

Immobilization of calix[6]arene bearing carboxylic acid and amide groups on aminopropyl silica gel and its sorption properties for Cr(VI)

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Abstract An aminopropyl silica gel-immobilized calix[6]arene (C[6]APS) containing both amide and acid moieties was prepared from *p-tert*-butylcalix[6]arene hexacarboxylate derivative and aminopropyl silica gel in the presence of *N,N'*-diisopropyl carbodiimide coupling reagent. C[6]APS was used to evaluate the sorption properties of Cr(VI) as a sorbent material. In sorption studies, it was observed that C[6]APS was highly effective at pH 1.5 for Cr(VI). The effect of parameters such as pH, sorbent dosage, contact time, initial Cr(VI) concentration and temperature on Cr(VI) sorption; the sorption isotherms were also studied. Maximum sorption capacity was obtained as 3.1 mg g^{-1} at pH 1.5 and $25 \text{ }^\circ\text{C}$ for 1 h and 10.4 mg L^{-1} initial Cr(VI) concentration. Thermodynamic parameters such as change in free energy, enthalpy, and entropy were also determined. In the isotherm studies, Langmuir and Freundlich isotherm models were applied and it was found that the experimental data confirmed to Freundlich isotherm model, and the batch sorption capacity of C[6]APS was calculated as 37.66 mg g^{-1} .

Keywords Calix[6]arene · Aminopropyl silica gel · Immobilization · Sorption · Chromium(VI)

Introduction

Chromium and its compounds are widely used in plating, leather tanning, dye, cement, and photography industries

producing large quantities of toxic pollutants [1]. Chromium can exist in the form of several oxidation states, however, only the trivalent and hexavalent forms are environmentally important [2]. Chromium(III) has been reported to be biologically essential to mammals as it maintains effective glucose, lipid, and protein metabolism. Chromium(VI) can be toxic as it can diffuse as $\text{Cr}_2\text{O}_7^{2-}$ or HCr_2O_7^- through cell membranes and oxidize biological molecules [3]. The maximum permissible levels of Cr(VI) in potable and industrial wastewater are 0.05 and 0.25 mg L^{-1} , respectively [2]. Due to its high solubility, Cr(VI) is very toxic to living organisms compared to Cr(III) [4]. When Cr(VI) is ingested beyond the maximum concentration, it can cause health disorders, such as vomiting and hemorrhage [5]. Therefore, treatment of wastewater containing Cr(VI) prior to discharge is essential. Conventional techniques for removing of metal ions from wastewater include chemical precipitation, membrane separation, reverse osmosis, evaporation, and electrochemical treatment. However the effectiveness of these methods for removing at low concentration is very low. Adsorption is one of the important alternatives available for such situation. The use of synthetic polymeric material as an adsorbent for the removal of Cr(VI) is reported in the literature [6, 7].

Calix[n]arenes (Fig. 1) are the third major class of supramolecular host systems along with the crown ethers and the cyclodextrins. Their facile preparation and relative simplicity of chemical modification have produced increased interest in the host-guest chemistry over the last few years. The ion binding properties of these molecules appear to be highly dependent upon the nature, number of donor groups, and the conformation of the calix[n]arene moiety [8, 9].

According to our knowledge to immobilize these compounds onto a polymeric support is very useful approach

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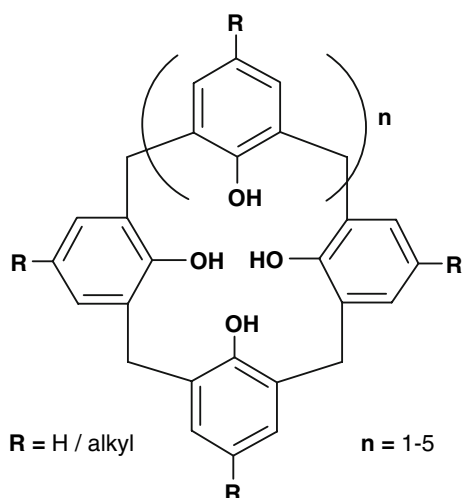


Fig. 1 The general molecular structures of calix[n]arenes

for the ion binding and/or sorption due to their rigid structures [10–13]. However, among these it was known that calixarenes bearing amide and/or carboxylic acid moieties were very effective materials for ions due to capability to form hydrogen bonding. Therefore, an aminopropyl silica gel-immobilized polymer with calix[6]arene (C[6]APS) containing both amide and acid functionalities was prepared and used as a sorbent for the batch sorption of dichromate anions ($\text{Cr}_2\text{O}_7^{2-}/\text{HCr}_2\text{O}_7^-$) included Cr(VI).

Experimental

Materials and equipments

High-purity aminopropyl silica gel (APS) and *N,N'*-diisopropyl carbodiimide (DIC) were purchased from Aldrich (No: 364258 and D125407, respectively) and used as support material and coupling reagent, respectively, for the immobilization of a *p-tert*-butylcalix[6]arene hexacarboxylate derivative. In the synthesis of monomeric calix[6]arenes, analytical thin layer chromatography was used for monitoring of the reactions on precoated silica gel plates (SiO_2 , Merck PF₂₅₄), while silica gel 60 (Merck, particle size 0.063–0.200 mm, 70–230 mesh) was used for preparative column chromatography. Generally, solvents were dried by storing them over molecular sieves (Aldrich; 4 Å, 8–12 Mesh). All chemicals were purchased from Merck or Aldrich. Aqueous solutions were prepared with deionized water (Millipore Milli-Q Plus water purification system).

IR spectra were recorded on a Perkin-Elmer 1605 FTIR spectrometer as KBr pellets. UV–Visible spectra were obtained on a Shimadzu 160A UV–visible recording spectrophotometer. Elemental analyses were performed on a Leco CHNS-932 analyzer.

Synthesis

Compounds 1–3 were prepared according to previously described procedures [14], while aminopropyl silica gel-immobilized calix[6]arene polymer (C[6]APS) employed in this work. The synthetic route for these compounds was illustrated in Scheme 1 and immobilization was performed as follows.

Immobilization of compound 3 onto APS (C[6]APS)

A mixture of compound 3 (1.0 g; 0.75 mmol), APS (1.5 g), coupling reagent (DIC; 0.13 mL; 0.85 mmol) and dichloromethane (300 mL) was stirred at room temperature for 3 days under nitrogen atmosphere. The cooled mixture was filtered and the solid was washed consecutively three times with dichloromethane, methanol, diluted HCl, and distilled water. The product was dried at 45 °C under vacuum for 3 h to give 1.85 g of C[6]APS, and kept in a desiccator before use.

Sorption studies

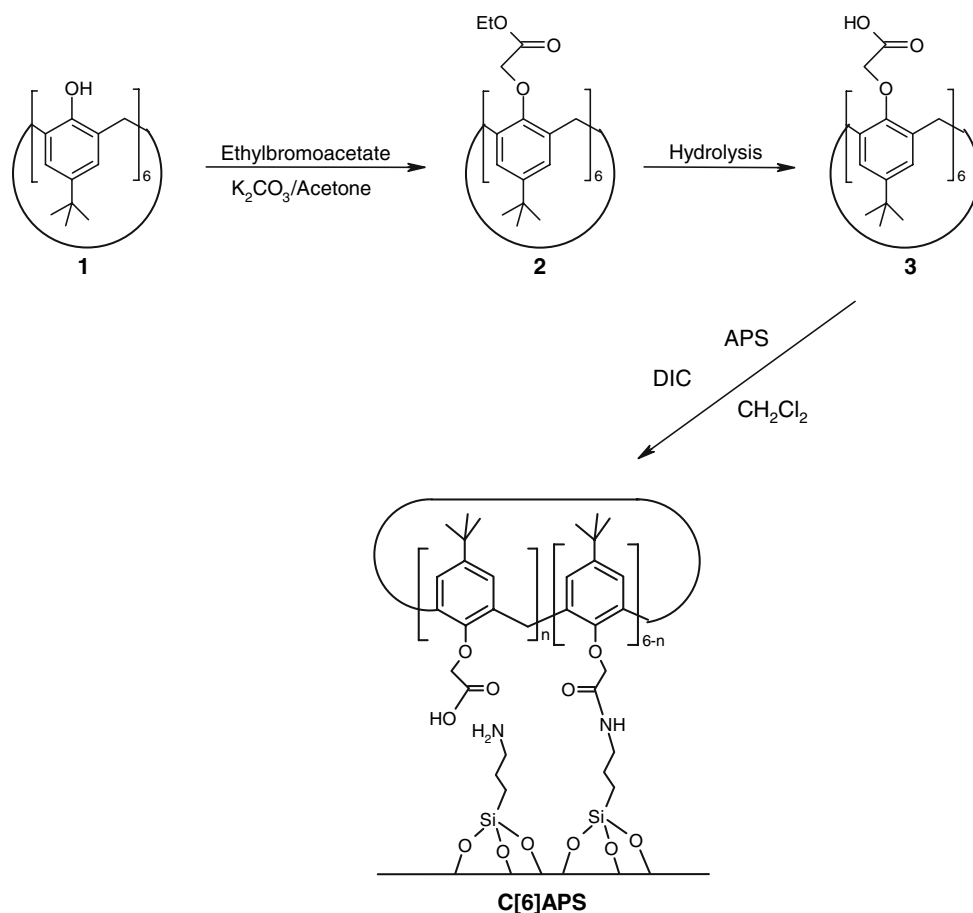
The solution of Cr(VI) was prepared in such a manner that the initial Cr(VI) concentration in sorption experiments was generally held at 10.4 mg L⁻¹. The pH values were measured with pH meter (Orion, 420A+). Generally, in batch sorption experiments, known weights of sorbents (0.025 g) were added to capped volumetric flasks each of which containing 10 mL of salt solution (10.4 mg L⁻¹ Cr(VI)) and shaken at 175 rpm, 25 °C and pH 1.5 in a temperature-controlled shaker (BINDER) for 1 h. After the sorption, samples were centrifuged and Cr(VI) in supernatants was determined spectrophotometrically. All tests were duplicated. The effect of pH was studied by adjusting the pH of Cr(VI) solutions using diluted HCl and NaOH solutions at 25 °C.

Results and discussion

Preparation and characterization of C[6]APS

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 [10–12]. Thus, having chosen the *p-tert*-butylcalix[6]arene as the basis for derivatives, synthetic scheme had to be developed to enable the derivatization of the molecule. Such synthetic routes were shown in Scheme 1. The syntheses of compounds 1–3 were based on the previously published procedures [14], while the reaction step leading to C[6]APS (Scheme 1) were

Scheme 1 The synthetic route of preparation of C[6]APS; $n = 3$ (suggested on the basis of elemental analysis)



reported for the first time. The hexaacid derivative of *p*-*tert*-butylcalix[6]arene **3** was obtained by hydrolysis of ester moieties of *p*-*tert*-butylcalix[6]arene (**2**). FTIR spectrums confirmed the hydrolysis of **2** due to appearing of carboxylic acid carbonyl band at $1,741\text{ cm}^{-1}$ in FTIR spectra of **3** and also disappearing of ester carbonyl band at $1,766\text{ cm}^{-1}$. From the FTIR results of C[6]APS, it was revealed that compound **3** was immobilized onto APS, due to appearing at $1,647\text{ cm}^{-1}$ and $1,100\text{ cm}^{-1}$ bands in its FTIR spectra corresponding to $NH-C=O$ and $-Si-O$, respectively. The band that at $1,753\text{ cm}^{-1}$ in FTIR spectra of C[6]APS was also an evidence for existence of carboxylic acid moieties on C[6]APS.

Elemental analysis data given in Table 1 showed that the loading of calix[6]arene moiety was 0.185 mmol g^{-1} on C[6]APS and it also led to consider us that the value of “ n ” would be corresponded to three unreacted carboxylate

groups. If it was that we could supposed that three amide units took place onto C[6]APS.

Fourier transform infrared spectroscopy (FTIR) investigations

The FTIR spectra before and after sorption of C[6]APS are shown in Fig. 2. The functional groups before and after adsorption on C[6]APS and the corresponding infrared absorption bands are shown in Table 2. As shown in Fig. 2 and Table 2, the spectra display a various absorption peaks, confirming structure of C[6]APS. These band shifts indicated that the bonded $-OH$ groups and/or $-NH$ stretching and carbonyl and/or carboxyl groups play a major role in Cr(VI) sorption on C[6]APS [15–17].

Effect of pH

The pH is one of the most important factors affecting the sorption process. The effect of pH on the sorption of Cr(VI) was studied as follows: 100 mL of Cr(VI) solution was taken in a flask. The pH of solution was adjusted by adding

Table 1 Results of elemental analysis for C[6]APS

	%C	%H	%N	Bonded amount (mmol g^{-1}) ^a
C[6]APS	21.42	2.56	1.57	0.185

^a Calculated according to the C and N content

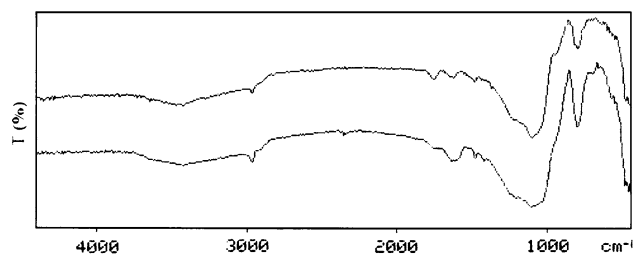


Fig. 2 FTIR spectrum of C[6]APS before and after sorption

dilute hydrochloric acid or sodium hydroxide. The concentration of Cr(VI) in this solution was then determined (initial concentration). Ten milliliters of Cr(VI) solution was taken in a conical flask and treated with 0.025 g of sorbent over the range of pH 1.5–7.5, and after equilibration, the final concentration of Cr(VI) was determined spectrophotometrically. The results show that the maximum uptake of Cr(VI) took place at pH 1.5 as 3.1 mg g^{-1} (Fig. 3).

In the present study, equilibrium solution pH was found to increase. The resultant equilibrium pH is shown in Table 3. Increase in pH can be explained by amino groups of sorbent. On the other hand, decreasing of acidity with increase of pH may be a reason of the decreasing of sorption.

In order to determine the sorption stoichiometry, $\log K_d$ versus pH graph was plotted as shown in Fig. 4, where, K_d is distribution coefficient, calculated according to Eq. 1. The plots were linear with the slopes nearly equal to 0.5, indicating a 2:1 stoichiometry between the sorbed species and calixarene moieties incorporating amide and/or carboxylic acid sites per unit.

$$K_d = \frac{\text{(amount of metal/g sorbent)}}{\text{(amount of metal/mL solution in contact)}} \quad (1)$$

Effect of contact time

The effect of time on the sorption of Cr(VI) by the C[6]APS was studied by taking 0.025 g sorbent with

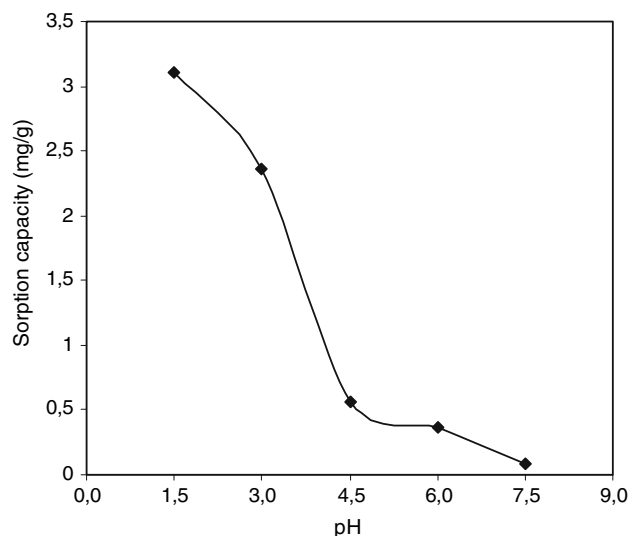


Fig. 3 Effect of pH for the sorption of Cr(VI) on C[6]APS

Table 3 Initial and equilibrium solution pH for C[6]APS

Initial pH	Equilibrium pH
1.5	1.5
3.0	5.1
4.5	6.9
6.0	7.2
7.5	7.9

10.0 mL of salt solution (in 10.4 mg L^{-1} initial concentration) in different stoppered flasks at pH 1.5 and 25°C for 1 h. The flasks were shaken for different time intervals in incubator. Sorption yield values were calculated from the following equation:

$$\text{Sorption yield(\%)} = \frac{[(C_0 - C_e)/C_0] \times 100}{1} \quad (2)$$

where C_0 is the initial Cr(VI) concentration (mg L^{-1}) and C_e is the Cr(VI) concentration (mg L^{-1}) in solution at equilibrium. Figure 5 shows the effect of contact time on

Table 2 FTIR spectral properties of C[6]APS before and after sorption

IR peak	Absorption bands (cm^{-1})			Assignments
	Before sorption	After sorption	Differences	
1	3,450	3,412	-38	Bonded -OH groups, -NH stretching
2	2,959	2,964	+5	Aliphatic C-H group
3	1,753	1,738	-15	Carboxylic acid C=O stretching
4	1,647	1,631	-16	Amide C=O stretching
5	1,480	1,479	-1	C=C group
6	1,413	1,370	-43	Carboxyl groups
7	1,165	1,170	+5	Ether C-O stretching
8	1,100	1,096	-4	-Si-O- group
9	880	887	+7	-C-C- group

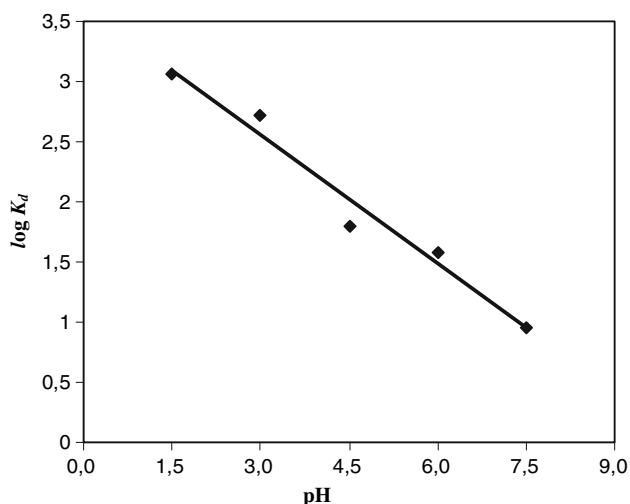


Fig. 4 Log K_d versus pH of Cr(VI) on C[6]APS

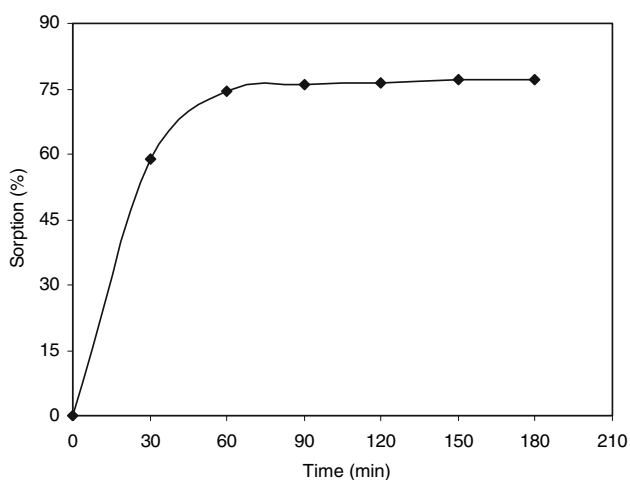


Fig. 5 Effect of contact time on the sorption of Cr(VI) by C[6]APS

the sorption of Cr(VI) using this sorbent. The results show that the percentage of metal ion sorption by C[6]APS increased with increasing time of equilibration and it reached the plateau value at about 60 min for Cr(VI).

Effect of initial Cr(VI) concentration

Solutions of different initial Cr(VI) concentrations (10.4, 20.8, 31.2, 41.6 mg L⁻¹) were used to investigate the effect of concentration on the removal of Cr(VI) by 0.025 g sorbent at pH 1.5 and 25 °C. Sorption percentages were calculated from Eq. 2. As seen from Fig. 6, the sorption yields (%) decrease with increase of initial Cr(VI) concentration. Although percent of sorption (%) decreased, the equilibrium sorption capacity of C[6]APS increased with increasing initial Cr(VI) ion concentration (Fig. 6). The initial concentration provides an important driving force to

overcome all mass transfer resistance of Cr(VI) ions between the aqueous and solid phases, hence a higher initial concentration of Cr(VI) ions may increase the sorption capacity. As it is known from the literature [18], at lower concentrations, all metal ions present in solution could interact with the binding sites and thus the percentage sorption were higher than those at higher initial metal ion concentrations. At higher concentrations, lower sorption percentage is due to the saturation of sorption sites.

The effect of sorbent dosage

Removal of the Cr(VI) ions from aqueous solutions (10.4 mg L⁻¹) was significantly depending on the amount of sorbent. Sorption percentages were calculated from Eq. 2. The efficiencies of sorption were increased (from 74.6 to 83.8%) with increasing of the amount of sorbent from 25 to 100 mg (contact time 1 h; 25 °C; pH 1.5). The reason for that is the availability of more binding sites for complexation of Cr(VI) ions. However, uptake of Cr(VI) showed a reverse trend to the removal percentage sorption. With increasing sorbent dosage, the sorption of Cr(VI) ion per unit weight of sorbent decreased from 3.10 to 0.87 mg g⁻¹.

Sorption isotherms

Several models have been published in the literature to describe experimental data of sorption isotherms. The Langmuir and Freundlich models are the most frequently employed models. In this work, both models were used to describe the relationship between the amount of sorbed Cr(VI) and its equilibrium concentration in solution.

Langmuir isotherm is represented by the following equation [19]:

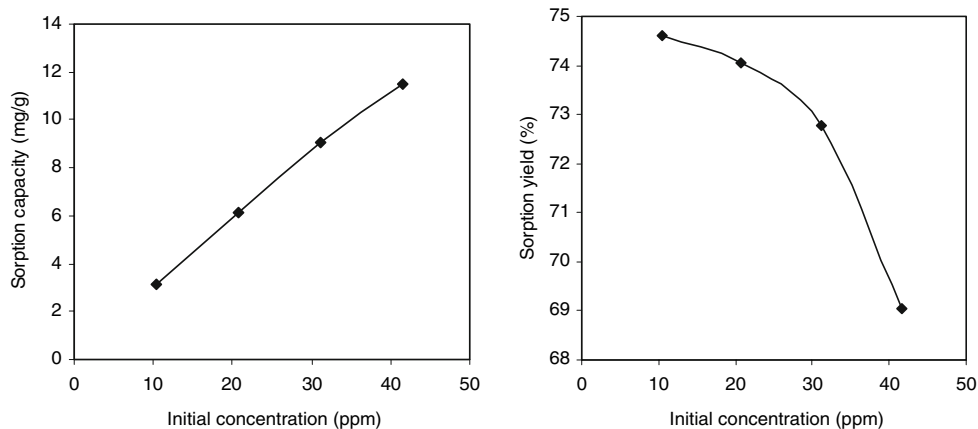
$$C_e/q_e = (1/q_0b) + (C_e/q_0) \quad (3)$$

where C_e is equilibrium concentration (mmol L⁻¹) in solution, q_e is sorption capacity (mmol g⁻¹) at equilibrium, the constant q_0 signifies the sorption capacity (mmol g⁻¹) and b is related to the energy of sorption (L mmol⁻¹).

The linear plot of C_e/q_e versus C_e shows that sorption follows a Langmuir isotherm (Fig. 7). Values of q_0 and b were calculated from the slope and intercept of the linear plots and are presented in Table 4. The applicability of the Langmuir isotherm suggests the monolayer coverage of the Cr(VI) sorption onto C[6]APS [19].

To determine if the Cr(VI) sorption process by C[6]APS is favorable or unfavorable for the Langmuir type sorption process, the isotherm shape can be classified by a term “ R_L ,” a dimensionless constant separation factor, which is defined below [20]:

Fig. 6 Initial concentration effect of Cr(VI) sorption on C[6]APS



$$R_L = 1/(1 + bC_0) \quad (4)$$

where b is Langmuir constant ($L \text{ mmol}^{-1}$). The parameter R_L indicates the shape of the isotherm accordingly:

$R_L > 1$, unfavorable; $R_L = 1$, linear; $0 < R_L < 1$, favorable; $R_L = 0$, irreversible.

The calculating of R_L value as 0.733 indicated that sorption of Cr(VI) on C[6]APS was favorable at 10.4 mg L^{-1} initial Cr(VI) concentration at 25°C and pH 1.5.

The Freundlich isotherm was also applied for the Cr(VI) removal by sorption. Freundlich isotherm model is given by the following equation [21]:

$$\ln q_e = \ln K_f + (1/n) \ln C_e \quad (5)$$

where K_f and n are Freundlich sorption isotherm constants, being indicative of the sorption capacity and intensity of sorption. The values of K_f and n were calculated from the intercept and slope of the plots of $\ln q_e$ versus $\ln C_e$ (Fig. 8). Freundlich isotherm data are given in Table 4. On the comparison of the R^2 values given Table 4, we can conclude that in sorption of Cr(VI) on C[6]APS Freundlich

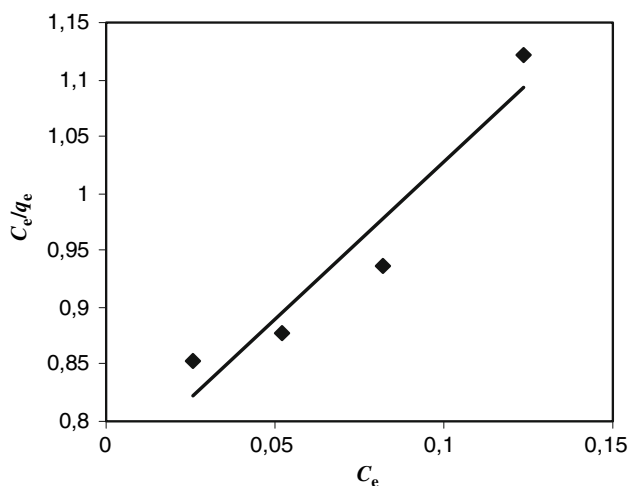


Fig. 7 Langmuir plot for the removal of Cr(VI) (at pH 1.5)

Table 4 Langmuir and Freundlich isotherm parameters

Langmuir isotherm parameters			Freundlich isotherm parameters			
q_0 (mmol/g)	b (L/mmol)	R^2	R_L	K_f	n	R^2
0.362	3.67	0.9167	0.731	0.176	0.903	0.9977

equation represents much better fit to the experimental data than the Langmuir equation.

Although direct comparison of C[6]APS with other sorbent materials is difficult, owing to the different applied experimental conditions, it was found, in general, the sorption capacity of C[6]APS for Cr(VI), using equilibrium experiments, determined to be around $37.66 \text{ mg Cr(VI)/g C[6]APS}$, is higher than beech sawdust [22], distillery sludge [4], sugarcane bagasse [23], soya cake [24], coconut shell carbon [25], and polyacrylonitrile fibers [26]. The values of sorption properties of Cr(VI) on different sorbents used in the literature with the sorbent of the present study are summarized in Table 5. It may be observed that the uptake of Cr(VI) on C[6]APS is greater than some other sorbents.

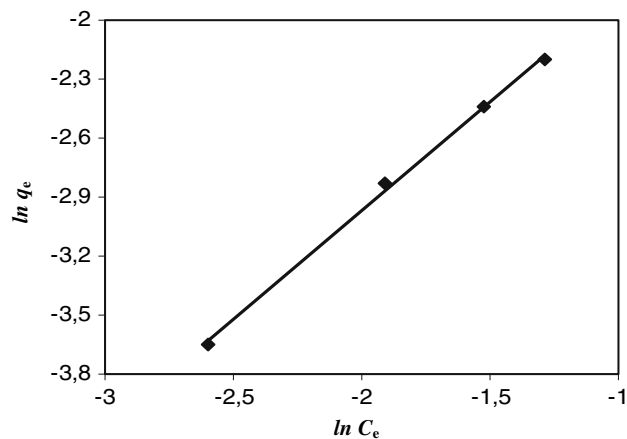


Fig. 8 Freundlich plot for the removal of Cr(VI) (at pH 1.5)

Table 5 Comparison of sorption capacity of other sorbents for Cr(VI) onto C[6]APS

Sorbent	Sorption capacity (mg g ⁻¹)	pH	Initial Cr(VI) concentration (mg L ⁻¹)	Reference
Beech sawdust	16.13	1.0	200	[22]
Distillery sludge	5.70	3.0	40	[4]
Sugarcane bagasse	13.40	2.0	500	[23]
Soya cake	0.28	1.0	34.25	[24]
Coconut shell carbon	10.88	4.0	25	[25]
Polyacrylonitrile fibers	35.0	5.0	50	[26]
C[6]APS	37.66	1.5	10.4	This work

Effect of temperature

The effect of temperature on the sorption of Cr(VI) on C[6]APS is shown in Fig. 9. The uptake of Cr(VI) was found to decrease with increasing temperature, indicating that Cr(VI) sorption on the sorbent surface was favored at lower temperatures. The Cr(VI) removal percent followed the order 25 °C > 35 °C > 45 °C > 55 °C. The change in standard free energy, enthalpy and entropy of sorption were calculated using the following equations:

$$\Delta G^0 = -RT \ln K \quad (6)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (7)$$

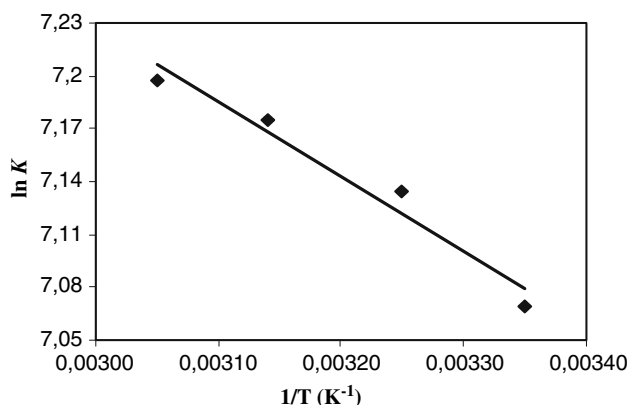
where R is gas constant (8.314 J mol⁻¹ K⁻¹) and K is the equilibrium constant (concentration of sorbed Cr(VI)/concentration of Cr(VI) remained at solution) and T is the temperature in K .

According to the van't Hoff equation:

$$\ln K = (\Delta S^0/R) - (\Delta H^0/RT) \quad (8)$$

where ΔS^0 and ΔH^0 are change in entropy and enthalpy of sorption, respectively.

A plot of $\log K$ versus $1/T$ is linear (Fig. 9). Values of ΔS^0 and ΔH^0 were evaluated from the slope and intercept of van't Hoff plots (Table 6). The positive values of ΔH^0 confirm the endothermic nature of sorption. ΔG^0 is

**Fig. 9** van't Hoff plot for the removal of Cr(VI) (at pH 1.5)**Table 6** Thermodynamic parameters for the removal of Cr(VI)

ΔH^0 (kJ mol ⁻¹ K ⁻¹)	ΔS^0 (kJ mol ⁻¹ K ⁻¹)	T (K)	ΔG^0 (kJ mol ⁻¹)
+3.51	+0.071	298	-17.65
		308	-18.36
		318	-19.07
		328	-19.78

negative and decreases further with increase in temperature indicating that the sorption of Cr(VI) on C[6]APS is spontaneous and spontaneity increases with temperature increase. The reorientation or restructuring of water around no polar solutes or surfaces is very unfavorable in terms of entropy, since it disturbs the existing water structure and imposes a new and less ordered structure on the surrounding water molecules. As a result of sorption of Cr(VI) onto C[6]APS surface, the number of the water molecules surrounding Cr(VI) ions decrease and thus the degree of the freedom of the water molecules increases. Therefore, the positive values of ΔS^0 suggest the increased randomness at solid-solution interface during the sorption of Cr(VI) on C[6]APS.

Conclusion

The preparation and characterization of an aminopropyl silica gel-immobilized *p-tert* butylcalix[6]arene polymer (C[6]APS) was successfully achieved. The sorption studies of Cr(VI) were performed by C[6]APS as sorbent material and the results appeared that 0.025 g of C[6]APS was effective sorbent in high yields at pH 1.5 and 25 °C in 10.4 mg L⁻¹ initial concentration for 1 h with 3.1 mg g⁻¹ sorption capacity. It was noticed that C[6]APS exhibited a stable sorption in all acidic conditions. Thermodynamic parameters indicated that the sorption process would be spontaneous and endothermic. In the isotherm studies, it was determined that the experimental data follow better Freundlich isotherm model than that Langmuir. Batch sorption capacity (q_0) was calculated as 37.66 mg g⁻¹.

Consequently, the immobilization of a *p-tert*-butylcalix[6]arene derivative bearing carboxylic acid groups onto APS became useful approach for Cr(VI) removal from aqueous media by sorption.

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References

1. Raji, C., Anirudhan, T.S.: Batch Cr(VI) removal by polyacrylamide-grafted sawdust: kinetics and thermodynamics. *Water Res.* **32**, 3772–3780 (1998)
2. Goyal, N., Jain, S.C., Banerjee, U.C.: Comparative studies on the microbial adsorption of heavy metals. *Adv. Environ. Res.* **7**, 311–319 (2003)
3. Krishna, P.G., Gladis, J.M., Rambabu, U., Rao, T.P., Naidu, G.R.K.: Preconcentrative separation of chromium(VI) species from chromium(III) by coprecipitation of its ethyl xanthate complex onto naphthalene. *Talanta* **63**, 541–546 (2004)
4. Selvaraj, K., Manonmani, S., Pattabhi, S.: Removal of hexavalent chromium using distillery sludge. *Bioresour. Technol.* **89**, 207–211 (2003)
5. Lalvani, S.B., Wiltowski, T., Hubner, A., Weston, A., Mandich, N.: Removal of hexavalent chromium and metal cations by a selective and novel carbon adsorbent. *Carbon* **36**, 1219–1226 (1998)
6. Zhao, D., Sengupta, A.K., Stewert, L.: Selective removal of Cr(VI) oxyanions with a new anion exchanger. *Ind. Eng. Chem. Res.* **37**, 4383–4387 (1998)
7. Sengupta, A.K., Clifford, D.: Important process variables in chromate ion exchange. *Environ. Sci. Technol.* **20**, 149–155 (1986)
8. Gutsche, C.D.: *Calixarenes Revisited*, Monographs in Supramolecular Chemistry. Royal Society of Chemistry, Cambridge UK (1998)
9. Asfari, Z., Böhmer V., Harrowfield, J.McB., Vicens, J. (eds.): *Calixarenes 2001*. Kluwer Academic Publishers, Dordrecht (2001)
10. Yilmaz, M., Memon, S., Tabakci, M., Bartsch, R.A.: Design of polymer appended calixarenes as ion carriers. In: Bregg R.K. (ed.) *New Frontiers in Polymer Research*, pp. 125–171. Nova Science Publishers, Hauppauge NY (2006)
11. Tabakci, M., Ersoz, M., Yilmaz, M.: A calix[4]arene-containing polysiloxane resin for removal of heavy metals and dichromate anion. *J. Macromol. Sci. Pure Appl. Chem.* **43**, 57–69 (2006)
12. Memon, S., Tabakci, M., Roundhill, D.M., Yilmaz, M.: Synthesis and evaluation of the Cr(VI) extraction ability of amino/nitrile calix[4]arenes immobilized onto a polymeric backbone. *React. Funct. Polym.* **66**, 1342–1349 (2006)
13. Tabakci, M., Erdemir, S., Yilmaz, M.: Preparation, characterization of cellulose-grafted with calix[4]arene polymers for the adsorption of heavy metals and dichromate anions. *J. Hazard. Mater.* **148**, 428–435 (2007)
14. Shinkai, S., Koreishi, H., Ueda, K., Manabe, O.: A new hexacarboxylate uranophile derived from calix[6]arene. *J. Chem. Soc. Chem. Commun.* 233–234 (1986)
15. Park, D., Yun, S.-Y., Park, J.M.: Studies on hexavalent chromium biosorption by chemically treated biomass of *Ecklonia* sp. *Chemosphere* **60**, 1356–1364 (2005)
16. Bai, R.S., Abraham, T.E.: Studies on enhancement of Cr(VI) biosorption by chemically modified biomass of *Rhizopus nigricans*. *Water Res.* **36**, 1224–1236 (2002)
17. Sheng, P.X., Ting, Y.-P., Chen, J.P., Hong, L.: Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. *J. Colloid Interf. Sci.* **275**, 131–141 (2005)
18. Ozer, A., Ozer, D., Ozer, A.: The adsorption of copper(II) ions on to dehydrated wheat bran (DWB): determination of the equilibrium and thermodynamic parameters. *Process Biochem.* **39**, 2183–2191 (2004)
19. Weber, W.J.: *Physicochemical Processes for Water Quality Control*. John Wiley and Sons Inc., New York (1972)
20. Hamdaoui, O.: Dynamic sorption of methylene blue by cedar sawdust and crushed brick in fixed bed columns. *J. Hazard. Mater.* **138**, 293–303 (2006)
21. Rao, M., Parwate, A.V., Bhole, A.G.: Removal of Cr and Ni from aqueous solution using bagasse and fly ash. *Waste Manage.* **22**, 821–830 (2002)
22. Acar, F.N., Malkoc, E.: The removal of chromium(VI) from aqueous solutions by *Fagus orientalis* L. *Bioresour. Technol.* **94**, 13–15 (2004)
23. Sharma, D.C., Forster, C.F.: A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents. *Bioresour. Technol.* **47**, 257–264 (1994)
24. Babel, S., Kurniawan, T.A.: Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere* **54**, 951–967 (2000)
25. Daneshvar, N., Salari, D., Aber, S.: Chromium adsorption and Cr(VI) reduction to trivalent chromium in aqueous solutions by soya cake. *J. Hazard. Mater.* **94**, 49–61 (2002)
26. Deng, S., Bai, R.: Removal of trivalent and hexavalent chromium with aminated polyacrylonitrile fibers: performance and mechanisms. *Water Res.* **38**, 2424–2432 (2004)