

Synthesis and oxoanions (dichromate/arsenate) sorption study of *N*-methylglucamine derivative of calix[4]arene immobilized onto poly[(phenyl glycidyl ether)-co-formaldehyde]

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Abstract The article describes synthesis as well as the evaluation of sorption properties of new *N*-methylglucamine substituted calix[4]arene and its poly[(phenyl glycidyl ether)-co-formaldehyde] immobilized product. Firstly, 5,17-bis-[(*N*-methylglucamine)methyl]-25,26,27,28-tetrahydroxy-calix[4]arene (**3**) was synthesized by the treatment of calix[4]arene with a secondary amine *N*-methylglucamine and formaldehyde via Mannich reaction. The immobilization of **3** onto poly[(phenyl glycidyl ether)-co-formaldehyde] to form calixarene based polymer (**4**) was carried out under suitable reaction conditions via nucleophilic substitution reaction. All the new compounds were characterized by a combination of FT-IR, ¹H-NMR spectroscopic and elemental analysis techniques. The sorption studies of **4** reveal that it is an excellent material for the removal of toxic oxoanions especially arsenate from aqueous environment. To understand the selectivity of **4**, we also examined the retention of dichromate anions in the presence of Cl⁻, NO₃⁻ and SO₄²⁻ anions at pH 1.5.

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

Introduction

Calix[*n*]arenes have received much attention in supramolecular chemistry over the last decade [1–3]. They represent a class of macrocycles widely used as typical third generation host compounds in supramolecular chemistry for the construction of various receptors or complexation agents for anions, cations and neutral molecules [4]. The complexation properties of calix[*n*]arene derivatives appear to be highly dependent upon the nature and number of donor atoms and in particular, upon the conformation of the calix[4]arene moiety [5–8]. Therefore, the potential as receptors depends on introducing various functional groups either to the upper or to the lower rim of the calixarene molecule [9–12]. Generally, calix[4]arene derivatives bearing amine or amide functions, capable of interacting with anions by hydrogen bonds are employed as selective anion extractant molecules [13]. Recently, we have reported calix[4]arene-based receptors, which effectively bind anions and can be useful for multiple applications such as laboratory, clinical, environmental, and industrial process analyses [14–19].

Toxic oxoanions (arsenite, arsenate, chromate, and dichromate) contamination of water is a serious hazard. Apart from the industrial and other anthropogenic activities, they also enter into the groundwater from natural sources [20]. Arsenic is one of the trace elements well-documented as groundwater contaminant and a serious public health concern in recent years due to its known carcinogenic as well as other adverse health effects [21, 22]. The European Commission [23], the US Environmental Protection Agency [24] and the World Health Organization (WHO) [25] have all recently revised the maximum arsenic concentration limit in drinking water by decreasing it from 50 to 10 μg L⁻¹ [26]. Therefore, various

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sophisticated methods [27–31] have needed to be improved and used for the removal of arsenic from the environment.

Chromium is also toxic, carcinogenic and harmful to human beings [32] in the form of Cr(VI) as As(V). Chromium and its compounds are widely used in plating, leather tanning, dye, cement, and photographic industries; producing large quantities of toxic pollutants [33]. Chromium can exist in several oxidation states, however, only the trivalent and hexavalent forms are environmentally important [34]. Chromium(III) has been reported to be biologically essential to mammals as it maintains effective glucose, lipid, and protein metabolisms. Moreover, chromium(VI) is toxic due to its diffusion as $\text{Cr}_2\text{O}_7^{2-}$ or HCr_2O_7^- through cell membranes and oxidize biological molecules [35].

The *N*-methyl- D -glucamin (NMDG) immobilized onto cross-linked polystyrene beads have been developed for boron removal from irrigation water in 1957 [36, 37]. Along with boron removal, NMDG containing several macroporous resins have been studied for its affinity for oxoanions of Ge(IV), V(V), Mo(VI), As(V), As(III), W(VI), Se(IV), Se(VI), and Sn(IV) [38, 39]; neither As(III) nor As(V) sorption was observed [40]. Herein, in view of the above fact **NMG-Calix (3)** was synthesized by following Mannich reaction. Then, **3** was immobilized onto poly[(phenyl glycidyl ether)-co-formaldehyde] (**PPGEF**) to obtain **PPGEF-NMG-Calix (4)**. The synthesized resin **4** was then applied for the sorption of oxoanions such as dichromate and arsenate from aqueous media.

Results and discussion

Synthesis

The main goal of this work was the design and synthesis of **3** and its immobilization onto PPGEF to obtain **4** as well as evaluation of their sorption properties toward dichromate and arsenate ions. All of the new compounds have been characterized through $^1\text{H-NMR}$, IR and Elemental analyses techniques. The synthetic route of new calixarene derivatives is given in Scheme 1.

To receive desired goal, *p*-*tert*-butylcalix[4]arene (**1**) and calix[4]arene (**2**) were prepared according to the known procedures [41]. The substitution of calix[4]arene (**2**) at its upper rim (Mannich reaction) was conducted in the presence of AcOH in THF with a secondary amine *N*-methylglucamine and formaldehyde to afford the cone conformer NMG-Calix (**3**) in 39% yield. The immobilization of **3** onto poly[(phenyl glycidyl ether)-co-formaldehyde] was carried out in the presence of potassium carbonate in CH_3CN to obtain polymeric calix[4]arene derivative (**PPGEF-NMG-Calix (4)**) in 63% yield. The

$^1\text{H-NMR}$ spectra of **3** has a typical AX pattern for the methylene bridge proton (ArCH_2Ar) of the calixarene moiety at 4.23 ppm ($J = 19.6$ Hz) which demonstrates that the compound **3** exists in the cone conformation [42]. The formation of PPGEF-NMG-Calix (**4**) was confirmed by the $^1\text{H-NMR}$ data that also demonstrates the presence of calix moieties in cone conformation in the backbone of **4**.

Dichromate anion sorption studies

The removal of the dichromate anion from wastewater sources gained high attention due to their high toxic effects. It is well known that as the pH of the aqueous solution is lowered ($\text{pH} < 6$), the oxoanion structure changes from the monomeric CrO_4^{2-} to the dimeric HCr_2O_7^- [43]. In view of that feature, we were interested in synthesizing novel polymeric calix[4]arene derivative as a host having proton-switchable binding lobes for anions and examining its sorption properties for anions at the varying range of pH, i.e. 1.5–4.5 pH. The solid–liquid sorption experiments for **3** were not performed due to its partial solubility in water. The sorption efficiency of **4** was investigated by solid-phase sorption system using aqueous solution of HCr_2O_7^- at different pH.

The sorption results given in Fig. 1 show that $\text{Na}_2\text{Cr}_2\text{O}_7$ could be extracted from aqueous solution at different pH. The results indicate that **4** has high anion sorption ability at low pH between 1.5 and 2.5. This high anion sorption ability can be explained by the fact that **4** is protonable in acidic conditions due to tertiary amine groups and it would form complex easily with dichromate anions by electrostatic interactions and hydrogen bonding. Moreover, calix[4]arene derivative may have gained a more rigid and appropriate structure for complexing with anions in the polymeric chain.

Consequently, the interfering effect of other anions on dichromate anion retention of **4** was examined by using additional different inorganic sodium salts (Cl^- , SO_4^{2-} and NO_3^-) and their mixture. The results are given in Table 1, showing the retention of dichromate ions with **4** in the presence of other anions. The sorption of $\text{Na}_2\text{Cr}_2\text{O}_7$ with **4** was not affected by the presence of other sodium salts. In view of these results, compound **4** could be used as selective ionophore for Cr(VI) in the presence of foreign anions.

Arsenate anion sorption studies

Arsenic is a serious public health concern because of its carcinogenic and other various health effects [21, 22]. For a molecule to be effective as a host, it is necessary that its structural features are compatible with those of the guest anions. The arsenate species occurs mainly in the form of

Scheme 1 The synthetic route for preparation of **PPGEF-NMG-Calix**. Reaction conditions: (i) AlCl_3 , phenol, toluene; (ii) *N*-methylglucamine, formaldehyde, CH_3COOH , THF; (iii) poly[(phenyl glycidyl ether)-co-formaldehyde], K_2CO_3 , CH_3CN

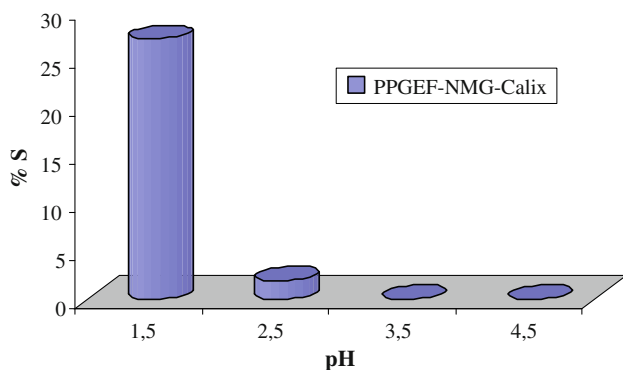
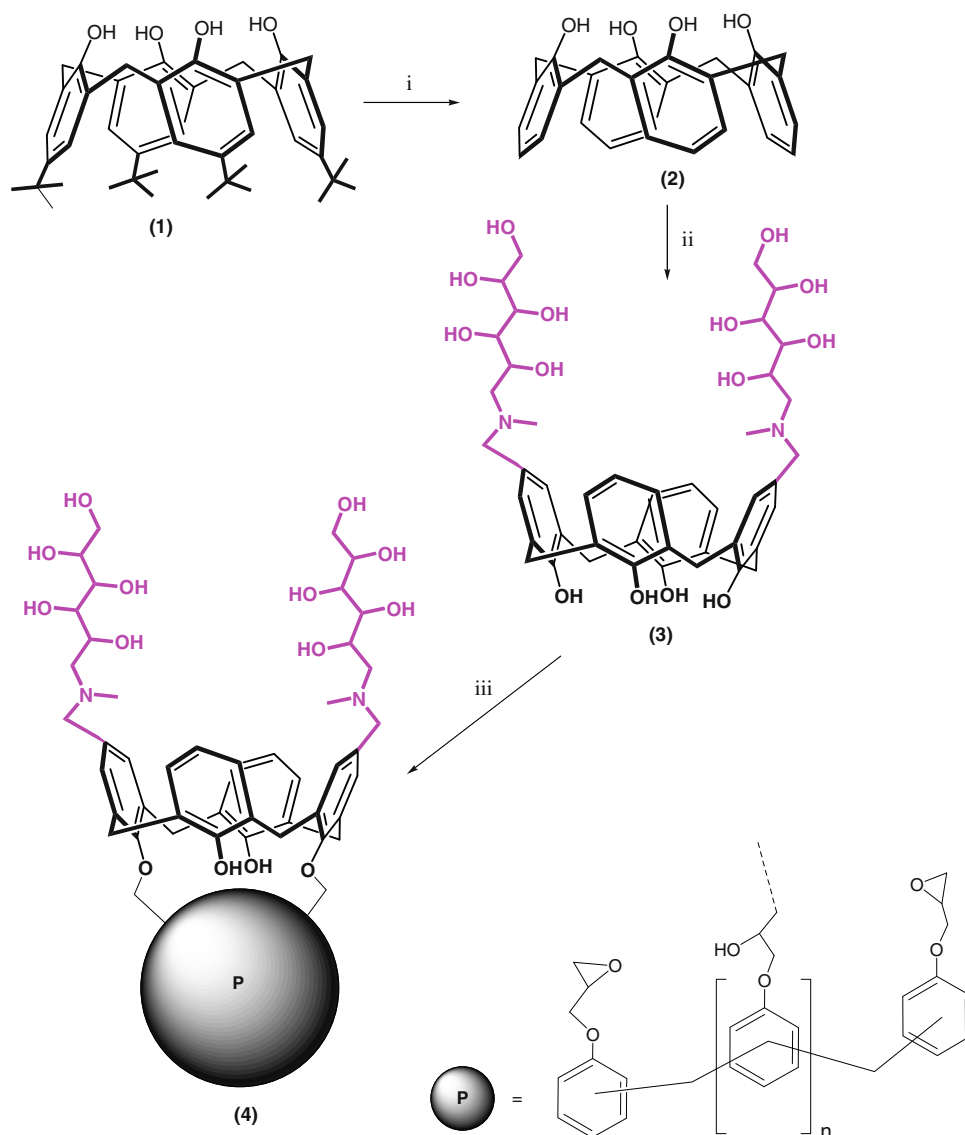


Fig. 1 Sorption percentages of dichromate anion with **PPGEF-NMG-Calix** at pH 1.5–4.5 (Solid phase, sorbent = 25 mg (**PPGEF-NMG-Calix**), aqueous phase, $\text{Na}_2\text{Cr}_2\text{O}_7 = 1.0 \times 10^{-4}$ M (10 mL) at 25 °C for 1 h)

Table 1 Dichromate retention results of **4** at 1.5 pH, in the presence of interfering anions (Cl^- , SO_4^{2-} and NO_3^-) and their mixture^a

	Different anions ^b				
	None	Cl^-	SO_4^{2-}	NO_3^-	Mixture
4	27	26.7	26.6	24.0	25.3

^a Solid phase, sorbent = 25 mg (**PPGEF-NMG-Calix**), aqueous phase, $\text{Na}_2\text{Cr}_2\text{O}_7 = 1.0 \times 10^{-4}$ M (10 mL) at 25 °C

^b The concentration of different anions = 1.0×10^{-2}

H_2AsO_4^- in the pH range between 3 and 6, while a divalent anion HAsO_4^{2-} dominates at higher pH values (such as between pH 8 and 11). Thus, it is evident that the adsorption of arsenate by calixarene is depending on pH ranges. In higher acidic conditions (pH 1–3) the arsenate

ions will be protonated in the H_3AsO_4 form. Besides this, the monoanion (H_2AsO_4^-) will have a smaller free energy of hydration as compared to its dianionic form HAsO_4^{2-} . In brief, the arsenate ions ($\text{H}_2\text{AsO}_4^-/\text{HAsO}_4^{2-}$) are mono/dianions having oxide moieties at the periphery of the anions. These oxides are potential sites for hydrogen bonding to the host molecule.

According to the literature [40], immobilized *N*-methyl-D-glucamine on poly(vinylbenzyl chloride) beads show high affinity towards arsenate ions. Therefore, we have designated and synthesized new **PPGEF-NMG-Calix (4)** and examined its sorption behavior toward arsenate ion. The results of sorption studies are summarized in Fig. 2. From the data given in Fig. 2, it is observed that arsenate anion was highly extracted by **4** at pH 3.5–5.5. This is not a surprising result because extractant **4** contains appropriate proton switchable amine binding sites and a great quantity of hydroxyl groups of NMG for aggregation of anions at low pH.

The maximum sorption (90%) of arsenate ions with **4** was observed at 3.5 pH and attained minimum (21%) at 5.5 pH. No sorption was observed when the pH increased to 7.0. The calix[4]arene based NMG derivative (**4**) provided suitable binding sites for interacting with the arsenate ions at low pH because of the presence of protonable amine groups. These interactions include electrostatic interactions and hydrogen bonding between protonable amine and the oxygens of arsenate anions [44]. The role of polymeric backbone may help in an increased interaction capability as well. The proposed interaction for the sorption of anions with **PPGEF-NMG-Calix** is given in Fig. 3 and Scheme 2.

Conclusion

The work reported here demonstrates the synthesis as well as dichromate and arsenate sorption studies of a new polymeric derivative (**4**) of NMG-Calix (**3**). The work

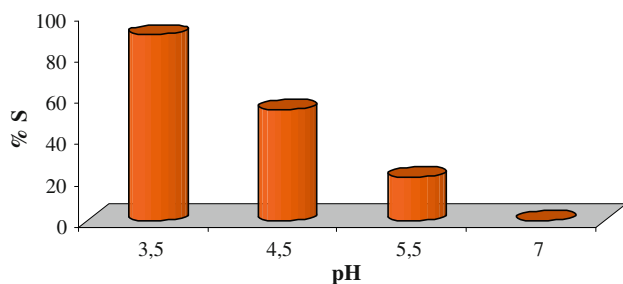


Fig. 2 Sorption percentages of arsenate anion with **PPGEF-NMG-Calix** at pH 3.5–7.0. (Solid phase, sorbent = 25 mg (**PPGEF-NMG-Calix**), aqueous phase, $\text{Na}_2\text{HAsO}_4 = 1.0 \times 10^{-5}$ M (10 mL) at 25 °C for 1 h)

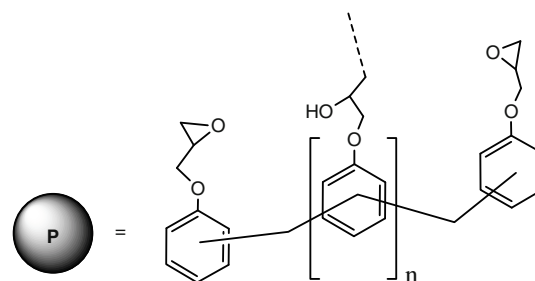
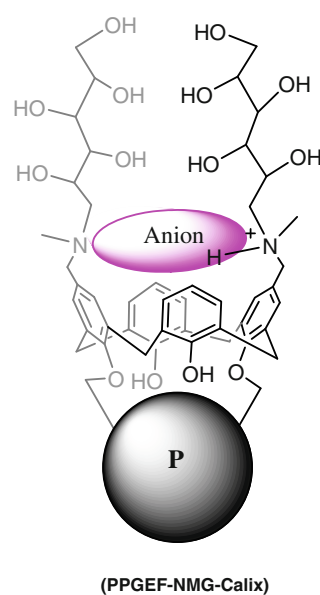


Fig. 3 Proposed interactions of **PPGEF-NMG-Calix** with anions (HCr_2O_7^- or H_2AsO_4^-)

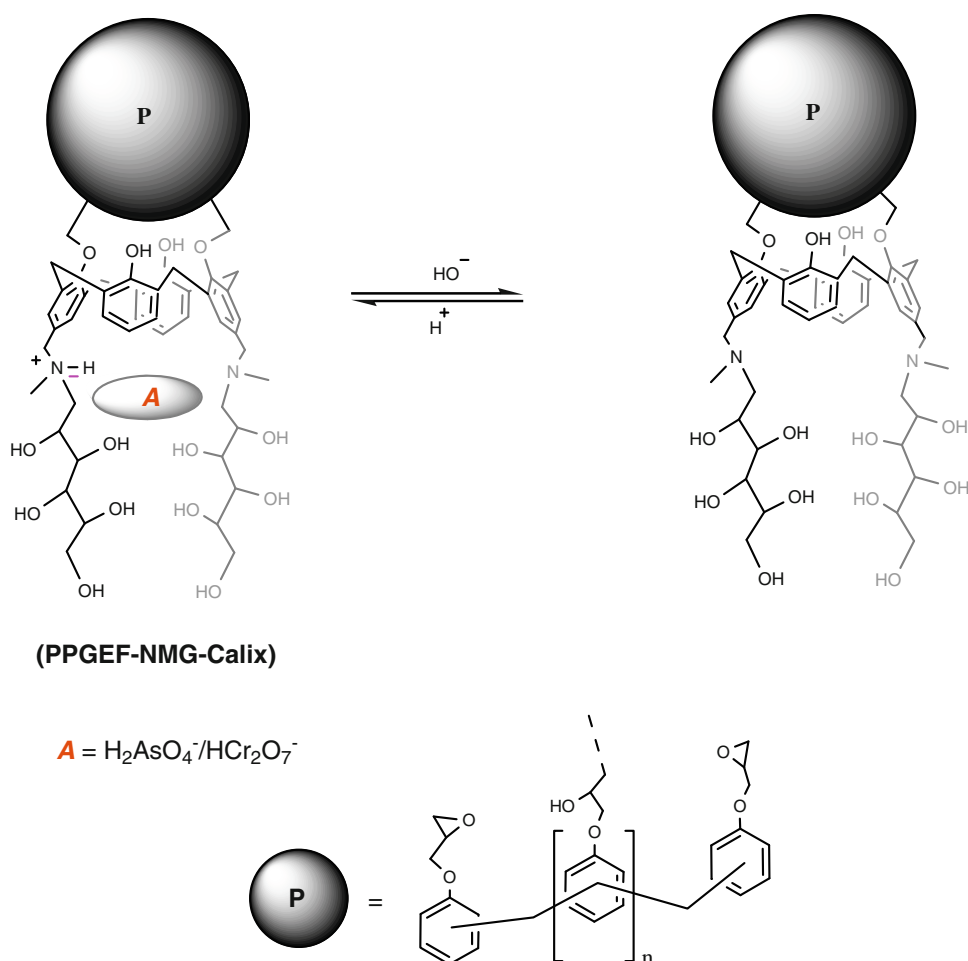
confirms good sorption efficiency of **4** toward dichromate and arsenate anions at low pH. The results can be explained on the basis of varying interactions, including electrostatic interactions and hydrogen bonding between protonable amine groups along with hydroxyl groups of the ligand and the oxygens of oxoanions. The work will find its applicability in various fields of analytical/environmental chemistry.

Experimental

General

Analytical TLC was performed on precoated silica gel plates (Merck, Darmstadt, Germany). All reactions, unless otherwise noted, were conducted under a nitrogen atmosphere. All starting materials and reagents used were of standard analytical grade from Fluka, Merck and Aldrich and used without further purification. The commercial grade solvents were distilled, and then stored over

Scheme 2 The suggested complexation phenomena of arsenate and dichromate ion with ion with **Calix-MN**



molecular sieves. Anions were used as their sodium salts. The drying agent employed was anhydrous MgSO_4 . All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli-Q Plus water purification system. Melting points were determined on a Gallenkamp apparatus in a sealed capillary and are uncorrected. Elemental analyses were performed using a Leco CHNS-932 analyzer. $^1\text{H-NMR}$ spectra were recorded on a Varian 400 MHz spectrometer. Chemical shifts are given in ppm relative to an internal standard tetramethylsilane ($\delta = 0.0$). IR spectra were recorded with a Perkin-Elmer 1605 FTIR spectrometer as KBr pellets. UV-vis spectra were obtained on a Shimadzu 160A UV-vis recording spectrophotometer. Atomic absorption spectra were obtained on High-Resolution Continuum Source AAS (ContrAA 300) (Analytikjena). An Orion 410A + pH meter was used for the pH measurements.

Synthesis

The syntheses of *p-tert*-butylcalix[4]arene (**1**) and calix[4]arene (**2**) were carried out according to the procedures described in Ref. [41].

Synthesis of 5,17-bis-[(*N*-Methyl-glucamine)methyl]-25,26,27,28-tetrahydroxycalix[4]arene (**3**)

4 mL of glacial acetic acid, *N*-methylglucamine (26.08 mmol), and 1.25 mL of aqueous formaldehyde (37%) were added into a solution of calix[4]arene (**2**) (4.7 mmol) in 150 mL of THF and the reaction mixture was stirred for 20 days at room temperature. The reaction mixture was monitored by TLC. The solvent was removed under vacuum, then methanol was added, the precipitates formed were filtered off and the received product was washed with water and dried in a vacuum desiccator. Yield 39%; m.p.: >350 °C. $^1\text{H-NMR}$ (400 MHz DMSO): δ 2.49 (s, 6H, $-\text{CH}_3$), 3.16–3.63 (br., 34H, $-\text{CH}_2-\text{N}-$, $-\text{CH}-$, $-\text{CH}_2-$, ArCH_2Ar , $-\text{OH}$, $\text{Ar}-\text{CH}_2-\text{N}-$), 4.23 (d, 4H, $J = 19.6$ Hz, ArCH_2Ar), 6.33–6.86 (br, 10H, ArH). Anal. Calcd. for $\text{C}_{44}\text{H}_{58}\text{N}_2\text{O}_{14}$; 62.99, C; 6.97, H; 3.34, N. Found: 63.02, C; 6.88, H; 3.32, N.

Synthesis of **PPGEF-NMG-Calix** (**4**)

A solution of compound **3** (0.238 mmol) in CH_3CN (30 mL) was stirred in the presence of K_2CO_3 (2.13 mmol)

at room temperature for half an hours. Then poly[(phenyl glycidyl ether)-co-formaldehyde] was added into reaction mixture and heated under refluxed for 16 h. The reaction was checked by TLC. The cooled mixture was filtered and evaporated. Resulting solid was washed three times with water. Yield of dark pink colour product comes out 63%; m.p. >350 °C. ¹H-NMR (400 MHz DMSO): δ 2.49 (s, 6H, -CH₃), 3.16–3.63 (br., 59H, -CH₂-, -CH-, -OH, ArCH₂Ar, -N-CH₂-), 4.23 (d, 4H, *J* = 19.6 Hz, ArCH₂Ar), 6.33–6.86 (br., 25H, ArH). Anal. Calcd. for C₈₀H₉₄N₂O₂₀: 68.46, C; 6.75, H; 2.00, N. Found: 68.53, C; 6.68, H; 2.06, N.

Sorption procedure

The sorption capacities of the synthesized calix[4]arene derivative (**4**) was determined by the following technique [14]: an aqueous solution (10 mL) containing Na₂Cr₂O₇ or Na₂HAsO₄ solution at a concentration of 1.0 × 10⁻⁴ M (for dichromate) and 1 × 10⁻⁵ (for Na₂HAsO₄·7H₂O) and 25 mg of the sorbent were mixed in a stoppered flask that was shaken at 175 rpm, 25 °C for 1 h. The sorbent was separated before measurements. The residual dichromate concentration of aqueous solute was determined spectrophotometrically by UV-vis analyses at 346 nm. The concentration of arsenate ion remaining in aqueous phase was determined by ContrAA 300 spectrometer. The effect of pH was studied by adjusting the pH of aqueous solutions using dilute HCl and KOH solutions at 25 °C. The experiments were performed in triplicate.

Blank experiments showed that no dichromate and arsenate sorption occurred in the absence of calix[4]arene.

The percent sorption (*S* %) was calculated according to Eq. 1;

$$S\% = (C_0 - C)/C_0 \times 100 \quad (1)$$

where C₀ and C are the initial and final concentrations of the dichromate ion before and after the sorption, respectively.

Selectivity Studies

Selectivity studies of **4** were performed in presence of nitrate (NO₃⁻), sulphate (SO₄²⁻) and chloride (Cl⁻) anions since they could be present more than dichromate anions in aqueous solutions. For this propose, anions were used as corresponded with one hundred-fold of dichromate anion concentration and determined according to literature [45].

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