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Removal of Dichromate Anions with Nanofiltration-Complexation by using Amino Calix[4]arene Derivative

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Abstract: Herein the removal and recovery of chromium anions from aqueous solutions by using nanofiltration pilot-scale equipment (Osmonics Sepa CF Membrane Cell) with a water-soluble amino calix[4]arene derivative was studied. To understand the selectivity, the authors also examined the retention of chromium anions in the presence of Cl^-, NO_3^-, SO_4^{2-}, HSO_4^-, CO_3^{2-}, PO_4^{3-}, $H_2PO_4^-$ anions in nanofiltration-complexation. From the results water-soluble amino calix[4]arene was effective and selective ligand for dichromate anions over nitrate anions, in a nanofiltration-complexation system at pH 2.5. Moreover, the recovery and reusability studies of dichromate and nitrate anions and also ligand were performed.

Keywords: Dichromate anions, water-soluble calixarene, nanofiltration-complexation, nitrate anions, membrane

INTRODUCTION

Chromium and derivatives are widely used in many industries dealing with electroplating, dye, textile, and leather. In wastewater from these industries, chromium is present either as hexavalent or trivalent. Due to its high

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toxicity, especially in the hexavalent form, the tolerated concentrations are controlled by strict norms. The recovery or removal of the chromium is interesting from both environmental and economic view points. Thus, several chromium removal methods have been proposed such as the adsorption (1, 2), liquid-liquid extraction (3), precipitation (4) and membrane processes, specially microfiltration (MF) (5), reverse osmosis (RO), and ultrafiltration (UF) (6, 7). Among these available separative methods, nanofiltration (NF) has attracted increasing attention over recent years due to the development of new applications. The properties of NF membranes lie between those of UF and RO membranes. It permits operation at low pressure and high permeate flux and does not require any chemical addition.

Moreover, to increase ionic separation, NF can be combined a complexation step (Fig. 1); retention of target ion is improved because the complex with the ligand (of larger size and mass than the target ion) prevents this ion from passing through the membrane (8). For such a purpose, water soluble ligands can be used in the case of NF-complexation association. For example, water-soluble calix[4]arene-bis(benzocrown-6) have been used in nanofiltration-complexation for caesium (9).

Calixarenes (Fig. 2) have generated considerable interest as useful building blocks for the synthesis of hosts for cations, anions, and neutral molecules. During the last two decades, they have attracted much attention as receptors in supramolecular chemistry. The increasing interest in these compounds is stimulated by the simple large-scale synthesis of calixarenes, and the different ways in which they can be selectively functionalized at the narrow (phenolic groups) or at the wide rim (aromatic nuclei) (10–13). Calixarenes have several advantages for use as extractants for oxoanions. One advantage is that their aromatic core structure is stable to oxidation. Other advantages are that multiple functionalities can be appended both for associating with the oxoanion and for binding to the cation. This association can be in the form of hydrogen bonding between substituents on the calixarene with one or more of the oxygen atoms on the periphery of the oxoanion.

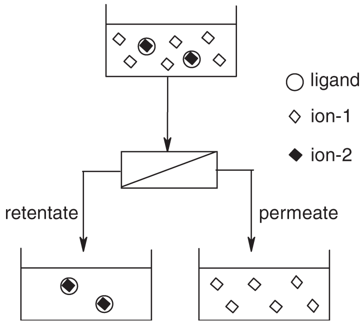


Figure 1. The principle of nanofiltration with a complexation step.

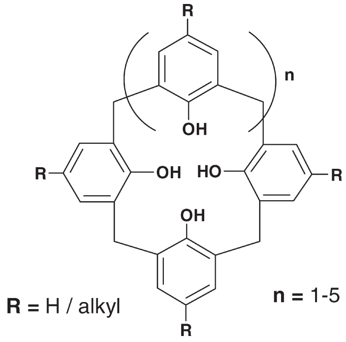


Figure 2. The general molecular structures of calix[n]arenes.

Significant efforts have been directed towards the use of calix[4]arene monomeric derivatives in the monitoring and remediation of chromate anions. An early use of a calixarene for the extraction of chromate anion employed amine substituents on the wide rim of the calix[4]arene which can hydrogen bond with the oxoanion (14). Subsequently the longer alkyl chain homologs have also been found to extract chromate anion as the protonated diaminocalix[4]arene derivative (15). The pyridine substituted calix[4]-arene derivatives have also been used to synthesize pH reversible chromium (VI) extractants (16, 17). Moreover, calixarenes with amide substituents have been used for hydrogen bonding with the oxoanion (18, 19). A recent development is the discovery that calix[4]arenes with nitrile substituents act as phase transfer extractants for chromate anion, and that their effectiveness is higher with aqueous solutions that are acidic (20). In addition to the functionalities that have previously resulted in them being extractants for chromate anion, a crown ether moiety incorporated into the structure of the calix[4]arene has also been proven a complementary binding site for oxoanion salts (21–23). In this paper, the removal of dichromate anions from aqueous solutions by using nanofiltration pilot-scale equipment (Osmonics Sepa CF Membrane Cell) with a water-soluble amino calix[4] arene (**3**) derivative was studied.

EXPERIMENTAL

Chemicals and Equipments

The water-soluble amino calix[4]arene derivative (**3**) was re-synthesized in our laboratory according to literature methods (24–27). For the characterization of compounds, melting points were determined on a Gallenkamp apparatus in a sealed capillary and are uncorrected, ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ with TMS as internal standard, IR spectra were recorded on a Perkin Elmer 1605 FTIR spectrometer as KBr pellets. UV-vis. data were obtained on a Shimadzu 160A UV-visible recording spectrophotometers. Elemental analyses were performed on a Leco CHNS-932 analyzer. Nanofiltration-complexation experiments were carried out by passing through nanofiltration pilot-scale equipment (Osmonics Sepa CF Membrane Cell).

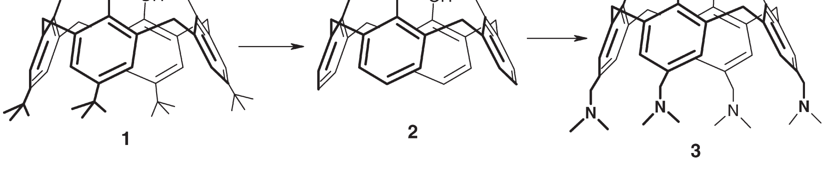
Analytical TLC was performed on precoated silica gel plates (SiO_2, Merck PF254), while silica gel 60 (Merck, particle size 0.040–0.063 mm, 230–240 mesh) was used for preparative column chromatography. Generally, solvents were dried by storing them over molecular sieves (Aldrich; 4 Å, 8–12 Mesh). The materials and reagents were standard analytical grade, purchased from Fluka or Merck, and used without further purification. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system. Osmonics Sepa CF II NF TF DK nanofiltration membrane (limited pH 2–11 range at 25°C and 19.1 × 14 cm dimensions) was used as membrane.

Synthesis

The compounds **1-3** (Scheme 1) were prepared by procedures published in the literature (24–27) and confirmed by re-characterizing with spectroscopic methods such as ^{1}H NMR and FTIR, and elemental analyses.

Nanofiltration-Complexation Studies

A schematic representation of nanofiltration (NF) used in our experiments is given in Fig. 3. By totally recycling permeate and retentate, the feed remains at constant composition during the experiment. Nanofiltration-complexation tests were carried out to measure ligand ability toward the



Scheme 1. The schematic representation of synthesis of water soluble amino calix[4]arene **3**.

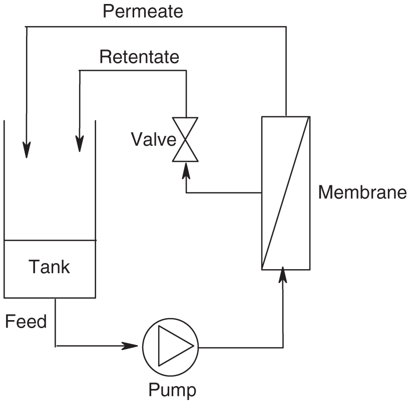


Figure 3. The scheme of the nanofiltration-complexation loop in this study.

dichromate anions in an aqueous medium containing low levels of sodium dichromate.

In order to see the permeability of nanofiltration membrane for the dichromate anions the known amount of sodium dichromate was preliminary passed through the NF membrane (Osmonics Sepa CF II NF TF DK). The samples of the permeate and the retentate were taken half an hour after sodium dichromate addition and the dichromate concentration was determined by spectrophotometrically (at 346 nm). It was observed that the NF membrane used in this study showed good permeability (almost 100%) toward dichromate anions. Also, the known amount of ligand was added to a solution containing fixed concentration of sodium dichromate which was filtered on a NF membrane at certain pH value. All nanofiltration tests were studied under 5 bar of pressure. The retention of chromium (VI) was calculated as follows Eq. (1):

$$R_{\mathrm{i}} = 100 \times (1 - C_{\mathrm{ip}}/C_{\mathrm{ir}}) \tag{1}$$

where C_{ip} is the concentration of i in the permeate, and C_{ir} is the concentration of i in the retentate.

Selectivity and Recovery Studies

Selectivity studies were performed in presence of nitrate anions (NO_3^-) since it could be present much more than dichromate anions in aqueous solutions. For this aim, sodium nitrate was used as corresponded with one hundred-fold of dichromate anion concentration. The nanofiltration process and determinations were carried out as described above. Recovery studies were realized after the separation of dichromate and nitrate anions. Finally, for the recovery of the ligand, the pH of the solution containing ligand:dichromate complex was increased toward basic pH values to precipitate the ligand.

RESULTS AND DISCUSSION

Synthesis of Water-soluble Calix[4]arene (3)

The calix[4]arene derivatives (Scheme 1) were prepared according to previously published literature methods (24–27). Among these, only the water-soluble amino calix[4]arene derivative (**3**) was subsequently used as specific ligand for dichromate anions in a nanofiltration-complexation process. Herein it is important that this calix[4]arene derivative is synthesized at only three steps.

Nanofiltration-Complexation Studies

The determination of the solubility of **3** for experimental studies has first been carried out at different pH conditions. Thus, it has been observed that this ligand is water-soluble below pH 3.0. Although it has been known that amino calixarenes are very effective ligands for dichromate anions in high acidic pHs, it could be tried only pH 2.5 in nanofiltration-complexation experiments since the membrane in this study is limited to use at pH 2–11 range. Aqueous solutions of $Na_2Cr_2O_7$ show no retention through the membrane in the absence of the ligand. When the addition of the ligand to the nanofiltration system, it has been observed that ligand **3** is an effective complexant for the retention of dichromate anions through the nanofiltration membrane at pH 2.5 in 33.3% yield. This result is in agreement with the literature where the extraction of the dichromate anions with an amino calix[4]arene (15). Also it has been reported previously (17) that **4** (Fig. 4), which contains similar

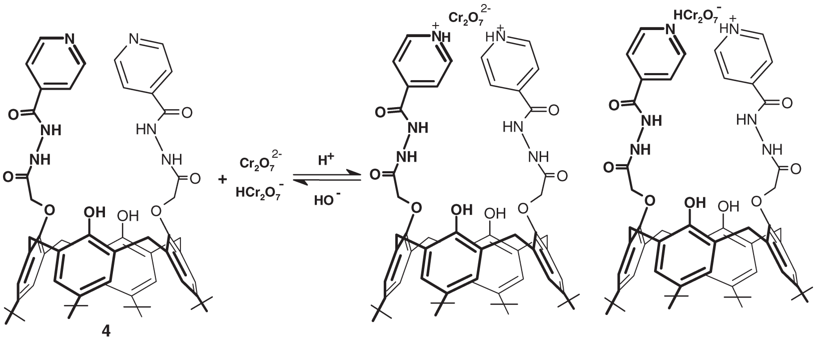


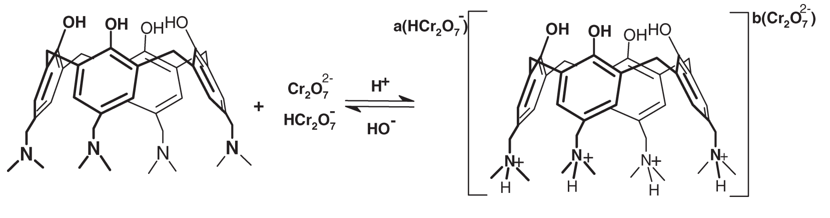
Figure 4. The proposed interactions of **4** with $HCr_2O_7^-/Cr_2O_7^{2-}$ ions.

proton-switchable binding sites (it contains nitrogen donor atoms) is an effective extractant for dichromate anions at low pH. Therefore, herein it can be demonstrated that due to the proton transfer to the nitrogen atom of amino unit in **3** an ion pair complex is formed in the nanofiltration-complexation system (Scheme 2). According to our knowledge the calixarene skeleton plays a very important role in the extraction phenomena due to its stable and macrocylic nature as to its monomeric analog (17). Moreover, this is an important advantage from the environmental view points because of the nanofiltration-complexation system use no organic solvent at removal.

Selectivity studies have also been performed by investigating the effect of nitrate anion on dichromate anion retention. From the results which are graphed in Fig. 5, it has been observed that there is no major change. This result indicates that dichromate anions can be removed over nitrate anions. This selectivity is another advantage from the for environmental view point because nitrate anion is present much more than the dichromate anion in aqueous solutions.

It is possible that the recovery of both separated species and ligand by using nanofiltration-complexation system so that it is also an advantage of this separation method. Therefore, when the pH of the retentate solution to basic pH values is changed, amino calix[4]arene starts to precipitate. Then the amino calix[4]arene is obtained and the separated dichromate anions with sequential filtration and washing operations. At the same time, nitrate anions which do not interact with the ligand remain in the permeate solution. Thus, the dichromate and nitrate anions could be separately recovered, and also amino calix[4]arene (Scheme 3).

Consequently, the foreign anion effect on dichromate anion retention of **3** by using additionally different sodium salts (Cl^-, NO_3, SO_4^{2-}, HSO_4^-, CO_3^{2-}, PO_4^{3-}, and $H_2PO_4^-$) with different concentration and their mixtures were also studied in the nanofiltration-complexation system although the nitrate anion effect had been mentioned in above specifically. The results summarized in Table 1 showed the retention of $Na_2Cr_2O_7$ with amino calix[4]arene **3** in the presence of other sodium salts. The major difference was that the extraction of $Na_2Cr_2O_7$ with **3** was not affected by the



Scheme 2. The schematic representation of possible interactions of **3** with $HCr_2O_7^-$/$Cr_2O_7^{2-}$ ions; **a** and **b** are related to protonable amino groups in aqueous solution.

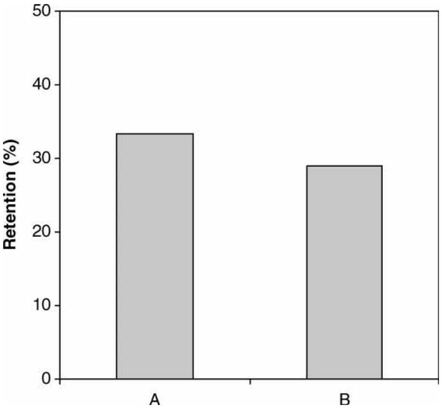
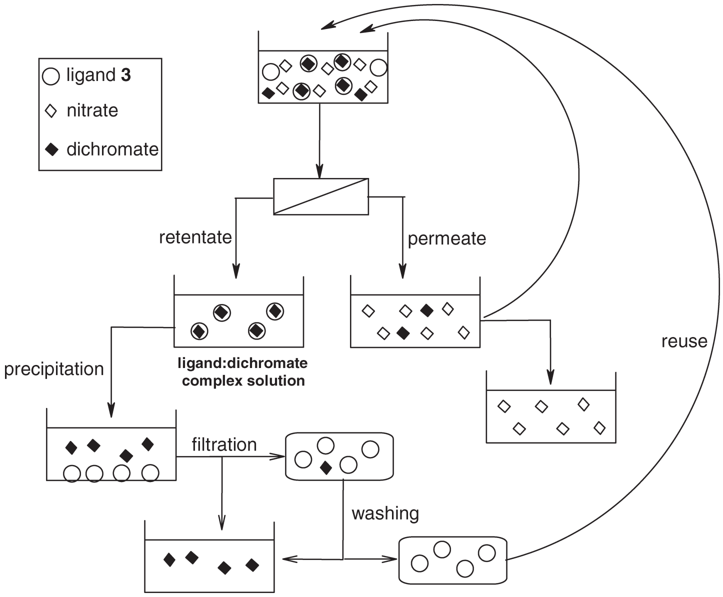


Figure 5. The effect of nitrate anion on dichromate anion retention with **3**; A: Dichromate anion retention in absence of nitrate anions; B: Dichromate anion retention in presence of nitrate anions.

presence of these other salts. This implied that the removal of dichromate anion in nanofiltration-complexation system by **3** could be almost selectively possible also in the presence of these foreign anions as in the presence of nitrate anions.



Scheme 3. The schematic representation of removal and recovery studies with nanofiltration-complexation with **3**.

Table 1. Dichromate retention results of **3** at pH 2.5, in the presence of different anions (Cl^-, NO_3^-, SO_4^{2-}, HSO_4^-, CO_3^{2-}, PO_4^{3-}, and $H_2PO_4^-$) and their mixtures[a]

	Different anions								
	None	Cl^-	NO_3^-	SO_4^{2-}	HSO_4^-	CO_3^{2-}	PO_4^{3-}	$H_2PO_4^-$	Mixture
3[b]	33.3	31.1	28.3	28.6	29.1	28.0	26.7	29.8	26.4
3[c]	33.3	26.9	29.0	25.9	28.6	26.2	25.3	28.7	25.9

[a] [Sodium dichromate] = 1.0×10^{-4} M; [ligand] = 2.0×10^{-5} water soluble calix[4]arene at 25°C, pH 2.5.

[b] The concentration of different anions = 1.0×10^{-3} M.

[c] The concentration of different anions = 1.0×10^{-2} M.

CONCLUSION

The removal and recovery of chromium anions was achieved over nitrate anions with water-soluble amino calix[4]arene (**3**). It has been noted that **3** can be a proton-switchable ligand for the dichromate anions that gains to it reusability. This study revealed that the nanofiltration-complexation system with **3** was a very useful approach for the recovery and removal of dichromate and nitrate anions, and also the recovery and the reusability of the ligand. Moreover, it is important that even the presence of foreign anions does not remarkably effect on dichromate anion retention in terms of selectivity. Consequently, this study is a contribution to environmental studies because it has some important advantages such as no organic solvents at removal, selective removal, recovery, and reusability.

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