



Preparation of Two Calix[4]arene-Functionalized Biopolymers and Evaluations of Their Extraction Abilities Against Cr(VI)/As(V) Anions

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 Extraction

Abstract: Two calixarene-functionalized biopolymers (calixarene-functionalized chitosan and calixarene-functionalized cellulose) have been synthesized and duly characterized using FTIR, TGA and elemental analysis techniques. Furthermore, their anion extraction behaviors at various pH values have been evaluated toward dichromate and arsenate anions. Results indicated that calixarene-functionalized chitosan against dichromate ion exhibited higher extraction capability than calixarene-functionalized cellulose. Intriguingly, although a less extraction efficiency against dichromate anion was obtained by calixarene-functionalized cellulose, the arsenate anion extraction results showed that calixarene-functionalized cellulose is more effective ionophore than calixarene-functionalized chitosan.

İki Kaliks[4]aren-Fonksiyonlu Biyopolimerlerin Hazırlanması ve Cr(VI)/As(V) Anyonlarına Karşı Ekstraksiyon Yeteneklerinin İncelenmesi

Anahtar Kelimeler

Kaliks[4]aren,
 Kitosan,
 Selüloz,
 Arsenat/dikromat,
 Ekstraksiyon

Öz: İki kaliksaren-fonksiyonlu biyopolimerler (kaliksaren-fonksiyonlu kitosan ve kaliksaren-fonksiyonlu selüloz) sentezlenmiş ve FTIR, TGA ve element analiz gibi teknikler kullanılarak uygun bir şekilde karakterize edilmişlerdir. Ayrıca, çeşitli pH lardaki anyon ekstraksiyon davranışları dikromat ve arsenat anyonlarına karşı incelenmiştir. Sonuçlar dikromat iyonuna karşı kaliksaren-fonksiyonlu kitosanın kaliksaren-fonksiyonlu selüloza göre daha büyük ekstraksiyon kabiliyetinin olduğunu gösterdi. İlginç bir şekilde, dikromat anyonuna karşı daha düşük bir ekstraksiyon verimliliği kaliksaren-fonksiyonlu selüloz ile elde edilmesine rağmen, arsenat anyon ekstraksiyon sonuçları kaliksaren-fonksiyonlu selülozun kaliksaren-fonksiyonlu kitosana göre daha etkin iyonofor olduğunu gösterdi.

1. INTRODUCTION

In recent years, oxyanions such as dichromate and arsenate have become two of the top 20 most hazardous ions that cause serious water pollution in the world [1,2]. It has been estimated that about 140 million people who supply with arsenic contaminated drinking water face to its crucial health problems such as lung, bladder, kidney, skin cancers, ischemic heart disease, abdominal pain, cardiovascular disease etc. [3-6]. Due to its carcinogenicity and great toxicity, it has been recommended that a higher level of arsenic contaminated drinking water than $10 \mu\text{g L}^{-1}$ should not be taken [5,7]. Water pollution based on dichromate compounds leakage leads similar serious issues to the environmental

like arsenic [8]. Therefore, the U.S. Environmental Protection Agency (EPA) listed dichromate compounds, which are extensively used in various industries such as electroplating, leather tanning, metal finishing, steels fabrication, pigments, textile etc., in as "Group A" human carcinogen [9,10]. Excessive or long-term dichromate exposure can bring out chronic chromium poisoning, and cause severe damage to human health [10-12]. Hereby, the World Health Organization (WHO) have recommended the allowable limit contaminant level of dichromate in natural water as 0.05 mg/L [13,14]. In this sense, several methods such as chemical precipitation, reverse osmosis, ion exchanger, bio/physisorption [15], adsorption, electrodialysis etc. have been developed [10,16]. However, considering hazardous and high toxicity of these oxyanions, it is still

urgent to design an efficient and low-cost material for the removal of these anions to meet the standards of the contaminated water discharge.

Cellulose and chitin are available as the most abundant bio-sourced polymer in nature [17]. Chitosan, which is a deacetylated derivative of naturally abundant chitin [18], and its compounds have been focused attention, leading wide range of usage in various fields such as pharmaceuticals, printing paper, textiles, medicine, health care products and agriculture with respect their great biocompatibility, low toxicity, shape flexibility, biodegradability, easy of processing, mechanical strength and efficient sorption properties [19-24]. Cellulose, which is a homopolymer comprised D-glucopyranose units [25], is also an important polysaccharide derivative like chitosan. Its unique features such as non-toxicity, biodegradable, renewable and biocompatibility makes cellulose attractive for industrial applications [26].

Over the years, a great deal of attentions has been devoted on calixarenes being a third generation of macrocycles due to their versatile three-dimensional structures, easy preparation and possible limitless functionalization with any kind of organic or inorganic substituents in their upper and lower rims [27,28]. Hereby, calixarenes have been successfully employed as the promising organic compounds for ion carriers, ion selective electrodes, catalysis applications, solid-phase support materials, enzyme-mimics, drug-delivery agents, gas sensors, and ion recognition [29-36].

In the present work, two biopolymers functionalized with calix[4]arene were prepared in order to use as potential ionophores for the removal of hazardous dichromate/arsenate ions from aqueous solutions. For this aim, the calix[4]arene dihydrazide derivative has been synthesized and then immobilized onto chitosan and/or cellulose biopolymer. Furthermore, the removal efficiencies of calix[4]arene-functionalized cellulose and calix[4]arene-functionalized chitosan towards dichromate/arsenate ions at different pH values have been investigated for the first time.

2. EXPERIMENTAL

2.1. Reagents and Instrumentation

A SRS OptiMelt MPA 100 instrument in a sealed capillary tube was used to determine melting points of compounds. NMR spectra of the compounds were recorded on a Bruker Avance III 400 MHz spectrometer. A Jasco FT/IR-6600 apparatus were employed to obtain ATR-FTIR spectra. Absorbance measurements were recorded on a Mapada UV-6100 PCS Double Beam UV-visible instrument. Elemental analyses were obtained using a Costech ECS 4010 analyzer. TLC analyses were performed on DC Alufolien Kieselgel 60 F₂₅₄ (Merck). All starting materials and reagents were purchased from Merck commercial source. Sodium salts of the anions were used in sorption studies. Doubly distilled water was used to prepare methyl violet solution (4.5×10^{-5} M),

ammonium molybdate solution (3.15×10^{-2} M) and HCl solution (6.85 M).

2.2. Synthesis

Literature procedures were used to synthesize the calixarene derivatives **1-3**, **Cel-iso**, **Chi-iso**, **Cel-Calix**, and **Chi-Calix** [35-38].

2.2.1. Synthesis of *p*-tert-butylcalix[4]arene dihydrazine amide (3)

Yield: 1.6 g (53.3%); m.p.: 330-333°C. IR (KBr): 1687 cm^{-1} (C=O). ¹H NMR (400 MHz CDCl₃): δ 1.02 (s, 18H, Bu^t), 1.26 (s, 18H, Bu^t), 2.15 (d, 4H, $J=1.6$ Hz, NH₂), 3.42 (d, 4H, $J=13.3$ Hz, ArCH₂Ar), 4.11 (d, 4H, $J=13.2$ Hz, ArCH₂Ar), 4.63 (s, 4H, OCH₂), 6.92 (s, 4H, ArH), 7.10 (s, 4H, ArH), 7.70 (s, 2H, OH), 9.61 (brs, 2H, NH). Anal. calcd. for C₄₈H₆₄N₄O₆: C; 72.70, H; 8.13, N; 7.06 (%). Found (%): C; 71.58, H; 8.27, N; 7.01.

2.2.2. General procedure for preparation of calix[4]arene-functionalized biopolymers (Chi-Calix and Cel-Calix)

Typically, a mixture of 0.2 g of calixarene derivative **3** and 0.6 g of biopolymer (**Chi-iso** or **Cel-iso**) in 10 mL of DMF was stirred at 70°C. The reaction completion was monitored by IR in which the peak of isocyanate group at around 2260 cm^{-1} needed to be disappeared. The reaction temperature was cool down, and the mixture was filtered off. Then, CH₂Cl₂ was used to remove excess of derivative **3**. The FTIR spectral data for **Chi-Calix** is as ATR cm^{-1} : 1651 (C=O). The FTIR spectral data for **Cel-Calix** is as ATR cm^{-1} : 1698 (C=O).

2.3. Dichromate/Arsenate Anion Extraction Studies

To estimate extraction capacities of calixarene-functionalized biopolymers toward arsenate and dichromate ions, a literature procedure was applied [2]. Generally, 10 mL of an aqueous solution of Na₂Cr₂O₇ or Na₂HAsO₄ (1.0×10^{-4} M) and 25 mg of calixarene-functionalized biopolymer (**Chi-Calix** or **Cel-Calix**) were shaken at 175 rpm, 25 °C for 1 h. The residual concentration of dichromate and/or arsenate anion in aqueous phase was estimated using UV-vis spectrometer at 346 and/or 610 nm according to the literatures [2,39]. HCl and KOH solutions were carried out to adjust the pH values of aqueous solutions at 25 °C. Eq. (1) was applied to calculate the extraction percentages (E %);

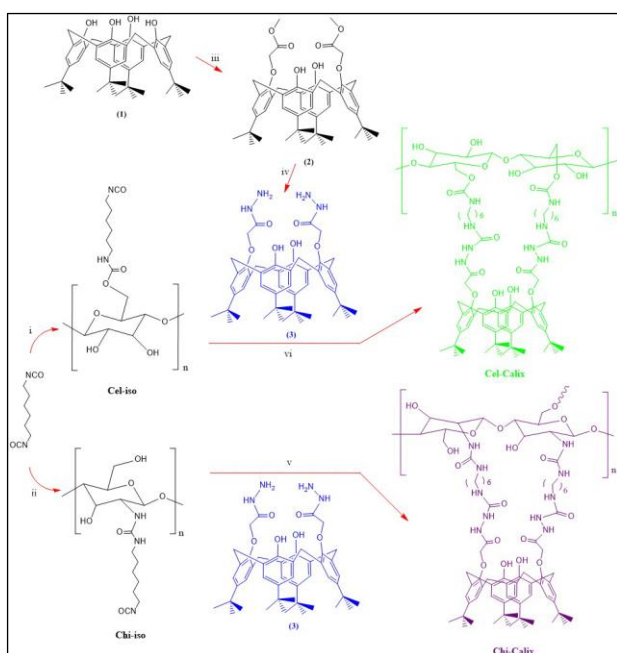
$$E \% = 100(A_0 - A)/A_0 \quad (1)$$

where A₀ and A are the concentrations of dichromate or arsenate ion before and after extraction.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of Calixarene-functionalized Biopolymers

The main goal of this study is to fabricate the efficient and selective ionophores for the removal of toxic and highly danger arsenate and dichromate anions from aqueous solutions. For the goal, two calix[4]arene-functionalized biopolymers (**Cel-Calix** and **Chi-Calix**) were prepared according to the literature procedures (see **Scheme 1**) [38]. The structures of two calix[4]arene-functionalized biopolymers were determined using FTIR (ATR), TGA and elemental analysis techniques. The FTIR spectra attributed that the characteristic vibration bands of isocyanate units of **Cel-iso** (2272 cm^{-1}) and **Chi-iso** (2263 cm^{-1}) were disappeared when they were treated with the calix[4]arene-dihydrazide **3** in order to afford their corresponding biopolymers. Moreover, the FTIR spectra of **Cel-Calix** and **Chi-Calix** confirmed the existence of carbonyl groups in which a characteristic vibration bands of C=O units were obtained at 1698 and 1651 cm^{-1} , respectively. Findings address the confirmation of the conversion of isocyanate subunits to amide moieties. The elemental analysis of **Cel-Calix** and **Chi-Calix** also contributed to assess their structure. As seen in Table 1, elemental analysis data in which 9.24 and 3.41 % nitrogen contents were found respectively for **Cel-Calix** and **Chi-Calix** showed the consistency with the expected formulas.



Scheme 1. Preparation of two calix[4]arene-functionalized biopolymers (**Cel-Calix** and **Chi-Calix**). Reaction conditions: (i) Chitosan, 70°C; (ii) Cellulose, 70°C; (iii) K_2CO_3 , methylbromoacetate, reflux; (iv) Hydrazine, r.t.; (v) **Chi-iso**, 70°C; (vi) **Cel-iso**, 70°C.

Table 1. Elemental analysis for two calix[4]arene-functionalized biopolymers (**Cel-Calix** and **Chi-Calix**)

	C(%)	H(%)	N(%)
Cel-Calix	45.71	6.81	3.41
Chi-Calix	43.12	7.33	9.24

Further evidence for calix[4]arene-functionalized biopolymers came from their thermal behaviors. The experimental results are illustrated in **Figure 1** imply that **Chi-Calix** and **Cel-Calix** exhibit high thermochemical stability, as evidenced by the 4.2 % and a minor weight-loss respectively at 50-200 °C, which are probably because of the loss of water and the external solvent molecules. Upon heating, the main weight loss of **Chi-Calix** was shown to be 62.3 % between the temperature of 200 and 525 °C, while a 83.4 % for the decomposition of both calix[4]arene and biopolymer groups of **Cel-Calix** were observed within a broad temperature of 274 and 525 °C.

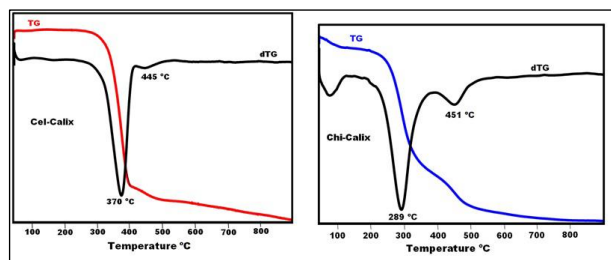


Figure 1. TGs and dTG curves of **Cel-Calix** and **Chi-Calix**.

3.2. Anion Extraction Studies

3.2.1 Dichromate anion extraction behaviors of calix[4]arene-functionalized biopolymers

The dimeric HCr_2O_7^- form of oxyanion species of dichromate ion becomes dominant when the pH value below of 6 in the solution [40]. So, this form of dichromate anion is capable to build hydrogen bonds with the ionophores. In view of the fact that, two calix[4]arene-functionalized biopolymers bearing amide moieties, which are able to perform the sites for hydrogen bonding as well as interaction with sodium cation [41], were employed as potential ionophores towards the sodium salt of dichromate at the pH ranges between 2.5 and 4.5.

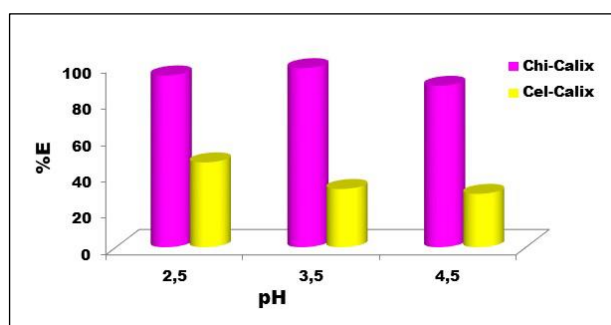


Figure 2. Extraction percentages of HCr_2O_7^- anion by **Chi-Calix** and **Cel-Calix**. Solid phase= 25mg; aqueous phase, $\text{Na}_2\text{Cr}_2\text{O}_7= 1.0 \times 10^{-4}\text{ M}$ at 25°C for 1h.

The dichromate binding efficiencies of two calix[4]arene-functionalized biopolymers were carried out using a solid-liquid extraction procedure. As illustrated in **Figure 2**, these ionophores are capable for the removal of dichromate anion from aqueous solution at the pH ranges between 2.5 and 4.5. Considering their rigid structures and containing amide moiety, which is

able to construct hydrogen bonding and interact with sodium cation, results were not a surprise. However, the maximum percentages of HCr_2O_7^- anion by **Chi-Calix** and **Cel-Calix** were 46.6 and 98.4%, respectively. This result indicates that **Chi-Calix** exhibited higher extraction efficacy than **Cel-Calix** at low pHs (2.5-4.5).

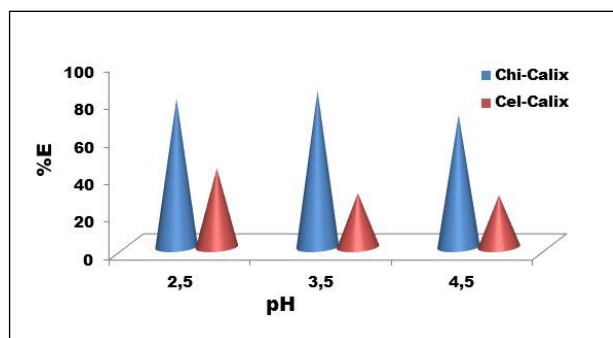


Figure 3. Percentage extraction of sodium cation by calix[4]arene-functionalized biopolymers at various pHs. Solid-phase, 25 mg **Chi-Calix**; aqueous-phase, $\text{Na}_2\text{Cr}_2\text{O}_7 = 1.0 \times 10^{-4}$ M at 25°C for 1h.

To investigate the role of sodium cation on dichromate anion extraction by calixarene-functionalized biopolymers, the levels of residual sodium cation in the aqueous solution after extraction were estimated by atomic absorption. The results are shown in **Figure 3** indicate that the pronounced sodium extraction attributes an ion-pair mechanism in which the amide moieties of **Chi-Calix** and **Cel-Calix** interact with sodium cation.

3.2.2 Arsenate anion extraction behaviors of calix[4]arene-functionalized biopolymers

It is well known that the pH values of the solution affect the formation of arsenate species. For instance, the H_2AsO_4^- form from the arsenate species occurs in the solution at a pH range of 3 and 6, while a higher pH value (8-11) in the solution leads the divalent HASO_4^{2-} form. The H_2AsO_4^- and HASO_4^{2-} forms among the arsenate species are potential to construct the hydrogen bonding along with their electrostatic attraction features to the host molecules. Therefore, two calix[4]arene-functionalized biopolymers bearing amide moieties were employed as potential ionophores towards the sodium salt of arsenate at pH 5-8.

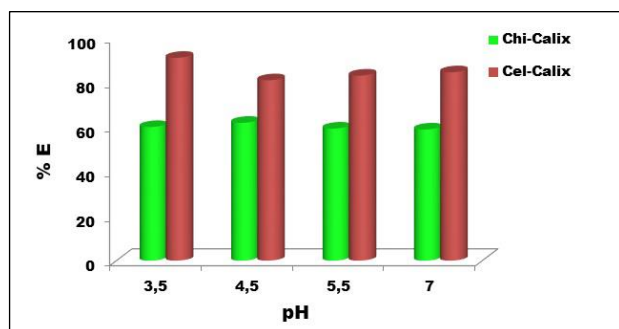


Figure 4. Extraction percentages of H_2AsO_4^- anion with **Chi-Calix** and **Cel-Calix** at pH 3.5-7.0. (ionophore = 25 mg, aqueous phase, $\text{Na}_2\text{HAsO}_4 = 1.0 \times 10^{-4}$ M (10 mL) at rt for 1 hour).

To assess the extraction binding characteristics of **Chi-Calix** and **Cel-Calix** towards arsenate anion at various

pHs, a solid-liquid extraction procedure was performed. Typically, 25 mg of calixarene-functionalized biopolymer (**Chi-Calix** or **Cel-Calix**) and 10 mL aqueous solution of Na_2HAsO_4 (1.0×10^{-4} M) interacted at 175 rpm and 25 °C for 1 h. The percentages of the removed arsenate from aqueous solution were estimated using UV-vis spectrometer at 610 nm according to the literatures [2,39]. The extraction results of **Chi-Calix** and **Cel-Calix** in **Figure 4** indicate that both calix[4]arene-functionalized biopolymers provide effective extraction properties towards arsenate ions at pH 3.5-7.0. However, it was found that **Cel-Calix** exhibited higher extraction efficiencies than **Chi-Calix** at all pH values. The maximum extraction percentage of **Cel-Calix** towards H_2AsO_4^- ion was 91.1% at pH 3.5, while a maximum extraction in 61.9% at pH 4.5 was obtained in the presence of **Chi-Calix**. The lowest values as 81 and 58.9% were received for **Cel-Calix** and **Chi-Calix**, respectively. Obtained results are in compatible with the data received from dichromate extraction by two calix[4]arene-biopolymers. Hence, findings clearly addresses that H_2AsO_4^- anion with sodium cation was effective extracted as an ion-pair from aqueous solutions in the presence of ionophores (**Chi-Calix** and **Cel-Calix**). The proposed interaction of **Cel-Calix** with these anions is given in **Fig. 5**.

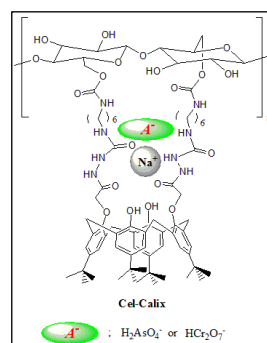


Figure 5. The proposed complexation phenomena of **Cel-Calix** with sodium salts of dichromate and arsenate ions.

4. CONCLUSION

In summary, two calix[4]arene-functionalized biopolymers (**Cel-Calix** and **Chi-Calix**) have been successfully prepared and characterized. Furthermore, the extraction capabilities of two calix[4]arene-functionalized biopolymers were evaluated with regard to arsenate and dichromate anions that are toxic and highly danger for human beings. The results showed that both calixarene-functionalized biopolymers exhibited considerable extraction properties for the removal of H_2AsO_4^- and HCr_2O_7^- ions at different pHs. Intriguingly, **Chi-Calix** showed higher affinity towards dichromate ion, while maximum extraction percentages for arsenate ion were obtained by **Cel-Calix**. Besides, the experimental results reflected that the extraction efficacies of calixarene-functionalized biopolymer against both anions were not depended on the pHs. Indeed, sodium cation detection experiments into residual aqueous solutions clearly illustrate that the ionophores (**Chi-Calix** and **Cel-Calix**) have an affinity

towards sodium ion, leading an efficient extraction of oxyanions as an ion-pair form from aqueous solutions.

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