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Review
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Calix[4]arene for the Extraction of Heavy Metal Contaminants

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Abstract

Detoxification of toxic species has become an increasingly important topic worldwide because these pollutants contribute significantly to environmental contamination. Industrialisation and population growth have led to pollution containing mixtures of metals and organic compounds, such as chromate, copper, arsenate, and aromatic compounds commonly found in wood-preserving pesticides. Such contamination can be controlled using macromolecules synthesised through various chemical reactions. In supramolecular chemistry, calix[4]arene macromolecules are particularly widespread because of their versatility in numerous applications. In this review, we summarise the synthesis reactions of macrocyclic compounds and their usefulness in extracting toxic metals through different supramolecular cavities. Most of the study was conducted using aqueous solutions of the molecules. The results demonstrated that macromolecules can effectively remove hazardous materials from the environment. These molecules are expected to play an even greater role in future toxin removal, as they can serve as building blocks for the design of novel compounds.

Keywords

Cavitand, supramolecule, extraction, toxic metals, calixarene

1 Introduction

Degradation of the environment is caused by the rapid increase in industrialisation and human population. Industrial activities release pollutants containing mixtures of metals and organic compounds, such as chromate, copper, arsenate, and aromatic compounds commonly present in wood-preserving pesticides. In various industrial wastewaters, heavy metals are often present together with complex-forming organic compounds. A number of synthesis reactions of calix[4]arene derivatives have been reported, designed for applications such as ion extraction.[1] In recent years, chemical separation techniques have focused on designing and synthesising new extraction reagents for metal ions.[2–7] Among these, chromate and dichromate anions present in soil and water are of particular concern due to their strong toxicity. Chromium(VI) is recognised as a carcinogen for both humans and animals. In industry, chromium(VI) is a widely used oxoanion, which is significantly more toxic, soluble, and more mobile than chromium(III). Furthermore, chromate and dichromate ions (CrO_4^{2-}, $Cr_2O_7^{2-}$) have potential sites for hydrogen bonding with host molecules as they are dianions with oxide functionalities.[8–10] A wide variety of azocalix[4]arene derivatives have been reported, containing ester, amide, bipyridyl, and bythiozoyal moieties. These azocalixarenes have been applied in cation extraction studies. To improve extraction efficiency, a β- ketoimine group was introduced on the lower rim of the molecule.[11] Rare earth metals have also been extracted using p-tert-octylcalix[4]arene-carboxyl derivatives. Cyclic calixarene ligands have proven effective in rare-earth metal separation via conventional solvent extraction methods.[12] In this review, we describe several synthetic strategies for calix[4]arene derivatives and highlight their utility as cavitands for the extraction of various toxic ions.

2 Synthesis of calix[4]arene for extraction of contaminant metals

The extraction of gold nanoparticles into organic solvents has been achieved using a variety of surfactants. However, small ligands are typically limited to stabilising only smaller nanoparticles (dimensions < 10 nm), during phase transfer into organic solvents. Consequently, surfactants alone are often insufficient to enhance van der Waals forces among the superior nanoparticles in organic media through steric repulsion. To address this challenge, *Sangbum Han et al.*, developed gold nanoparticles functionalised with resorcinarenes. They synthesised tetrapyridiniumtetrabromide, tetratrimethylammonium tetrabromide, and tetratributyl-ammonium tetrabromide, which were characterised using TEM, EDS, UV-Vis, and IR spectroscopy. Citrate-stabilised dispersions of gold nanoparticles were successfully extracted by the synthesised resorcinarene molecules (Fig. 1).[13] The extraction behaviour of nanoparticles was monitored using UV-visible spectroscopy in various solvents, including water-acetonitrile, toluene-acetonitrile, and diluted dispersions of gold nanoparticles. Among these, the toluene-acetonitrile solvent was found to be the most effective for extraction of gold nanoparticles. Nanoparticles extracted with resorcinarene **1** exhibited an absorption maximum at 530 nm, while resorcinarene **2** and **3** showed maxima at 580 nm.[13]

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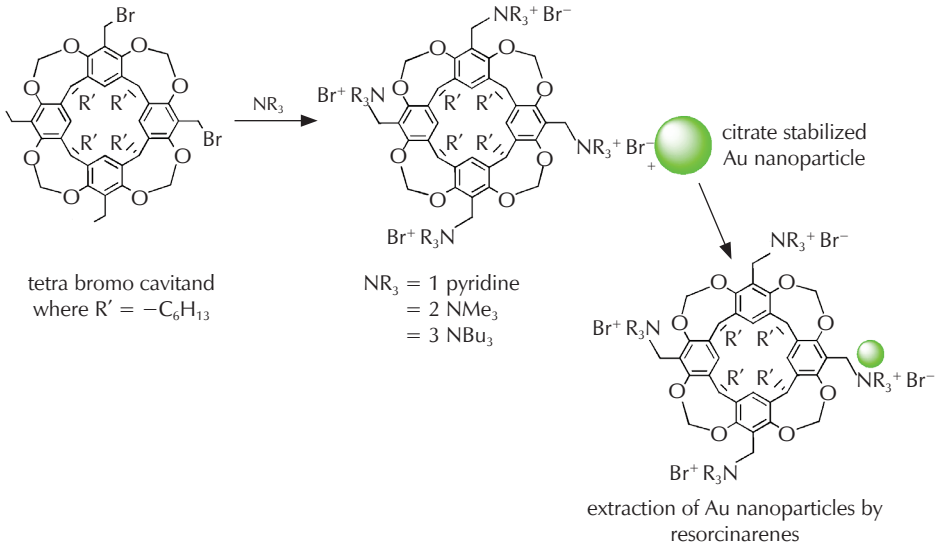

Fig. 1 – Extraction of Ag nanoparticles by resorcinarene cavitands[13]

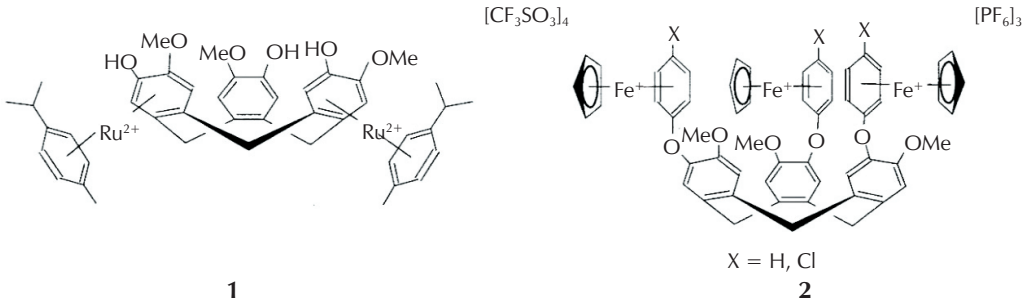

Fig. 2 – Extraction of TcO_4^- using a biphasic system composed of nitromethane[18]

The construction of artificial molecular receptors has been developed using three-dimensional building blocks of azocalix[4]arenes. These receptors are capable of recognising neutral molecules, cations, and anions, and their thermal behaviour has also been studied. *Sulak et al*. reported the synthesis of a new azocalix[4]arene by coupling with *p*-tert-butylcalix[4]arene. They described its complexation, extraction ability, and thermal properties. Four new diazo-coupled calix[4]arene derivatives, containing two groups in their structures, were synthesised for the recognition of diazo (−N=N−) and neighbouring groups (−OH, $-NH_2$). Azocalix[4]arenes were employed in two-phase solvent extraction studies (chloroform and water) of transition-metal picrate anions (Ag^+, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+} and La^{3+}). The results showed that complexation between azocalix[4]arene and Ag^+, and Hg^{2+} was significantly superior compared to other metal cations.[14,15] *Podyachev et al*. described the extraction properties of novel hydrazone derivatives of calix[4]resorcinol for alkali, earth, and transition metals. The binding properties of these receptors with metals were examined using liquid-liquid extraction in aqueous solutions of metal picrates. They also examined extraction efficiency, selectivity, complexation stoichiometry, and extraction constants for various transition metals.[16] *Rubio et al*. explored supramolecular assemblies for extraction studies, including conservation, hemimicelles/admicelles, and amphiphilic-templated mesoporous silica methods, which were shown to be useful for extracting and concentrating organic compounds.[17] *Gawenis et al*. designed host complexes of the cyclotriveratrylene macrocycle (**a**), produced on a metalation for guest TcO_4^- (Fig. 2). Their extraction studies were performed using a biphasic nitromethane system. Anion transport experiments of nitromethane/saline in two phases were carried out with host (**a**) and in competition with other anions to regulate the degree of TcO_4^- and ReO_4^- complexation. Anion was extracted from aqueous phase when the host molecule (**a**) acted as a phase-transfer agent and more than 90 % remained in the organic phase. This host also showed selective extraction of other tetrahedral oxoanions. Furthermore, development of a similar host of macrocyclic arene complex with a trimer ring (**b**) of stretched cavity at the upper rim was reported. Host (**b**) displayed improved selectivity and productivity of binding with TcO_4^- in solution.[18–22] Ion extraction studies have also been carried out using various calixarene nanoemulsions.[23]

The calix[4]pyrrole polymeric backbone receptor has been shown to be effective for anion binding and has been successfully applied in a variety of ion-binding and extraction applications.[24] Recognition studies of divalent toxic metals (Cd^{2+}, Hg^{2+}, and Pb^{2+}) by different functionalised calix[n]

arenes using the liquid-liquid extraction method have also been reported in the literature. Extractants were designed based on two strategies: 1. steric stabilisation, generally achieved with non-ionic extractants or polymers; and 2. electrostatic stabilisation generally achieved with ionic extractants or polymers. Anionic extractants display strong electrostatic interactions with metal ions, thereby attracting divalent cations such as Cd^{2+}, Hg^{2+} and Pb^{2+} (Fig. 3). The extractant binding site depends on the nature of the anion-cation interaction: polarisable (soft) anions tend to bind with polarisable (soft) cations, whereas non-polarisable (hard) anions bind with non-polarisable (hard) cations.

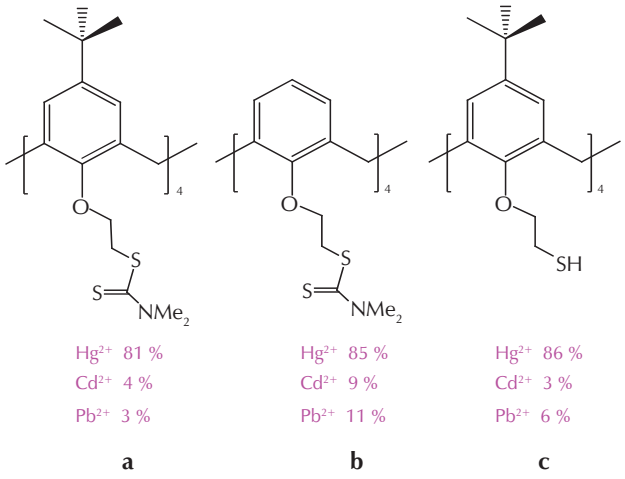

Fig. 3 – Extraction of Hg^{2+}, Cu^{2+} and Pb^{2+} with calix[4]arenes[25]

Hg^{2+} was found to have greater extraction ability (between 80 and 87 %) than Cd^{2+} and Pb^{2+} (between 3 and 12 %) using compounds **a-c**.[25] *Asfari et al.* reported the synthesis of a Schiff base of *p*-tertbutylcalix[4]arene for the complexation of alkali, alkaline- earth, transition, and heavy metal cations, as well as lanthanides. Their extraction studies revealed complexation of Cu^{2+}, Pb^{2+} and Eu^{2+} in aqueous phase, and stability constants for these cations were determined.[26] Furthermore, Schiff bases of tetra amino calix[4]resorcinarenes have been synthesised with various aromatic aldehydes. These Schiff base derivatives were used to investigate the complexation behaviour of Cu^{2+} using liquid-liquid extraction in a two-phase solvent chloroform–water system, monitored by UV-visible spectroscopy. Fig. 4 shows the different derivatives of tetraamino calix[4]resorcinarene Schiff bases used in the extraction of Cu^{2+} ion.[27]

Upadhyay et al. synthesised 2,6 dihydroxyacetophenone[4] arene using different aliphatic aldehydes.[28] The resulting macrocyclic molecules were further reacted with benzylamine to produce Schiff base derivatives. These compounds were then applied in extraction studies for various toxic metals and chromate ion in aqueous solution (Fig. 5). The Schiff base compounds proved effective for toxic ions such as Co^{2+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, and Na^{+}, as well as dichromate anion, using liquid–liquid solvent extraction. These macromolecules, synthesised with benzylamine in chloroform solvent, feature an imine group of amine capable of binding with transition metals. Consequently, these macromolecules have been proven to be best in extracting both anions and cations at different pH values.[29]

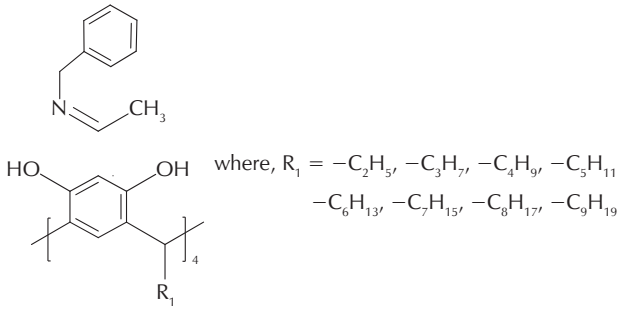

Fig. 5 – Extraction of cations/anions by benzylamine Schiff base derivatives[29]

Similarly, Schiff bases of benzylamine with 2,6 dihydroxyacetophenone[4]arene have also been applied in metal extraction studies. The solutions of Co^{2+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, and Na^{+} cations were prepared at a concentration of $1 \cdot 10^{-4}$ M, while a solution of sodium dichromate $(Cr_2O_7^{2})^{-}$ anion was prepared at a concentration of $1 \cdot 10^{-5}$ M. In the experiments, resorcin[4]arene Schiff base ligands were prepared at $1 \cdot 10^{-3}$ M in CH_2Cl_2. The most effective extraction of the dichromate ion was observed at the lowest pH value, as shown in Fig. 6.[30]

Different macrocyclic ligands of 5,11,17,23-tetrabutyl-25,27-bis(carboxymethoxy) calix[4]arene crown have been synthesised and applied for the extraction of various

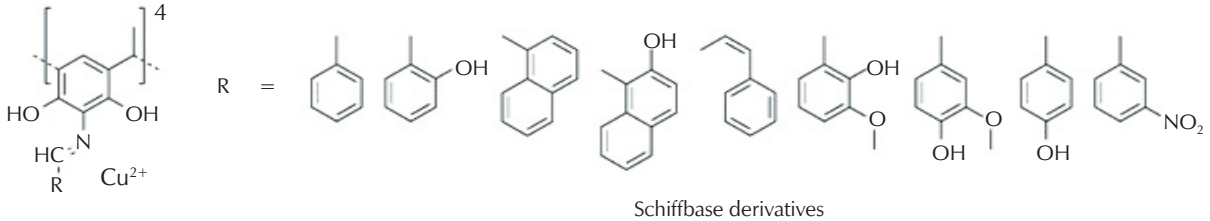

Fig. 4 – Extraction of Cu^{2+} by Schiff bases of tetraaminocalix[4]resorcinarenes[27]

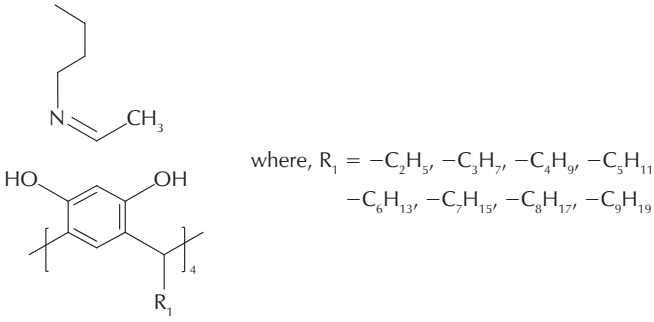

Fig. 6 – Extraction of cations/anions by *n*-butylamine Schiff base derivatives[30]

toxic heavy metals from water, as shown in Fig. 7. Extraction studies were carried out over a pH range of 2.4 to 3.7 for Zn^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, and Pb^{2+} from weakly acidic solutions. Compounds containing a $-CH_2COOH$ group facilitated cation extraction. Small cations were extracted by crown-5 derivatives, whereas larger cations were extracted by crown-6 derivatives. The extraction efficiency was evaluated using distribution ratios, as reported in the article.[31]

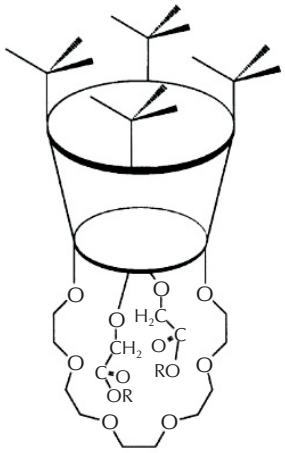

Fig. 7 – Extraction of cations by calix[4]arene based crown-6[31]

3 Conclusion

Various calix[4]arenes have been synthesised using different reaction techniques and have shown significant applicability in the removal of hazardous materials such as heavy metals. Many toxic ions have been successfully separated from their waste sources using these macrocycles. The unique structural features of calix[4]arenes, particularly their concave cavities, allow them to accommodate small molecules, making them highly advantageous for extraction procedures. Different separation methods have been explored, demonstrating that ions can be effectively hosted within the calixarene cavity. This highlights the potential of host-guest chemistry as a promising strategy for removing other environmental pollutants in the future. In this approach, ions act as a guest material and the receptor acts as a suitable host. Several cation and anion wastes present in water can be removed through different functionalisation on cavitands in the future.

ACKNOWLEDGEMENTS

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Conflict of interest

The authors report no conflict of interest.

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SAŽETAK

Kaliks[4]aren za ekstrakciju teških metala

Juhi B. Upadhyay [a*] i *Hitesh M. Parekh* [b]

Detoksikacija toksičnih tvari postaje sve važnija na globalnoj razini jer ta onečišćivala znatno doprinose zagađenju okoliša. Industrijalizacija i rast stanovništva doveli su do pojave složenih onečišćenja koja sadrže mješavine metala i organskih spojeva poput kromata, bakra, arsenata i aromatskih spojeva prisutnih u pesticidima za zaštitu drva. Takvo onečišćenje moguće je ukloniti primjenom makromolekula dobivenih različitim kemijskim reakcijama. U području supramolekulske kemije posebno se ističu kaliks[4]areni zbog svoje svestranosti i široke primjene. U ovom preglednom radu dan je sažet prikaz metoda sinteze makrocikličkih spojeva te njihove primjene u uklanjanju toksičnih metala pomoću različitih supramolekulskih šupljina. Većina istraživanja provedena je u vodenim otopinama. Rezultati pokazuju da makromolekule mogu učinkovito ukloniti štetne tvari iz okoliša. Očekuje se da će u budućnosti imati još veću ulogu u uklanjanju toksina jer mogu poslužiti kao osnova za razvoj novih, naprednih spojeva.

Ključne riječi
Kavitand, supramolekula, ekstrakcija, toksični metali, kaliksaren

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