Calix[4]arene Embedded Polyamide Supported Liquid Membrane for Separation of Heavy Metals from Aqueous Solutions

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In this study, we aimed to prepare new calixaren embedded mercapto groups supported liquid membranes and to use them in the transport of heavy metals. For this purpose 5,11,17,23-tetra-tetra-tert-buty1-25,27-bis(3-thiol-1-oxypropane)-26,28-dihydroxycalix[4]arene was synthesized. The synthesized calixarene compounds were fully characterized by spectroscopic and other techniques. The prepared compounds were supported polyamide liquid membranes and obtained calix[4]arene embedded supported liquid membranes (C@PSMs). The characterization of C@PSM was carried out by FTIR, TGA and elemental analysis techniques. Transport experiments were carried out with Pb(II), Cd(II) and Zn(II) as trace metals, to transport from donor phase to accept phase. From the results, it was calculated flux (J) and recovery (RF) values. The affinity (the percentage of metal ion transferred from the source solution) of a PIM towards a range of divalent cations was found to follow the order Zn(II)> Cd(II)> Pb(II).

Introduction

It is known that environmental pollution is caused by very high levels of heavy metal pollution from industrial sources (Cay et al., 2004; Ugur et al., 2015). Technologies used in various branches of industry require the use of large amounts of heavy metals, if introduced directly or indirectly to the environment, causing the potential to contaminate both surface and groundwater (Konczyk et al., 2016; Wu et al., 2016). Heavy metals are toxic substances known to trigger adverse health effects, including cardiovascular diseases, neurological disorders, diabetes, hearing loss, hematological and immunological disorders, and various types of cancer in humans (Kir et al., 2015).

There are many ways to extract heavy metals from waste waters. Some of these ways are chemical precipitation, biosorption, adsorption, ion exchange, electrolysis, distillation, reverse osmosis, ultrafiltration, solvent extraction, and liquid membranes (Sap et al., 2012). The increasing severity of environmental regulations affecting the discharge of effluents has created a sustained interest in the development of novel technologies that could improve the efficiency of the separation of toxic materials from very dilute solutions (Engin et al., 2019).

According to many studies, liquid membranes have become an attractive alternative to selective separation and low concentration of target metals (Konczyk et al., 2016). These membranes include emulsion liquid membranes, supported liquid membranes, bulk liquid membranes and polymer inclusion membranes (Ugur et al., 2015). Among these, polymer inclusion membranes and support liquid membranes stands out due to high transport rates, good selectivity and long-term stability. Supported liquid membranes are, in particular, considered to be one of the types of liquid membranes suitable for the removal and recovery of toxic metals from aqueous solutions. The use of supported liquid membranes containing carrier and microporous membranes has been proposed as an alternative to solvent extraction processes for the selective separation and concentration of metal ions. A supported liquid membrane contains an organic carrier solution immobilized in a porous hydrophobic support membrane. Since they are stable under the test conditions used and have suitable chemical properties, any membrane material can be used as the support membrane. Indeed, highly stable materials such as polypropylene, polyethylene, polysulfone, polyamide, and polyvinylidene fluoride are often used as supports (Kir et al., 2015).
The calixarene derivatives have been used as extractant for the removal of toxic ions. They are also form selective and stable complexes with anions, cations or neutral molecules (Sayin et al., 2011). Because of the specificity of the structure and the diversity of the derivates, calixarenes have attractive expectations for chemical sensors, ion transport, separation and analysis, recovery of precious metals, molecular recognition and incorporation, molecular catalysis and enzyme simulation, ion selective electrodes. Research on calixarenes is particularly important for chemistry, environmental chemistry, the development of life chemistry and structural chemistry in supramolecular chemistry (Tabakci and Yilmaz, 2008; Liu and Zhong, 2018).

In this paper, the affinity of supported liquid membranes containing mercapto groups derivative towards heavy metals from aqueous solutions. For this purpose, p-tetra-butylcalix[4]arene, p-tetra-butylphenol and formaldehyde in basic environment by condensation reaction was synthesized. The synthesized p-tetra-butylcalix[4]arene in the presence of K2CO3 into the reaction with 1,3-dibromopropyl derivative of dialky bromide of calixarene was synthesized. The obtained derivative of dialkyl bromide of calixarene into the reaction with thiourea and dialkythiol functional of calixarene was synthesized. The synthesized calixarene compounds were fully characterized by spectroscopic and the other techniques. The prepared compounds were supported different liquid membranes especially polyamide and obtained calix[4]arene embedded supported liquid membranes (C@PSMs). The characterization of C@PSM was carried out by FTIR, TGA and elemental analysis techniques. Transport experiments were carried out with Pb(II), Cd(II) and Zn(II) as heavy metals, to transport from donor phase to accept phase. From the results, it was calculated flux (J) and recovery (RF) values.

**Material and Method**

**Chemicals and Materials**

All of the starting materials and reagents were obtained from Merck (Merck, Darmstadt, Germany) and Aldrich companies (Aldrich; Steinheim, Germany) and used without further purification. Ultra-pure water obtained from a Milli-Q (Millipore Corp.) was used to prepare all solutions. Melting points were determined using a Gallenkamp apparatus in a closed capillary tube. NMR spectra were recorded on a Bruker 400 MHz spectrometer. TLC silica gel plates (SiO 2, Merck PF254) were used for analytical thin layer chromatography studies. A Burker (820-MS) Inductive Coupled Plasma Mass Spectrometer (ICP-MS) was used to determine the heavy metals transfer of the novel C@PSM.

**Synthesis**

The compounds p-tetra-butylcalix[4]arene (1), 5,11,17,23-tetra-tetra-butyl-25,27-bis (bromopropoxy)-26,28-dihydroxy cyclene [4] arene (2) and 5,11,17,23-tetra-tetra-butyl-25,27-bis(3-thiol-1-oxypropane)-26,28-dihydroxy calix[4] arene (3) were synthesized according to the published procedures (Gutsche, 1990; Sayin et al., 2011; Demirkol et al., 2014).

**Preparation of C@PSM**

Microporous polyamide membrane filter, (NL17, 0.45 μm, 25 mm) was used as the support. Polyamide supported membranes (PSM) were incubated overnight in 5,11,17,23-tetra-tetra-butyl-25,27-bis(3-thiol-1-oxypropane)-26,28-dihydroxy calix[4] arene (10 mg) as ion carrier dissolved in chloroform, membrane saturated with carrier solution and provided to achieve a more stable structure. Lastly, before being used in transport experiments, the C@PSM was immersed in distilled water for 2 hours. In the absence of the ion carrier, it did not show a clear flow from the C@PSM with empty experiments for transport.

**Characterization**

The characterization of C@PSMs was carried out by Fourier Transform Infrared spectroscopy (FT-IR). Thermo Gravimetric Analysis (TGA) and elemental analysis techniques.

**Transport Experiments**

The aqueous solution transport of heavy metals was performed using a cell of two separable sections made of Teflon (Koseoglu et al., 2010). All measurements were made at room temperature. The feed phase contained heavy metals (104 M) solutions and the receptor phase contained deionized water. Experiments on the transport of heavy metals through the C@PSM from the feed phase to the strip phase were specified for 2 hours each or otherwise. The transport of heavy metals from the feed phase to the strip phase was measured at regular time intervals by taking samples from the feed and strip solutions and analyzed for the analysis of heavy metal concentrations. At the C@PSM / solution interface, the value of the initial flow (J0, mol m^-2 s^-1) was used to evaluate the rate of removal of the C@PSMs and was calculated using the following equation:

\[
J_0 = \frac{V}{A} \left( \frac{dC}{dt} \right)_{t=0} = \frac{V}{A} \left( \frac{C_t - C_{t=0}}{t} \right)
\]

Where, V is the volume of feed solution (m^3); A is the effective contact area of membrane (m^2); C is the change in heavy metal concentration over time (molL^-1); t is elapsed time (s) (Venkateswaran et al., 2007).

The recovery factors (RF%) of the trace metals were calculated from the following equation:

\[
\text{RF%} = \left( 1 - \frac{C_r}{C_t} \right) \times 100
\]

C_r and C_t (molL^-1) are dichromate concentrations in the receiver and feed phases, respectively.
Result and Discussion

**Synthesis**

The objective of this article is to investigate the dichromate anion transport property of a mercapto functionalized calix[4]arene-embedded polymer inclusion membrane. For this purpose, \(p\)-tert-butylcalix[4]arene, dialkyl bromide derivative of \(p\)-tert-butylcalix[4]arene, and 5,11,17,23-tetra-tert-butyl-25,27-bis(3-thiol-1-oxypropane)-26,28-dihydroxycalix[4]arene (3) were synthesized according to the published literature procedures (Gutsche, 1990; Sayin et al., 2011; Demirkol et al., 2014).

**Characterization of C@PSMs**

The infrared spectrum of PSM (Fig. a) and the C@PSM (Fig. b) were obtained and are shown in Figure 1. When we look at the FT-IR spectrum of the C@PSM in which the PSM and the calix[4]arene are absorbed, the characteristic peaks of the calix[4]arene are generally clouded because the intensity of the PSM is greater than the calix[4]arene compound.

Figure 2 demonstrates thermogravimetric analysis (TGA) result of the C@PSMs. The thermal decomposition temperature, at about 242, 351 and 483°C, all corresponds to the high weight loss of mercapto groups calix[4]arene derivative and thermal depolymerization of polyamide for C@PSM.

According to the elemental analysis results of C@PSM given in Table 1, mercapto groups calix[4]arene derivatives are absorbed into the PSM. From the results, C@PSM contained 0.41% S, which shows that 0.26 mmol of mercapto groups calix[4]arene derivatives are present in 1 g of PSM.

**Transport Studies**

**Effect of contact time**

The contact time required to achieve equilibrium is an important factor in membrane processes. The contact time required to achieve equilibrium for the metals is shown in Figure 3. In the first few minutes, the uptake of metals was very rapid since there were initially more C@PSM sites available for uptake of metals. As time passed, the metals did not occupy any space and therefore a slow transfer process took place. Therefore, 150 minutes was chosen as the appropriate contact time for the systems.

**Effect of pH**

It is well known that pH, as well as various physicochemical effects, is an important variable in which membrane surface processes can or can be altered. To observe the effect of this parameter on transport, the C@PSMs were contacted with metal solutions at pH 2.0–5.5. Lower pH values (acidic) were not investigated because of change of C@PSMs structure and higher pH values were not investigated because of the insolubility of the cations, so the best results are measured at pH 5.5. Also the pHs of prepared metal solutions are approximately the same value.
Table 1. Elemental analysis results of C@PSM

|        | C(%) | H(%) | S(%) | N(%) | Immobilized amount of calix[4]arene (mmol/g)* |
|--------|------|------|------|------|---------------------------------------------|
| PSM    | 39.18| 3.73 | -    | 0.13 |                                             |
| C@PSM  | 39.56| 3.20 | 0.41 | 0.10 | ~0.26                                       |

*Calculated according to the S content

Table 2. RF and J values of heavy metals for C@PSMs

| pH     | J×10^{11} (mol cm^{-2}.s^{-1}) | RF values (180 min.) |
|--------|-------------------------------|----------------------|
| Zn(II) |                               |                      |
| 2.05   | 0.321 (± 0.011)               | 20.161               |
| 3.05   | 0.528 (± 0.014)               | 28.534               |
| 4.15   | 0.517 (± 0.004)               | 29.179               |
| 5.50   | 0.732 (± 0.011)               | 42.755               |
| Cd(II) |                               |                      |
| 2.15   | 0.241 (± 0.008)               | 20.203               |
| 3.00   | 0.219 (± 0.017)               | 22.429               |
| 4.15   | 0.306 (± 0.011)               | 25.807               |
| 5.40   | 0.430 (± 0.016)               | 31.866               |
| Pb(II) |                               |                      |
| 2.00   | 0.193 (± 0.021)               | 20.161               |
| 3.05   | 0.308 (± 0.019)               | 20.959               |
| 4.20   | 0.327 (± 0.012)               | 24.172               |
| 5.50   | 0.401 (± 0.015)               | 30.123               |

**Conclusion**

The calix[4]arene embedded mercapto groups supported liquid membranes and to use them in the transport of heavy metals. The results are summarized as follows:

- The structure and surface morphology of C@PSMs were determined by FT-IR, TGA and elemental analysis techniques.
- The transfer capacities of the three metal ions under the same conditions was in the following order Zn(II)> Cd(II)> Pb(II).
- As a result of regeneration cycles and four repeated transporting, the C@PSMs retained almost the same transfer ability that indicates that the C@PSMs own good stability.
- For the transfer of metal ions from aqueous solutions in further operations, the experiments conducted in this study provided encouraging results to apply these C@PSMs.

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