N NaOH solution and agitated for 4 h at 300 rpm to allow the neutralization of carboxylic acid groups. Then, the suspension was titrated with 0.1 N oxalic acid solution and the volume of NaOH consumed for neutralization of the resin was determined from the difference. Since excess NaOH was used initially, all Na⁺ ions were practically completely taken up by the resin and displaced the H⁺ ions. Hence, the amount of

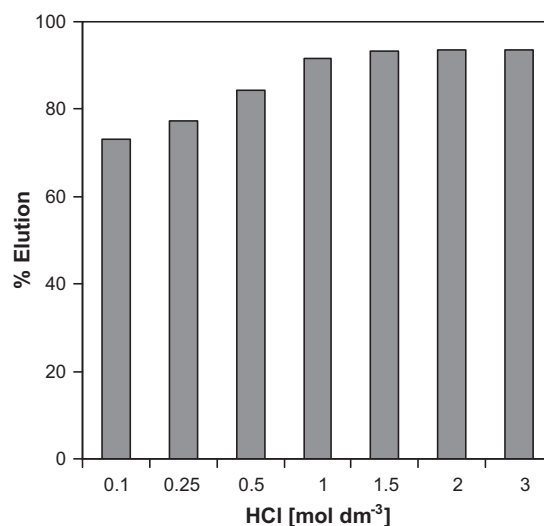


Fig. 7. Effect of hydrochloric acid concentration on percentage elution of the loaded lead from the resin **4**. [Pb(II)]_{loaded} = 213.42 mg g⁻¹ resin, solid/liquid ratio = 1, shaking time = 6 h at 303 K.

Experimentally, the maximum lead loading capacity of the resin was found to be 1.30 mmol per gram resin. Thus, formation of 1:1 host–guest complexes is quite obvious.

3.4. Elution of loaded lead and reusability of the resin

For real time application, the resin should be recyclable, *i.e.* it should not only extract the target metal ion but also be able to conveniently and quantitatively release the extracted metal cation in response to mild changes in the environment such as pH. The elution process not only regenerates the resin but also recovers the loaded metal in pre-concentrated form. Consequently, the elution test of loaded lead on **4** was examined by contacting the lead loaded resin with various concentrations of hydrochloric acid solutions and the results are summarized in Fig. 7. The results indicate that more than 90% elution of loaded lead was achieved with 2 M hydrochloric acid solution even at high loading of lead (more than 200 mg lead per gram resin was loaded in present case). However, it may be emphasized here that quantitative elution of loaded lead was achieved with dilute HCl solution at low loading of lead.

For keeping the process cost down in routine operations, the repeated use of resin is essentially important and subsequent regeneration of the resin for another cycle of application is desirable. It is also mandatory that the elution process should restore the resin identical to the original condition for effective reuse with undiminished metal uptake. The FT-IR spectra of **4** (free resin, lead loaded resin and after elution) are presented in Fig. 8. It is worth mentioning that the C=O stretching band of free resin **4** at 1736 and 1624 cm⁻¹ were totally absent with the appearance of new band at 1577 cm⁻¹ upon lead loading, presumably due to C=O...Pb²⁺ stretching vibrations indicating the participation of carbonyl group for coordination with loaded lead ion. After elution, the spectrum became commensurate of the original resin with the appearance of C=O stretching band at 1734 and 1618 cm⁻¹ suggesting that elution of loaded lead with 2 M HCl restores the resin identical to the original condition. It is inferred from the FT-IR spectra of lead loaded and eluted resin that the resin **4** is regenerated without any physical/chemical damage and can be used repeatedly.

NaOH consumed by the resin is stoichiometrically equivalent to the amount of H⁺ ions released by the resin.

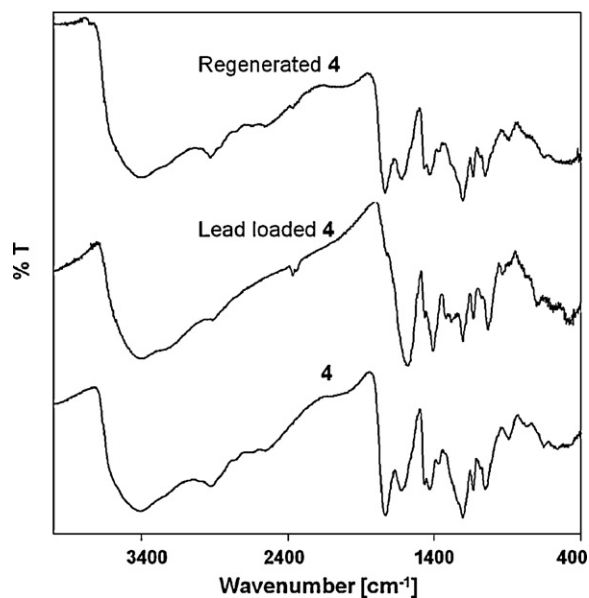


Fig. 8. FT-IR spectra of free, lead loaded and regenerated 4.

The practical reusability of the resin 4 for successive cycles was also examined by extraction/elution cycles using conventional batchwise method for at least five repeated cycles and the results are presented in Fig. 9. It is obvious that quantitative extraction and elution of lead was achieved for at least 5 repeated cycles with undiminished metal uptake thus opening up the possibility of repeated use of resin 4 for the removal and recovery of lead.

3.5. The column experiment

It is usually required to remove the trace amount of lead from the waste containing large amount of other metal ion, for instance the waste solution of zinc plating, which contains trace amount of lead ion as a contaminant. The tailings and associated overburden materials usually contain elevated concentration of copper and zinc with relatively small quantity of lead. So, it is desirable to selectively scavenge lead ions in presence of varying concentration of other metal ions for cleansing and processing of such materials. For this,

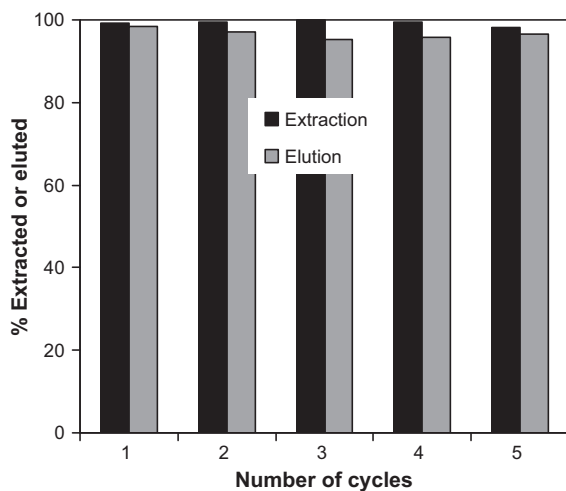


Fig. 9. Successive extraction/elution cycles for extraction of Pb(II) with resin 4. $[Pb(II)]_{initial} = 184.12$ ppm, initial pH in extraction experiment = 4.1, eluent = 2.0 M HCl, shaking time = 10 h for extraction and 5 h for back extraction, solid/liquid ratio = 2 in extraction as well as elution.

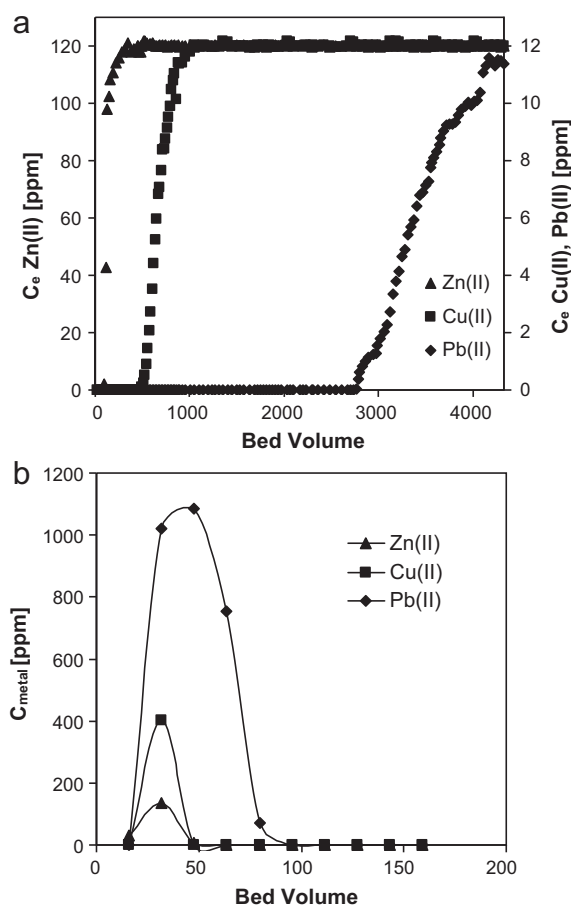


Fig. 10. (a) Breakthrough and (b) elution profiles of lead, copper and zinc ions. $[Pb(II)] = 12$ ppm; $[Cu(II)] = 12$ ppm $[Zn(II)] = 120$ ppm, wt of resin = 0.15 g, flow rate = $6.0 \text{ cm}^3 \text{ h}^{-1}$, liquid hourly space velocity (LHSV) = 15.91, pH of feed solution = 4.1, eluent = 2.0 M HCl.

highly effective ion exchangers are needed for efficient removal of small quantities of a counter ion species from a large excess of competitive counter ions. One of the several possibilities to achieve this is the selective uptake of metal cations by simple ion exchange on the packed bed of the cation exchange resin and elution of the loaded metal cations with dilute mineral acids.

It is obvious from the results of Fig. 5 that the resin 4 shows high selectivity to lead ion over the other ions studied. Therefore, it is reasonable that this resin is suitable for the removal of lead present even in minute quantity from the waste containing large amount of other metal ions. By means of breakthrough followed by elution using the continuous column experiment, even the small amount of lead ion should be adsorbed on the packed bed of the resin and separated from the excess amount of other metal ions studied. The breakthrough profile of lead, copper and zinc are shown in Fig. 10(a) where bed volume is the volume ratio of the feed solution that passes through the column to the volume of the resin. As expected from the results of batchwise experiment, breakthrough of zinc ion took place immediately after the starting of the feed while that of copper took place after bed volume 500. On the contrary, the breakthrough of lead began to take place after as late as about 2700 bed volume. From the results shown in Fig. 10(a), the breakthrough volume of lead under the present experimental conditions was evaluated to be 2700 indicating that the amount of analyte that can be safely passed through the column expecting complete separation and preconcentration with 100% efficiency corresponds to 2700 bed volume. The results of breakthrough profile clearly suggested that the complete separation of trace amount of lead from

excess zinc was successfully achieved by using the column packed with the resin **4**. From the results, one can also infer that the resin can be applied for mutual separation of lead and copper by adjusting the solution pH. Continuation beyond breakthrough resulted in incomplete separation of the mixture, however, with complete displacement of hydrogen ions from the resin with lead ions and the whole bed was in equilibrium with the feed solution at about bed volume 4200.

After saturation of the bed, the column was regenerated by elution. The elution profiles of the loaded metal ions from the column with 2 M hydrochloric acid solution are shown in Fig. 10(b). The elution profile depicts different patterns corresponding to different concentrations of metal ions eluted from the column. A very sharp elution profile of lead was observed at about bed volume 50 which demonstrates that lead concentration reaches as high as 90 times that of the feed solution. On the other hand, the elution of copper is in small quantity and that of zinc is insignificant compared with that of lead. These results are promising on the grounds that they suggest the present resin would be useful in achieving selective and effective removal of trace amount of lead from the polluted water and industrial streams.

4. Conclusions

We have developed a calix[6]arene-based cation exchange resin by methylene crosslinking of calixarene units. The resin is highly efficient for selective and quantitative scavenging of lead from aqueous environment. The maximum lead binding capacity of the resin is reasonably higher than those reported in literature. Since the loaded lead is easily and quantitatively eluted with acid solution regenerating the resin identical to the original condition, the resin is industrially useful in routine operations for achieving preconcentration and removal of trace amount of lead and holds promise for cleansing lead bearing effluents.

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