ORIGINAL ARTICLE

Preparation of calix[4]arene-based sporopollenin and examination of its dichromate sorption ability

Serkan Sayin · Ilkay Hilal Gubbuk ·
Mustafa Yilmaz

Abstract The present study describes the preparation of a new calix[4]arene-based sporopollenin material and its application for the removal of $Na_2Cr_2O_7$ from aqueous solution. The novel calix[4]arene-based sporopollenin material was prepared via the immobilization of dihydrazine amide derivative of *p-tert*-butylcalix[4]arene (**3**) onto the modified sporopollenin. The newly prepared calix[4]arene-based sporopollenin is characterized by using different analytical techniques such as FT-IR spectroscopy, scanning electron microscope and Elemental analysis. The batch wise sorption study was carried out to optimize various experimental parameters such as the effect of sorbent dosage, pH, temperature and Cr(VI) anion concentration. It has been found that the sorption of Cr(VI) anion on calix[4]arene-based sporopollenin was highly pH dependent and maximum sorption was achieved at pH 1.5. The sorption behavior was also evaluated by Langmuir, Freundlich and Dubinin Radushkevich isotherms. The value of correlation coefficient (R^2) showed a good agreement with Freundlich isotherm model. Result of study demonstrated that calix[4]arene-based sporopollenin proved to be highly effective for the removal of Cr(VI).

Keywords Calix[4]arene · Sporopollenin · Sorption · Dichromate · Proton-switchable

Introduction

Calixarene is a well-known family of synthetic macromolecular compounds, and from last more than three decades have got much more interest of many researchers due to its easy and targeted derivatisation [1, 2]. Until now, calixarenes have been effectively used as an extractant for the transferring of anion and cation as well as neutral molecules from aqueous phase to organic phase [3–6]. The anion selective calixarenes are the robust class of synthetic macromolecules, furthermore their extensive use as a trapping agent makes them hottest and very important research field of the present era. The selectivity towards the selected ions is mainly depends upon the conformation of the calix[4]arene moiety as well as the nature and number of the donor atoms [7, 8].

The biological and chemical properties of sporopollenin such as, biocompatible, bioactive and polycationic are generally produced due to the oxidative polymerization of carotenoids and carotenoid esters [9]. Sporopollenin by virtue of its outer wall which is made up by spores and pollen can survive in a geological stratum more than millions of years with fully retained morphology [10].

Although the chromium exists in several oxidation states, out of them only the trivalent and hexavalent states of chromium due to their impact on human being and environment are important [4]. It is well known that Cr(VI) is highly toxic, carcinogenic, and harmful to human beings, while Cr(III) is essential for mammals, as it maintains effective glucose, lipid, and protein metabolism [11]. Therefore the remediation technology that can remove the Cr(VI) from groundwater is the most imperative needed of the modern world and still a technological challenge [12]. Up to now, many types of removal methods such as precipitation, coprecipitation, ion-exchange, sorption, ultra filtration,

S. Sayin · I. H. Gubbuk (✉) · M. Yilmaz
Department of Chemistry, Selcuk University,
Konya 42075, Turkey
e-mail: ihilalg@gmail.com

S. Sayin
Department of Chemistry, University of Massachusetts,
710 North Pleasant St., Amherst, MA 01003, USA

and reverse osmosis have been used [13]. Among all these remediation methods, sorption and the solvent extraction have proven to be as effective and attractive process for the decontamination of Cr(VI) from groundwater.

Herein, we have synthesized hydrazide amide derivative of calix[4]arene (**3**) and than it has been immobilizated onto the surface of modified sporopollenin with isocyanate in order to obtain a new calix[4]arene-based sporopollenin sorbent and to enhance the sorption capability of the pure sporopollenin towards dichromate anion. Furthermore, the sorption capability of calix[4]arene-based sporopollenin towards dichromate anion by means of solid–liquid extraction process at various pHs have been investigated for the first time.

Experimental

Materials and procedures

The syntheses of compounds **1**–**3** were carried out according to the known procedures [14–16]. The **SP-iso** and **SP-Calix** are herein reported firstly. TLC analyses were carried out on DC Alufolien Kieselgel 60 F_{254} (Merck, Darmstadt, Germany). Generally, solvents were dried by storing them over molecular sieves (Aldrich; 4 Å, 8–12 mesh). All reactions, unless otherwise noted, were conducted under nitrogen atmosphere. All starting materials and reagents used were of standard analytical grade from Merck (Darmstadt, Germany) and Aldrich (Steinheim, Germany) and used without further purification. *Lycopodium clavatum* spores (sporopollenin) with 20 μm particle size are obtained from Fluka Chemicals. The pH of the solution was adjusted by mixing appropriate amount of (0.1 N) HCl and/or KOH. Anion was used as its sodium salt. All aqueous solutions were prepared with deionized water that was passed through a Millipore milli-Q Plus water purification system. Melting points were determined on a Gallenkamp apparatus (UK) in a sealed capillary glass tube. ^{1}H NMR spectra were recorded on a spectrometer (Varian 400 MHz, UK) at room temperature unless otherwise specified. IR spectra were recorded with a (FT-IR, Perkin-Elmer 1605, USA) spectrometer as KBr pellets. UV–Vis spectra were obtained on a (UV-160A, Shimadzu, Japan) UV–Vis recording spectrophotometer using standard 1.00 cm quartz cells (to analyze Cr(VI) in aqueous solution). In order to obtain information about the surface morphologies of **Sp** and **Sp-Calix**, scanning electron microscopy, SEM was performed in a ZEISS EVO LS 10 SEM at accelerating voltage of 20 kV. Before scanning process, all samples were dried and coated with gold to enhance the electron conductivity. Elemental analyses were performed using a Leco CHNS-932 analyzer. An "Orion 410A+" pH meter was used for the pH measurements.

Synthesis of *p-tert*-butylcalix[4]arene diester (**2**)

Yield: 14 g (63.4 %); mp: 202–207 °C. IR (KBr): 1,750 cm^{-1} (C=O). ^{1}H NMR (CDCl$_3$): δ 0.97 (s, 18H, Bu^t), 1.24 (s, 18H, Bu^t), 3.35 (d, 4H, $J = 12.6$ Hz, ArCH$_2$Ar), 3.85(s, 6H, OCH$_3$), 4.45 (d, 4H, $J = 12.6$, ArCH$_2$Ar), 4.78 (s, 4H, OCH$_2$CO), 6.85 (s, 4H, ArH), 7.05 (s, 4H, ArH), 7.10 (s, 2H, OH).

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

Yield: 1.6 g (53.3 %); mp: 330–333 °C. IR (KBr): 1,687 cm^{-1} (amide carbonyl band, N–C=O). ^{1}H NMR (400 MHz CDCl$_3$): δ 1.02 (s, 18H, Bu^t), 1.26 (s, 18H, Bu^t), 2.15 (d, 4H, $J = 1.6$ Hz, NH$_2$), 3.42 (d, 4H, $J = 13.3$ Hz, ArCH$_2$Ar), 4.11 (d, 4H, $J = 13.2$ Hz, ArCH$_2$Ar), 4.63 (s, 4H, OCH$_2$), 6.92 (s, 4H, ArH), 7.10 (s, 4H, ArH), 7.70 (s, 2H, OH), 9.61 (brs, 2H, NH). Anal. calcd. for C$_{48}$H$_{64}$N$_4$O$_6$: C, 72.70; H, 8.13; N, 7.06 (%). Found (%): C, 71.58; H, 8.27; N, 7.01.

Preparation of sporopollenin containing active sides (**SP-iso**)
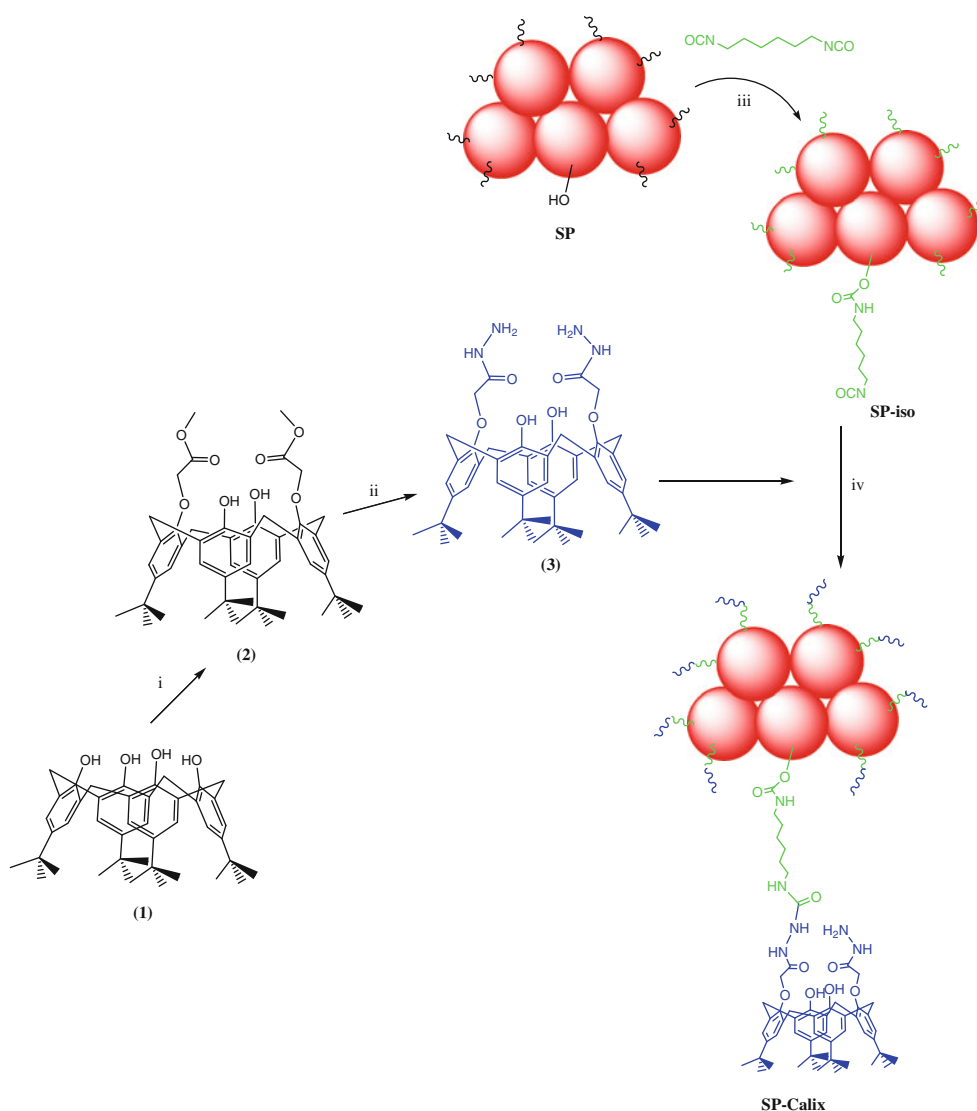
Sporopollenin (2.0 g) was mixed with 20 cm^3 of dry DMF at room temperature. Then 10 cm^3 of hexamethylene diisocyanate was added dropwise and stirred at 70 °C for 2 h and 20 min. The precipitated solution was filtered and washed with acetone. The product was dried under vacuum. The IR spectral data is as (KBr disk) cm^{-1}: 2,263 (isocyanate N=C=O), 1,724 and 1,661 (C=O).

Preparation of calix[4]arene-based sporopollenin (**SP-Calix**)

0.5 g of dihydrazine amide derivative **3** was dissolved in 20 cm^3 of DMF. 1.5 g of sporopollenin was added to that solution and stirred and heated at 70 °C for 2 h. The reaction was monitored by IR. After cooling to room temperature, that mixture was filtered off and washed with CH$_2$Cl$_2$ to remove excess of **3** and with deionized water to neutral pH. The IR spectral data is as (KBr disk) cm^{-1}: 1,719 and 1,609 (C=O) (see Fig. 1).

Dichromate anion extraction studies

The extraction capacity of the newly synthesized calixarene-based sorbent (**SP-Calix**) were determined through the batch wise sorption methods [17]. For liquid–liquid extraction, the 10 cm^3 aqueous solution of Na$_2$Cr$_2$O$_7$ (1.0×10^{-4} mmol dm^{-3}) and 10 cm^3 solution of ligand **3** (1×10^{-3} mmol dm^{-3} in CH$_2$Cl$_2$) were taken into the Erlenmeyer flask. While for solid–liquid extraction, the 25 mg of sorbent

Fig. 1 The IR spectrum of **3**, **SP-iso** and **SP-Calix**

(**SP-Calix**) was added to the Erlenmeyer flask containing 10 cm^3 aqueous solution of $Na_2Cr_2O_7$ (1.0×10^{-4} mmol dm^{-3}). The Erlenmeyer flasks were stirred on a horizontal shaker operating at a constant speed (175 rpm) at 25 °C for 1 h. The sorbents were separated from sorbate, the residual concentration of dichromate ion in aqueous phase was analyzed by UV–Vis spectrophotometer at 346 nm.

The % extraction (E%) of dichromate ion was calculated as follows:

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

where as C_o and C are the initial and final concentrations of the dichromate ion before and after the extraction, respectively.

The sorption capacity was calculated as follows:

The amount of Cr(VI) ions sorbed were computed from the difference between the C_o and the C using the relationship [18],

$$q = \frac{(C_o - C)V}{W} \quad (2)$$

where q is the amount of Cr(VI) ion sorbed onto unit amount of the sorbent (mmol g^{-1}), C_o and C (mmol dm^{-3}), V the volume of the aqueous phase (dm^3), and W is the dry weight of the sorbent (g).

Results and discussion

Synthesis and characterization of new host molecules

The main goal of this work was the synthesis of new calix[4]arene-based sporopollenin (**SP-Calix**) sorbent and evaluation of its binding ability towards dichromate anion. All new compounds have been characterized through IR, SEM and Elemental analyses techniques.

Scheme 1 shows the modification of sporopollenin (**SP-iso**) bearing the active isocyanate sides. The **SP-Calix** was prepared by the reaction of **SP-iso** and hydrazine amide substituted calix[4]arene (**3**) after the formation of **SP-iso**. The formation of **SP-iso** was confirmed by the appearance of the characteristic isocyanate and carbonyl bands at about 2,263 and 1,724, and 1,661 cm^{-1}, respectively in the FT-IR spectra (Fig. 1).

p-tert-Butylcalix[4]arene (**1**), a diester derivative of *p-tert*-butylcalix[4]arene (**2**) and hydrazine-substituted *p-tert*-butyl-calix[4]arene (**3**) were synthesized by a modification of the literature route (see Scheme 1) [14–16]. The substitution of diester derivative of *p-tert*-butylcalix[4]arene (**2**) was conducted in the presence of CH_2Cl_2/CH_3OH with hydrazine to afford the cone conformer hydrazine-substituted calix[4]arene (**3**). The formation of the hydrazine-substituted calix[4]arene (**3**) was confirmed by the appearance of the characteristic amide bands at about 1,687 cm^{-1} and by the disappearance of an ester carbonyl band at 1,750 cm^{-1} in the IR spectra. The ^{1}H NMR spectra of **3** has a typical AX pattern for the methylene bridge proton (ArCH$_2$Ar) of the calixarene moiety, at 3.42 and 4.10 ppm ($J = 13.2$ Hz) respectively, which demonstrates that **3** exists in the cone conformation [19].

The dihydrazine-substituted calixarene-based sporopollenin (**SP-Calix**) was prepared as mention in Scheme 1. The formation of **SP-Calix** was confirmed through the FT-IR spectroscopy, the appearances of some additional characteristic carbonyl bands at about 1,719 and 1,609 cm^{-1}, and the disappearance of isocyanate band at 2,263 cm^{-1} in the FT-IR spectrum (Fig. 1) clearly indicates the formation of **SP-Calix**.

Scheme 1 The synthetic route for the preparation of **SP-Calix**. Reaction conditions: (*i*) methyl bromoacetate chitosan, DMF, 70 °C, 5 h; (*ii*) cellulose, DMF, 70 °C, 4.5 h; (*iii*) methylbromoacetate, K₂CO₃, CH₃CN, reflux; (*iv*) hydrazine, CH₂Cl₂/CH₃OH, r.t.; (*v*) **Chi-iso**, DMF, 70 °C; (*vi*) **Cel-iso**, DMF, 70 °C

The elemental analysis results for **SP**, **SP-iso** and **SP-Calix**, as given in Table 1 confirmed the immobilization of the hydrazine-substituted calix[4]arene (**3**) was accomplished. The amount of loaded calix[4]arene (**3**) onto the sporopollenin was evaluated from the results of elemental analysis. According to the elemental analysis, the resulting **SP-Calix** contains 1.71 % nitrogen, corresponding to 0.5 mmol of **3**/g of support.

To verify changes in the immobilized chemical preparation during this reaction, a SEM image obtained sporopollenin (Fig. 2a) was compared with image of **SP-Calix** (Fig. 2b). Figure 2b exhibits a porous surface structure caused by the crosslinking of sporopollenin chains with calixarene units, which hampered the formation of the intramolecular hydrogen bonds. This type porous structure

Table 1 Results of elemental analysis for **SP**, **SP-iso** and **SP-Calix**

Compounds	C (%)	H (%)	N (%)
SP	56.8	7.55	–
SP-iso	66.8	8.51	1.01
SP-Calix	44.01	5.27	1.71

confirms that a calixarene unit onto the surface of modified sporopollenin has been successfully immobilized.

Evaluation of extraction capabilities of both 3 and SP-Calix

It is well known that under the acidic conditions $Na_2Cr_2O_7$ is converted into $H_2Cr_2O_7$ and following the ionization in an
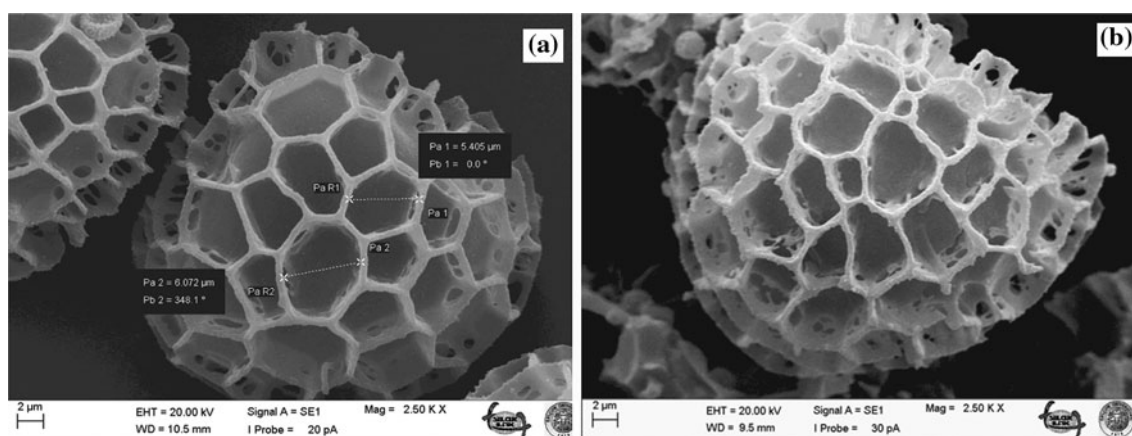
Fig. 2 SEM micrographs of **a** sporopollenin and **b** SP-Calix

aqueous solution it exists as $HCr_2O_7^-/Cr_2O_7^{2-}$ form [4]. Moreover, at highly acidic conditions the $HCr_2O_7^-$ as well as $Cr_2O_7^{2-}$ dimers become the dominant Cr(VI) form and pK_{a1} and pK_{a2} values of these equations are 0.74 and 6.49, respectively [4]. At pH < 6, the oxyanions structure changes from the monomeric CrO_4^{2-} to the dimeric $HCr_2O_7^-$ [20]. These oxides might be incorporated with the host molecules via hydrogen bonding and ionic interactions. For this reason, we have examined the extraction abilities of **3** and **SP-Calix** for dichromate anions at a wide range of pH 1.5–4.5. A preliminary evaluation of the binding efficiency of **3** was carried out by liquid–liquid extraction system of $Na_2Cr_2O_7$ from aqueous solution.

The extraction results showed that dihydrazine-substituted calixarene (**3**) is an effective extractant at low pH between 1.5 and 4.5. The percentage of dichromate ions extracted was 99.7 % when the pH of the aqueous solution was 1.5 and attained a minimum of 11.6 % when the pH of the aqueous solution increased to 4.5. Extractant **3** provides suitable binding sites for dichromate anions at low pH due to the presence of protonable amine moieties.

The binding efficiency of the other host **SP-Calix** was also examined through the solid-phase sorption of $HCr_2O_7^-$ from aqueous solution at different pH. The Fig. 3 represents the sorption results of **SP-Calix.** From these results it is concluded that, due to the rigid structure **SP-Calix** is a most effective sorbent for the removal of dichromate anions. This sorption behavior can be easily explained by the fact that **SP-Calix** is protonated from free amine moieties under acidic conditions and it would be easily form complexes with dichromate anions by electrostatic interactions as well as hydrogen bonding.

Effect of the pH

The pH value of the metal ions solution is one of the most important factors influencing the sorption behavior of
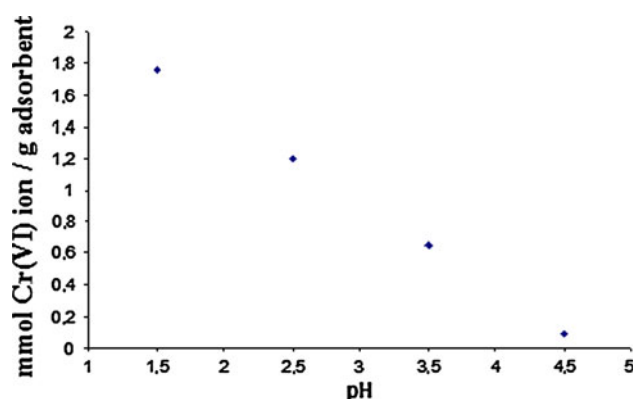

Fig. 3 Effect of solution pH on sorption of Cr(VI) ion by using **SP-Calix**

metal ions on sorbents. It impact not only the surface structure of sorbents and the formation of metal ions, but also it may influence the interaction between the sorbents and sorbets i.e. Cr(VI) ions [21]. The Fig. 3 show the pH effect during the sorption of Cr(VI) onto the **SP-Calix**. From the Fig. 3, it can be obviously conclude that, by increasing the pH from (1.5–4.5), sorption decreases i.e. the amount of absorbed Cr(VI) ions decreases. Whereas by decreasing the pH percent sorption increases and a significant sorption (97.9 %) of Cr(VI) ions by using **SP-Calix** occurred at pH 1.5. In addition, the low percent sorption observed at pH 3.5 and 4.5. Therefore the pH 1.5 has been selected to study the sorption characteristics of **SP-Calix** for Cr(VI) ion.

Sorption isotherm

The sorption isotherms are important to understand the mechanism of the sorption systems. Analysis of isotherm data plays a vital role to predict the sorption capacity of sorbent. In this study, for the explanation of interactive behavior between the sorbate and the sorbent the

Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms models have been used [18].

The Langmuir sorption isotherm model assumes monolayer coverage of sorbate over a homogenous sorbent surface. A basic assumption is that sorption takes place at specific homogeneous sites within the sorbent, and can be successfully use to study the behavior of monolayer sorption. The linearized form of the Langmuir isotherm models is represented as follows [18];

$$\frac{C_e}{q_e} = \frac{C_e}{q_o} + \frac{1}{q_o b} \qquad (3)$$

where q_e is the amount of sorbate (mmol g^{-1}) at sorbent surface, C_e is the amount of sorbate in the liquid phase at equilibrium (mmol dm^{-3}), q_o is the maximum surface density at monolayer coverage (mmol g^{-1}) and b is the Langmuir sorption constant (dm^3 mmol^{-1}). The plot of C_e/q_e versus C_e for the sorption gives a straight line of slope $1/b\,q_o$ and intercepts $1/q_o$ (Fig. 4a).

The Freundlich model assumes a heterogeneous sorption surface with sites that have different energies of sorption and are not equally available [18]. The Freundlich isotherm is more widely used but provides no information on the monolayer sorption capacity, in contrast to the Langmuir model. Its linearized form can be written as;

$$\ln q_e = \ln K_F + 1/n \ln C_e \qquad (4)$$

where q_e is the amount of sorbate (mmol g^{-1}) at sorbent surface, C_e is the amount of sorbate in the liquid phase at equilibrium (mmol dm^{-3}), q_o is the maximum surface

density at monolayer coverage and b is the Langmuir sorption constant (L mmol^{-1}), K_F is the Freundlich constant (mmol g^{-1}) which indicates the sorption capacity and represents the strength of the sorptive bond and n is the heterogeneity factor which represents the bond distribution. The plot of $\ln q_e$ versus $\ln C_e$ should give a straight line with a slope of $1/n$ and the intercept of log K_F (Fig. 4b).

The D–R isotherm can be used to describe sorption on both homogenous and heterogeneous surfaces. For the extensive investigate of the sorption mechanism, the sorption data have been also analyzed by D–R isotherm model [18]. A linearized form of D–R isotherm is as follow;

$$\ln q_e = \ln q_m - k\varepsilon^2 \qquad (5)$$

where ε (Polanyi potential) is $\left[RT \ln\left(1 + {}^1/_C\right)\right]$, q_e is the amount of solute sorbed per unit weight of sorbent (mol g^{-1}), k is a constant related to the sorption energy (mol^2 (kJ^2)$^{-1}$), and q_m is the sorption capacity (mol g^{-1}). Hence by plotting $\ln q_e$ versus ε^2 it is possible to generate the value of q_m from the intercept, and the value of k from the slope (Fig. 4c).

E (kJ mol^{-1}) is defined as the free energy change that is required to transfer 1 mol of ions from solution to the solid surfaces. The relation is the following;

$$E = \frac{1}{\sqrt{2\beta}} \qquad (6)$$

The magnitude of E can be related to the reaction mechanism. If E value lies between 8 and 16 kJ mol^{-1}, the sorption process takes place by chemically while

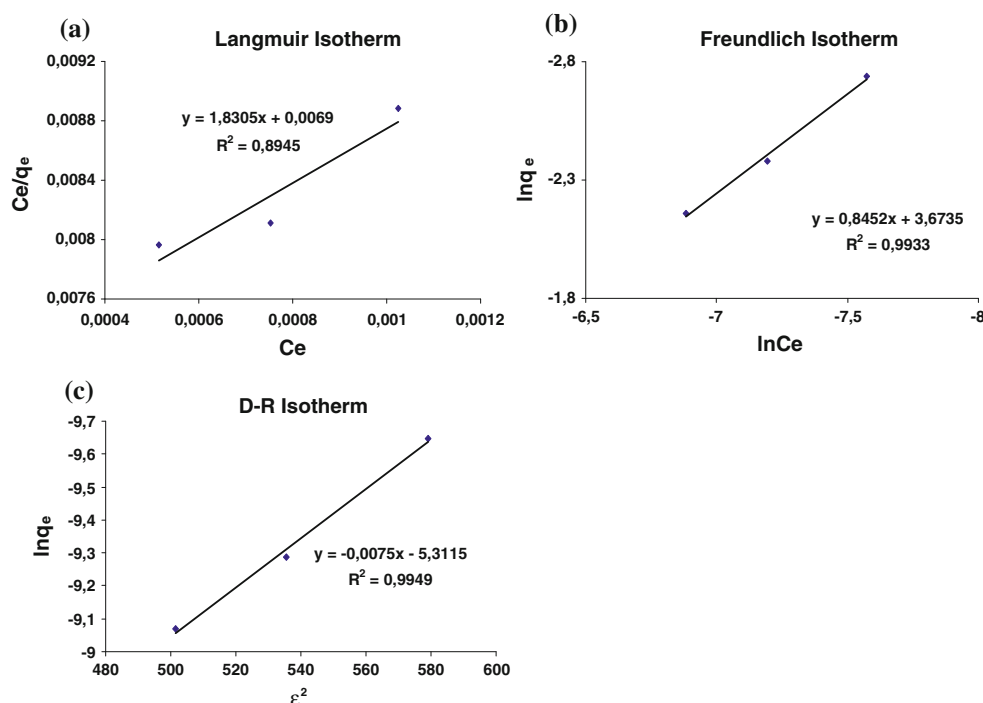Fig. 4 Langmuir, Freundlich and D–R isotherm curves for the sorption of Cr(VI) ion by using **SP-Calix**

Table 2 Isotherms parameters for Cr(VI) by **SP-Calix** (temperature = 298 K, pH = 1.5)

Ion	Freundlich isotherm		Langmuir isotherm		D–R isotherm		
	n	K_F	q_o	b ($\times 10^2$)	k	q_m	E
Cr(VI)	1.19	9.38	0.54	1.44	0.0075	4.93	15.43

Table 3 Thermodynamic parameters for Cr(VI) sorption by **SP-Calix** (Cr(VI) ion concentration: 5 mmol dm^{-3}, pH: 1.5)

Ion	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	$-\Delta G^o$ (kJ mol^{-1})		
			291	298	323
Cr(VI)	41.01	222.48	23.76	25.32	30.88

$E < 8$ kJ mol^{-1}, the sorption process is carried out physically. The mean sorption energy was calculated as a 8.16 kJ mol^{-1} for Cr(VI). This value indicated that removal of Cr(VI) ion on **SP-Calix** mainly proceeds chemically due to its value of E [18].

The Langmuir, Freundlich and D–R isotherm parameters for the sorption of Cr(VI) ion onto **SP-Calix** are listed in Table 2. Based on the correlating coefficients, the Freundlich model was found to be the most appropriate to describe the sorption process of this ion on **SP-Calix**.

For the Langmuir isotherm model, The R^2 value was found to be 0.8945. This result indicates that the this model was not able to adequately to describe the relationship between the sorbed amount of Cr(VI) and its equilibrium concentration in the solution. However, the Freundlich and D–R isotherm models best fitted with the equilibrium data since it presents higher R^2 value. From the results of Langmuir isotherm, the maximum sorption capacity of **SP-Calix** was obtained 0.54 mmol g^{-1} (28.07 mg g^{-1}). The value of b, is related to affinity of the binding cites was calculated 144 dm^3 mmol^{-1}. K_F and n the Freundlich isotherm parameters related to the sorption capacity and sorption intensity of the sorbent, respectively. The values of n and K_F were calculated 1.19 and 39.38, respectively. When n values approached zero, the surface site heterogeneity increased. The value of $n > 1$ ($1/n$ less than 1) indicated favorable sorption of Cr(VI).

Thermodynamic study

The thermodynamic parameters including change in the enthalpy (ΔH^o), entropy (ΔS^o), and Gibbs free energy (ΔG^o), are the actual indicators for practical application of a process. In the present work, the effect of temperature on sorption was studied at different temperatures (i.e. 291, 298 and 323 ± 1 K). ΔH^o and ΔS^o were calculated from the slope and intercept of the linear plot of ln(q_e/C_e) versus $1/T$. ΔG^o by using Eq. (9) [22]:

$$K_D = \frac{(C_o - C)}{C} \times \frac{V}{W} \tag{7}$$

$$\log K_D = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT} \tag{8}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{9}$$

where C_o and C are the initial and equilibrium concentrations of the metal ions in aqueous phase (mmol dm^{-3}), V is the volume of the aqueous phase (dm^3), and W is the dry weight of the sorbent (g). Where ΔG^o is the change in Gibbs free energy (kJ mol^{-1}), ΔH^o is the change in enthalpy (kJ mol^{-1}), ΔS^o is the change in entropy (kJ (mol K)$^{-1}$), T is the absolute temperature (K), R is the gas constant (8.314 × 10^{-3} kJ mol^{-1} K^{-1}).

The values obtained from Eqs. (7–9) are listed in Table 3. The ΔG^o value is negative as expected for a spontaneous process under the applied conditions. The more negative values of ΔG^o with increase of temperature indicate more efficient sorption at higher temperature. The positive value of (ΔH^o) enthalpy change confirms that sorption process is endothermic in nature. The positive value of entropy (ΔS^o) suggests the increase in randomness at the solid–solution interface by the fixation of dichromate ions on the sorbent during the sorption. Dichromate ions in aqueous media are hydrated. The ions were sorbed on the sorbent surface, water molecules previously bounded to the Cr(VI) ions were released and dispersed in solution, resulting in an increase in entropy [23]. And also, the magnitude of sorption enthalpy change may give an idea about the type of sorption. In physical sorption, the process is fast and usually reversible due to the small energy requirement. Energies of 4–8 kJ mol^{-1} are required by London Van der Waals interactions compared from 8 to 40 kJ mol^{-1} for hydrogen bonding. But sometimes the enthalpy associated with chemical sorption according to is 40 kJ mol^{-1}, a value that has been recognized in the literature as the transition boundary between both types of sorption processes [24]. In this study, ΔH^o values for Cr(VI) sorption was calculated as 41.01 kJ mol^{-1}, indicating a surface chemical reaction control mechanism.

Conclusions

Preparation and characterization of **SP-iso** and **SP-Calix** were successfully achieved in order to perform both more rigid structural features and to bring about stabilization. The extraction/sorption studies of dichromate anion were performed using **3** and **SP-Calix**. The extraction results indicated that the complexation of dichromate anions depends on the structural properties of the receptors such as

proton-switchable ability and hydrogen-binding ability for **3**. The sorption results also reflected that the complexation of dichromate anions with **SP-Calix** depends on the structural properties of the receptors, such as stability or rigidity, proton-switchable and hydrogen-binding abilities depending on medium pHs, especially pH 1.5. Besides, thermodynamic parameters depicted that sorption process was thermodynamically favorable which means the combination of a calix[4]arene dihydrazine derivative with sporopollenin became a useful approach to remove of dichromate oxyanions from aqueous solutions via sorption.

References

1. Shinkai, S.: Molecular recognition of calixarene-based host molecules. J. Incl. Phenom. **7**, 193–201 (1989)
2. Cuřínová, P., Pojarová, M., Budka, J., Lang, K., Stibor, I., Lhoták, P.: Binding of neutral molecules by *p*-nitrophenylureido substituted calix[4]arenes. Tetrahedron **66**, 8047–8050 (2010)
3. Akkuş, G.U., Memon, S., Sezgin, M., Yilmaz, M.: Synthesis of calix(aza)crown and its oligomeric analogue for the extraction of selected metal cations and dichromate anions. Clean Soil Air Water **37**, 109–114 (2009)
4. Sayin, S., Yilmaz, M.: Synthesis of a new calixarene derivative and its immobilization onto magnetic nanoparticle surfaces for excellent extractants toward Cr(VI), As(V), and U(VI). J. Chem. Eng. Data **56**, 2020–2029 (2011)
5. Stastny, V., Lhoták, P., Michlová, V., Stibor, I., Sykora, J.: Novel biscalix[4]arene-based anion receptors. Tetrahedron **58**, 7207–7211 (2002)
6. Deligöz, H., Erdem, E.: Comparative studies on the solvent extraction of transition metal cations by calixarene, phenol and ester derivatives. J. Hazard. Mater. **154**, 29–32 (2008)
7. Ghidini, E., Ugozzoli, F., Ungaro, R., Harkema, S., Abu El-Fadl, A., Reinhoudt, D.N.: Complexation of alkali metal cations by conformationally rigid, stereoisomeric calix[4]arene crown ethers: a quantitative evaluation of preorganization. J. Am. Chem. Soc. **112**, 6979–6985 (1990)
8. Sayin, S., Ozcan, F., Yilmaz, M.: Synthesis and evaluation of chromate and arsenate anions extraction ability of a *N*-methyl-glucamine derivative of calix[4]arene immobilized onto magnetic nanoparticles. J. Hazard. Mater. **178**, 312–319 (2010)
9. Tutar, H., Yilmaz, E., Pehlivan, E., Yilmaz, M.: Immobilization of *Candida rugosa* lipase on sporopollenin from *Lycopodium clavatum*. Int. J. Biol. Macromol. **45**, 315–320 (2009)
10. Brooks, J., Shaw, G.: Chemical structure of the exine of pollen walls and a new function for carotenoids in nature. Nat. Lond. **219**, 532–533 (1968)
11. Losi, M.E., Amrhein, C., Frankenberger, W.T.: Environmental biochemistry of chromium. Rev. Environ. Contam. Toxicol. **136**, 91–121 (1994)
12. Liu, T., Rao, P., Mak, M.S.H., Wang, P., Lo, I.M.C.: Removal of co-present chromate and arsenate by zero-valent iron in groundwater with humic acid and bicarbonate. Water Res. **43**, 2540–2548 (2009)
13. Ranjan, D., Talat, M., Hasan, S.H.: Biosorption of arsenic from aqueous solution using agricultural residue 'rice polish'. J. Hazard. Mater. **166**, 1050–1059 (2009)
14. Gutsche, C.D., Nam, K.C.: Calixarenes. 22. Synthesis, properties, and metal complexation of aminocalixarenes. J. Am. Chem. Soc. **110**, 6153–6162 (1988)
15. Collins, E.M., McKervey, M.A., Madigan, E., Moran, M.B., Owens, M., Ferguson, G., Harris, S.J.: Chemically modified calix[4]arenes, regioselective synthesis of 1,3-(distal) derivatives and related compounds. X-ray crystal structure of a diphenol-dinitrile. J. Chem. Soc. Perkin Trans. **1**(12), 3137–3142 (1991)
16. Alekseeva, E.A., Bacherikov, V.A., Gren, A.I.: Synthesis of *p-tert*-butylcalix[4]arene derivatives containing amino acid residues. Russ. J. Gen. Chem. **70**, 490–492 (2000)
17. Sayin, S., Ozcan, F., Memon, S., Yilmaz, M.: Synthesis and oxoanions (dichromate/arsenate) sorption study of *N*-methylglucamine derivative of calix[4]arene immobilized onto poly [(phenyl glycidyl ether)-co-formaldehyde]. J. Incl. Phenom. **67**, 385–391 (2010)
18. Gubbuk, I.H., Gup, R., Kara, H., Ersoz, M.: Adsorption of Cu(II) onto silica gel-immobilized Schiff base derivative. Desalination **249**, 1243–1248 (2009)
19. Jaime, C., de Mendoza, X., Prados, P., Nieto, P.M., Sanchez, C.: Carbon-13 NMR chemical shifts. A single rule to determine the conformation of calix[4]arenes. J. Org. Chem. **56**, 3372–3376 (1991)
20. Memon, S., Roundhill, D.M., Yilmaz, M.: Remediation and liquid–liquid phase transfer extraction of chromium(VI). A review. Collect. Czech. Chem. Commun. **69**, 1231–1250 (2004)
21. Zong, G., Chen, H., Qu, R., Wang, C., Ji, N.: Synthesis of polyacrylonitrile-grafted cross-linked N chlorosulfonamidated polystyrene via surface-initiated ARGET ATRP, and use of the resin in mercury removal after modification. J. Hazard. Mater. **186**, 614–621 (2011)
22. Ahmad, S., Khalid, N., Daud, M.: Adsorption studies of lead on lateritic minerals from aqueous media. Sep. Sci. Technol. **37**, 343–362 (2002)
23. Bhadoria, R., Singh, B.K., Tomar, R.: Sorption of toxic metals on sodium aluminosilicate (NAS). Desalination **254**, 192–200 (2010)
24. Cea, M., Seaman, J.C., Jara, A., Mora, M.L., Diez, M.C.: Kinetic and thermodynamic study of chlorophenol sorption in an allophanic soil. Chemosphere **78**, 86–91 (2010)