

Preparation, characterization of cellulose-grafted with calix[4]arene polymers for the adsorption of heavy metals and dichromate anions

Mustafa Tabakci^{a,*}, Serkan Erdemir^b, Mustafa Yilmaz^b

^a Selçuk University, Department of Chemical Engineering, 42075 Konya, Turkey

^b Selçuk University, Department of Chemistry, 42031 Konya, Turkey

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Abstract

In this paper, the adsorbents were prepared from cellulose-grafted with calix[4]arene polymers (CGC[4]P-1 and CGC[4]P-2) and their sorption properties studied. The polymers were characterized by Fourier transform infrared spectroscopy, elemental analysis, thermal gravimetric analysis and scanning electron microscopy. They were then used to evaluate the sorption properties of some heavy metal cations (Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Hg^{2+} and Pb^{2+}) and dichromate anions ($\text{Cr}_2\text{O}_7^{2-}/\text{HCr}_2\text{O}_7^-$). Results showed that CGC[4]P-2 was a good sorbent for heavy metal cations while CGC[4]P-1 was ineffective. In the studies of dichromate anion sorption, it was observed that CGC[4]P-2 was a more highly effective sorbent at pH 1.5 than was CGC[4]P-1.

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1. Introduction

Heavy metal ion removal from waters has been the subject of extensive technological research and recovering processes [1]. Several different types of methods have been studied for the treatment of aqueous streams contaminated with heavy metals, among them polymers [2–5], amorphous silica [6–9], clays [10–14] and zeolites [15–17]. Nevertheless these materials have shown several problems like low mechanical and thermal stability, weak chemical union with the metals, poor removal efficiency, high cost, *etc.* These factors have led the scientific community to develop new techniques to remove heavy metals from the environment. The majority of the effective and economic methods are based on adsorption process, so the synthesis of adsorbents for the removal of toxic heavy metal ions from wastewater is a continuing research objective of environmental pollution control processes.

Chromate and dichromate anions are important because of their high toxicity and because of their presence in soils and

waters. In designing complexants for these particular guest anions a number of structural features can be incorporated into the host molecule that may be important in achieving selective binding. For such a molecule to be effective as a host it is necessary that its structural features are compatible with those of the guest anion. The chromate and dichromate (CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$) ions are dianions with oxide functionalities at their periphery. Since the metal center does not bind to additional ligands there is no advantage in designing a host that can act as a complexant to it. Nevertheless, since the periphery of the anions has oxide moieties; these are potential sites for hydrogen bonding to the host molecule [18–20].

Cellulose is one of the most abundant organic materials that can be easily obtained in nature. Various researches were focused on preparing all kinds of cellulose derivatives with good sorption properties towards transition metals and heavy metal ions, which could be applied as chelating resins in metal cation separation and extraction of water, *etc.* [21–25]. On the other hand, calixarenes (Fig. 1), a family of cavity-shaped cyclic molecules obtained from formaldehyde and *para*-substituted phenols *via* ring-closing condensation under alkaline conditions, have also attracted much attention. They have demonstrated outstanding complex ability towards ions, organic molecules, *etc.*, and are

* Corresponding author. Tel.: +90 332 2232142; fax: +90 332 2410635.
E-mail address: mtabakci@selcuk.edu.tr (M. Tabakci).

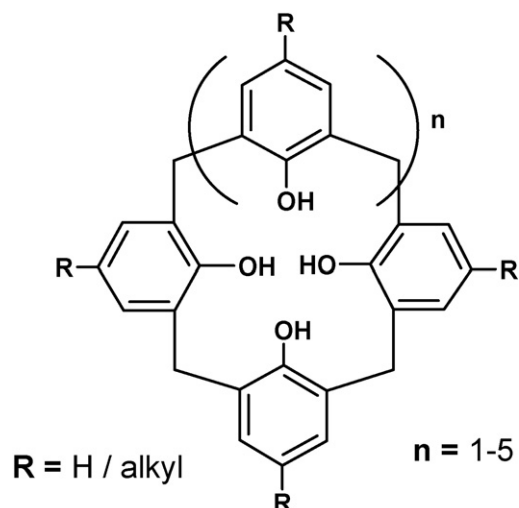


Fig. 1. The general molecular structures of calix n arenes.

considered the third best host molecules, after crown ethers and cyclodextrins. Thus, it is interesting to see what happens when these two kinds of molecules are combined. To the best of our knowledge, no report concerning this topic has been published to date. This paper firstly reports the preparation, characterization, and sorption properties towards some selected heavy metal cations (Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Hg^{2+} and Pb^{2+}) and dichromate anions (HCr_2O_7^- or $\text{Cr}_2\text{O}_7^{2-}$) of cellulose-grafted calix[4]arene polymers.

2. Experimental

2.1. Materials

High-purity cellulose was purchased from Aldrich (no.: 435236) and used as a support material. In the synthesis of monomeric calix[4]arenes, analytical thin layer chromatography was performed on precoated silica gel plates (SiO_2 , Merck PF₂₅₄) for the monitoring of reactions. In order to purification of compounds, silica gel 60 (Merck, particle size 0.040–0.063 mm, 230–240 mesh) was used for preparative column chromatography. Generally, solvents were dried by storing them over molecular sieves (Aldrich; 4 Å, 8–12 mesh). Acetone, CH_2Cl_2 and MeOH was distilled from CaSO_4 , CaCl_2 and over Mg, respectively. Tetrahydrofuran (BDH) and toluene were dried by refluxing over sodium/benzophenone and CaH_2 , fractionally distilled, respectively and then stored over molecular sieves. NaH was used as an 80% dispersion in oil and washed twice with *n*-hexane before use. All the chemicals were purchased from Merck or Aldrich. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system. Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Hg^{2+} and Pb^{2+} picrates were prepared according to previously studies [19].

2.2. Instrumentation

IR spectra were recorded on a Perkin-Elmer 1605 FTIR spectrometer as KBr pellets. UV–vis spectra were obtained on a

Shimadzu 160A UV–vis recording spectrophotometer. Sodium cation determinations were made on a JENWAY PFP7 flame photometer. Elemental analyses were performed on a Leco CHNS-932 analyzer. SEM images were taken by a JSM-5600 scanning electron microscope. TG-DTG thermograms were taken by a Perkin-Elmer Pyris 1 thermogravimetric analyzer. The sample weight was almost 10.0 mg. Analysis was performed from 16 to 900 °C at a heating rate of 20 °C/min in a nitrogen atmosphere with a gas flow rate of 40 mL/min.

2.3. Synthesis

Compounds 1 and 4–7 were prepared according to known previous procedures [19,26]. The preparation of compounds 2 and 3, and cellulose-grafted with calix[4]arene polymers (CGC[4]P-1 and CGC[4]P-2) employed in this work, as illustrated in Figs. 2 and 3, have been prepared as follows.

2.3.1. Modification of the Cell/Ti-OH surface with organosilicones

Cell/Ti-OH (4 g) was suspended in 40 mL of dry toluene and stirred for 30 min at room temperature. To this suspension organosilicones 3-glycidoxypropyl triethoxysilane (GPTES) (2.9 mL) or 3-aminopropyl triethoxysilane (APTES) (3.1 mL) was added and stirred at 90 °C for 6 h under a nitrogen atmosphere. After the addition of a little distilled water, the reactant was stirred continuously at 90 °C for 1 h under a nitrogen atmosphere. The residue was filtered and extracted with alcohol in a Soxhlet apparatus for 4 h and then dried at 80 °C under reduced pressure to a constant weight to give compounds 2 and 3 as a light-yellow powder.

2.3.2. Grafting of compound 2 with *p*-tert-butylcalix[4]arene (CGC[4]P-1)

A mixture of 0.5 g *p*-tert-butylcalix[4]arene and 0.02 g NaH in 50 mL anhydrous toluene was heated with stirring under an inert atmosphere at 80 °C for 30 min. Subsequently, 1.0 g 2 and 0.27 g tetrabutylammonium bromide (TBAB) were added to the suspension and heated immediately to reflux for 24 h. The bonded-material was filtered and washed in sequence with toluene, dichloromethane, acetone, doubly distilled water. After dried at 120 °C, CGC[4]P-1 (1.0 g) was obtained.

2.3.3. Grafting of compounds 3 with 6 (CGC[4]P-2)

Compound 3 (1.0 g) was added to a solution of 6 (0.5 g) dissolved in dry THF (50 mL). The mixture was stirred and refluxed for 5 days and then filtered and in sequence with toluene, dichloromethane, acetone, doubly distilled water to give CGC[4]P-2 (1.1 g).

2.4. Sorption studies

Cellulose-grafted calix[4]arene polymer (0.025 g (*W*)) was shaken with 10 mL of aqueous solution containing 10 mL (*V*) of a metal picrate solution or a NaCr_2O_7 solution with known concentration (C_i) at 175 rpm in a 50 mL-closed glass flask at 25 °C for 1 h and filtered off. The concentration of the picrate

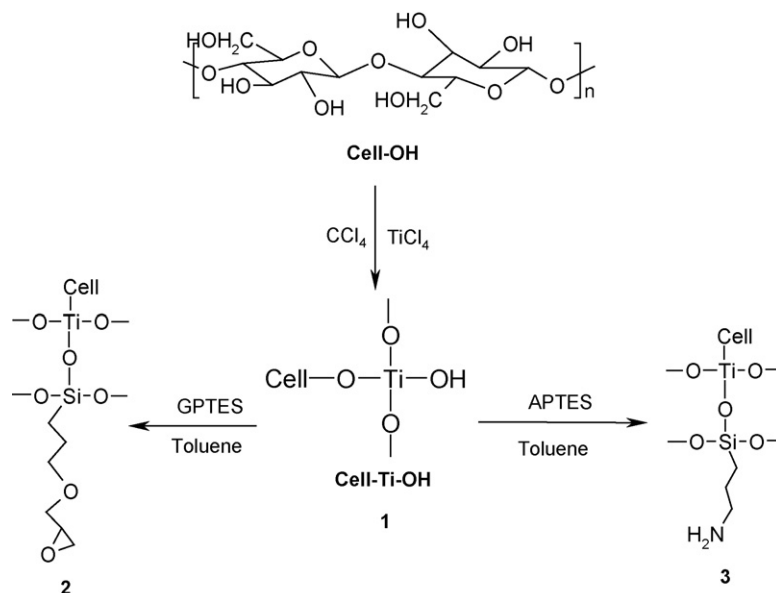


Fig. 2. The synthetic route of preparation of cellulose derivatives (2 and 3).

or dichromate ion remaining (C_e) in aqueous phase after the sorption was then determined spectrophotometrically [19].

The amount of metal cation sorbed by calixarene polymer (q) was calculated as

$$q = \frac{(C_i - C_e)V}{nW(\text{mmol/g})} \quad (1)$$

where n is valence of metal ion.

The percent sorption of ion ($S\%$) has been calculated as

$$S\% = \left[\frac{C_i - C_e}{C_i} \right] \times 100 \quad (2)$$

The distribution coefficients (K_d) were calculated as

$$K_d = \frac{\text{amount of ion sorbed by resin/g of dry resin}}{\text{amount of metal remaining in solution/mL of solution in contact}} \quad (3)$$

3. Results and discussion

3.1. Synthesis

Calixarenes have been widely used as three-dimensional building blocks for the construction of artificial molecular receptors capable of recognizing neutral molecules, cations and more recently anions [6–8]. Thus, having chosen the *p*-tert-butylcalix[4]arene as the basis for derivatives, synthetic way had to be developed to enable the derivatization of the molecule. Such synthetic routes were shown in Figs. 2 and 3. The syntheses of compounds 1 and 4–7 were based on the previously published procedures [19,26], while the reaction steps leading to cellulose derivatives 2 and 3, cellulose-grafted with calix[4]arene polymers CGC[4]P-1 and CGC[4]P-2 (Figs. 1 and 2) were reported for the first time. The modification of Cell/Ti-OH with organosilicones GPTES or APTES in dry toluene was performed to give 2 and 3, respectively. The elemental analysis results of 2 and

3 given Table 1 confirmed that the modification of native cellulose was accomplished. The cellulose-grafted with calix[4]arene polymer-1 (CGC[4]P-1) was obtained from the grafting of cellulose derivative 2 with *p*-tert-butylcalix[4]arene in the presence of TBAB and NaH in toluene. Also the cellulose-grafted calix[4]arene polymer-2 (CGC[4]P-2) was prepared from the grafting of cellulose derivative 3 with compound 6 in dry THF via aminolysis reaction [27]. FTIR spectra of 2, 3, CGC[4]P-1 and CGC[4]P-1 were demonstrated in Fig. 4. Comparing with IR spectra of them showed distinct absorption peaks especially for phenyl groups, which indicated that the cellulose derivatives had been grafted with calix[4]arenes successfully. Also the ele-

mental analyses of CGC[4]P-1 and CGC[4]P-1 confirmed that the grafting of cellulose derivatives with calix[4]arenes.

Thermogravimetric analysis (TGA) of CGC[4]P-1 and CGC[4]P-2 was determined and their TG and DTG curves presented in Figs. 5 and 6, respectively. As seen in Fig. 5, the weight-loss of CGC[4]P-1 occurred at four regions explained in Table 2. At range of this temperature the remaining of the

Table 1
Results of elemental analysis for 2, 3, CGC[4]P-1 and CGC[4]P-2

	%C	%H	%N	Bonded amount (mmol/g) ^a
2	39.18	4.62	–	–
3	36.86	4.60	1.7	–
CGC[4]P-1	42.48	4.88	–	0.640
CGC[4]P-2	32.57	3.56	1.86	0.440

^a Calculated according to the C or N content.

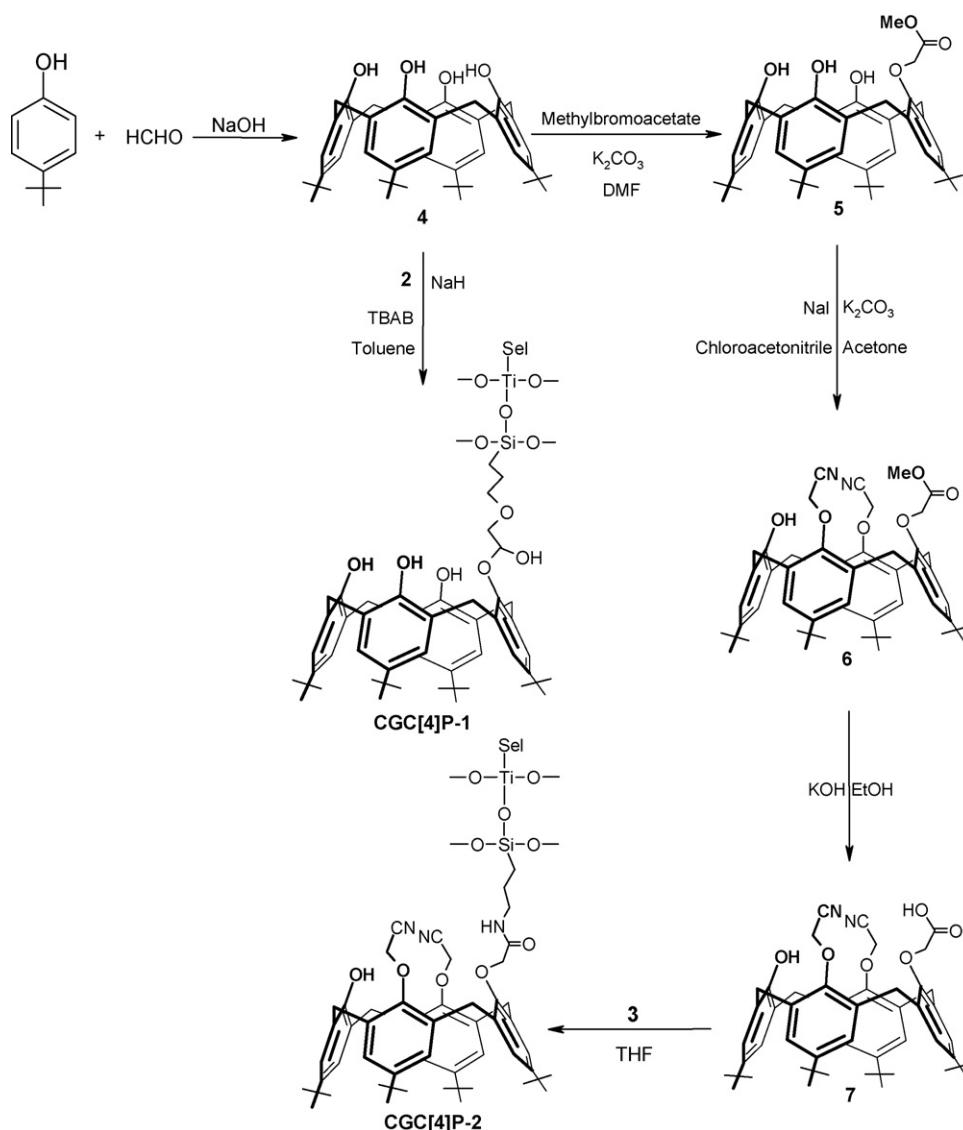


Fig. 3. The synthetic route of preparation of cellulose-grafted with calix[4]arene polymers (CGC[4]P-1 and CGC[4]P-2).

29.4% of material without decomposed showed the presence of Si–O– and Ti–O– units. Fig. 6 displayed that the weight-loss of CGC[4]P-2 occurred at three regions explained in Table 3. At range of this temperature the remaining of the 13.1% of mate-

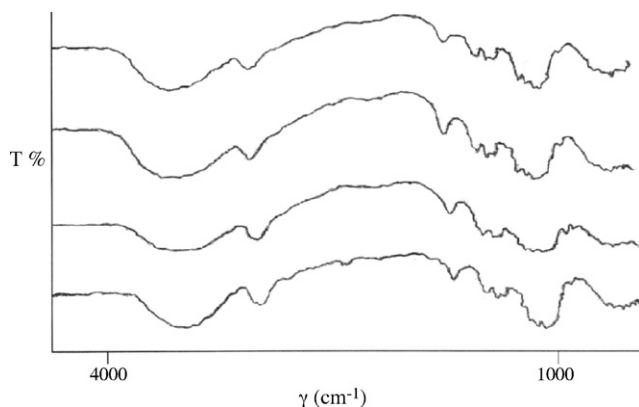


Fig. 4. FTIR spectra of 2, CGC[4]P-1, 3, and CGC[4]P-2, respectively, from above.

rial without decomposed indicated the presence of Si–O– and Ti–O– units. From these data, it is revealed that CGC[4]P-1 and CGC[4]P-2 are strong grafting polymers to heat although their preparation process requires slightly a long synthetic route leading to cost. Moreover, the SEM images of CGC[4]P-2 were taken to evaluate its surface morphology and displayed in Fig. 7. According to our knowledge the image of cellulose

Table 2
Thermogravimetric analysis results of CGC[4]P-1^{a,b}

Region (°C)	Weight-loss (%)	Assignment
16–160	3.6	Moisture
160–425	52.2	Calix[4]arene and cellulose units
425–501	7.4	Propoxy units
501–900	7.2	Unreacted ethoxy units

^a The sample weight was almost 10 mg.

^b Analysis was performed from 16 to 900 °C at a heating rate of 20 °C/min in a nitrogen atmosphere with a gas flow rate of 40 mL/min.

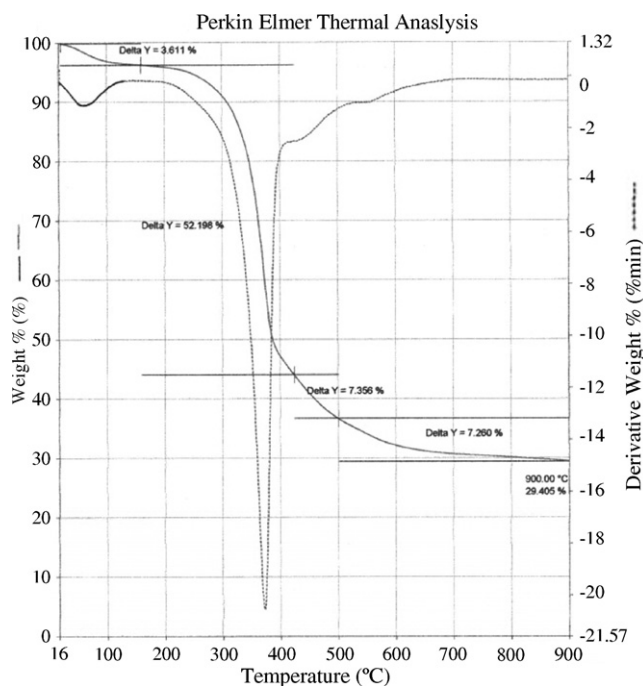


Fig. 5. TG and DTG curves of CGC[4]P-1.

(not displayed here) exhibits distinct flake and lumpish structure because of the strong intra-molecular hydrogen bonds. However, the porous SEM image of CGC[4]P-2 indicated that the adding calixarene units into cellulose units hampered the formation of the intra-molecular hydrogen bonds. This kind of loose and porous structures was favorable for producing good sorption properties.

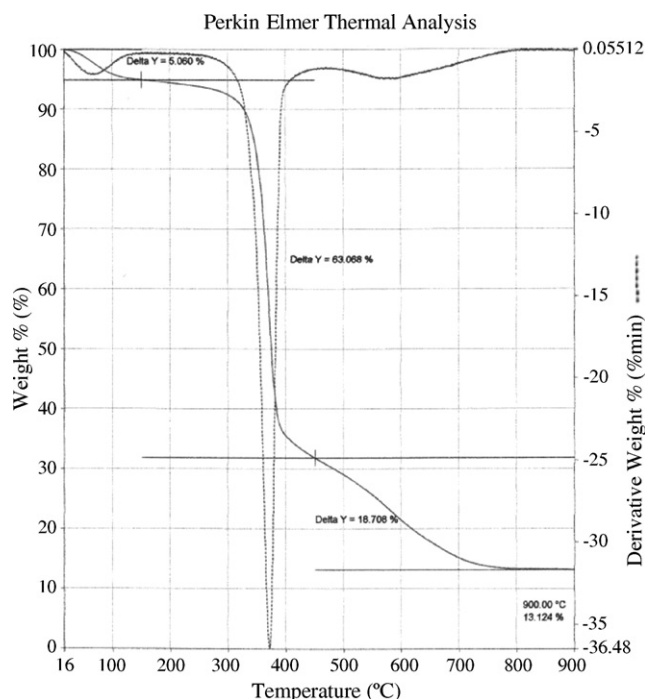


Fig. 6. TG and DTG curves of CGC[4]P-2.

Table 3
Thermogravimetric analysis results of CGC[4]P-2^{a,b}

Region (°C)	Weight-loss (%)	Assignment
16–150	5.1	Moisture
150–458	63.1	Aminopropyl, calix[4]arene and cellulose units
458–900	18.7	Unreacted ethoxy units

^a The sample weight was almost 10 mg.

^b Analysis was performed from 16 to 900 °C at a heating rate of 20 °C/min in a nitrogen atmosphere with a gas flow rate of 40 mL/min.

3.2. Evaluation of sorption capabilities

In this study it was also aimed the evaluation of sorption abilities by cellulose-grafted with calix[4]arene polymers (CGC[4]P-1 and CGC[4]P-2) toward some selected heavy metal cations (Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Hg^{2+} and Pb^{2+}) and dichromate anions ($\text{Cr}_2\text{O}_7^{2-}/\text{HCr}_2\text{O}_7^-$).

3.2.1. Sorption of heavy metal cations

We performed solid–liquid sorption studies of some heavy metal cations (Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Hg^{2+} and Pb^{2+}) by using CGC[4]P-1 and CGC[4]P-2 as sorbents. The sorption capac-

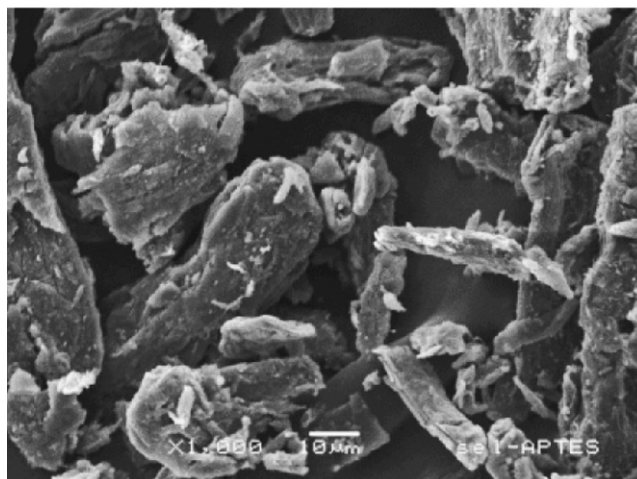
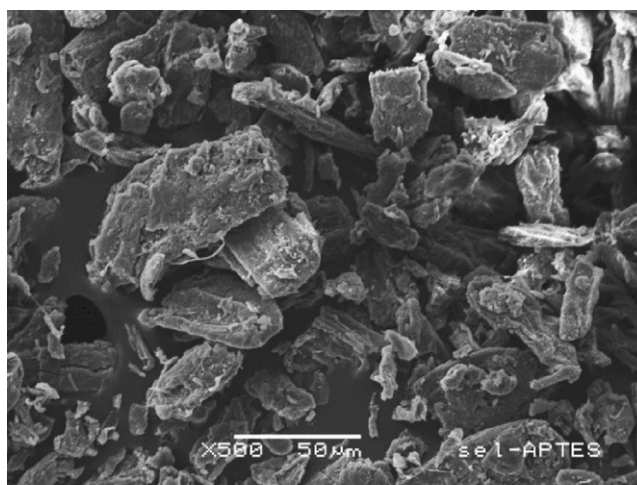


Fig. 7. SEM micrographs of CGC[4]P-2, 50 μm (above); 10 μm (below).

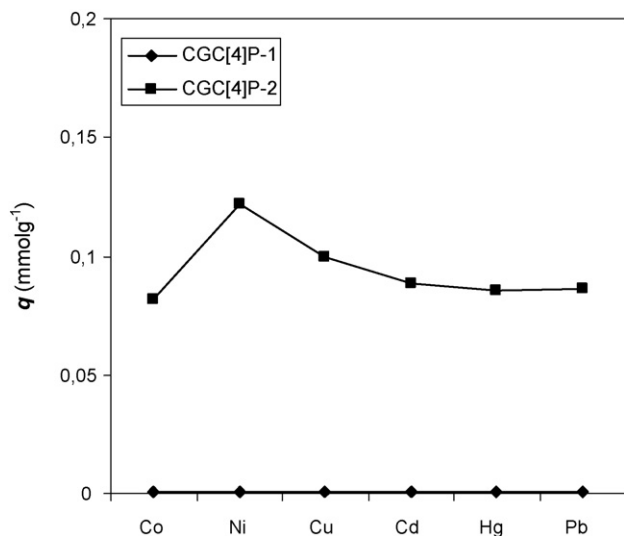


Fig. 8. Sorption capacities (q) of CGC[4]P-1 and CGC[4]P-2 towards heavy metal cations (25 °C, 1 h, $C_0 = 0.02 \text{ mmol L}^{-1}$).

ities, sorption percentages and distribution coefficients were calculated equations (1)–(3), respectively, and given in Fig. 8, Tables 4 and 5, respectively. These data have been obtained by using a 0.025 g of the polymers for sorption of metal cations from aqueous solution. The equilibrium concentration of picrate in the aqueous phase has been determined spectrophotometrically [19].

From the results, it was observed that CGC[4]P-2 was an effective sorbent, while CGC[4]P-1 did not display any remarkable sorption for heavy metal. The sequence of sorption efficiency of CGC[4]P-2 for heavy metal cations was $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+} > \text{Hg}^{2+} > \text{Co}^{2+}$. From our previous works and various studies [18–20], it was deduced that amide

Table 4
Sorption percentages of heavy metal cations by CGC[4]P-1 and CGC[4]P-2^{a,b}

	Sorbed metal cations					
	Co^{2+}	Ni^{2+}	Cu^{2+}	Cd^{2+}	Hg^{2+}	Pb^{2+}
CGC[4]P-1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
CGC[4]P-2	20.4	30.5	25.0	22.1	21.4	21.5

^a Solid phase, sorbent = 25 mg polymer; aqueous phase, metal picrate = $2.0 \times 10^{-5} \text{ M}$ at 25 °C for 1 h.

^b Averages and standard deviations calculated for data obtained from three independent sorption experiments.

Table 5
Distribution coefficients for heavy metal cations (K_d) by CGC[4]P-2^a

Sorbed metal cations	K_d
Co^{2+}	51
Ni^{2+}	88
Cu^{2+}	67
Cd^{2+}	57
Hg^{2+}	54
Pb^{2+}	55

^a Solid phase, sorbent = 25 mg polymer; aqueous phase, metal picrate = $2.0 \times 10^{-5} \text{ M}$ at 25 °C for 1 h.

derivatized calixarenes are effective sorbents for these cations. Because $\text{NHC}=\text{O}$ group is preferable to complex the more polarizable transition metal ions especially Pb, Hg, Cd and Cu due to cation- π interactions. The phenomenon may also reflect the “principle of hard and soft acids and bases” introduced by Pearson [28]. Furthermore, the grafting groups also may help to the sorption of dichromate anions supplying conformational stability to polymer in sorption process along their partial interactions with heavy metal cations. Consequently, it was clearly found out that grafting of cellulose with 6 was useful approach for heavy metal sorption.

3.2.2. Sorption of dichromate anions

We also examined the sorption properties of CGC[4]P-1 and CGC[4]P-2 for dichromate anions at the range of pH 1.5–4.5. The sorption percentages and distribution coefficients were calculated (Eqs. (2) and (3)) and given in Tables 6 and 7, respectively. These data have been obtained by using a 0.025 g of the polymers for sorption of dichromate anions from aqueous solution. The equilibrium concentration of dichromate in the aqueous phase has been determined spectrophotometrically [19].

The sorption data revealed that CGC[4]P-1 and CGC[4]P-2 were effective sorbents and the sorption efficiency of CGC[4]P-2 was highly more than CGC[4]P-1 for dichromate anions at pH 1.5. However, the sorption efficiencies of sorbents decreased with increasing at the pH of solution. From this it was clearly understood that optimum sorption pH value by these sorbents was 1.5. The sorption abilities of CGC[4]P-1 and CGC[4]P-2 can be attributed to these polymers possess some atoms such as oxygen and nitrogen lead to make hydrogen bond with dichromate anion. One reason of high sorption ability of CGC[4]P-2 may be that it contains amide and nitrile moieties lead to interact with sodium cations in aqueous solution. Because, from the literature

Table 6
Sorption percentages of dichromate anion by CGC[4]P-1 and CGC[4]P-2^{a,b}

	pH			
	1.5	2.5	3.5	4.5
CGC[4]P-1	32.3	13.9	<0.1	<0.1
CGC[4]P-2	91.1	66.6	33.9	2.1

^a Solid phase, sorbent = 25 mg polymer; aqueous phase, $\text{Na}_2\text{Cr}_2\text{O}_7 = 1.0 \times 10^{-4} \text{ M}$ at 25 °C for 1 h.

^b Averages and standard deviations calculated for data obtained from three independent sorption experiments.

Table 7
Distribution coefficients for dichromate anions (K_d) by CGC[4]P-1 and CGC[4]P-2^a

	pH			
	1.5	2.5	3.5	4.5
CGC[4]P-1	95	32	–	–
CGC[4]P-2	2047	399	103	4

^a Solid phase, sorbent = 25 mg sorbent; aqueous phase, $\text{Na}_2\text{Cr}_2\text{O}_7 = 1.0 \times 10^{-4} \text{ M}$ at 25 °C for 1 h.

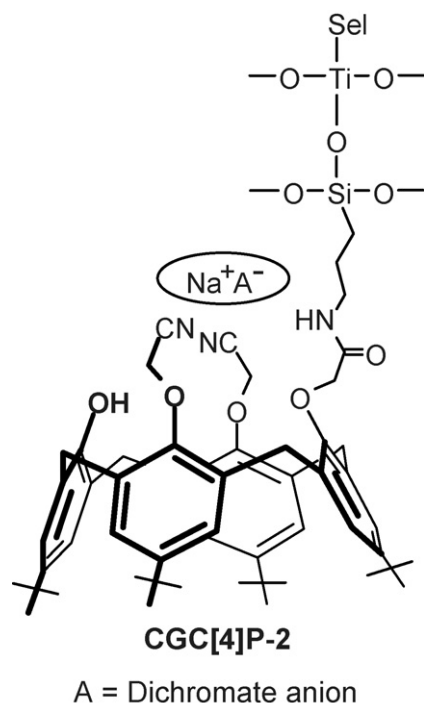


Fig. 9. The proposed interactions of CGC[4]P-2 with Na^+ cation and dichromate anions.

[18–20] it is well known that the calixarenes with amide and nitrile functionalities are effective sorbents for sodium cation. Therefore, in order to seek the sorption abilities of CGC[4]P-2 toward sodium cation, it was also performed sodium sorption studies under same conditions with that of dichromate anions. The results demonstrated that CGC[4]P-2 was an excellent sorbent for sodium cation. Thus the sorption of dichromate anion realized with together sodium cation as shown in Fig. 9 by CGC[4]P-2. Another reason may be that unreacted amino moieties of C[4]BP-2 remaining from 3 can be protonated. This also implies decreasing in sorption efficiency of CGC[4]P-2 with increasing at the pH of solution due to the fact that protonation decrease under this condition. One another reason can be that amide oxygen can be protonated [29] at low pH although this is more difficult as to amino groups. Furthermore, the grafting groups also may help to the sorption of dichromate anions supplying conformational stability to polymer in sorption process along their partial interactions with dichromate anions. Thus, these causes cooperatively can contribute to sorption efficiencies of CGC[4]P-2. As a result it revealed that CGC[4]P-1 and CGC[4]P-2 were useful sorbents especially CGC[4]P-2 for dichromate anions at pH 1.5. This also indicated that the grafting of a calix[4]arene based compound onto a cellulose-based support was a good approach.

4. Conclusions

The preparation and characterization of cellulose-grafted with calix[4]arene polymers was achieved. The sorption studies of some heavy metal cations and dichromate anions were performed by CGC[4]P-1 and CGC[4]P-2 as sorbent materials.

From the sorption results of heavy metal cations it was revealed that CGC[4]P-2 exhibited excellent sorption properties while the CGC[4]P-1 could not be effective for these cations. As for the sorption studies of dichromate anions by CGC[4]P-1 and CGC[4]P-2, it was appeared that CGC[4]P-2 was more effective sorbent than CGC[4]P-1 at pH 1.5. Consequently, CGC[4]P-2 exhibited good sorption properties for both heavy metal cations and especially dichromate anions. After all, the grafting of a cellulose derivative with a calix[4]arene derivative became useful approach for heavy metal cations and dichromate anions removal from aqueous media by sorption.

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