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Preparation of calix[4]arene-embedded polysulphone membranes, and utilisation of its Cr(VI) transport efficiency

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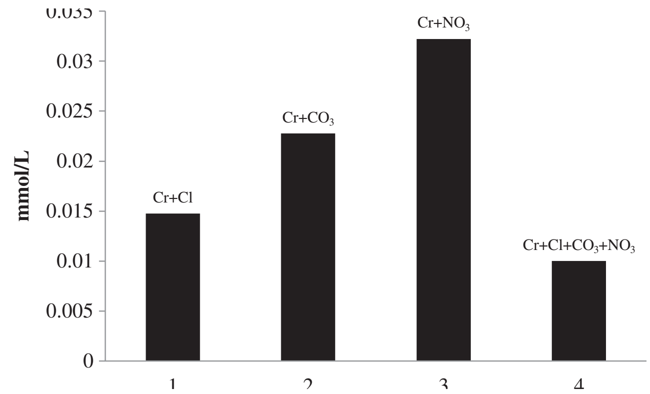
ABSTRACT

In this study, a tetramine-substituted calix[4]arene derivative, which was synthesised from calix[4] arene by treatment with dimethylamine in one step via Mannich reaction, was used to fabricate a new calix[4]arene-embedded polysulphone membrane (**calix@membrane**). Its structure and surface morphology were determined using thermogravimetric analysis and scanning electron microscopy, and elemental analysis techniques. Moreover, a Donnan dialysis system was employed to investigate Cr(VI) transport efficacy of calix@membrane at different pH values. Results showed that calix@membrane represented a promising transport capability for $HCr_2O_7^-$ due to their efficient complexation behaviour.



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KEYWORDS
Calixarene; polysulphone membrane; Cr(VI); ion transportation; Donnan dialysis system

1. Introduction

In the developing countries, in terms of industry and urbanisation, heavy metal pollution has been increasing day by day. This increasing heavy metal pollution became a worldwide problem, and was paid attention by researchers all around the world. With the development of industry and urbanisation, heavy metal pollution has been a worldwide problem and attracts more attention from all the countries. Because of the harm to rivers and lakes, the pollutants can be an important threat for public safety, especially for drinking water. Among them, hexavalent chromium (Cr(VI)) is extremely harmful because of its high solubility, toxicity and non-biodegradable nature (*1–4*). Industrial sources of Cr(VI) are: plating, leather tanning, electroplating, rinse waters, anodising baths and cement and steel industries. The US EPA has set the concentration of 0.1 mg $L^{-1}$of total chromium for drinking water as 'a maximum contaminant level goal' (*5*) while the World Health Organization (WHO) states a lesser guideline value of 0.05 mg L^{-1}exclusively for Cr(VI) (*6*). According to the WHO, long-term exposure to chromium (VI) levels over 0.1 ppm can be a reason for kidney and liver damage and respiratory problems(*7*).

Varied methods for the removal of chromium ions based on ion exchange (*8*), precipitation (*9*, *10*) and adsorption (*10–12*) were used. However, in separation, the membrane

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transport and solvent extraction seem to be the most efficient techniques (*13–15*). In membrane separation, care should be taken to balance the selectivity and productivity of the membrane and hence the performance (*16–21*). Some important conventional membrane technologies are: nanofiltration, ultra-filtration, microfiltration, fuel cell applications, reverse osmosis, gas separations, electro- and hemodialysis and Donnan dialysis (*22*). The Donnan dialysis has a great importance for recovery or extraction of valuable metals in ionic form from the aqueous solution (*23*).

Different polymeric materials, polysulfone (PSf), polyethylene, polyvinylamine, poly(vinylidene fluoride), etc., have been used as membranes because of their good chemical, mechanical and heat-resistance performances (*24–27*). Polysulfonated ion-exchange membranes are truly microporous with controlled ion-exchange capacities and excellent mechanical wet strength and are particularly patented for the post-treatment process (*28*). The choice of the carrier is an important factor in facilitated transport. If the carrier is very specific to one solute, high selectivity is obtained. In the literature, it was found that those liquid ion carriers could be oximes, (*29*) thiacrown ethers, (*30*) calixarenes, (*31*) azo-compounds, (*32*) and thiophosphorus species (*33*).

The objective of this study is to develop an easy and convenient tool for efficiently removing Cr(VI) anion from its contaminants. For this purpose, a tetramine-substituted calix[4]arene derivative, whose dichromate anion extraction efficacy is known to be extremely high (*34*), was synthesised and characterised using NMR and elemental analysis techniques. Owing to good extraction properties, tetramine-substituted calix[4]arene derivative was used to fabricate a new calix[4]arene-embedded polysulphone membrane (**calix@membrane**). In order to elaborate its dichromate anion transportation capability, a Donnan dialysis system was employed. Moreover, different parameters such as various pH levels, Cr(VI) concentrations, dialysis durations and foreign anions affect the performance of **calix@membrane**.

2. Experimental

2.1. Chemicals and materials

PSf (MW~35,000 g mol^{-1}) was purchased from Sigma–Aldrich. Other chemicals like hydrochloric acid, dimethylformamide (DMF), $Na_2Cr_2O_7$, NaCl, Na_2CO_3, $NaNO_3$ and NaOH were purchased from Merck chemicals and Fluka. All solutions were prepared using ultra-pure water obtained from a Milli-Q (Millipore Corp.). A Gallenkamp apparatus in a sealed capillary tube was used to determine melting points. NMR spectra were recorded on a Bruker 400 MHz spectrometer. TLC silica gel plates (SiO_2, Merck PF_{254}) were used for analytical thin-layer chromatography studies. All materials and reagents were purchased from Alfa Aesar, Merck and Sigma–Aldrich, and used without further purification.

2.2. Synthesis

Compounds **1–3** were synthesised by procedures published in the literature (*35*, *36*).

2.2.1. Synthesis of 5,11,17,23-tetrakis[(dimethyl amine)methyl]-25,26,27,28-tetrahydroxycalix[4]arene (3)

Typically, the reaction of calix[4]arene **2** and dimethylamine in the presence of acetic acid in THF gave the desired white coloured derivative **3** in 78% yield. M.p.; 159–161 °C. ^{1}H-NMR (400 MHz, DMSO): δ 2.14 (s, 24H, -CH_3), 3.13 (d, 4H, $J = 12.4$ Hz, Ar-CH_2-Ar), 3.21 (s, 8H, -CH_2-), 4.25 (d, 4H, $J = 12.4$ Hz, Ar-CH_2-Ar), 6.81 (s, 8H, ArH).

2.3. Preparation of PSf membrane and calix@membrane

Phase inversion method was used to prepare PSf membrane. Typically, 1 g PSf was dissolved in 10-mL DMF and then vigorously stirred for 6 h until a clear homogeneous solution was obtained. The **calix@membrane** was prepared as follows. One-gram PSf was dissolved in 10-mL DMF and then vigorously stirred for 6 h until a clear homogeneous solution was obtained. Then, 10-mg tetramine-substituted calix[4]arene derivative **3** was added and stirred for 6 h until a clear homogeneous solution was obtained. Both of them were then casted onto a glass plate using an applicator with a precise gap of 200 μm between the applicator knife and the glass plate. Defect-free membrane was achieved by immersing the plate in a pure water bath.

2.4. Transport experiments

The transport of Cr(VI) ion from an aqueous solution was performed using a cell consisting of two detachable compartments made of Teflon (*22*). The membrane was clamped tightly between two compartments of 40 mL capacity, and the surface area of the membrane was 7 cm^2. Both phases were stirred at 500 rpm with a magnetic stirrer, during the experiment. All of the measurements were carried out at 24 °C. The feed phase contained 10^{-3}–10^{-6} mol/L $Na_2Cr_2O_7$ solutions (Between pH 2 and 5) and the receiver phase contained HCl solution (Between pH 2 and 5). The sampling of the solution (1 mL) was carried out at certain intervals (each 30 min) and the amount of Cr(VI) ions transported across the membrane was determined by the use of an ICP–MS (Perkin Elmer 5300 DV model). The experiments of Cr(VI) have been carried out at optimum pH 3 and optimum concentration 10^{-4} mol/L.

3. Result and discussion

The main theme of this study is to design a new **calix@membrane** that would be easily accessible, and has an effective transportation property towards heavy metals such as Cr(VI). For this goal, 5,11,17,23-tetrakis[(dimethylamine)methyl]-25,26,27,28-tetrahydroxycalix[4]arene (**3**) has been synthesised by treating calix[4]arene **2** with dimethylamine in the presence of acetic acid according to the literature procedure (Scheme 1) (*28*). Its structure has been characterised using NMR techniques, and compared with the literature. The NMR data revealed that calixarene derivative **3** was successfully synthesised. Synthesised tetramine-substituted calixarene derivative was used to prepare **calix@membrane**. Its structure and surface morphology have been evaluated using thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) techniques (*37*).

Figure 1 represents the TGA results of both **calix@membrane** (Figure 1(b)) and calixarenefree membrane (Figure 1(a)). In their TGA curves, there is a sharp peak at about 521 °C, which corresponds to mass loss of calixarene and thermal depolymerisation of polysulphonemoieties (mass loss 49%), whereas decomposition peak of the membrane without calixarene is attributed to only thermal depolymerisation of polysulphone moieties of approximately 22%.

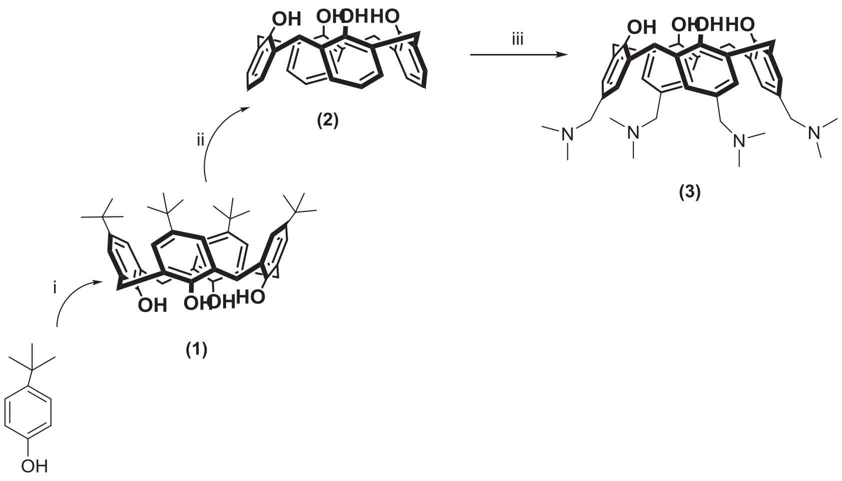
Figure 2(a) bears SEM images of fabricated membrane without calixarene derivative **3**, and membrane with calixarene derivative (**calix@membrane**). In these figures, significant differences associated with the shape and distribution on the surface of fabricated membranes are obvious as the surface of one is embedded with calixarene which is represented in Figure 2(b). These differences on the surface morphologies of prepared membranes provide an evidence that embedding of calixarene **3** onto membrane was accomplished.

To determine the amount of the loaded calixarene on **calix@membrane**, an elemental analysis technique was performed. The results, which were measured by the nitrogen contents of the calixarene derivative **3**, indicated that **calix@membrane** contained the amount of nitrogen with 0.10% corresponding to 0.29 mmol of **calix@membrane**/g of support (Table 1).

The effect of pH on the chromium (VI) transport was investigated in the pH range 2–5 while the feed phase was 10^{-3} mol/L. By the way, pH of the receiver phase was also kept constant between 2 and 5. The effect of pH on removal efficiency for Cr(VI) with time using **calix@membrane** is shown in Figure 3. It is clearly seen that the maximum transport amount was obtained at pH 3.05. Thus, the optimum pH was chosen as 3.05 for transport of Cr(VI) from aqueous solution. This might be because of proton-binding amino groups of calixarene derivative. It is well known that amino units of calixarene derivative that are embedded in the membrane are protonated in acidic conditions, and the protonated sides of **calix@membrane** would form complexes with $HCr_2O_7^-$ by electrostatic attraction and hydrogen bonding.

The flux values of the Cr(VI) were calculated from the time profile of receiver phase concentration by initial rate technique, and the results are given in Table 2. The results are obtained at 95% confidence level ($N = 3$). The RF values of the Cr(VI) are also shown in Table 2. It can be seen that the highest flux and RF values of Cr(VI) ion were obtained at pH 3.05.

The effect of initial concentration in the feed phase with time for removal of Cr(VI) from the aqueous solution through **calix@membrane** is presented in Figure 4. It is clearly seen that the transport of Cr(VI) increased with increase in concentration of Cr(VI) in the feed phase.



Scheme 1. Synthesis of 5,11,17,23-tetrakis[(dimethylamine)methyl]-25,26,27,28-tetrahydroxycalix[4]arene (**3**). Reaction conditions: (i) HCHO; NaOH; (ii) $AlCl_3$; Phenol; and (iii) dimethylamine; HCHO; AcOH.

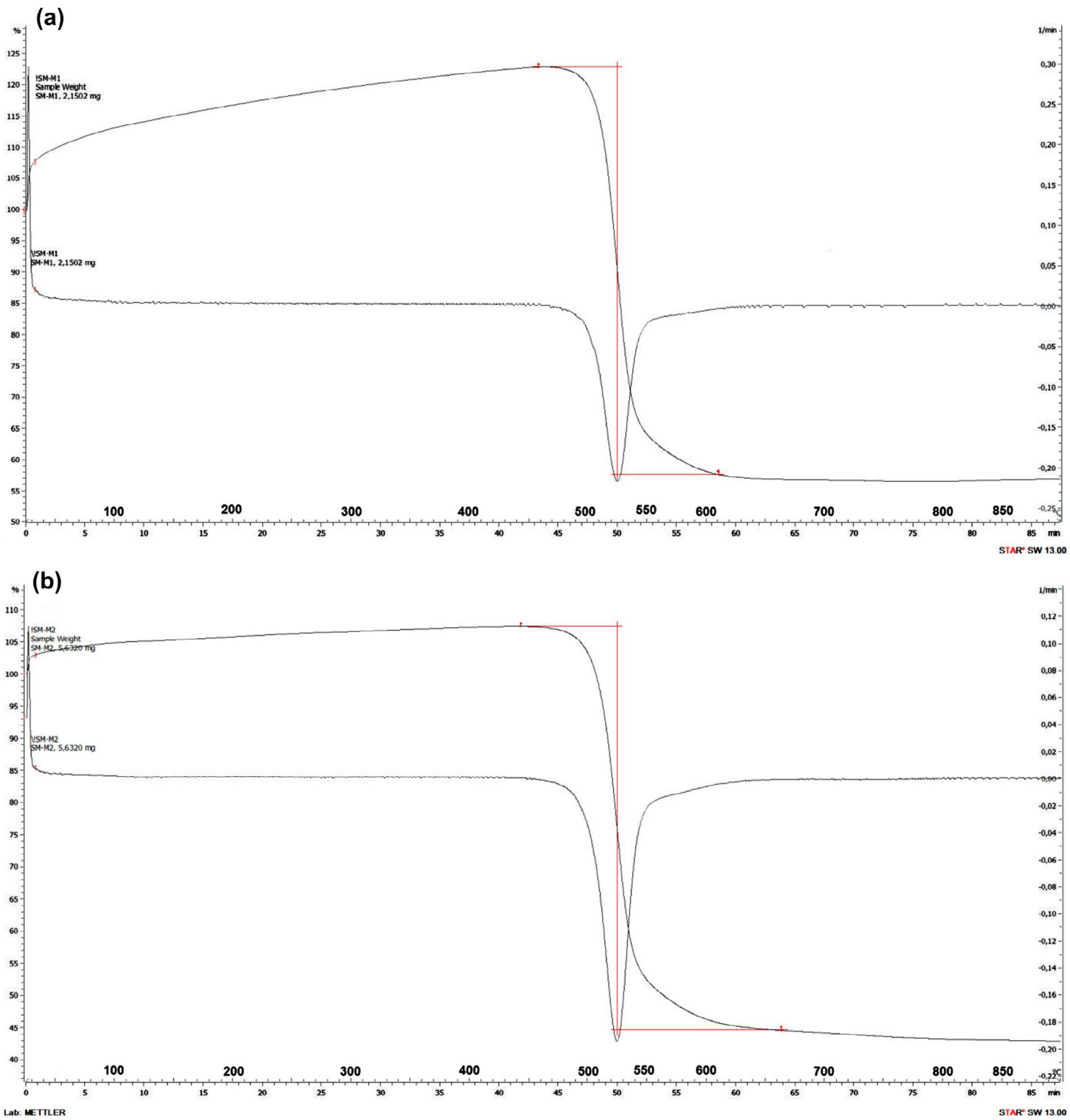


Figure 1. (Colour online) The TGA curves of (a) membrane without calixarene, (b) **calix@membrane**.

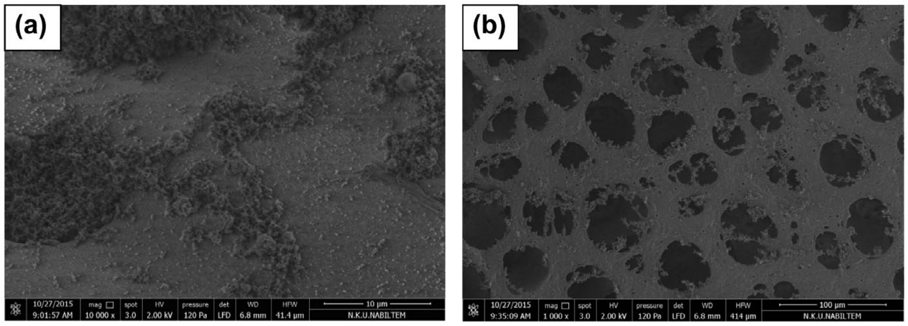


Figure 2. The SEM images of prepared membranes: (a) membrane without calixarene, (b) **calix@membrane**.

Table 1. Elemental analysis results of **calix@membrane**.

	C (%)	*H* (%)	*S* (%)	*N* (%)	Embedded amount of calixarene (mmol/g)[a]
calix@membrane	72.25	4.72	6.78	0.10	0.29
Membrane without calixarene	71.54	5.02	6.44	–	–

[a] Calculated according to the *N* content.

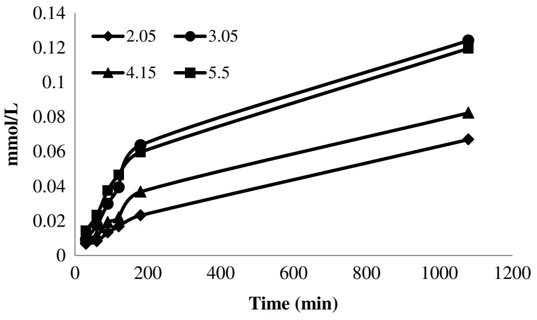


Figure 3. Time dependence of the pH of Cr(VI) in receiver phase with **calix@membrane**.

Table 2. Fluxes and RF values of Cr(VI) for calixarene membrane in the different pHs.

	pH	$J \times 10^{11}$ (mol cm^{-2} s^{-1})	RF values (at 1080 min)
Cr(VI)	2.05	0.521 (±0.001)	26.161
	3.05	0.928 (±0.014)	48.534
	4.15	0.617 (±0.004)	32.179
	5.50	0.832 (±0.011)	46.755

3.1. Effects of competing anions

To assess the interfering behaviours of other anions such as chloride (Cl^-), carbonate (CO_3^{2}) and nitrate ions (NO_3^-) on dichromate ion transportation of **calix@membrane**, an aqueous solution of various sodium salts (NaCl, Na_2CO_3, $NaNO_3$) was additionally mixed with the solution into the feed phase at pH 3.05. The results represented in Figure 5 clearly indicate that **calix@membrane** exhibits a transport efficacy towards those foreign anions in an order of Cl^-, CO_3^{2-} and NO_3^-. This transportation affinity for other anions caused drastically to decrease its dichromate anion transportation efficacy. Figure 5 shows the effects of these anions on the Cr(VI) removal efficiency. As seen from Figure 5, in the presence of these anions, the removal of Cr(VI) decreased compared to the Cr(VI) alone case.

The Cl^- anion is the most initiative one among Cl^-, CO_3^{2-} and NO_3^- anions. As there is Cl^-anion in both supply and receiver sides, it could have had much more influence at attempts to get away. When the hydration volume is considered, CO_3^{2-} ion has the highest hydration volume. Compared with NO_3^- Cr(VI), it has made more attempts to get away. Hydration volumes: Cl^-: 93.6 cm^3/mol, NO^{3-}: 95.3 cm^3/mol, CO_3^{2-}: 137.1 cm^3/mol (38).

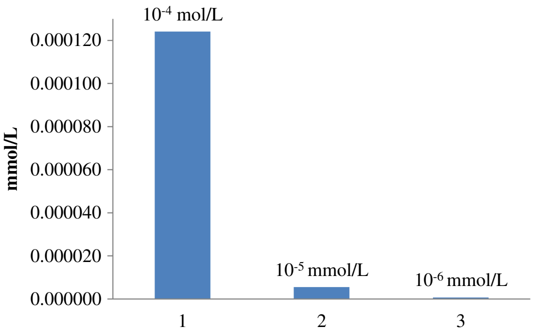


Figure 4. (Colour online) Effect of concentration on Cr(VI) concentration.

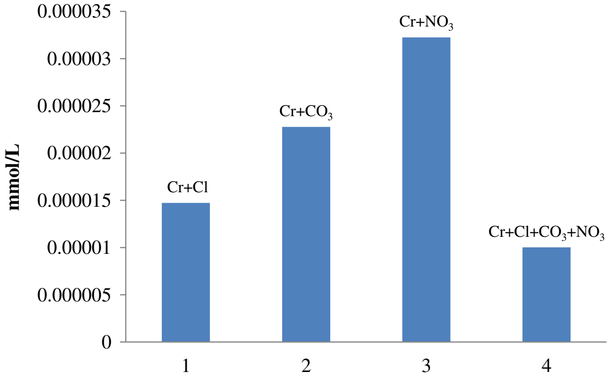


Figure 5. (Colour online) Effects of competing anions on Cr(VI) concentration.

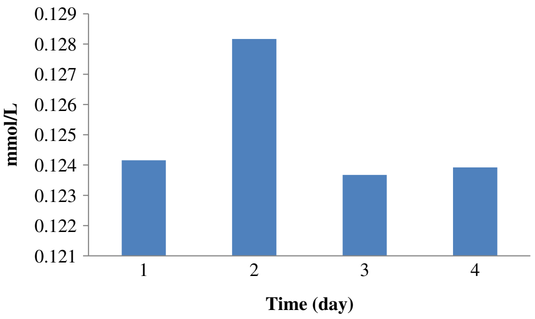


Figure 6. (Colour online) Investigation of the stability of **calix@membrane**.

3.2. Stability of calix@membrane

To evaluate the lifetime of **calix@membrane**, transport capacity of the membrane for Cr(VI) was examined under same experimental conditions (Feed phase: 0.1 mol/L HCl solution; Receiver phase: 10^{-4} mol/L Cr(VI) solution; pH: 3.05). The transport experiments were performed using the same membrane and renovated solutions in four runs of 24-h duration.

Cr(VI) mmol amounts obtained for the number of runs are shown in Figure 6. It was observed that the transport of Cr(VI) ions decreased with number of runs; the resulting Cr(VI) amount was about 50% lower than the initial concentration. These transport experiments were performed at a time of 2 months. When the experiments were completed, no structural deformation was observed in the membranes. Besides, membranes were preserved in purified water after each experiment.

4. Conclusion

In the presented study, a new **calix@membrane** was obtained from chemically synthesised tetramine-substituted calix[4]arene derivative by casting method. The Donnan dialysis method was evaluated to remove Cr(VI) ions from aqueous solutions using calix@membrane. The results are summarised as follows:

1. SEM images, comparing membrane without calixarene membrane to **calix@membrane**, indicate that the surface morphologies of the membranes are different.
2. The Donnan dialysis was carried out for transport of Cr(VI) ions from aqueous solution using **calix@membrane**. It can be seen that the highest flux and RF values of Cr(VI) ions were obtained at pH 3.05.
3. The removal of Cr(VI) in the presence of competing anions (Cl^-, CO_3^{2-}, NO_3^-) was investigated. The flux of Cr(VI) decreased in the presence of different anions in the feed phase and the order of flux was found as $Cl^- > CO_3^{2-} > NO_3^-$.
4. The transport experiments were performed using the same membrane four times with 24-h periods. It was observed that the transport of Cr(VI) ions decreased with the number of runs. The resulting Cr(VI) amount was about 50% lower than the initial concentration.
5. Using Donnan dialysis method for removing Cr(VI) from aqueous solution seems to be a feasible method, especially with the **calix@membrane**.
6. The amino units of **calix@membrane** are protonated in acidic conditions, and the protonated sides of **calix@membrane** would form complexes with $HCr_2O_7^-$ by electrostatic attraction and hydrogen bonding. In addition, the cooperative effect of free dimethylamine units of calixarene derivative also contributed a critical role in the construction of this complex.

Disclosure statement

No potential conflict of interest was reported by the authors.

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