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Removal of Chromium Anions with Nanofiltration-Complexation by Using p-Sulfonated Calix[4]arene

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This article describes the removal of chromium anions from aqueous solutions by using nanofiltration-complexation consisting of pilot-scale nanofiltration equipment (Osmonics Sepa CF Membrane Cell) and water-soluble p-sulfonated calix[4]arene ligand. For the determination of optimum removal conditions of the chromium anions, the effect of pH, ligand cavity size, and foreign anions on the retention of the chromium anions in nanofiltration-complexation system was also evaluated. The results showed that water-soluble p-sulfonated calix[4]arene was an effective and selective ligand for the chromium anions over Cl^-, SO_4^{2-} and NO_3^- anions in nanofiltration-complexation system at pH 9.4.

Keywords: Chromium anions; p-Sulfonated calix[n]arenes; Nanofiltration-complexation; Membrane separation

INTRODUCTION

Chromium and its derivatives are widely used in many industries dealing with electroplating, dye, textile and leather. In waste-water from these industries, chromium is present either as hexavalent or trivalent ions, and the tolerated concentrations are controlled by strict norms especially in the hexavalent form since it posseses high toxicity. 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 adsorption [1,2], liquid–liquid extraction [3], precipitation [4] and membrane processes, special 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.

Calix[n]arenes (Fig. 1) 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 from the narrow (phenolic groups) or wide rim (aromatic nuclei) [8–11]. Calixarenes have several advantages for use as extractants for dichromate anions. 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 binding to the cation. This association can be effective 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.

However, in order to increase ionic separation, NF can be combined in a complexation step (Fig. 2), where the retention of the target ion is improved because the complex with the ligand (possess larger size and mass than the target ion) prevents this ion from passing through the membrane [12]. 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) has been used in nanofiltration-complexation for cesium [13].

Significant efforts have been directed towards the use of calix[4]arene derivatives in the monitoring and remediation of the chromium anions [14]. In this article, the removal of the chromium anions from

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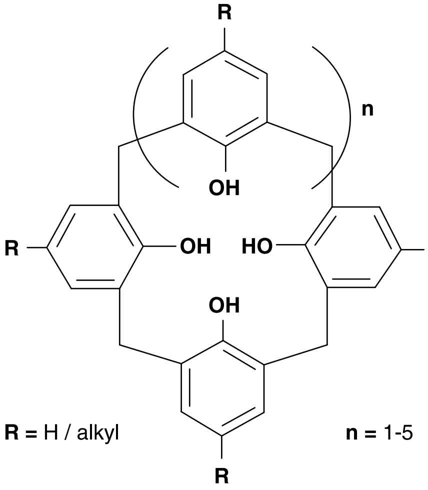

FIGURE 1 The general molecular structures of calix[n]arenes.

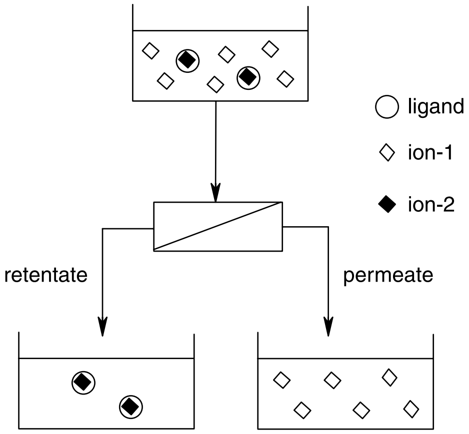

FIGURE 2 The principle of nanofiltration with a complexation step.

aqueous solutions by using nanofiltration pilot-scale equipment (Osmonics Sepa CF Membrane Cell) with water-soluble p-sulfonated calix[4]arene (p-SC[4]) is reported.

RESULTS AND DISCUSSION

Synthesis of Water-soluble p-Sulfonated Calix[n]arenes (n = 4, 6 and 8)

Water-soluble p-sulfonated calix[n]arenes (Fig. 3) were prepared as described by previously published methods [15–18]. They were subsequently used as ligands due to their water-solubility to see their complexation behaviors toward chromium anions via nanofiltration-complexation process.

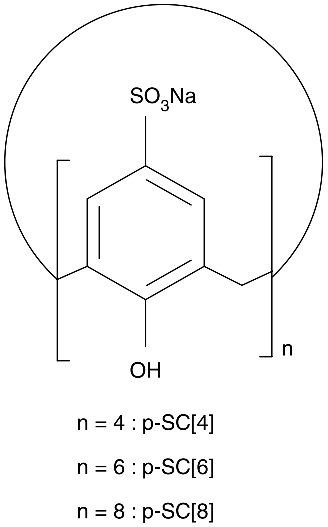

FIGURE 3 Water soluble p-sulfonated calix[n]arenes.

Nanofiltration-complexation Studies

Effect of PH

The aqueous solutions of sodium dichromate show no retention through the membrane in the absence of the ligand. When addition of the ligand to nanofiltration systems at different pH values (2.7–9.4) has happened it has appeared that p-SC[4] is an effective complexant for the retention of chromium anions through the NF membrane at pH 9.4 with 77.6% yield (Table I and Fig. 4). It is known that chromium anions can exist in different forms according to pH of the solution as shown in Eq. (1) [19]. Thus, it is clear that the form of the chromium anions is CrO_4^{2-} at pH 9.4. On the other hand, it was noticed that this method has an important advantage from the environmental view points since nanofiltration-complexation processes do not use any organic solvent for removal.

$$HCr_2O_7^-(aq) \underset{pH>1}{\overset{pH<1}{\rightleftharpoons}} Cr_2O_7^{2-}(aq) \underset{pH>7}{\overset{pH<7}{\rightleftharpoons}} CrO_4^{2-}(aq) \qquad (1)$$

TABLE I The chromium anions retention results of p-SC[4] at different pH values[a]

	PH								
	2.7	3.4	4.2	5.0	6.2	7.1	7.6	8.3	9.4
%	13.7	13.6	15.7	31.11	30.36	28.57	30.2	65.7	77.6

[a] [Sodium dichromate] = 1.0×10^{-4} M; [ligand] = 2.0×10^{-5} M water soluble p-SC[4] at 25°C.

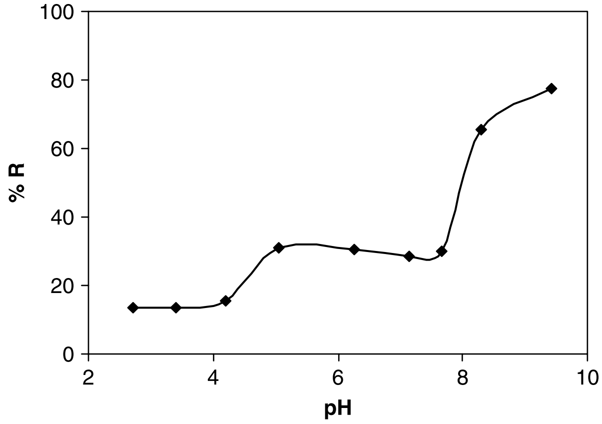

FIGURE 4 Chromium anions retention of p-SC[4] at different pH values.

Effect of Ligand Cavity Size

In order to observe the effect of calixarene cavity size on the removal of chromium anions, we used p-sulfonated calix[6]arene (p-SC[6]) and p-sulfonated calix[8]arene (p-SC[8]), they have larger cavity sizes than p-SC[4], in the nanofiltration-complexation system at pH 9.4. From the results, given in Table II, it has been deduced that p-SC[6] and p-SC[8] are very ineffective ligands for the removal of chromium anions. This may be attributed to the disappearing of effective interaction between chromium anions and calixarene rings due to the expansion of cavity size. This result indicates that the cavity size of the ligand is an important factor on the removal of the chromium anions under these experimental conditions.

Effect of Diverse Anions

Selectivity studies investigating the effect of diverse anions such as Cl^-, SO_4^{2-} and NO_3^- on the retention of the chromium anions with p-SC[4] at pH 9.4 have also been performed. The results, summarized in Table III, show that the retention of the chromium anions with p-SC[4] is not influenced by the presence of these anions. This may show that these diverse anions can not form a stable complex with calixarene rings within the calixarene cavity due to their structural features such as size and conformation. However, this result implies that the selective removal of the chromium anions in nanofiltration-complexation systems by using p-SC[4] would be possible in the presence of these anions.

TABLE II The chromium anions retention results of p-SC[4], p-SC[6] and p-SC[8][a]

Ligand	Chromium anions retention (%)
p-SC[4]	77.6
p-SC[6]	<0.1
p-SC[8]	<0.1

[a][Sodium dichromate] = 1.0×10^{-4} M; [ligand] = 2.0×10^{-5} M water soluble p-SC[n] at 25°C.

TABLE III The chromium anions retention results of p-SC[4] in the presence of different anions (Cl^-, NO_3^- and SO_4^{2-}) and their mixtures[a]

	Chromium anions retention (%)				
Ligand	A	B	C	D	E
3[b]	77.6	76.1	73.3	75.6	72.7
3[c]	77.6	70.9	74.0	72.9	69.2

[a][Sodium dichromate] = 1.0×10^{-4} M; [ligand] = 2.0×10^{-5} M water soluble p-SC[4] at 25°C, pH 9.4.

A: The percentage of dichromate ion extracted in the absence of any other anion.

B: The percentage of dichromate ion extracted in the presence of Cl^- anions.

C: The percentage of dichromate ion extracted in the presence of NO_3^- anions.

D: The percentage of dichromate ion extracted in the presence of SO_4^{2-} anions.

E: The percentage of dichromate ion extracted in the presence of Cl^-, NO_3^- and SO_4^{2-} anions.

[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 of the chromium anions from aqueous solutions with water-soluble p-sulfonated calix[4]arene in the nanofiltration-complexation system was demonstrated. Some parameters such as effect of pH, ligand cavity size, and diverse anions on the retention of the chromium anions were studied to examine optimum removal conditions. It was concluded that the water-soluble p-sulfonated calix[4]arene was an excellent and selective ligand for the removal of the chromium anions from aqueous solutions by nanofiltration-complexation system at pH 9.4. Consequently, this study revealed that nanofiltration-complexation system with p-sulfonated calix[4]arene was a very useful approach for the selective removal of the chromium anions. We think that this study can contribute to the environmental studies since it has some important advantages, such as not using organic solvents in the removal process and selective removal of anions.

EXPERIMENTAL

Chemicals and Equipment

To characterize the ligands, ^1H NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ with TMS as internal standard and IR spectra were recorded on a Perkin Elmer 1605 FTIR spectrometer as KBr pellets. UV-vis spectra were obtained on a Shimadzu 160A UV-visible recording spectrophotometers. Nanofiltration-complexation experiments were carried out by passing through nanofiltration pilot-scale equipment (Osmonics Sepa CF Membrane Cell).

In the synthesis, generally, solvents were dried by storing them over molecular sieves (Aldrich; 4 Å, 8–12 Mesh). The materials and reagents were purchased from Fluka or Merck, were used without further purification, and were standard analytical grade. 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 with pH 2–11 and 19.1 × 14 cm dimensions) was used as the NF membrane.

Synthesis

Water soluble p-sulfonated calix[n]arenes (n = 4, 6 and 8) (Fig. 3) were prepared by the procedures published in the literature [15–18], and their structures were confirmed by re-characterizing with spectroscopic methods such as ^{1}H NMR and FTIR.

Nanofiltration-complexation Studies

The schematic representation of nanofiltration (NF) used in our experiments is seen in Fig. 5. By totally recycling permeate and retentate, the feed remains at constant composition during the experiment. Nanofiltration-complexation tests were carried out to learn the complexation abilities of p-sulfonated calix[n]arenes toward the chromium anions in aqueous medium containing low levels of sodium dichromate.

The known amount of sodium dichromate was firstly passed through the NF membrane (Osmonics Sepa CF II NF TF DK) without ligand. The samples of permeate and retentate were taken half an hour after sodium dichromate addition, and then the chromium concentration was determined spectrophotometrically (at 346 nm). It was observed that the NF membrane used in this study exhibited good permeability (almost 100%) toward chromium anions. Afterwards, the known amount of ligand was added to a solution containing fixed concentration of sodium dichromate which was filtered on a NF membrane at particular pH value. The pressure was 5 bars in all of the nanofiltration experiments, and the retention of chromium (VI) was calculated according to Eq. (2).

$$R_\mathrm{i} = 100 \times (1 - C_\mathrm{ip}/C_\mathrm{ir}) \qquad (2)$$

Where C_ip is the concentration of i in the permeate, and C_ir is the concentration of i in the retentate.

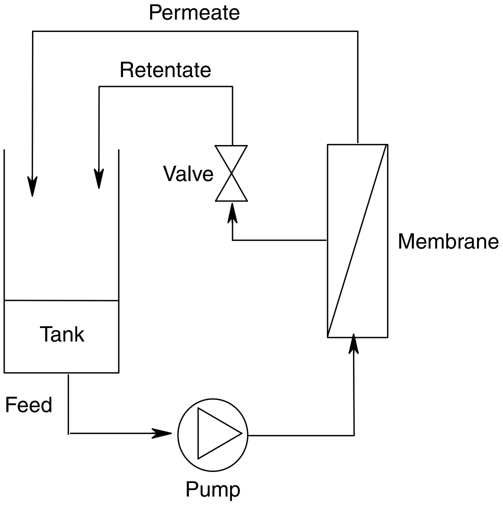

FIGURE 5 The scheme of the nanofiltration-complexation loop in this study.

Effect of PH

In order to observe the effect of pH on the retention of the chromium anions, pH was adjusted between 2.5 and 9.5 with NaOH or HCl. Then the nanofiltration-complexation process was performed by using sodium dichromate solutions at different pH values, and the chromium anions retention was calculated as described above.

Selectivity Studies

In order to understand the selectivity of the ligand for the chromium anions over some diverse anions, the selectivity studies were carried out in the presence of Cl^-, SO_4^{2-} and NO_3^- anions. For this aim, sodium salts of these anions were used in amounts corresponding to one hundred fold of sodium dichromate concentration. Then the nanofiltration-complexation process was performed by using sodium dichromate solutions at different pH values, and the chromium anions retention was calculated as described above.

Acknowledgements

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