

Preparation of calix[4]arene methylene crosslinked resins with 2-pyridyl pendant group and their adsorption behavior towards silver ion

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Abstract Three different resins namely 1:5 MC-resin, 1:3 MC-resin and 1:1 MC-resin have been synthesized by methylene crosslinking of 2-pyridylcalix[4]arene. Adsorption behavior of these resins towards the metal ions existing in photographic waste was investigated. The resins show absolute efficiency for adsorption of silver ion with no affinity for other coexisting ions. First two resins form 1:1 complex whereas the third one forms 2:1 complex with silver ion. Maximum loading capacity of silver ion on the present resins was found to be 1.15, 1.29 and 0.69 mol kg⁻¹, respectively. Column chromatographic separation of silver ion in presence of excess of sodium ions was also carried out with 1:5 MC-resin. Selective adsorption of silver ions over excess of sodium ions was achieved.

Keywords 2-Pyridylcalix[4]arene · Crosslinked resin · Impregnated resin · Adsorption · Silver ion · Column chromatography

Introduction

The conventional approaches to heavy metal removal are chemical precipitation and filtration, chemical oxidation or reduction, electrochemical treatment, reverse osmosis, chemical coagulation, use of chelating ion exchangers,

solvent extraction, adsorption, etc. [1–5]. Over the years, calixarenes, the phenolic metacyclophanes [6, 7], and their derivatives are receiving increasing attention as a versatile class of macrocyclic compounds that have been studied extensively as potential ionophores for solvent extraction [8]. Because of their specific ion binding properties with well-organized cavity, they are frequently employed as a platform for design and synthesis of novel ionophores with specific ligating sites. A number of calixarene derivatives containing various pendant groups such as ester, ketone [9–11], carboxylic acids [12–20], amine [5], amides [21, 22], nitriles [23], phosphonyl [24, 25], etc. have been developed at lower rim to study their ionophoric behavior. Ionic recognition and discrimination is one of their remarkable feature and they have been emerged as powerful extractants for various metal ions including alkali and alkaline earth cations [11, 22, 26], transition metal ions [5, 12–19, 27–30], lanthanides and actinides [12–19, 24, 25]. Our interest lies on the removal and recycling of toxic and valuable heavy metal ions.

Bottino et al. [31] reported the synthesis of calix[4]arenes bearing pendant pyridine groups at the lower rim as potential ligands for transition metals. Higuchi et al. developed pyridine-functionalized proton-switchable calix[4]arenes which performed good extractability towards silver ion in acidic solution [12–19]. They also investigated the structural effects of three isomers, 2-, 3-, and 4-pyridylcalix[4]arenes towards the extraction of silver ion and the results revealed that 2-pyridylcalix[4]arene shows excellent silver extraction behavior. Marcos et al. [32] developed dihomooxalix[4]crown-6 bearing pyridyl pendant groups and found very strong affinity for Ag⁺ ion. Zaghbani et al. prepared thiacalix[4]arene derivative having amide group at the lower rim and found high selectivity for silver ion. The results were explained on the basis of great

Molecular recognition across disciplines—a special issue dedicated for Drs. Jack Harrowfield and Jacques Vicens.

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affinity of complexing agents containing sulphur and nitrogen towards d^{10} transition metals such as Ag^+ [33]. Shimojo et al. solubilized calix[4]arene bearing pyridinium units in typical room temperature ionic liquid (RTIL) and found high extraction ability and selectivity for silver ion. They reported that the extraction performance of calixarene was greatly enhanced by dissolution in RTIL compared to chloroform [34]. Despite their good extraction abilities, solubility of calixarenes in non-toxic solvents used in industrial processes such as kerosene and aliphatic hydrocarbons is poor, which is the significant barrier for using them as solvent extraction reagents in industrial application [35]. Because of their limited solubility in organic diluents, the steady increase is in the development of calixarene-based sorbents for solid phase extraction. The sorption processes are probably the most attractive methods due to their high efficiency in a wide range of metal ion concentration, easy handling with more flexible working conditions together with good stability and selectivity [36]. Solid phase extraction using good sorbent offers a number of important benefits such as reduction in solvent use and exposure to toxic solvent, their disposal cost and extraction time [37]. Generally, calixarene based solid phase extractants are developed either by linking them onto various supports such as polymeric resins [12–19, 38, 39] silica [40], or by impregnation onto commercial resin [12–19, 41], or through crosslinking of calixarene themselves [12–19].

Treatment of industrial wastes containing substantial quantities of toxic and valuable components often receives the utmost priority. Industrial waste streams contaminated with heavy metal ions are frequently produced as effluents from various industrial processes. Consequently, toxic heavy metal ions are being increasingly released into environment leading to severe contamination of the later. The environmental pollution caused by toxic heavy metals in industrial effluents is one of the widely posed threat and a topic of much interest in recent years. Transition metal ions (Ag^+ , Hg^{2+} , Pb^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pd^{2+} , Cd^{2+}) are recognized as highly toxic which makes their presence in environment undesirable. Since they are non degradable, such metals can accumulate in environment and cause deleterious effects in plants and animals even at low concentrations [42]. Hence, there is the need of renewed interest in processing of industrial effluents containing such toxic metal ions. On the other hand, the heavy metal resources could run out in few years based on the current consumption rate. Therefore, from the resource reservation point of view, recovery and recycle of heavy metal ions are equally obligatory.

Photographic waste contains high concentration of silver (2,490 ppm), sodium (3,630 ppm), potassium (6,240 ppm) and iron (1,480 ppm) along with some zinc, copper, lead and cadmium [43]. High concentration of silver in photographic

wastes, its high value and its toxicity are worthy of consideration. Increasing price of silver and increasing pressure concerning the environmental issues make preconcentration and recovering of silver an attractive approach. Previously, we had reported the extraction behavior of resin impregnating pyridylcalix[4]arene towards silver ion [12–19]. Our previous results indicate that 2-pyridyl derivative of calix[4]arene hardly forms complex with sodium, copper, lead and zinc ions, but selectively makes complex with silver ion. Such compound has advantage to remove or recover silver from the waste containing silver along with other ions, such as photographic drainage. However, the impregnated resin shows only low loading capacity due to the polymeric matrices which are quite ineffective towards silver adsorption. In an extension of our previous studies to develop the resins with increased loading capacity for silver ion, we decided to synthesize methylene crosslinked resin of 2-pyridylcalix[4]arene which would be applied for selective removal of silver from photographic waste. In this paper, we report the synthesis of 2-pyridylcalix[4]arene methylene crosslinked resins and their adsorption behavior towards silver ion. Column chromatographic separation of silver ion in presence of sodium ion is also reported.

Experimental

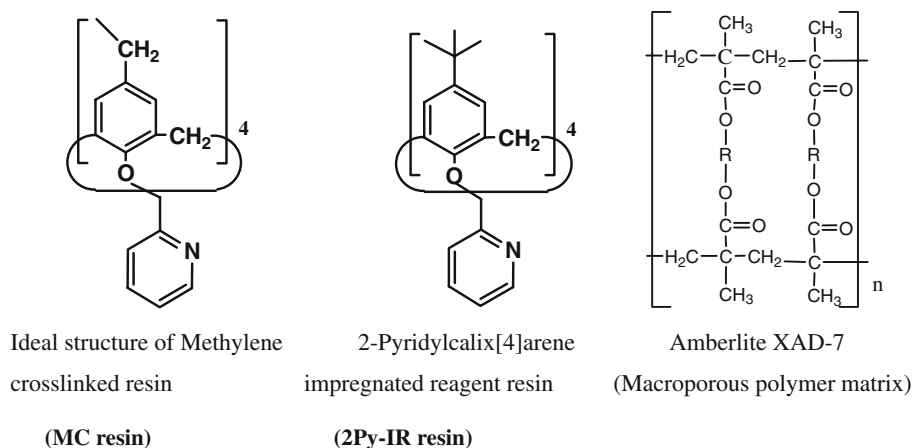
Materials and methods

IR spectra were recorded by JASCO FT-IR 410 spectrophotometer as KBR pellets. 1H -NMR spectra were recorded by Jeol, JNM-AL300 spectrophotometer in $CDCl_3$ with TMS as an internal standard. All reagents and solvents, purchased from Wako chemical company, were of reagent grade and used without further purification unless mentioned otherwise. Analytical TLC was performed on precoated silica gel plates (SiO_2 , 60 F_{254}). In NMR spectra, the Ar notation indicates the aromatic nuclei of calixarene backbone. The compounds 5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetrahydroxycalix[4]arene ($^tBu[4]H$) and 25,26,27,28-tetrahydroxy-calix[4]arene ([4]H) were synthesized as described in literature [44, 45] and analyzed for their purity by TLC, FT-IR and 1H -NMR. Structures of reagents employed in this study are shown in Fig. 1.

Preparation of 2-(chloromethyl)pyridine

To 10.3 g (61.6 mmol) of 2-(chloromethyl)pyridine hydrochloride salt in 100 cm^3 dry DMF was added 6.23 g (61.6 mmol) triethylamine in 50 cm^3 dry DMF and the mixture was stirred for 30 min. After removal of triethylamine hydrochloride salt by filtration, 2-(chloromethyl)pyridine in dry DMF was obtained.

Fig. 1 Structures of the reagents employed in the present studies



Synthesis

Synthesis of 25,26,27,28-tetrakis(2-pyridylmethoxy)calix[4]arene ([4]CH₂²Py)

Under nitrogen atmosphere, [4]H (3.00 g, 7.07 mmol) was added to 60 cm³ dry DMF in a salt ice bath. Sodium hydride (5.66 g, 171 mmol) was added to the mixture and stirred for 3 h at room temperature. Then, 2-(chloromethyl)pyridine (141 mmol, 20 mol eq.) in 300 cm³ dry DMF was carefully added dropwise to the mixture solution, also in a salt ice bath and stirred for 1 h at 25 °C and for more than 14 h at 35 °C. Excess of sodium hydride was deactivated by adding methanol and the resulting mixture was evaporated in vacuo. The residue was dissolved in chloroform and 50 cm³ of 1 M hydrochloric acid was added to neutralize. Chloroform layer was separated, washed successively with distilled water and dried over anhydrous magnesium sulfate. The solvent was evaporated and residue was recrystallized from methanol; white powder 4.20 g (75.5%). IR (KBr) $\nu_{\text{ArC-H}}$ 2,960–2,919 cm⁻¹, $\nu_{\text{C=C}}$ and $\nu_{\text{C=N}}$ 1,570–1,430 cm⁻¹, $\nu_{\text{ArC-H}}$ (out of plane bending) 754 and 777 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃, TMS, 27 °C), δ 3.07 (4H, d, ArCH₂Ar(*exo*)), 4.38 (4H, d, ArCH₂Ar(*endo*)), 5.13 (8H, s, OCH₂), 6.57 (12H, s,

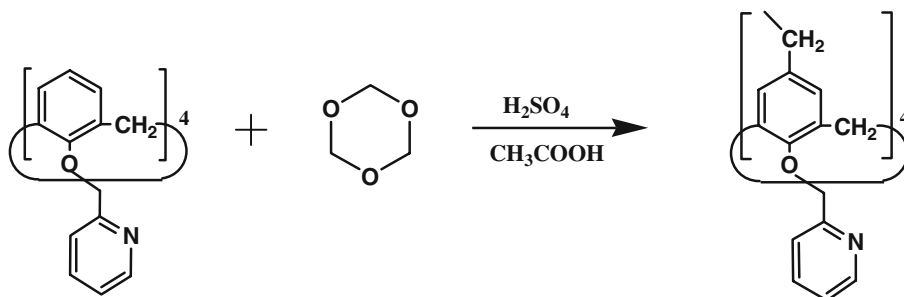
ArH), 7.12 (4H, t, 4-PyArH), 7.46 (4H, t, 5-PyArH), 7.71 (4H, d, 6-PyArH), 8.47 (4H, d, 3-PyArH).

Synthesis of methylene crosslinked resin (MC-[4]CH₂²Py)

General procedure for crosslinking of pyridylcalix[4]arene units to get the desired resins is as shown in Scheme 1.

Pyridylcalix[4]arene and *s*-trioxane, according to the desired mole ratio, were mixed in acetic acid and heated at 80 °C for 30 min. Then, the mixture of sulphuric acid (catalytic amount) and acetic acid was added dropwise to the solution for 30 min. which was followed by heating at 110 °C for 8 h. When cooled to room temperature, the reaction mixture was poured in small aliquots into 5% (w/v) sodium bicarbonate solution. Insoluble solid was collected by filtration and successively washed with hot water, 1 mol dm⁻³ HCl and distilled water. The crude resin was heated at 80 °C for 12 h in an oven and stirred in 0.05 mol dm⁻³ sodium hydroxide solution for several hours to remove unreacted feed materials. The resulting solid was again washed as mentioned in above operations and dried at 80 °C for 12 h. By varying the molar ratio of pyridylcalix[4]arene: trioxane to be 1:5, 1:3 and 1:1, three different resins namely 1:5 MC resin, 1:3 MC resin and 1:1 MC resin were synthesized. IR (KBr) $\nu_{\text{C-H}}$ 3,020–2,990 cm⁻¹, $\nu_{\text{C=C}}$

Scheme 1 Synthesis of methylene crosslinked [4]CH₂²Py resin



and $\nu_{\text{C=N}}$ 1,590–1,470 cm^{-1} , $\nu_{\text{ArC-H}}$ (out of plane bending) 755 cm^{-1} .

Adsorption test

The adsorption tests were carried out by the conventional batch method. Aqueous metal solutions (0.1 mmol dm^{-3}) were prepared by dissolving metal nitrate or metal chloride into 0.1 M ($M = \text{mol dm}^{-3}$) nitric acid and 0.1 M HEPES [2-[4-(2-hydroxyethyl)-1-piperazinyl]-ethanesulphonic acid] buffer solution. Both solutions were arbitrarily mixed to adjust pH. The resin (0.020 g) was added to 10 cm^3 of metal solution and the mixture was shaken for 24 h at 303 K. After phase separation followed by filtration of resin, metal concentration and pH of the aqueous solution were measured by an atomic absorption spectrophotometer (AAS, Shimadzu AA-6650) and a pH meter (Orion A-720), respectively.

Stripping of silver ion

The silver loaded resin was washed with small portions of distilled water and dried prior to the elution. The elution tests of the loaded silver ion on the resin were carried out by using various concentrations of aqueous hydrochloric acid (10 cm^3). After filtration of the acid solution, the silver concentration was measured by AAS and eluted percentage of silver ion was calculated by mass balance.

The column experiment

In column experiment, the aqueous feed solution was prepared by dissolving silver nitrate and sodium chloride in 0.1 M nitric acid solution. The pH was adjusted to 3.0 and the concentrations of silver and sodium were 50 ppm and 100 ppm, respectively. The feed solution was passed through the packed bed of 0.201 g of the 1:5 MC-resin supported by glass beads (average diameter = 1.3 mm). Once the adsorption was completed, the resin was washed with small portions of distilled water and adsorbed metal was eluted with 3 mol dm^{-3} hydrochloric acid. In both cases, the feed rate was 5.53 cm^3/h . The metal concentrations in the collected sample solutions were determined by AAS.

Results and discussion

Synthesis of MC-[4] CH_2Py resins

Synthesis of [4] CH_2Py is a three-step reaction. AlCl_3 catalyzed debutylation of *p-tert*-butylcalix[4]arene gave calix[4]arene. Treatment of calix[4]arene with 2-(chloromethyl)pyridine in presence of NaH in a manner similar to Williamson's synthesis of ether afforded the

pyridylcalix[4]arene in 76% yield. The $^1\text{H-NMR}$ spectrum of [4] CH_2Py contains the typical doublets in AB pattern of cone conformation of calixarene conferring that introduction of pyridyl group at lower rim has locked the cyclooligomer in cone conformation. It is likely that in resin also, the calixarene moiety maintains the cone conformation. Crosslinking of calixarene units with methylene chains was accomplished as in scheme 1. Solubility behavior and IR spectra of resins were used as identification tool to ensure the crosslinking of oligomers. Table 1 lists the solubility pattern of [4] CH_2Py and crosslinked resins on different media checked by visual inspection. The oligomer is soluble in chloroform but the crosslinked resins are insoluble in all the solvents studied. Since the resins are insoluble in organic diluents of varying polarity as well as in inorganic solvents of different concentrations, it confers that resinification has taken place.

Crosslinking of calixarene units by methylene chain is also confirmed according to the IR spectra of three different resins compared to that of [4] CH_2Py itself. IR spectrum of [4] CH_2Py , which is equivalent to 1,2,3-trisubstituted aromatic hydrocarbon, consists of two out of plane C–H bending peaks at 754 and 777 cm^{-1} . The Crosslinking of [4] CH_2Py units should occur from 5-position and the product must be equivalent to 1,2,3,5-tetrasubstituted aromatic hydrocarbon. This must be marked by the disappearance of one of the out of plane C–H bending peak for [4] CH_2Py after cross linking. As expected, the spectra of MC resins consist only one such peak at 755 cm^{-1} . Disappearance of a peak at 777 cm^{-1} region of the IR spectrum is the strong indication of crosslinking of calixarene oligomers. All the resins have similar pattern of IR spectra indicating that they have similar functionality.

Table 1 Solubility test of resins on different media

Solvent	[4] CH_2Py	1:1 MC resin	1:3 MC resin	1:5 MC resin
Toluene	○	×	×	×
Acetone	○	×	×	×
CHCl_3	○	×	×	×
Ethyl acetate	○	×	×	×
Ethanol	○	×	×	×
Methanol	○	×	×	×
H_2O	×	×	×	×
1 M NaOH	×	×	×	×
0.1 M H_2SO_4	○	×	×	×
1 M HNO_3	○	×	×	×
1 M HCl	○	×	×	×
3 M HCl	○	×	×	×
5 M HNO_3	○	△	△	△
5 M HCl	○	△	△	△

○, Soluble; ×, insoluble; △, partially soluble

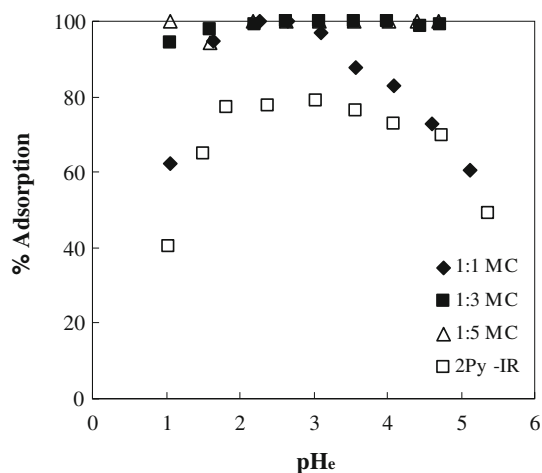


Fig. 2 Effect of pH on percentage adsorption of silver ions on different resins. Wt. of resin = 0.02 g; [Metal] = 0.1 mM; adjustment of pH = 0.1 M HNO₃ – 0.1 M HEPES

Adsorption of silver ion on different resins

The degree of silver adsorption at different pH values determined by batch equilibrium method on different resins is shown in Fig. 2, where the percentage of adsorption, %A is defined by,

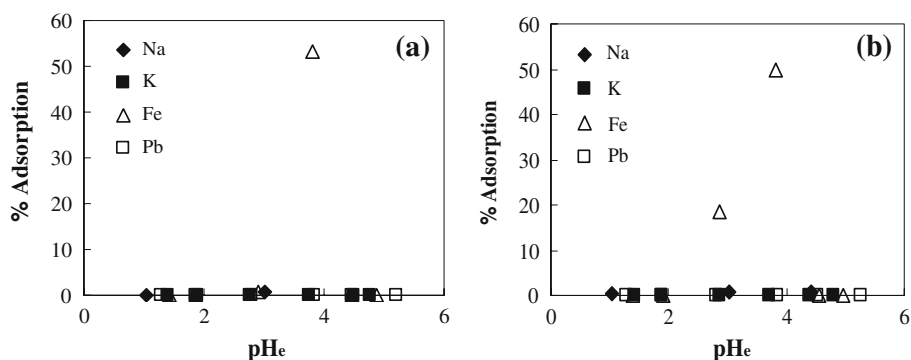
$$\%A = \frac{C_i - C_e}{C_i} \times 100$$

where C_i and C_e (mol dm⁻³) are initial and equilibrium concentrations of metal ions, respectively, in aqueous solution. Absolute adsorption of silver ion is achieved with both 1:5 MC-resin and 1:3 MC-resins from pH 1–5. Compared to the resin impregnating 2-pyridylcalix[4]arene, cross linked resins are found to be superior towards adsorption of targeted metal ion. This is attributed to the effect of polymer matrix of impregnated resin which is quite ineffective for silver adsorption.

Adsorption of other ions

As 1:5 MC and 1:3 MC resins show absolute adsorption of silver ion, adsorption behavior of these resins towards other

Fig. 3 Effect of pH on percentage adsorption of different ions on **a** 1:5 MC-resin and **b** 1:3 MC-resin. Wt. of resin = 0.02 g; [Metal] = 0.1 mM; adjustment of pH = 0.1 M HNO₃ – 0.1 M HEPES



metal ions which coexist with silver ion in photographic waste was also carried out. Figure 3a and b show the percentage adsorption behavior of 1:5 MC and 1:3 MC resins towards these ions, respectively. Both the resins do not adsorb sodium, potassium and lead ions at all but show about 50% adsorption of iron at pH around 4. However, at pH less than 3, adsorption of the iron on the resin is also zero. Taking the advantage of difference in pH range for the adsorption of silver and iron, these two metals can be separated using either resin.

Shimojo et al. [35] reported that the inclusion and chelating effects are predominant factors in the exceptionally high Ag⁺ extraction by calixarenes having pyridyl groups. However, our results indicate that the chelating effect of pyridyl nitrogen is predominant and the match between the cation size and the calixarene cavity dimensions is not an evident factor in exceptionally high silver selectivity, which was also observed by Ak et al. [9]. The ionic radii of Ag⁺ and Na⁺ are comparable and similar selectivity pattern would be expected for these ions based on their size fitting effect and inclusion behavior of calixarene moiety. In contrary to this expectation, the present resins preferably and selectively adsorb silver ion showing no affinity for sodium, potassium and lead ions. Such an interesting discriminating effect of these resins for silver ion is attributed to HSAB principle in which the soft donor atom nitrogen prefer to form complex with silver ion. Deligoz et al. [27] also concur with the participation of nitrogen atom in complex formation with soft silver ion.

Maximum loading capacity of different resins and stoichiometry of complex formation

Since the resins selectively and effectively adsorb silver ion, the maximum loading capacity of silver on different resins was also studied. Adsorption isotherm of silver on four different resins is shown in Fig. 4 where the amount of silver adsorbed, q (mol kg⁻¹) is given by,

$$q = \frac{C_i - C_e}{W} \times V$$

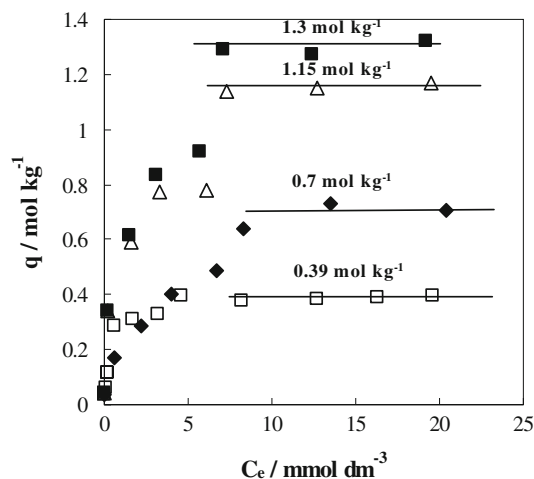


Fig. 4 Adsorption isotherms of silver on different resins. *Filled square* 1:3 MC resin, *triangle* 1:5 MC-resin, *filled diamond* 1:1 MC-resin, *square* IR-resin. Wt. of resin = 0.020 g, Initial pH = 3.0, Vol. of AgNO₃ solution = 10 cm³; adjustment of pH = 0.1 M HNO₃ – 0.1 M HEPES

where C_i and C_e (mol dm⁻³) are initial and equilibrium concentrations of metal ions in aqueous solutions, respectively. W (kg) and V (dm³) are weight of resin and volume of aqueous solution, respectively. The amount of silver adsorption increases with increasing concentration and reaches a constant value, which is the maximum adsorption capacity of the resins.

In order to find out the complex ratio of calixarene and silver ion, content of calix[4]arene in the resin and maximum adsorption amount of silver ion was correlated. Table 2 lists the relation between content of calix[4]arene in the resin and the maximum adsorption amount of silver ion.

The adsorption isotherm of different resins towards silver ion is in the order 1:3 MC resin > 1:5 MC resin > 1:1 MC resin > IR resin. The high silver loading capacity of crosslinked resins than that of the impregnated resin is due to high content of calixarene per gram of the resin. Both 1:5 MC and 1:3 MC resins form 1:1 complex with silver ion whereas 1:1 MC resin forms 2:1 complex with silver ion. As 1:3 MC and 1:5 MC resins form 1:1 complex with silver ion, their silver loading capacities are higher than that of 1:1 MC resin which forms 2:1 complex with silver ion.

Table 2 Relation between content of calix[4]arene in the resin and maximum amount of silver adsorption

Resins	CR	CCR/mol kg ⁻¹	MAAS/mol kg ⁻¹	Complex ratio
	1:5	1.19	1.15	1:1
MC	1:3	1.21	1.29	1:1
	1:1	1.23	0.69	2:1
2Py IR	–	0.40	0.39	1:1

CR Crosslinked ratio, CCR content of calix[4]arene in the resin, MAAS maximum adsorption amount of the silver ion

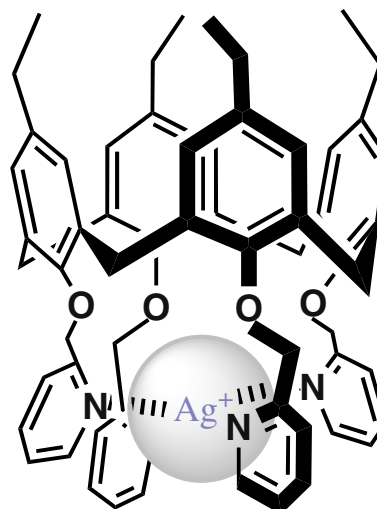


Fig. 5 Proposed 1:1 structure of the resin and silver ion

Higuchi et al. [12–19] studied the ¹HNR spectra of *t*-octylcalix[4]arene tetra-²pyridyl derivative complexed with silver ion and reported the 1:1 complex of pyridylcalix[4]arene with silver ion. Formation of 1:1 complex by calixarene having pyridyl groups with silver ion is also suggested by Marcos et al. [32] and Shimojo et al. [34]. As soft metal ions tend to coordinate with soft ligands such as nitrogen and sulphur, the coordination sites for silver ion are just the four pyridyl nitrogen atoms where silver ion should be encapsulated into the cavity composed by tetra-²pyridyl groups as proposed in Fig. 5.

Stripping test

From practical point of view, endurance property and repeated use of the resin is important. Hence, the stripping test of loaded silver ion from the resin was examined by contacting the silver loaded resin with various concentrations of hydrochloric acid. Table 3 lists the relation between acid used and elution percentage of loaded silver ion from the resin, where the percentage of elution is given by the relation,

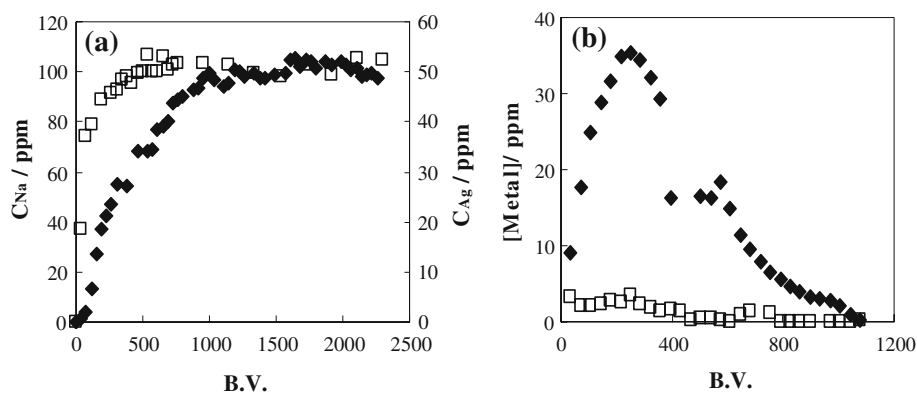
$$\% \text{Elution} = \frac{C_E}{C_i - C_e} \times 100$$

where C_E is the eluted concentration of the loaded silver.

Table 3 Relation between the hydrochloric acid concentration and elution percentage of the loaded silver ion from the resin

Acid solution	Percentage elution		
	1:5 MC	1:3 MC	1:1 MC
1 M HCl	62.4	75.8	71.9
2 M HCl	81.0	79.0	81.5
3 M HCl	97.9	91.2	91.8

Fig. 6 a Breakthrough and **b** elution profiles of silver and sodium ions. [Ag^+ , filled diamond] = 50 ppm, [Na^+ , square] = 100 ppm; Wt. of resin = 0.201 g; flow rate = $5.39 \text{ cm}^3/\text{h}$; pH of feed solution = 3.0; eluent = $3 \text{ mol dm}^{-3} \text{ HCl}$



The results indicate that 3 mol dm^{-3} hydrochloric acid solution is enough to elute the loaded silver ion from the resin.

The column experiment

Since the resin shows excellent selectivity for silver ion over other metal ions, it is reasonable that this resin is suitable for the recovery and removal of trace amount of silver from the waste effluent contaminated with large amount of other metals. For instance, the photographic waste which contains relatively less amount of silver ion as compared to sodium. By means of breakthrough followed by elution using the packed column, silver ion should be adsorbed on resin and separated from the excess amount of sodium ion. The breakthrough profiles of the silver and sodium are shown in Fig. 6a where bed volume (B.V.) represents the volume ratio of the solution to the resin. As expected from the results of batch experiment, breakthrough of sodium ion took place immediately after the starting of the feed without being trapped in the bed. On the contrary, the breakthrough of silver began to take place after as late as about 150 B.V. It clearly suggested that the complete separation of trace amount of silver from excess amount of sodium is successfully achieved by using a column packed with 1:5 MC resin. The elution profiles of the loaded metal ions from the column with 3 mol dm^{-3} hydrochloric acid are shown in Fig. 6b. A very sharp elution profile of silver is observed at about B.V. 250, which demonstrates that preconcentration factor of silver reaches as high as 35 times that of the feed solution. On the other hand, the elution of sodium ion is in very small quantity compared with that of silver. These results are promising in the sense that they suggest the present resin would be useful in achieving selective and effective removal of a trace amount of silver from the polluted water and photographic waste.

Conclusion

Methylene crosslinked resins of pyridylcalix[4]arene show specific selectivity for silver ions with no affinity for sodium, potassium and lead ions. This high selectivity of the resins for silver ion is due to the chelating effect of soft donor atom in which the silver ion is encapsulated within the cavity composed by pyridyl groups forming 1:1 complex. As sodium and silver ions have similar ionic radii, our results indicate that the cavity size of calixarene does not seem to be an evident factor for complexation with silver ion. Preorganization and chelating effect of functional group seems to be the absolute factors for silver adsorption. The maximum loading capacity of crosslinked resins for silver ion are higher than that of impregnated resin. The resin shows promising results for industrial application for the preconcentration and separation of silver ion from photographic waste and other industrial effluents.

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