



## Estimation of chromium(VI) sorption efficiency of novel regenerable *p*-*tert*-butylcalix[8]areneoctamide impregnated Amberlite resin

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### ABSTRACT

The article describes a convenient synthesis and Cr(VI) extraction efficiency of a novel *p*-*tert*-butylcalix[8]areneoctamide impregnated Amberlite (XAD-4) resin. Using *p*-*tert*-butylcalix[8]arene macrocyclic building block, two strategies have been developed; i.e., derivatization of *p*-*tert*-butylcalix[8]arene framework with sophisticated ionophoric groups having efficiency to extract oxoanions from aqueous media and, impregnation of *p*-*tert*-butylcalix[8]arene derivative onto the polymeric support. Liquid–liquid and solid–liquid extraction experiments have been performed to evaluate the Cr(VI) extraction efficiency of both *p*-*tert*-butylcalix[8]arene derivative and the impregnated resin. From the results, it has been deduced that solid-phase extraction method is more convenient and efficient than liquid–liquid extraction process. The impregnated XAD-4 resin has been found regenerable with better extracting efficiency as compared to the simple *p*-*tert*-butylcalix[8]areneoctamide ionophore.

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### 1. Introduction

Hexavalent chromium is extensively used by various industries in particular stainless steel welding, chromate production, electroplating, chrome pigment, catalysts, refractory or corrosion-resistant products, leather tanning, textile dyeing, wood preserving, oil drilling, or locations where large tanks have been cleaned with chromium(VI) solutions [1–3]. When chromium(VI) is ingested higher than its permissible level, it causes health disorders; such as vomiting and hemorrhage [4]. It can easily cross the cell wall and exerts its toxic influence on the cell. Therefore, chromium(VI) is known to exhibit carcinogenic properties; attacks liver, kidney and lungs [5]. Due to the extreme toxicity of Cr(VI), its selective determination and removal from the polluted sites is of particular importance.

Calixarenes have been proven to be very useful precursors for the synthesis of host molecules. During the last three decades, they have attracted much attention as key receptors in ‘Supramolecular Chemistry’. Immense interest in these compounds was stimulated by their simple large-scale synthesis and the different ways in which they can be selectively functionalized at the narrow or wide rim [6–9]. Moreover, calixarenes have several advantages for

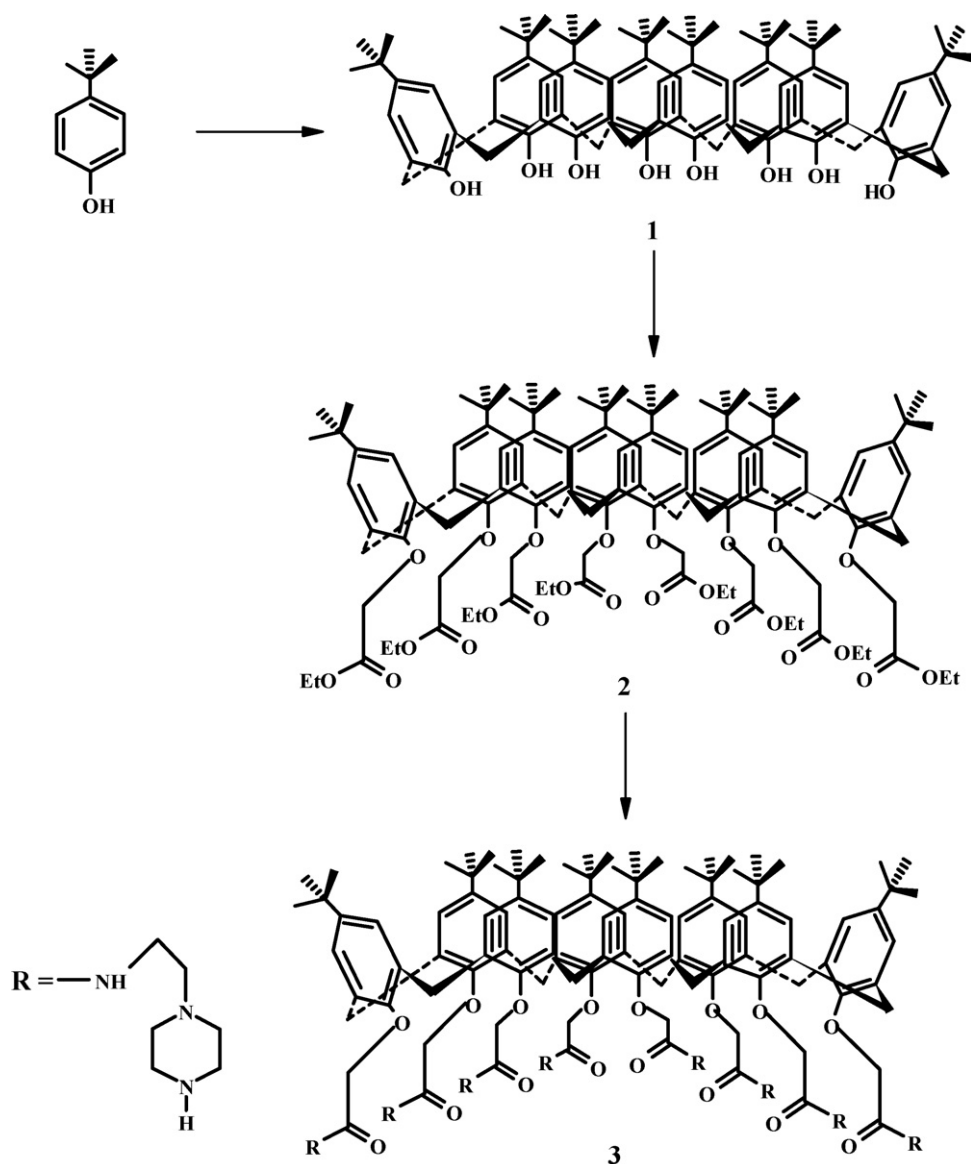
their application as extractants for chromium(VI), e.g., their aromatic core structure is stable against oxidation, and the association of oxoanion with multiple functionalities present onto the aromatic core. This association may arise due to the hydrogen bonding between substituents on the calixarene moiety and one or more of the oxygen atoms on the periphery of the oxoanion [10].

Generally, two strategies have been adopted to enhance the affinity of calixarenes toward metal ions and anions. Either different ionophoric groups including carbonyl, amide, nitrile and other suitable functionalities have been incorporated onto the calix-platform, or the calix[*n*]arene units have been fixed in a polymeric matrix [11–14]. Thus, calixarenes need to be modified chemically to reduce their solubility characteristics by immobilization on polymeric supports. The preparation of such insoluble polymeric calixarenes is made by linking the calixarene units to the polymeric matrix covalently or by connecting a polymerizable spacer group to calixarene unit to give a resin-like substance after polymerization.

Amberlite XAD series resins have been extensively used for the solid-phase extraction and often modified for designing chelating resins [15–17]. Amberlite XAD-4 is a cross-linked polymer which has excellent adsorptive properties for neutral small molecules onto its macroreticular structure and higher surface area. These structures provide excellent chemical, physical and thermal stability. The modification with calixarenes makes them the best choice for the removal of a variety of metal ions [18,19]. In our previous

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**Scheme 1.** Synthesis of 5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octa-(2-piprazinoethylamino)carbonylmethoxycalix[8]arene (3).

work [10,20–23] we have reported several polymeric calixarenes, and have investigated their ionophoric properties. Based on the previous studies, herein we report the extended research work regarding designing of structures for the extraction of dichromate anions. Thus, in the present work two strategies were adopted, i.e. loading calix[8]arene moiety with ionophoric groups (e.g. amide) and impregnation of that calix[8]arene derivative onto the resin in order to extract chromium(VI) from aqueous media efficiently.

## 2. Material and methods

### 2.1. Reagents

Analytical TLC was performed on precoated silica gel plates ( $\text{SiO}_2$ , Merck PF<sub>254</sub>). Ethanol was distilled over CaO and toluene was dried and distilled using sodium wire. Dichloromethane and *n*-hexane used were distilled from  $\text{CaCl}_2$  and stored under  $\text{N}_2$  over molecular sieves (4 Å). Potassium dichromate and sodium bicarbonate all Merck (Darmstadt, Germany) were used as supplied. All aqueous solutions were prepared with deionized water that

had been passed through a Millipore Milli-Q Plus water purification system. The Amberlite XAD-4 resin (styrene-divinylbenzene copolymer), surface area  $725 \text{ m}^2 \text{ g}^{-1}$ , pore diameter 4 nm and bead size 20–50 mesh was supplied by Fluka (Buchs, Switzerland). The resin obtained from the supplier contains organic and inorganic material. Therefore, before impregnation the resin was washed with ethanol followed by excessive water then with 15% HCl solution and finally again with water till neutralized. It was dried in oven at  $110^\circ\text{C}$  and was stored in polyethylene container.

### 2.2. Instrumentation

Melting points were determined on a Gallenkamp apparatus (UK) in a sealed glass capillary tube and are uncorrected. IR spectra were recorded on a Thermo Nicolet AVATAR 5700 FTIR spectrometer using KBr pellets in the spectral range 4000–400. UV–visible spectra were recorded on a PerkinElmer Lambda 35 UV/VIS spectrophotometer using standard 1.00 cm quartz cells. For pH measurement 781-pH/ion meter (Metrohm Switzerland) was used. Gallenkamp mechanical shaker with temperature controller

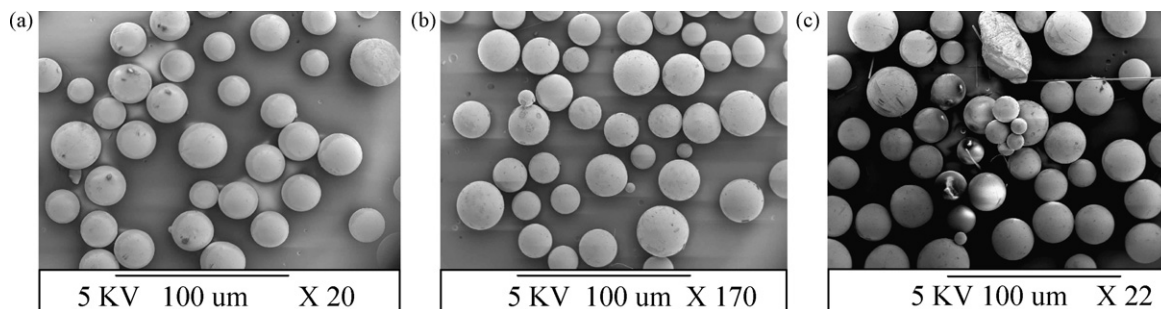


Fig. 1. SEM micrographs of (a) pure resin (5 kV, 100  $\mu\text{m}$ , 20 $\times$ ), (b) impregnated resin (5 kV, 100  $\mu\text{m}$ , 170 $\times$ ) and (c) loaded impregnated resin (5 kV, 100  $\mu\text{m}$ , 22 $\times$ ).

was used for shaking. Elemental analyses were performed using a CHNS instrument model Flash EA 1112 elemental analyzer. Scanning electron microscopic (SEM) studies were performed using JSM-6380 instrument.

### 2.3. Synthesis

Compounds **1** and **2** were prepared according to the reported methods [24,25], while compound **3** as illustrated in Scheme 1 was prepared as follows.

#### 2.3.1. Synthesis of 5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octa-(2-piprazinoethylamino)carbonylmethoxycalix[8]arene (**3**)

Compound **2** (4.9 g, 2.64 mmol) and *N*-(2-aminoethyl)pipazine (6.8 g, 52.8 mmol, 8 mL) were mixed with 100 mL of dry ethanol/toluene (1:1) and refluxed for 72 h. After removing solvent

through rotary evaporator 2N HCl aqueous solution (100 mL) was added into the crude product. The precipitates formed were filtered and washed with distilled water followed by 10% NaHCO<sub>3</sub>. Finally, the precipitates were washed with water and dried in vacuum desiccator. The compound **3** was recrystallized from dichloromethane and *n*-hexane to obtain **3** as pure product in 76% yield, m.p.  $\geq 210^\circ\text{C}$  (dec.). IR(KBr) 3399 and 3300  $\text{cm}^{-1}$  (NH), and 1667  $\text{cm}^{-1}$  (HNC=O).

<sup>1</sup>H NMR (CDCl<sub>3</sub>);  $\delta$  0.70–1.27 (m, 72H, Bu<sup>t</sup>); 2.34 (s, 48H, NCH<sub>2</sub>); 2.67 (s, 32H, NCH<sub>2</sub>); 3.21–3.38 (m, 24H, NH, NCH<sub>2</sub>); 3.52–4.30 (m, 40H, Ar-CH<sub>2</sub>-Ar, OCH<sub>2</sub>, CONH); 6.20–7.23 (m, 16H, ArH). Calculated for: C<sub>152</sub>H<sub>232</sub>N<sub>24</sub>O<sub>16</sub>; C, 68.85; H, 8.82; N, 12.68; found: C, 68.79; H, 8.85; N, 12.73%.

#### 2.3.2. Impregnation procedure

2 g of XAD-4 resin was taken in 10 mL of ethanol–water system (1:1). Then  $6.6 \times 10^{-3}$  M of ligand **3** was added and continuously stirred for 60 h. After that the resin was filtered through sintered glass funnel, washed with ethanol and water in order to remove

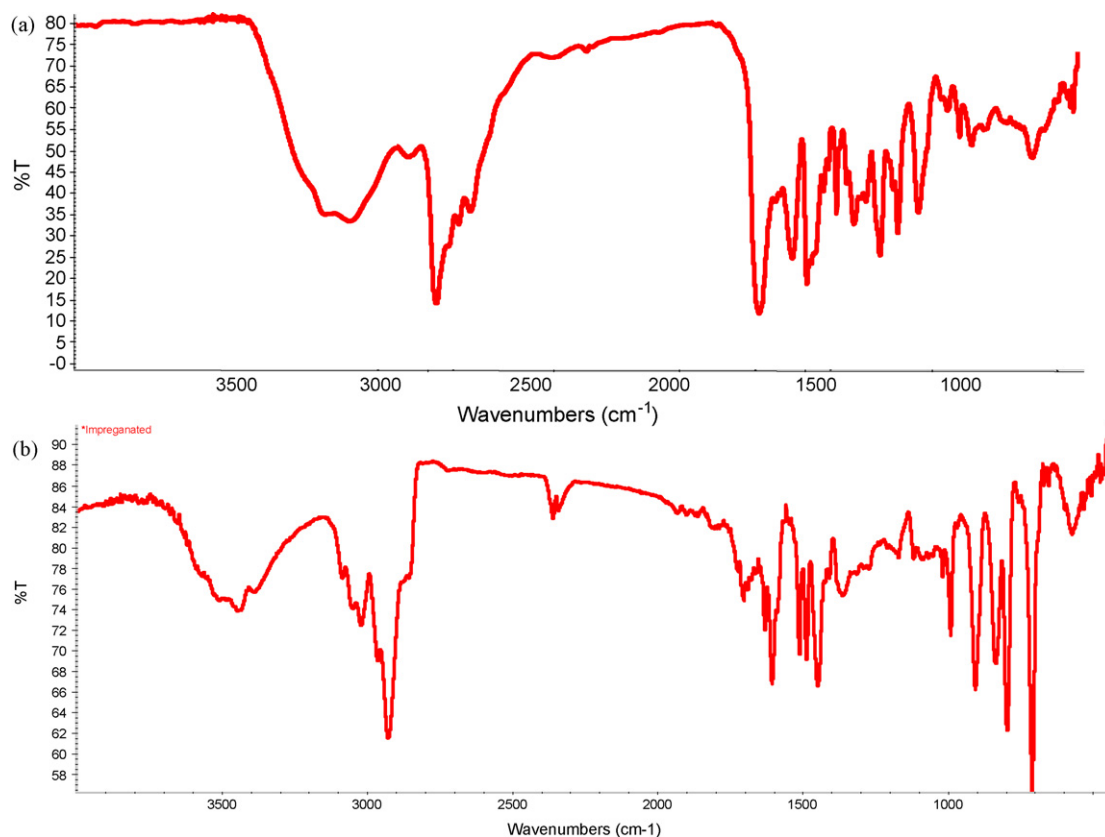


Fig. 2. FT-IR spectra of (a) *p*-*tert*-butylcalix[8]areneoctamide and (b) *p*-*tert*-butylcalix[8]areneoctamide impregnated Amberlite XAD-4 resin.

unimpregnated ligand **3**. The ligand content was checked after solvent evaporation through gravimetric analysis. The amount of impregnated resin was calculated from the material balance. Maximum amount of ligand **3** impregnated onto dry resin was  $1 \times 10^{-4} \text{ mol g}^{-1}$ .

### 2.3.3. Extraction procedure

**2.3.3.1. Liquid–liquid extraction.** Dichromate extraction experiments were performed using Pederson's experimental procedure [26]. 10 mL of  $1 \times 10^{-4} \text{ M}$  aqueous dichromate solution (pH of dichromate solution has been maintained by 0.01 M KOH/HCl solution) and 10 mL of  $1 \times 10^{-3} \text{ M}$  solution of calixarene in  $\text{CH}_2\text{Cl}_2$  were vigorously agitated in a stoppard glass tube with a mechanical shaker for 2 min then magnetically stirred in a thermostated water-bath at  $25^\circ\text{C}$  for 1 h, and finally left standing for an additional 30 min so that the two phases separate distinctively. The concentration of dichromate ion remaining in the aqueous phase was then determined spectrophotometrically. Blank experiments showed that no dichromate extraction occurred in the absence of calixarene. The percent extraction ( $E\%$ ) has been calculated as

$$E(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where  $C_0$  and  $C$  are initial and final concentrations of dichromate ions before and after the extraction, respectively.

**2.3.3.2. Solid–liquid extraction (column procedure).** In solid–liquid extraction experiment a glass column (1.0 cm i.d. 10.0 cm length) filled with 1 g of impregnated resin was used. It was cleaned by passing ethanol, and doubly distilled water. Then the column was conditioned to the desired pH with 0.01 M HCl/KOH solutions. 10 mL of  $1 \times 10^{-4} \text{ M}$  aqueous dichromate solution was passed through the column at a flow rate of  $2 \text{ mL min}^{-1}$ . The analyte in the eluents was determined spectrophotometrically. After each run the impregnated resin was regenerated by passing 4 M HCl solution followed by distilled water.

## 3. Result and discussions

The main focus of this work was to design a new easily accessible calixarene-based ionophoric resin; capable of binding specific anions effectively and could be useful for multiple applications; such as laboratory, clinical, environmental and industrial process analyses. To achieve the desired goal, we have synthesized 5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene **1** as a starting material through the base catalyzed condensation reaction [24]. The compound **1** was treated with ethyl bromoacetate in dry acetone in the presence of  $\text{K}_2\text{CO}_3$  to obtain 5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octaethoxycarbonylmethoxycalix[8]arene **2** [25]. The compound **3** was obtained in 76% yield by the treatment of the compound **2** with *N*-(2-aminoethyl)piperazine in dry ethanol/toluene (1:1). Compound **3** was impregnated onto the resin as described above. The new compound **3** and impregnated resin were characterized by a combination of analytical techniques described in Section 2.3 and some of them are illustrated in the following sections.

### 3.1. SEM of the resin

Generally, SEM is used to study the morphology and surface characteristics of adsorbent material [27]. In this work, SEM is used to study the morphological changes on the surface of adsorbent resin in its various forms (i.e. pure, impregnated and loaded impregnated), which are shown in Fig. 1a–c. Perusal of the scanning

electron micrographs of pure, impregnated and loaded resins indicates morphological features. The morphology of the impregnated and loaded resins shows some important observations. Coverage of the surface of the resins due to the impregnation of the calixarene molecules and adsorption/loading of Cr(VI), i.e. potassium dichromate, presumably leading to formation of mono/multi-layers over the adsorbent surface is evident from the formation of white layer(s) (cloud) of uniform thickness and coverage.

### 3.2. FT-IR analysis of the resin in its various forms

Fig. 2a and b show FT-IR spectra of the *p*-*tert*-butylcalix[8]areneoctamide **3** and impregnated resin. An examination of the adsorbent surface before and after impregnation possibly provides information regarding the surface groups that might have participated in the impregnation and also indicates the surface sites on which adsorption has taken place. IR spectrum of impregnated resin (Fig. 2b) shows two merged peaks at  $3300$  and  $3399 \text{ cm}^{-1}$ , which correspond to the presence of *sec.* amine and amide (N–H) functionalities; while a peak at about  $1679 \text{ cm}^{-1}$  shows the presence of carbonyl (C=O) functionality. From these observations it can be concluded that **3** has been impregnated onto the surface of XAD-4 resin. The IR spectrum of **3** (Fig. 2a) shows the carbonyl peak at  $1667 \text{ cm}^{-1}$ . The IR spectrum of pure resin does not show any of these peaks [27].

### 3.3. Method profile

The chromium(VI) extraction efficiency of novel compound **3** and impregnated resin were evaluated experimentally and the results are discussed as follows. The liquid–liquid and solid–liquid extraction % of dichromate at different pH values is shown in Fig. 3a and b.

#### 3.3.1. Effect of pH and flow rate on dichromate ion uptake

According to column procedure, metal ion uptake was determined in the pH range of 1–6 and its absorbance was measured at  $\lambda_{\text{max}} = 257 \text{ nm}$ . 1 g of impregnated resin was packed in column and 10 mL of  $1 \times 10^{-4} \text{ M}$  metal solution was passed at optimum flow rate at different pH values. Fig. 3b shows that the maximum Cr(VI) sorption (80%) occurs at pH 3. However, it is well known that at higher acidic conditions  $\text{K}_2\text{Cr}_2\text{O}_7$  is converted into the  $\text{H}_2\text{Cr}_2\text{O}_7$  form, and after the ionization in aqueous solution it exists in the  $\text{HCr}_2\text{O}_7^-$  and/or  $\text{Cr}_2\text{O}_7^{2-}$  form as shown in the following equation:



In acidic conditions the equilibrium shifts toward left-hand side of Eq. (2) and in such conditions mostly there is an extraction of  $\text{HCr}_2\text{O}_7^-$ . These findings have been reported by several investigators [28–30], favorable effect of low pH can be attributed to the neutralization of negative charges on surface of the adsorbents by excess hydrogen ions, thereby facilitating the diffusion and the subsequent adsorption of hydrogen dichromate ions ( $\text{HCr}_2\text{O}_7^-$ ).

The dependence of metal ion sorption at various flow rates was optimized at pH 3. Maximum percent sorption was observed at  $2 \text{ mL min}^{-1}$ . An increase in flow rate decreases the sorption gradually, because of less contact time and weak hydrogen bonding. It was found that resin extracts Cr(VI) more efficiently as compared to the ligand **3** may be due to larger surface area provided for the interaction by the resin.

#### 3.3.2. Effect of concentration of eluting agents for desorption

The elution studies were performed with HCl and  $\text{HNO}_3$  at different molar concentrations ranging 1–4 and 3–5, respectively [31]. A sample solution of 10 mL was taken. It was then passed through

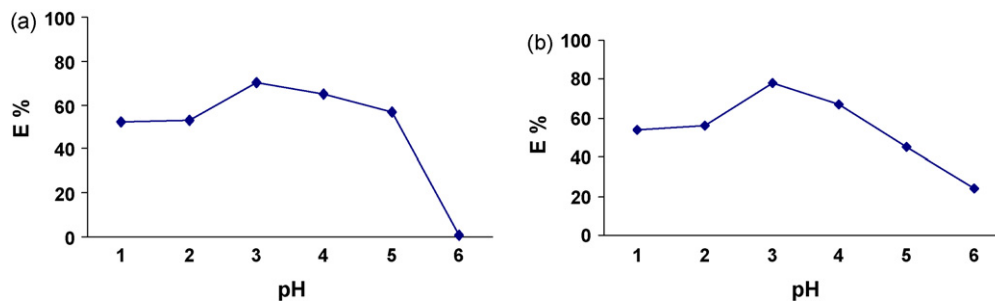


Fig. 3. Study of the pH effect on (a) liquid-liquid extraction and (b) solid-phase extraction.

column at optimum flow rate. Again, the metal ions were desorbed with HCl and/or HNO<sub>3</sub> at different molar concentrations separately and determined through UV/vis spectrophotometer. The recovery of the adsorbed Cr(VI) with HNO<sub>3</sub> solutions was not very good as compared to the recovery of adsorbed Cr(VI) by using 4 M HCl. Thus, 4 M HCl was used for all desorption and regeneration processes.

### 3.3.3. The stability and potential reusability of the column

The stability and potential reusability of the column was investigated by monitoring the change in recoveries of chromate ion through several sorption and desorption cycles. It was found that after 10 repetitions there is no change in sorption capacity of the resin. In desorption experiment it has been observed that almost total recovery of Cr(VI) occurs, suggesting that the resin is regenerable and can be used again and again. The resin can be regenerated by passing 4 M HCl followed by distilled water.

## 3.4. Sorption isotherms

### 3.4.1. Langmuir and Freundlich models

Sorption isotherm is a functional expression that correlate the amount of solute adsorbed per unit amount of sorbent and the concentration of sorbate in bulk solution at given temperature under equilibrium conditions. The most common and frequently used models are Langmuir and Freundlich model.

The Langmuir model assumes uniform energies of sorption on the surface and no transmigration of sorbate in the plane of the surface. Langmuir isotherm is represented by the following equation [32]:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0}$$

where the constants  $q_0$  is the sorption capacity ( $\text{mg g}^{-1}$ ) and  $b$  is related to the surface energy of sorption. A plot of  $C_e/q_e$  versus  $C_e$  as shown in Fig. 4 exhibits favorable sorption. Where  $q_0$  ( $87.7 \text{ mg g}^{-1}$ ) and  $b$  (0.19) represent the intercept and slope, respectively. From

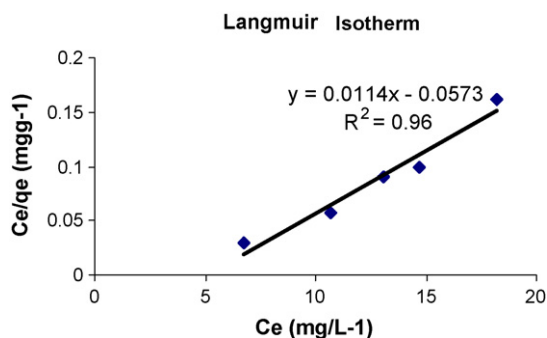


Fig. 4. Application of Langmuir model to the experimental data.

the value of  $q_0$  and  $b$ , dimensionless factor  $R_L$  was estimated by using the relationship:

$$R_L = \frac{1}{1 + bC_0}$$

where  $R_L$  is the separation factor and  $b$  is the Langmuir constant  $\text{L mg}^{-1}$ . Separation factor shows the nature of sorption process and its value indicate that the sorption process could be favorable, linear, unfavorable, when  $0 < R_L < 1$ ,  $R_L = 1$ ,  $R_L > 1$ , respectively. The value of  $R_L = 0.175$  showing that sorption of Cr(VI) on impregnated resin is favorable at pH 3. The model seems to be more agreeable with respect to the correlation coefficient  $R^2 = 0.9151$ , resulting monolayer sorption. The plot of specific sorption ( $C_e/q_e$ ) against the equilibrium concentration ( $C_e$ ) for Cr(VI) sorption is shown in Fig. 5.

The Freundlich isotherm model is in empirical expression describing the exponential distribution of active centers, characteristic of heterogeneous surface and infinite surface coverage:

$$\log q_e = \log K + \frac{1}{n} \log C_e$$

where  $q_e$  is the amount of the sorbed analyte per unit weight of the solid phase at equilibrium concentration  $C_e$ ,  $K$  is the Freundlich constant related to the sorption capacity, while  $1/n$  shows the sorption intensity.

A plot of  $\log q_e$  versus  $\log C_e$  would exhibit in straight line with slope of  $1/n$  and intercept of  $\log K$ . If the value of  $1/n$  is less than unity, it indicates that significant adsorption is taking place at low concentration. The situation  $1/n < 1$  is the most common and corresponds to a normal L-type Langmuir isotherm [33], while  $1/n > 1$  is indicative of a cooperative sorption [34], which involves strong interactions between the molecules of adsorbate. For  $1/n = 1$  indicates that the partition between two phases is independent of concentration. Moreover, the greater the value of  $K$  the greater the uptake of chromium [35]. The value of  $1/n$  and  $K$  are 1.48 and 858.8, respectively.

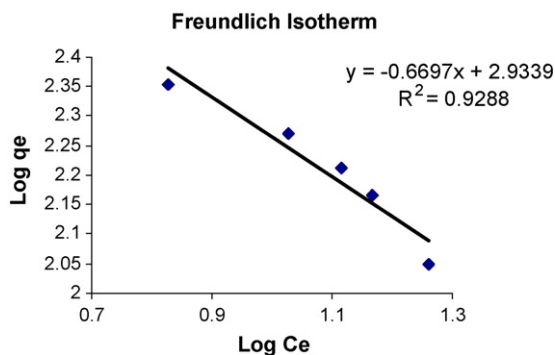


Fig. 5. Application of Freundlich model to the experimental data.

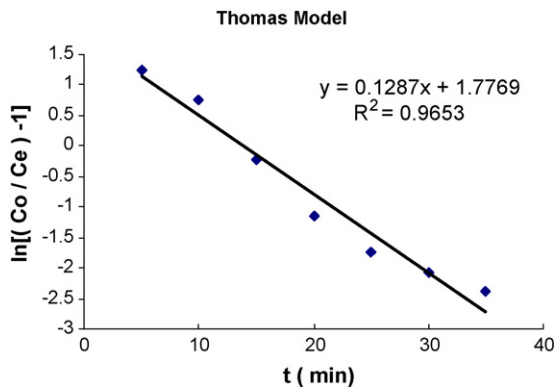


Fig. 6. Application of Thomas model to the experimental data.

This is an expected result due to the adoption of an excellent strategy by anchoring sophisticated functional groups onto the lower rim of calix moiety followed by its impregnation onto the resin. Since the resin provides greater surface area to the calix moiety to expose its ionophoric groups for interaction with the anions, which ultimately represent the Freundlich isotherm for Cr(VI).

#### 3.4.2. Thomas model

Thomas model is one of the widely used mathematical modeling methods for fixed bed column studies [36]. Efficient design of a column sorption process requires prediction of the concentration–time profile or breakthrough curve for the effluent. In the present study, the Thomas model was used to correlate the experimental and theoretical data for chromium(VI) sorption. The linearized form of the Thomas model can be expressed mathematically as

$$\ln\left(\frac{C_0}{C_e} - 1\right) = K_{th}C_0 + K_{th}\frac{q_0m_s}{Q}$$

where  $C_0$  is the initial Cr(VI) concentration ( $\text{mg L}^{-1}$ ),  $C_e$  the eluents Cr(VI) concentration ( $\text{mg L}^{-1}$ ),  $K$  the Thomas rate constant ( $\text{L min}^{-1} \text{mg}$ ),  $m_s$  the mass of the adsorbent (g),  $q_0$  the maximum adsorption capacity ( $\text{mg of Cr(VI) g}^{-1}$  of impregnated resin) and  $Q$  is the flow rate ( $\text{mL min}^{-1}$ ).

From the plot of  $\ln[(C_0/C_e) - 1]$  against  $t$  at a given flow rate [37], the intercept  $(k_{th}q_0m_s)/Q$  and the slope  $(k_{th}C_0)/Q$  were calculated (Fig. 6). Thomas adsorption capacity  $q_0$  for Cr(VI) sorption was found to be 408.8 mg and the value of  $K$  is  $8.7 \times 10^{-3} \text{ L min}^{-1} \text{ mg}$ . The observations based on experimental and theoretical parameters are compared in Fig. 7.

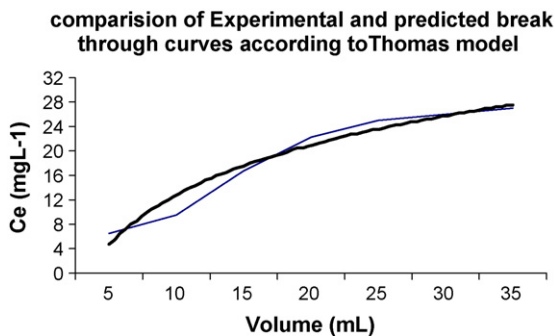


Fig. 7. Comparison of experimental and predicted breakthrough curves according to Thomas model.

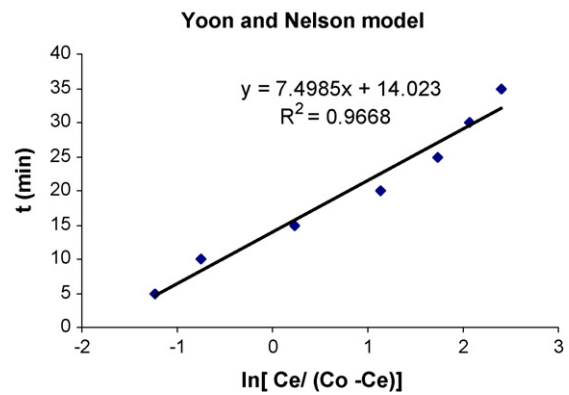


Fig. 8. Application of Yoon and Nelson model to the experimental data.

#### 3.4.3. Yoon and Nelson model

The model is based on the assumption that the rate of decrease in probability of sorption for each sorbate is proportional to the probability of sorbent sorption and the probability of sorbate breakthrough on the sorbent. The Yoon and Nelson model not only is less complicated than other models but also requires no detailed data concerning the characteristics of sorbate, the type of sorbent and the physical properties of sorption bed. The Yoon and Nelson equation regarding to a single component system is expressed as [38]:

$$\frac{C_e}{C_0} = \frac{1}{1 + \exp[k(T - t)]}$$

where  $k$  is the rate constant ( $\text{min}^{-1}$ ),  $T$  the time required for 50% sorbate breakthrough (min) and  $t$  is the breakthrough (sampling) time (min). The linearized form of the Yoon and Nelson model is as follows:

$$t = T + \frac{1}{k} \ln \frac{C_0}{C_0 - C_e}$$

The theoretical breakthrough curves calculation for a single component system need the determination of the parameters  $k$  and  $T$  for the sorbate of interest. The available experimental data may be helpful in the determination of these values. A simple theoretical model developed by Yoon and Nelson was applied to describe the breakthrough behavior of chromium(VI). The values of  $k$  and  $T$  were determined from plots  $\ln[C_0/(C_0 - C_e)]$  against  $t$  at different inlet chromium(VI) concentrations. The theoretical curves are compared with the corresponding experimental data in Fig. 8, and it could be concluded that the experimental breakthrough curves are followed very closely by those predicted by the Yoon–Nelson model.

#### 3.4.4. Temkin isotherm

Temkin isotherm assumes that decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies. Temkin isotherm is expressed by the following equation:

$$q_e = \frac{RT}{b} \ln(K_t C_e) \quad \text{or} \quad q_e = B_1 \ln K_t + B_1 \ln C_e$$

where  $K_t$  is equilibrium binding constant ( $\text{L g}^{-1}$ ),  $b$  is related to heat of adsorption ( $\text{J mol}^{-1}$ ),  $R$  is the gas constant ( $8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$ ) and  $T$  is the absolute temperature (K).

The isotherm assumes that (1) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that (2) the adsorption is characterized by a uniform distribution of binding energies, up to

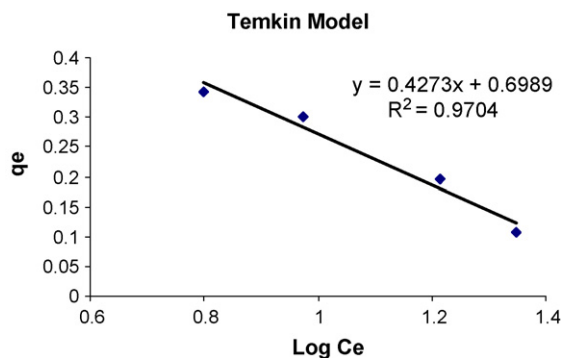


Fig. 9. Application of Temkin model to the experimental data.

some maximum binding energy. A plot of  $q_e$  versus  $\ln C_e$  as shown in Fig. 9 enables to determine the isotherm constant  $K_t$ ,  $b$  and  $T$ . Typical binding energy for ion-exchange mechanism is reported to be in the range of 8–16 kJ mol<sup>-1</sup>, while physisorption processes are reported to have low adsorption energies [39]. A very low value of  $b$  (5.7 kJ mol<sup>-1</sup>) obtained in the present study reveals weak ionic interactions between sorbate and the sorbent which indicates the physisorption of chromium(VI).

#### 4. Conclusion

In this study, *p*-*tert*-butylcalix[8]areneoctamide was synthesized and used to evaluate its chromium(VI) extraction capacity. It was found a good extractant for chromium(VI), however; to enhance its extraction ability as well as high thermal stability, it was impregnated onto the Amberlite XAD-4 resin. In impregnated form, it exhibited excellent sorption properties toward chromium(VI). The important features of this study are that the work done in this contest may help not only to recover the particular targeted metal from the industrial effluents for reuse, but also to restore the polluted sites in their original state. Moreover, the regeneration of impregnated resin offers another advantage in this contest.

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