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ARAŞTIRMA MAKALESİ **RESEARCH PAPER**

Preparation and Characterization of Polymer Supported Lewis Acid-type Calix[4]arene for Transport of Dichromate Anions

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Abstract: The article describes the fabrication and characterization of a new 25,27-bis[5-(trimethyl ammonium bromide)pentyloxyl]-26,28-dihydroxyl-5,11,17,23-tetra-*tert*-butylcalix[4]arene-embedded polymer inclusion membranes (TMAC[4]Bu^t@PI membrane). TGA, SEM and DSC techniques were performed to determine its structures. Moreover, the anion transport capacity of TMAC[4]Bu^t@PI membrane against Cr(VI) anion was investigated.

Keywords: Calixarene, cellulose triacetate, dichromate, membrane, poly vinyl chloride.

Dikromat Anyonlarının Taşınması için Polimer Destekli Lewis Asit Tipi Kalikserenlerin Hazırlanması ve Karakterizasyonu

Öz: Makale, 25,27-bis[5-(trimetil amonyum bromür)pentiloksi]-26,28-dihidroksi-5,11,17,23-tetra-ter-bütilkaliks[4]aren katkılı polimer içerikli membran (TMAC[4]Bu^t@PI) hazırlanmasını ve karakterizasyonu açıklamaktadır. TGA, SEM ve DSC teknikleri kullanılarak membranların yapıları belirlenmiştir. Ayrıca Cr(VI) anyonuna karşı TMAC[4]Bu^t@PI membranının taşıma kapasitesi araştırılmıştır.

Anahtar sözcükler: Dikromat, kalikseren, membran, poli vinil klorür, selüloz triasetat.

INTRODUCTION

Since drinking water is contaminated with toxic substances such as some oxyanions, drinking quality water has been the target of humanity for years. Toxic oxyanions, such as dichromate anions, are toxic compounds that can harm many living organisms and the environment, even in small amounts (Bozkurt & Turkmen, 2018).

Chromium which is found in animals, rocks, soil, plants, volcanic dust and gases is a naturally occurring element. It is mostly encountered in the oxidation states of Cr(III) and Cr(VI) which are known as “chromite” and “chromate”, respectively. Two of them get into the body by the way of dermal contact, ingestion and inhalation. Trivalent and hexavalent forms are believed to be biologically active species; however, their impact on health is not the same. Cr(VI) can easily penetrate biological membranes, while Cr(III) does not usually penetrate (Bozkurt et al., 2009; Krishna et al., 2004). Chrome plating industry generally use Cr(VI). Chrome plating is the operation of electroplating a thin chrome layer to a metal surface (Bayrakci et al., 2017; Kaya et al., 2016).

There are many ways to extract Cr(VI) from waste waters. Some of these ways are chemical precipitation, biosorption, adsorption, ion exchange, electrolysis, distillation, reverse osmosis, ultrafiltration, solvent extraction, and liquid membranes (Hsu et al., 2010; Sap, Tabakci & Yilmaz, 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). In recent years, researchers have been paying attention to polymer addition membranes (PIMs), a new type of liquid membrane. PIMs are formed by pouring a solution containing an extractor, a plasticizer, and a base polymer to form a thin, flexible and stable film (Nghiem et al., 2006). 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).

Due to the specificity of the structure and the diversity of derivative, Calixarenes have attractive prospects in ion transport, chemical sensors, recovery of precious metals, separation and analysis, molecular recognition and inclusion, ion-selective electrodes, molecular catalysis and enzyme simulation studies. Research on calixarene is important to the development of life chemistry, chemistry, environmental chemistry and structural chemistry, especially in supramolecular chemistry (Liu & Zhong, 2018; Tabakci & Yilmaz, 2008)

In this paper, the affinity of PIMs containing Lewis acid-type calix[4]arene derivative towards dichromate anions from aqueous solutions. For this purpose, *p-tert*-butylcalix[4]arene and 25,27-bis[5-(trimethylammonium bromide)pentyloxyl]-26,28-dihydroxyl-5,11,17,23-tetra-*tert*-butylcalix[4]arene were synthesized according to the published procedures (Gutsche, 1990; Sayin & Yilmaz, 2017). Synthesized Lewis acid-type calix[4]arene was then employed as an additive in the membrane producing process, in which cellulose triacetate (CTA) or polyvinyl chloride (PVC) and o-NPOE are typically used to prepare polymer inclusion membrane. Thermo gravimetric analysis (TGA), scanning electron microscopy (SEM) and Differential Scanning Calorimeter (DSC) techniques were performed to determine the structure of Lewis acid-type calix[4]arene-embedded membrane (TMAC[4]Bu^t@PI membrane). Furthermore, a Donnan dialysis system was used to study the carrying capacity of dichromate anions with the novel TMAC[4]Bu^t@PI membrane.

MATERIAL and METHODS

Chemicals and Materials: All starting materials and reagents were purchased 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 by using a Gallenkamp apparatus in a closed capillary tube. NMR spectra were recorded on a Bruker 400 MHz spectrometer. For analytical thin layer chromatography studies, TLC silica gel plates (SiO_2, Merck PF254) were used. A Mapada UV-6100 PCS double beam ultraviolet–visible spectrophotometer (Shanghai Mapada Instruments, China) was used to state extraction of dichromate anions efficacy of the novel TMAC[4]Bu^t@PI membrane.

Synthesis. *p-tert*-butylcalix[4]arene (**1**), and 25,27-bis[5-(trimethylammonium bromide)pentyloxyl]-26,28-dihydroxyl-5,11,17,23-tetra-*tert*-butylcalix[4]arene (**2**) were synthesized according to the literature procedures (Gutsche, 1990; Sayin & Yilmaz, 2017).

25,27-bis[5-(trimethyl ammonium bromide) pentyloxyl] -26,28-dihydroxyl-5,11,17,23-tetra-tert-butylcalix [4]-arene (2): Yield: 85%, melting point: 241–242 °C. ^{1}H-NMR (400 MHz, $CHCl_3$): δ 0.91 (s, 18H, Bu^t), 1.26 (s, 18H, Bu^t), 1.75–1.79 (m, 4H, $–CH_2–$), 2.04–2.07 (m, 8H, $–CH_2–$), 3.30 (d, 4H, J = 13.2 Hz, Ar-CH_2-Ar), 3.45 (s, 18H, $–CH_3$), 3.76 (t, 4H, J = 8.0 Hz, O–CH_2–), 3.96 (t, 4H, J = 5.6 Hz, N–CH_2–), 4.17 (d, 4H, J = 13.2 Hz, Ar-CH_2-Ar), 6.73 (s, 4H, ArH), 7.03 (s, 4H, ArH), 7.11 (s, 2H, –OH). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 22.8, 23.0, 29.2, 31.0, 31.7, 33.8, 33.9, 53.5, 66.6, 125.3, 125.5, 127.8, 132.1, 142.0, 147.0, 149.7, 150.1. Anal. calcd for $C_{60}H_{92}Br_2N_2O_4$ (%): C, 67.65; H, 8.71; N, 2.63. Found (%); C, 67.59; H, 8.76; N, 2.49

Preparation of Polymer inclusion membranes: TMAC[4]Bu^t@PI membrane-I; 0.2 g of CTA was dissolved in 10 mL of dichloromethane at room temperature. The plasticizer (o-NPOE, 0.3 mL) in dichloromethane (5 mL) and Lewis acid-type calix[4]arene as an ion carrier (13.3 mg) were then added. Part of this solution was poured into a membrane mold consisting of a 9.0 cm glass ring attached to a glass plate with CTA dichloromethane adhesive (Engin et al., 2018). The solution was allowed to evaporate dichloromethane overnight and the final membrane was immersed in cold water and separated from the glass plate (Zawierucha et al., 2013). The resulting membranes were recovered by immersion in cold water from the surface of the glass plate. The thickness of the membrane with a standard deviation of 0.1 m over 10 readings was measured by the help of a digital micrometer (Mitutoyo). Lastly, the TMAC[4]Bu^t@P**I** membranes were immersed in distilled water for 2 hours before being used in transport experiments. In the absence of the ion carrier, it did not show a clear flow from the TMAC[4]Bu^t@PI membranes with empty experiments for transport, ie, membranes containing only CTA / PVC and o-NPOE.

TMAC[4]Bu^t@PI membrane-II; 0.3 g of PVC was dissolved in 20 mL of dichloromethane at room temperature. The plasticizer (o-NPOE, 0.4 mL) in dichloromethane (5 mL) and Lewis acid-type calix[4]arene as an ion carrier (13.3 mg) were then added. Then, similar procedures in TMAC[4]Bu^t@PI membrane-I were applied to the TMAC[4]Bu^t@PI membrane-II.

Characterization: Thermo gravimetric analysis (TGA), Scanning electron microscope (SEM), and Differential Scanning Calorimeter (DSC) techniques were used to characterize the TMAC[4]Bu^t@PI membranes.

***Transport experiments*:** The aqueous solution transport of the dichromate anions was carried out using a cell consisting of two separable sections made of Teflon (Koseoglu et al., 2010). Both the volumes of the welding and receiving stages are equal to 40 cm^3. On the experiments, membrane samples having an effective membrane area of 7.00 cm^2 were used and both phases were mixed with a magnetic stirrer at 500 rpm. All measurements were made at room temperature. The feed phase contained dichromate (10^{-4}M) solutions and the receptor phase contained deionized water. The penetration rate of the dichromate anions was determined by sampling the source phase. Samples were then analyzed at regular intervals (every 2 hours) and dichromate anion concentrations in the receptor phases were measured by UV-VIS analysis at 610 nm (Bozkurt & Turkmen, 2018).

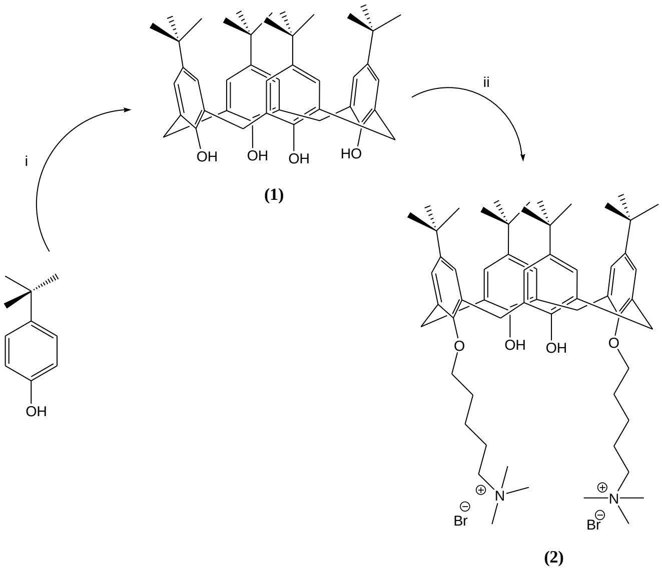
The recovery factors (RF%) of the trace metals were calculated from the following equation:

$$RF\% = \left(1 - \frac{C_r}{C_f}\right).100$$

C_r and C_f (molL^{-1}) are dichromate concentrations in the receiver and feed phases, respectively

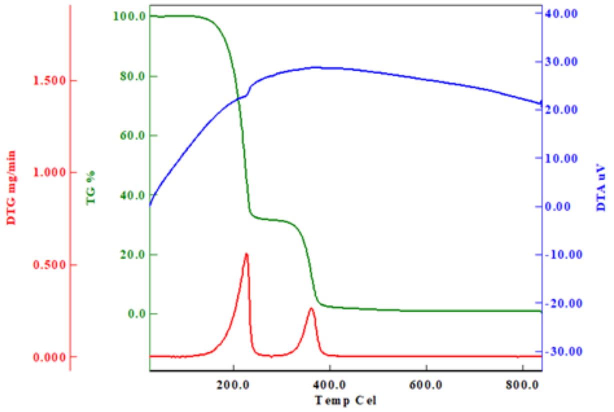
RESULT and DİSCUSSİON

Synthesis: This articles lies on the fabrication and investigation dichromate anion transport efficiency of a new Lewis-acid type calix[4]arene-embedded polymer inclusion membrane. In order to receive this goal, an effective as well as selective Lewis-acid type calix[4]arene derivative was synthesized by the reaction of *p-tert*-butylcalix[4]arene with (5-bromopentyl)trimethylammonium bromide in the presence of K_2CO_3 according to the applied literature method (Sayin & Yilmaz, 2017).

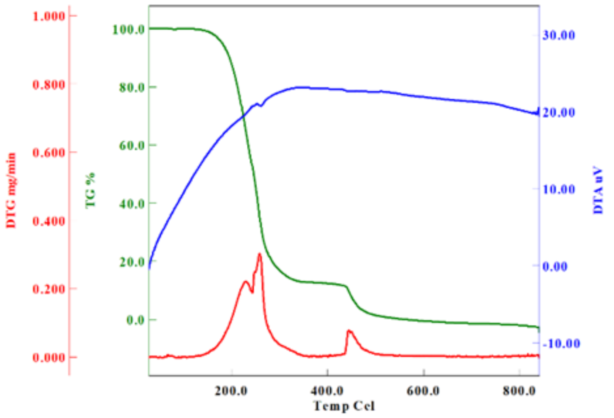


Scheme 1. Synthesis of Lewis acid-type calix[4]arene derivative (2). Reaction conditions; (i) HCHO, NaOH; (ii) (5-bromopentyl)trimethylammonium bromide, K_2CO_3.

Characterization of TMAC[4]Bu^t@PI membrane-I and TMAC[4]Bu^t@PI membrane-II:



TMAC[4]Bu^t@PI membrane-**I**



TMAC[4]Bu^t@PI membrane-II

Figure 1. The TGA curves of TMAC[4]Bu^t@PI membrane-I and TMAC[4]Bu^t@PI membrane-II

Figure 1 depicts thermogravimetric analysis (TGA) result of the TMAC[4]Bu^{t}@PI membranes. TMAC[4]Bu^{t}@PI membrane-I was found to exhibit the thermal decomposition temperature at about 227 and 361 °C; all correspond to high weight loss of the Lewis acid type calix[4]arene derivative and thermal depolymerization of CTA. The thermal decomposition temperature, at about 259, 300 and 444 °C, all corresponds to the high weight loss of the Lewis acid type calix[4]arene derivative and thermal depolymerization of PVC for TMAC[4]Bu^{t}@PI membrane-II.

The morphologies of TMAC[4]Bu^{t}@PI membranes and without calixarene TMAC[4]Bu^{t}@PI membranes were appraised by scanning electron microscopy (SEM) in Figure 2. As shown in Figures 2b and 2d, TMAC[4]Bu^{t}@PI membranes exhibit substantially different morphology in their distribution over shapes and surfaces. This finding showed that the Lewis acid type calix[4]arene derivative was successfully embedded in the polymer-containing membrane.

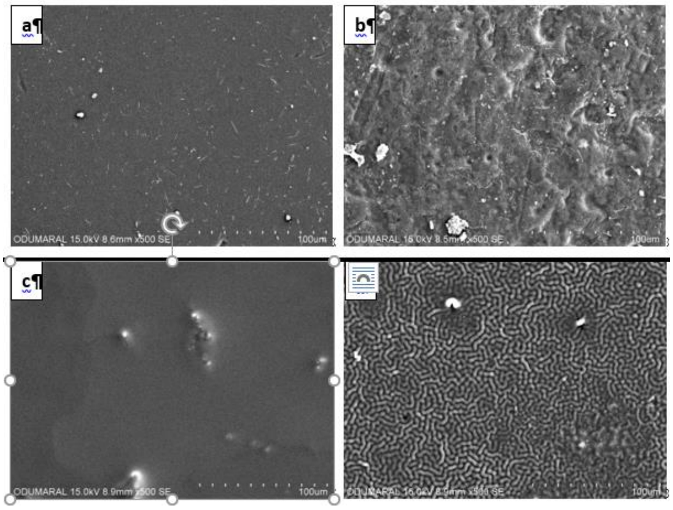


Figure 2. The SEM images a) TMAC[4]Bu^{t}@PI membranes-I without calixarene b) TMAC[4]Bu^{t}@PI membranes-I c) TMAC[4]Bu^{t}@PI membranes-II without calixarene d) TMAC[4]Bu^{t}@PI membranes

The Tg is the glass transition temperature of the polymers in DSC experiments (the midpoint of the change in heat capacity). Glass transition temperatures (Tg) of the PIMs were investigated on a Hitachi DSC 7020 double-furnace differential scanning calorimeter (DSC) under nitrogen flow (20 mL min^{-1}) at a heating rate of 20 °C min^{-1} from -100 °C to 200 °C.

The calixarenes decrease the glass transition temperature of PIMs and improve their flexibility (see Table 1). Glass transition temperatures of TMAC[4]Bu^{t}@PI membranes without calixarene in this study was detected as -79.0±1.2 °C and TMAC[4]Bu^{t}@PI membrane-I was detected as -81.1±1.4 °C. For TMAC[4]Bu^{t}@PI membrane-II was detected as -70.8±1.6 °C and TMAC[4]Bu^{t}@PI membrane-I was detected as -74.8±1.5 °C. The calixarenes have been shown to reduce Tg values and increase the flexibility of TMAC[4]Bu^{t}@PI membranes.

Table 1. Glass transition temperatures of TMAC[4]Bu^{t}@PI membranes.

Membranes	Glass transition temperatures (°C)
TMAC[4]Bu^{t}@PI membrane-I without calixarene	-79.0±1.2
TMAC[4]Bu^{t}@PI membrane-I	-81.1±1.4
TMAC[4]Bu^{t}@PI membrane-II without calixarene	-70.8±1.6
TMAC[4]Bu^{t}@PI membrane-II	-74.8±1.5

Transport studies: The RF values of the dichromate anions were calculated from the receiver phase concentration divided to initial phase concentration, and the results are given in Table 1. The results are obtained at 95% confidence level (N=3). It can be seen that the highest RF values of dichromate anions are obtained by TMAC[4]Bu^{t}@PI membrane-I.

Table 1. RF values of dichromate anions for TMAC[4]Bu^{t}@PI membranes.

Membranes	RF values
TMAC[4]Bu^{t}@PI membrane-I	44,118±0,125
TMAC[4]Bu^{t}@PI membrane-II	36,420±0,141

CONCLUSION

Lewis acid type calix[4]arene, cellulose triacetate (CTA) or polyvinyl chloride (PVC) was used to make novel TMAC[4]Bu^{t}@PI membranes. The obtained TMAC[4]Bu^{t}@PI membranes were used for dichromate anions transfer capabilities. The results are summarized as follows:

- The structure and surface morphology of PIMs were determined by TGA, SEM and DSC techniques. SEM images comparing calixarene membrane-free membrane with TMAC[4]Bu^{t}@PI membrane-I and TMAC[4]Bu^{t}@PI membrane-II show that the calixaren derivative has been successfully embedded in the membrane.
- Donnan dialysis was performed to transport the dichromate anions from the aqueous solution using TMAC[4]Bu^{t}@PI membranes. It can be seen that the highest RF values of dichromate anions are obtained by TMAC[4]Bu^{t}@PI membrane-I.
- The use of the Donnan dialysis method for the removal of dichromate anions from the aqueous solution appears to be a viable method, especially in TMAC[4]Bu^{t}@PI membranes.

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