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Synthesis of A New Calixarene Derivative and Its Immobilization Onto Magnetic Nanoparticle Surfaces for Excellent Extractants Toward Cr(VI), As(V), and U(VI)

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ABSTRACT: This article describes the synthesis of 5,11,17,23-tetra-*tert*-butyl-25,27-di(benzhydrazidylmethoxy)-26,28-dihydroxy-calix[4]arene (**3**) through the treatment of a dialkyl bromide derivative of *p*-*tert*-butylcalix[4]arene with benzhydrazide under mild reaction conditions. 5,11,17,23-Tetra-*tert*-butyl-25,27-di(benzhydrazidylmethoxy)-26,28-dihydroxy-calix[4]arene (**3**) was characterized by a combination of FTIR, ^{1}H NMR, and elemental analyses. The macrocyclic building block of the calixarene derivative (**3**) has been immobilized on silica-based magnetic nanoparticles to receive a new magnetic calixarene derivative (BHCB-MN). 5,11,17,23-Tetra-*tert*-butyl-25,27-di(benzhydrazidylmethoxy)-26,28-dihydroxy-calix[4]arene immobilized silica-based magnetic nanoparticles (BHCB-MN) were characterized by a combination of Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), and thermogravimetric analyses (TGA). Studies regarding the removal of arsenate, dichromate, and uranyl ions from aqueous solutions have also been carried out by using these extractants in both liquid−liquid extraction and solid−liquid sorption experiments. The extraction results depict that these new calixarene derivatives have good extraction abilities toward dichromate/arsenate and uranyl ions.

INTRODUCTION

Recently, Cr(VI) and inorganic arsenic, such as As(V) and As(III), have been counted among the top 20 most hazardous substances.[1] It is a well-known fact that these oxyanions are among the most serious sources of environmental pollution.[2−4] In particular, long-term arsenic exposure via drinking water has been proven to increase the risk of lung, bladder, kidney, and skin cancers.[5−10] About 150 million people are threatened by this serious health hazard.[11,12] In order to guarantee safe drinking water, worldwide health organizations, including the U.S. Environmental Protection Agency, have reduced the maximum contaminant level for arsenic from (50 to 10) μg L^{-1}.[5]

Although chromium can exist in several oxidation states, only the trivalent and hexavalent forms are important in regard to the environment and humans.[13] Cr(VI) is highly toxic, carcinogenic, and harmful to human beings, like As(V), while Cr(III) is essential for mammals, as it maintains effective glucose, lipid, and protein metabolism.[14]

Owing to uranium's dangerous and harmful fundamental properties toward the health of human beings, the extraction of uranium is a very important task.[15,16] Since the 1950s, great effort has focused on new materials and technologies for the separation of uranium(VI) from aqueous solution.[17] In order to design a material which can selectively extract the uranyl ion, one has to overcome a difficult problem: that is, the ligand must certainly discriminate between U(VI) and other metal ions present in great excess in water, especially in seawater, where uranium has a concentration of about 3.3 μg L^{-1}.[18,19] The unusual coordination structure of U(VI) complexes provides a possibly unique solution to this difficult problem.

Calixarenes are important building blocks in supramolecular chemistry.[20−22] They can be selectively functionalized both at phenolic OH groups (*lower rim*) and at the *para* positions of phenol rings (*upper rim*).[23−25] Chemical modification of *the upper* or *lower rim* has made this class of synthetic ionophores effective extractants for transferring anionic[26,27] and cationic ions[28,29] or neutral molecules from aqueous solution into an organic layer. Calixarene based materials are also used as uranophiles.[30] Extraction mechanisms can be explained in terms of the complexation of metal ions with the functional groups of the sorbent. It is well-known that U(VI) is a hard acid and therefore is expected to react preferentially with a hard base.[31] Not surprisingly, the most efficient uranophile chelating functions are oxygen-containing,[32] such as hydroxyl-pyridones,[33] sulfocatecholamides,[34] and carbamoylmethylphosphine oxide.[35]

Recently, magnetic nanoparticles of iron oxide have shown great potential applications in many fields like bioseparation,[36,37] tumor hyperthermia,[38] magnetic resonance imaging (MRI), diagnostic contrast agents,[39] magnetically guided site-specific drug delivery agents,[40] and biomolecule immobilization,[41,42] as well as being used as support materials for some selective calixarene derivatives toward arsenate or dichromate ions.[4,43]

In this study, we investigate the extraction ability of new calixarene materials (**3** and **4**) toward As(V), Cr(VI), and U(VI). For this purpose, we synthesized a new calix[4]arene derivative and its magnetic nanoparticles. The magnetic Fe_3O_4 nanoparticles and [3-(2,3-epoxypropoxy)-propyl]-trimethoxysilane-modified Fe_3O_4 nanoparticles (EPPTMS-MN) were prepared according to the literature.[4,44] To obtain the final material (**4**), the di-substituted *p*-*tert*-butylcalix[4]arene derivative (**3**) was grafted onto the surface of the modified nanoparticles. Using this strategy, the separation capability of the calixarene composite

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silica carriers is provided improved efficiency. Hence, 5,11,17,23-tetra-*tert*-butyl-25,27-di(benzhydrazidylmethoxy)-26,28-dihydroxy-calix[4]arene immobilized silica-based magnetic nanoparticles BHCB-MN (**4**) can easily be separated from the aqueous phase of both reaction mixtures and complexation studies due to their magnetism. Finally, the affinity of the new calixarene derivative and its magnetic nanoparticles BHCB-MN toward As(V), Cr(VI), and U(VI) was investigated.

■ MATERIALS AND METHOD

Apparatus. UV−vis spectra were obtained on a Shimadzu 160A UV−visible spectrophotometer. Melting points were determined on a Gallenkamp apparatus in a sealed capillary glass tube and were uncorrected. ^{1}H NMR spectra were recorded on a Varian 400 MHz spectrometer. IR spectra were obtained on a Perkin−Elmer 1605 FTIR spectrometer using KBr pellets. Elemental analyses were performed using a Leco CHNS-932 analyzer. An Orion 410A+ pH meter was used for the pH measurements.

Materials. TLC analyses were carried out on a DC Alufolien Kieselgel 60 F_{254} (Merck). Generally, solvents were dried by storing them over molecular sieves (Aldrich; 4 Å, 8−12 mesh). All reactions, unless otherwise noted, were conducted under a nitrogen atmosphere. All starting materials and the reagents used were of standard analytical grade from Merck or Aldrich and used without further purification. Dry THF was distilled from the ketyl prepared from sodium and benzophenone. CH_2Cl_2 was distilled from $CaCl_2$, while MeOH was distilled over Mg and stored over molecular sieves. All commercial grade solvents were distilled and then stored over molecular sieves. The drying agent employed was anhydrous magnesium sulfate. All aqueous solutions were prepared with deionized water that was passed through a Millipore milli-Q Plus water purification system. Anions were used as their sodium salts. An ammonium molybdate solution ($3.15 \cdot 10^{-2}$ M), violet solution ($4.5 \cdot 10^{-5}$ M), and hydrochloric acid solution (6.85 M) were prepared by dissolving the reagents in doubly distilled water. Arsenazo III and uranyl acetate dihydrate were purchased from Fluka. A standard stock solution of 0.9787 μg mL^{-1} uranium(VI) was prepared by dissolving appropriate amounts of uranyl acetate dihydrate in deionized water. A stock arsenazo III solution (0.01 %) was prepared by dissolving the reagent in deionized water. The effect of pH was studied by adjusting the pH of the aqueous solutions using diluted HCl and KOH solutions at 25 °C. Adjustment of the pH values of the working solutions was carried out using a 5 M sodium acetate buffer to determine U(VI) in aqueous solution.

Synthesis. The compounds **1**, **2**, Fe_3O_4 nanoparticles, and [3-(2,3-epoxypropoxy)-propyl]-trimethoxysilane-modified Fe_3O_4 nanoparticles (EPPTMS-MN) were synthesized by procedures published in the literature.[4,44−46] The syntheses of compound **3** and 5,11,17,23-tetra-*tert*-butyl-25,27-di(benzhydrazidylmethoxy)-26,28-dihydroxy-calix[4]arene immobilized silica-based magnetic nanoparticles (BHCB-MN) are herein reported for the first time.

Synthesis of 5,11,17,23-Tetra-*tert*-butyl-25,27-di(benzhydrazidylmethoxy)-26,28-dihydroxy-calix[4]arene (3). To a solution of dialkyl bromide of *p-tert*-butylcalix[4]arene (**2**; 1.0 g, 1.12 mmol) in 40 mL of CH_3CN were added 0.7 g of K_2CO_3, 0.67 g of NaI, and benzhydrazide (2.53 g, 18.57 mmol), and the reaction mixture was stirred and heated under reflux. The reaction was monitored by using a TLC. After 4 days, the reaction mixture was filtered off, and the solvent was removed under reduced pressure. The residue was dissolved in 150 mL of CH_2Cl_2. The organic layer was extracted three times with water. The organic phase was dried (anhydrous $MgSO_4$); the solvent was removed under reduced pressure. In order to remove impurities, the crude product was precipitated by the addition of CH_3OH and filtered off. The solvent was evaporated and dried. A brown powder remained with 98 % yield, m.p.: (161 to 164) °C. The IR spectral data of **3** are (KBr disk) cm^{-1}: 1638 (−NC═O). ^{1}H NMR (400 MHz $CDCl_3$): δ 1.18 (s, 18H, Bu^t), 1.22 (s, 18H, Bu^t), 2.38−2.42 (m, 4H, $-CH_2-$), 3.37 (d, 4H, J = 12.8 Hz, Ar−CH_2−Ar), 3.54−3.57 (m, 2H, −NH−), 3.76 (t, 4H, J = 6.8 Hz, $-CH_2-$), 4.18 (t, 4H, J = 4.8 Hz, $-CH_2-$), 4.29 (d, 4H, J = 12.8 Hz, Ar−CH_2−Ar), 7.01 (s, 4H, ArH), 7.06 (s, 4H, ArH), 7.39 (s, 2H, −OH), 7.47 (t, 4H, J = 7.2 Hz, ArH), 7.54 (t, 2H, J = 7.2 Hz, ArH), 7.88 (d, 4H, J = 8.0 Hz, ArH), 9.10 (s, 2H, −NH). Anal. Calcd for $C_{64}H_{80}N_4O_6$ (%): C, 76.77; H, 8.05; N, 5.60. Found (%); C, 76.94; H, 7.91; N, 5.77.

Preparation of 5,11,17,23-Tetra-*tert*-butyl-25,27-di(benzhydrazidylmethoxy)-26,28-dihydroxy-calix[4]arene Immobilized Silica-Based Magnetic Nanoparticles (4). A mixture of a functionalized *p-tert*-butylcalix[4]arene derivative (**3**; 0.3 g) and NaH (0.05 g) in a solution of THF/DMF (20 mL, 3/1) was stirred for 30 min; then, 0.9 g of EPPTMS-MN was added to that solution and heated under reflux for 5 days. After magnetic separation, the resulting compound was washed with dichloromethane three times to remove an excess of the functionalized *p-tert*-butylcalix[4]arene derivative, then washed with water and dried under a vacuum. The IR spectral data of BHCB-MN (**4**) are (KBr disk) cm^{-1}: 2927, 2866, 1646 (−NC═O), 1476, 1410 (aromatic C═C), 1198, 1046, 948, 791 (Si−O), and 574 (Fe−O).

Dichromate/Arsenate Anion Extraction Studies. The extraction capacities of the synthesized calixarene derivatives (**3** and **4**) were determined using the following technique.[2] An aqueous solution (10 mL) containing a $Na_2Cr_2O_7$ or Na_2HAsO_4 solution at a concentration of $1.0 \cdot 10^{-4}$ M and the calixarene derivative (10 mL of a $1 \cdot 10^{-3}$ M solution of **3** in CH_2Cl_2 for liquid−liquid extraction, 25 mg of **4** for solid−liquid extraction) were mixed in a stoppered flask that was shaken at 175 rpm and 25 °C for 1 h. The ligands were separated before measurements. The residual dichromate concentration of the aqueous solute was determined spectrophotometrically by UV−vis analyses at 346 nm, as described previously.[47] The concentration of the arsenate ion remaining in the aqueous phase was determined spectrophotometrically at 610 nm as described previously.[48] The effect of pH was studied by adjusting the pH of the aqueous solutions using diluted HCl and KOH solutions at 25 °C. The experiments were performed in triplicate.

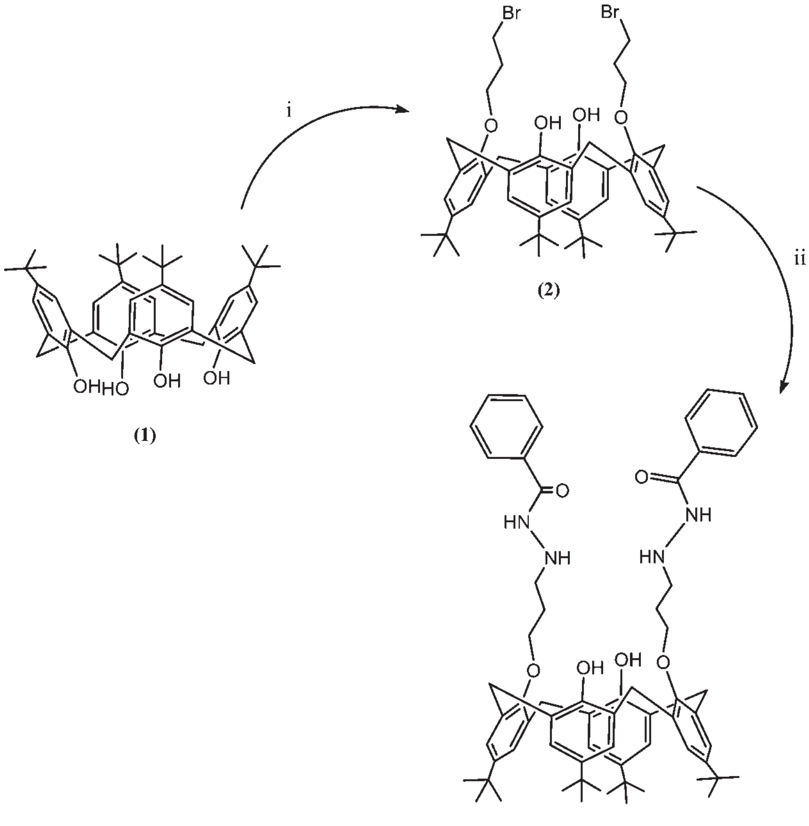
The percent extraction (E %) was calculated according to eq 1:

$$(E\%) = \frac{A_0 - A}{A_0} \times 100 \tag{1}$$

where A_0 and A are the initial and final concentrations of the dichromate/arsenate or uranyl ion before and after the extraction, respectively.

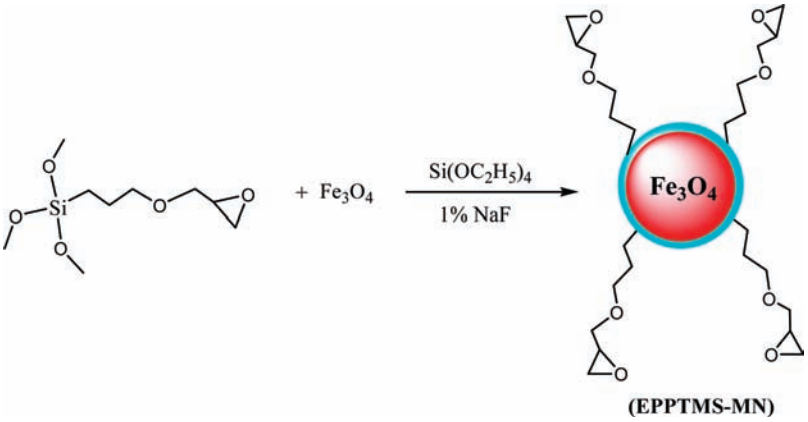
Uranyl Cation Extraction Studies. Into a vial was pipetted an aqueous solution (10 mL) containing $UO_2(AcO)_2 \cdot 2H_2O$ at a concentration of $1.15 \cdot 10^{-5}$ M, a few drops of 0.01 M KOH/HCl solution in order to obtain the desired pH at equilibrium and maintain the ionic strength, and calix[4]arene derivatives (10 mL of $1 \cdot 10^{-3}$ M solution of **3** in CH_2Cl_2 for liquid−liquid extraction, 25 mg of **4** for solid−liquid sorption). The mixture was

Scheme 1. Synthetic Route for Synthesis of 3[a]



[a] Reaction conditions: (i) K_2CO_3, CH_3CN, NaI, 1,3-dibromopropane; (ii) CH_3CN, K_2CO_3, NaI, benzhydrazide.

Scheme 2. Preparation of the EPPTMS-MN



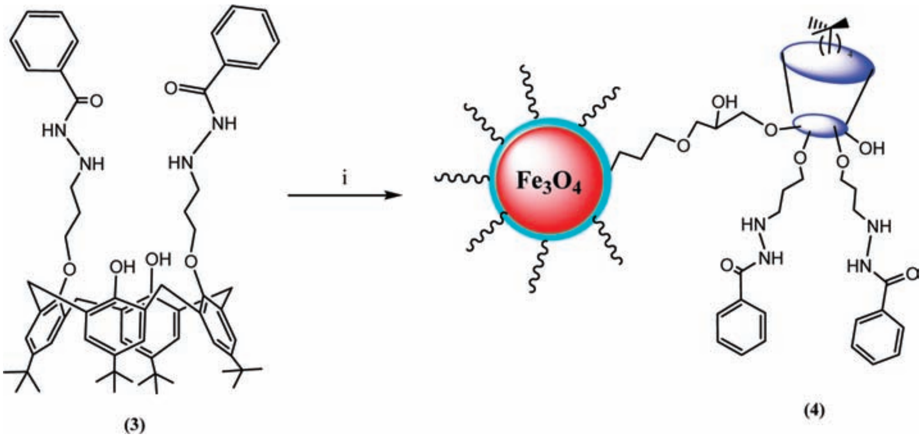
vigorously agitated in a stoppered glass vial with a mechanical shaker for 2 min, then was shaken at 175 rpm and 25 °C for 1 h. The ligands were separated before measurements. The residual uranyl concentration of the aqueous solute was determined spectrophotometrically.[49]

Blank experiments showed that no uranyl extraction occurred in the absence of calixarene. The uranyl cation in the aqueous phase was measured at 652 nm (for pH 5.5 to 8.5). The percent sorption (E %) was calculated[50] according to eq 1.

Anion Selectivity Studies. Selectivity studies of **3** were performed in the presence of different inorganic sodium salts of nitrate (NO_3^-), sulfate (SO_4^{2-}), and chloride (Cl^-) anions since they could be present more than dichromate anions in aqueous solutions. For this purpose, anions were used at 100-times the dichromate anion concentration and determined according to the literature.[2]

Cation Selectivity Studies. Selectivity studies of **3** were performed in the presence of Fe^{3+}, Ca^{2+}, K^+, and Na^+ cations

Scheme 3. Synthetic Route for the Preparation of BHCB-MN[a]



[a] Reaction conditions: (i) EPPTMS-MN, NaH, THF/DMF.

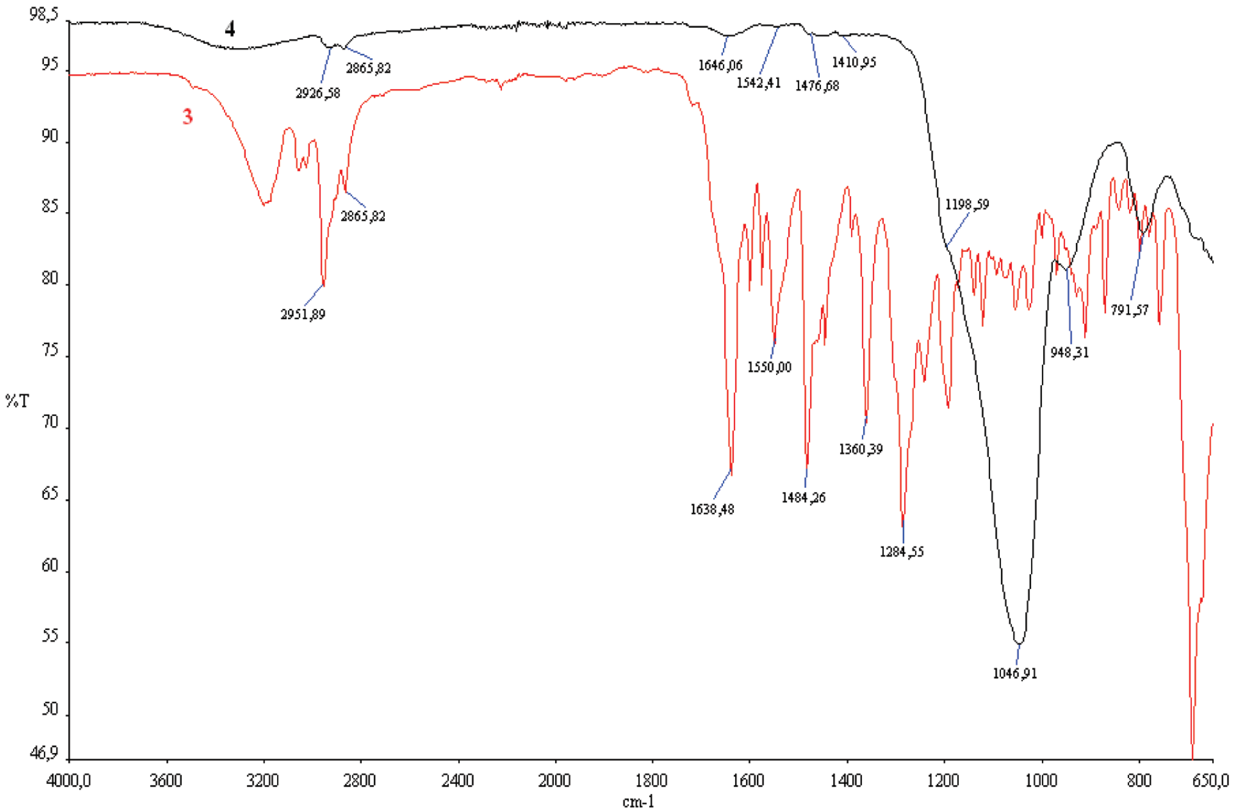


Figure 1. The IR spectrum of **3** and **4**.

since they could be present more than uranyl cations in aqueous solutions. For this goal, cations were used at 100-times the uranyl cation concentration.

RESULTS AND DISCUSSION

Design and Synthesis of New Host Molecules. The main goal of this work was the design and synthesis of new calixarene derivatives (**3** and **4**) and exploration of their binding properties toward the arsenate/dichromate anions and uranyl cation. For this purpose, *p-tert*-butylcalix[4]arene (**1**) and the dialkyl bromide derivative of *p-tert*-butylcalix[4]arene (**2**) were synthesized using a modification of the literature route.[45,46] 5,11,17,23-Tetra-*tert*-butyl-25,27-di(benzhydrazidylmethoxy)-26,28-dihydroxy-calix-[4]arene (**3**) was obtained in 98 % yield through the condensation of **2** with benzhydrazide in the presence of K_2CO_3 and NaI (see Scheme 1). Derivative **3** was fully characterized by ^{1}H NMR, IR, and element analysis techniques. The cone conformation of the macrocycles was confirmed by ^{1}H NMR, which displays two doublets at (3.37 and 4.29) ppm (J = 12.8 Hz) corresponding to the resonance signals of H_{ax} and H_{eq} of the methylene bridge proton ($ArCH_2Ar$).[51]

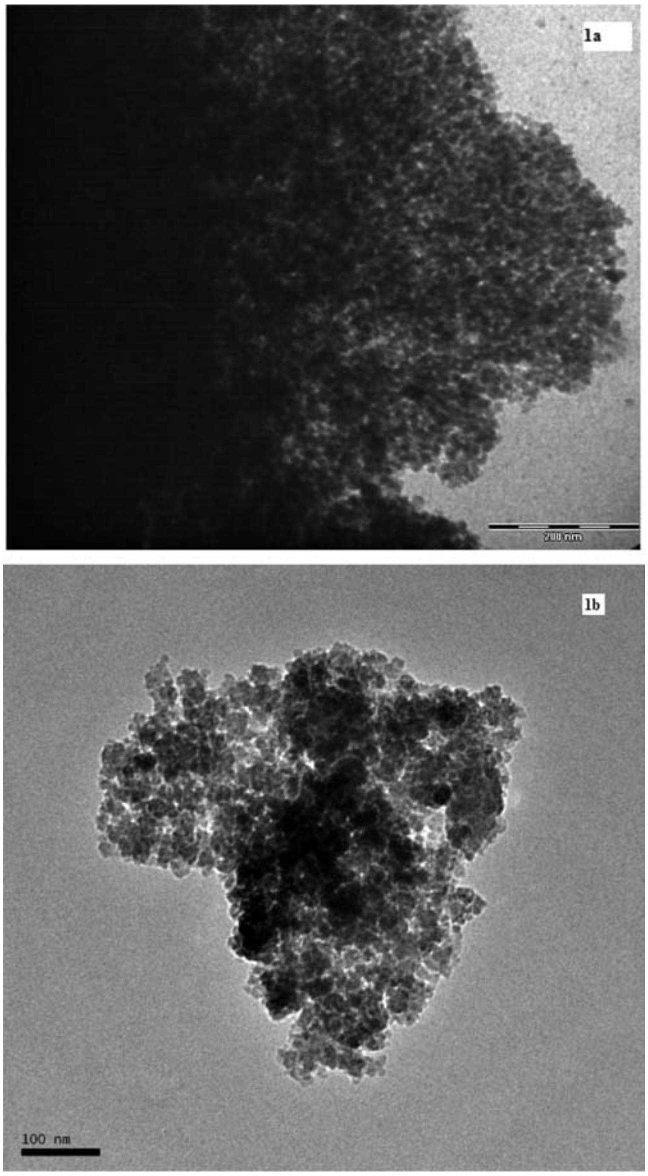


Figure 2. TEM micrographs of (a) pure Fe_3O_4 nanoparticles and (b) BHCB-MN.

The magnetic (Fe_3O_4) nanoparticles and [3-(2,3-epoxypropoxy)-propyl]trimethoxysilane-modified Fe_3O_4 nanoparticles (EPPTMS-MN) were prepared according to the published procedures[4,44] (see Scheme 2). The final compound (**4**) was prepared through the treatment of EPPTMS-MN with a *p-tert*-butylcalix[4]arene derivative (**3**) in the presence of NaH in a solution of THF/DMF (see Scheme 3). BHCB-MN (**4**) was characterized by a combination of FT-IR, TEM, TGA, and elemental analysis.

FT-IR spectroscopy was used to elaborate the structures of Fe_3O_4, EPPTMS-modified Fe_3O_4, and BHCB-MN. The IR peak at 568 cm^{-1} belongs to the stretching vibration mode of Fe−O bonds in Fe_3O_4. Compared with the IR spectrum of EPPTMS-modified Fe_3O_4, that of BHCB-MN possessed peaks at 1646 cm^{-1}, which is a stretching vibration of the amide carbonyl (N−C=O), and at (1476 and 1410) cm^{-1}, which are attributed to the bending vibration of aromatic C=C bonds of *p-tert*-butylcalix[4]arene derivatives. Additional peaks centered at (1198, 1047, 948, and 791) cm^{-1} (for BHCB-MN) and (1116, 1090, and 955) cm^{-1} (for EPPTMS-MN) were most probably due to the symmetric and asymmetric stretching vibration of framework and terminal Si−O− groups (see Figure 1).

Transmission electron microscopy (TEM) micrographs of pure Fe_3O_4 nanoparticles and BHCB-MN were used to receive more direct information on particle size and morphology (Figure 2a and b). The TEM micrographs (Figure 2a) show that the nanoparticles are seen as dense aggregates due to the lack of any repulsive force between the magnetic nanoparticles, which is mainly due to the nanosize of the EPPTMS-modified Fe_3O_4, which is nearly (10 ± 2) nm. This may be considered indirect evidence that the magnetic core of the EPPTMS-modified magnetic particles consisted of a single magnetic crystallite with a typical diameter of (8 ± 3) nm, and that difference corresponds to the EPPTMS coating. After *p-tert*-butylcalix[4]arene derivatives were immobilized, the dispersion of particles was improved greatly (Figure 2b), which can easily be explained by the electrostatic repulsion force and steric hindrance between the calix[4]arenes on the surface of the Fe_3O_4 nanoparticles.

The indication of coating formation on the magnetic nanoparticles surface can be obtained from the TGA measurement. Upon heating, the weight loss of EPPTMS-modified magnetite nanoparticles (EPPTMS-MN) was shown to be about 5 % within a broad temperature range of (250 and 650) °C. The decomposition of both calix[4]arene units and 3-(2,3-epoxypropoxy)-propyl groups of BHCB-MN was observed in between (275 and 650) °C (see Figure 3.).

The elemental analysis results of BHCB-MN given in Table 1 confirmed that the immobilization of the calix[4]arene derivative was accomplished. The amount of loaded 5,11,17,23-tetra-*tert*-butyl-25,27-di(benzhydrazidylmethoxy)-26,28-dihydroxy-calix-[4]arene (**3**) onto the silica based magnetic nanoparticles was evaluated from the results of elemental analysis. According to the elemental analysis, the resulting BHCB-MN contains 0.32 % nitrogen, corresponding to 0.92 mmol of **4**/g of support.

Dichromate Anion Extraction Studies. Under acidic conditions, $Na_2Cr_2O_7$ is converted into $H_2Cr_2O_7$, and after ionization in an aqueous solution, it exists in the $HCr_2O_7^-/Cr_2O_7^{2-}$ form. Under more strongly acidic conditions, $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ dimers become the dominant Cr(VI) form, and the pK_{a1} and pK_{a2} values of these equations are 0.74 and 6.49, respectively. At a pH < 6, the oxyanions' structure changes from the monomeric CrO_4^{2-} to the dimeric $HCr_2O_7^-$.[52] These oxides are potential sites for hydrogen bonding to the host molecule. In this case, we synthesized new selectively ligands as a host having proton-switchable binding lobes for extraction studies. The binding efficiency of **3** was carried out in a liquid−liquid extraction system of $HCr_2O_7^-$ from an aqueous solution over the pH range of 1.5 to 4.5.

The results show that **3** has a high binding effect at a low pH, as depicted in Figure 4. The percentage of dichromate ions extracted was 89 % when the pH of the aqueous solution was 1.5 and attained a minimum 11 % when the pH of the aqueous solution increased to 4.5. Extractant **3** provides suitable binding sites for dichromate anions at a low pH due to the presence of protonable amine moieties.

The binding efficiency of other host (BHCB-MN) magnetic nanoparticles was carried out in a solid-phase sorption system of $HCr_2O_7^-$ from an aqueous solution at different pH's. The sorption results of **4** are summarized in Figure 5. It is clear that the receptor (BHCB-MN) is most effective for the removal of dichromate anions. Magnetic calixarene nanoparticles (**4**) that have a rigid structure have notably increased the anion sorption

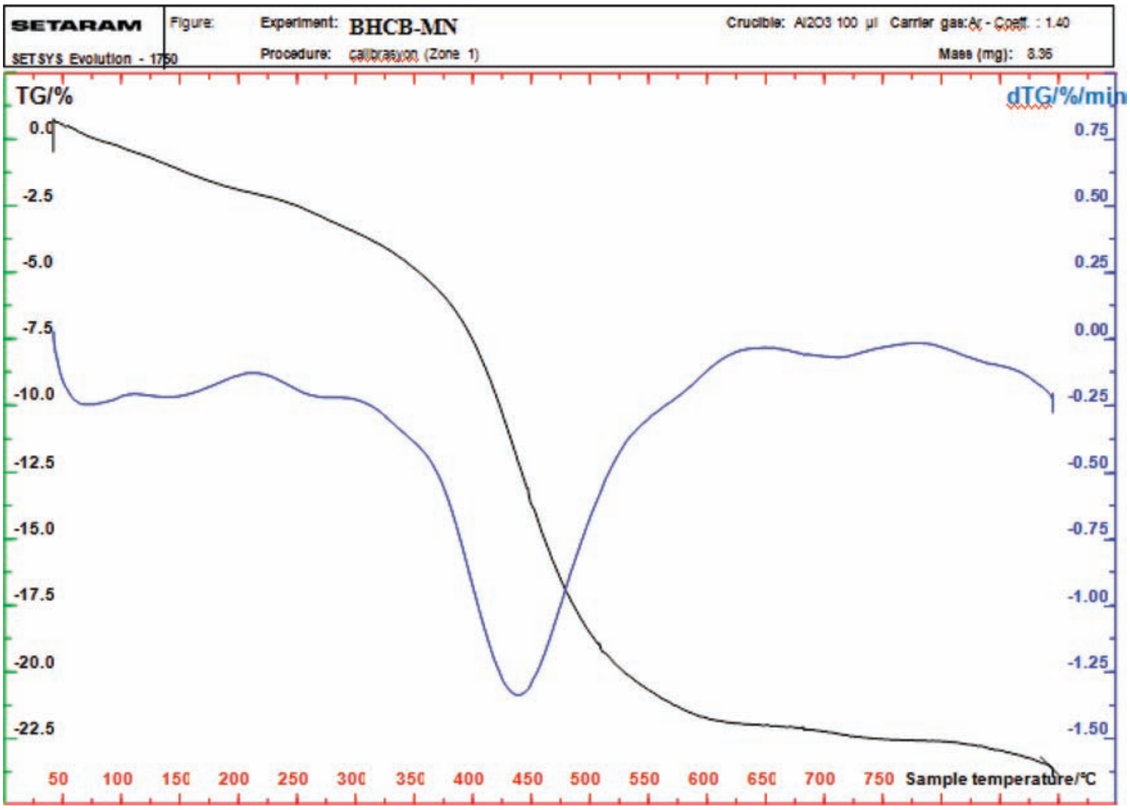


Figure 3. TG and their first derivatives (dTG) of BHCB-MN.

Table 1. Results of Elemental Analysis for EPPTMS-MN and BHCB-MN

	C (%)	H (%)	N (%)	bounded amount (mmol/g)[a]
BHCB-MN	15.81	3.01	0.32	~0.92
EPPTMS-MN	13.20	2.61		

[a] Calculated according to the N content.

ability. This increase can be explained by the fact that BHCB-MN is protonable under acidic conditions due to amine groups, and it would easily form complexes with dichromate anions through electrostatic interactions and hydrogen bonding.

The maximum percentage of extracted dichromate ions was found to be 66 % when the pH of the aqueous solution was 1.5. However, the minimum percentage of extracted ions (11 %) was attained when the pH of the aqueous solution was increased to 3.5. As a result, the BHCB-MN provided suitable binding affinity for dichromate anions at a low pH, due to the proton-switchable amine moiety. The proposed interaction for the sorption of anions with BHCB-MN is given in Figure 6.

To understand the foreign anion effect on the dichromate anion, dichromate anion retentions of 3 different inorganic sodium salts (Cl^-, SO_4^{2-} and NO_3^-) were investigated. Table 2 shows the retention of the dichromate anion with **3** in the presence of foreign anions. The extraction of $Na_2Cr_2O_7$ with **3** was not accomplished via the presence of sodium salts. This new calixarene derivative, **3**, could selectively be in the presence of foreign anions.

Arsenate Anion Extraction Studies. It is well-known that As(V) speciation is affected by the solution pH through the following equilibrium:[53]

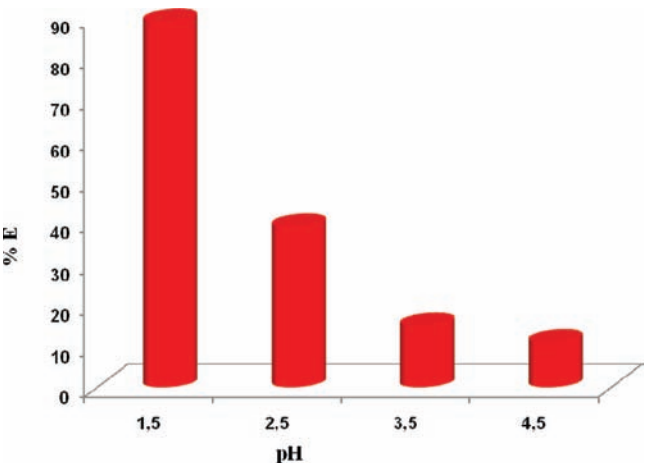


Figure 4. Extraction percentages of the dichromate anion with **3** at a pH of 1.5 to 4.5. H_2O/CH_2Cl_2, 10/10 (v/v); sodium dichromate, $1 \cdot 10^{-4}$ M; ligand, 1.10^{-3} M; 1 h; 25 °C.

$$H_3AsO_4 \leftrightarrow H_2AsO_4^- + H^+ \quad pKa_1 = 2.3 \tag{2}$$

$$H_2AsO_4^- \leftrightarrow HAsO_4^{2-} + H^+ \quad pKa_2 = 6.8 \tag{3}$$

$$HAsO_4^{2-} \leftrightarrow AsO_4^{3-} + H^+ \quad pKa_2 = 11.6 \tag{4}$$

From eqs 2 to 4, the arsenate species occurs mainly in the form of $H_2AsO_4^-$ 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 depends on pH. Under more acidic conditions (pH 1 to 3), the arsenate ions will be in the protonated form H_3AsO_4. Besides this, the monoanion ($H_2AsO_4^-$) will have a smaller free energy of hydration compared to its dianionic form $HAsO_4^{2-}$.[53]

In view of that feature, we have synthesized a new protonable calixarene derivative (**3**) and its magnetic nanoparticles (BHCB-MN) and evaluated their extraction/sorption behavior toward the arsenate ion.

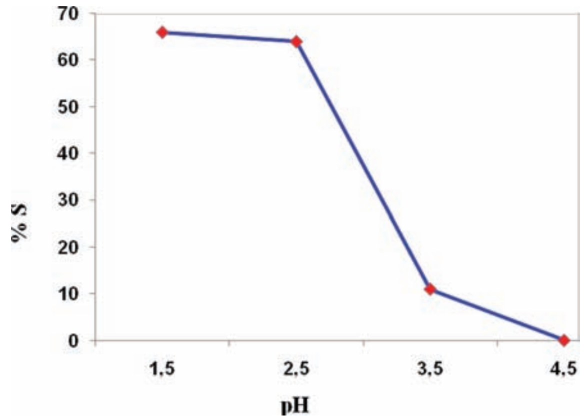


Figure 5. Sorption percentages of the dichromate anion with BHCB-MN at a pH of 1.5 to 4.5. Solid phase, sorbent = 25 mg, aqueous phase, $Na_2Cr_2O_7 = 1.0 \cdot 10^{-4}$ M (10 mL) at 25 °C for 1 h.

The percentage of arsenate ions extracted was 73 % for **3** when the pH of the aqueous solution was 3.5 and attained a minimum 1 % for the nanoparticles when the pH of the aqueous solution increased to 7.0 (see Figure 7). The binding efficiency of its magnetic nanoparticles (**4**) was found to be 78.2 % when the pH was 3.5 and 16 % when the pH increased to 5.5 (see Figure 8). This indicates that the best interaction between the ligand and arsenate ions occurs at a pH of 3.5. These interactions include electrostatic interactions and hydrogen bonding between protonable amine and the oxygen of arsenate anions.[4]

Uranyl Ion Extraction Studies. Benzhydrazide was chosen as the chelating component because it is known to have strong tendencies to form complexes with uranyl ions through the NH−NH−CO−Ph chelating ligand like benzoylthiourea.[17]

The binding efficiency of **3** was carried out in a liquid−liquid extraction system of U(VI) from an aqueous solution over a pH range of 5.5 to 8.5, showing the dependence of the degree of extraction of uranyl ions as a function of the pH (Figure 9). The

Table 2. Dichromate Retention Results of 3 pH 1.5, in the Presence of Foreign Anions (Cl^-, SO_4^{2-} and NO_3^-) and Their Mixtures[a]

	different anions				
	none	Cl^-	SO_4^{2-}	NO_3^-	mixture
3	89	87.8	87.8	78.6	70.5

[a] [Sodium dichromate] = $1.0 \cdot 10^{-4}$ M; ligand **3** = $1.0 \cdot 10^{-3}$ M at 25 °C, pH 1.5. The concentration of different anions = $1.0 \cdot 10^{-2}$ M.

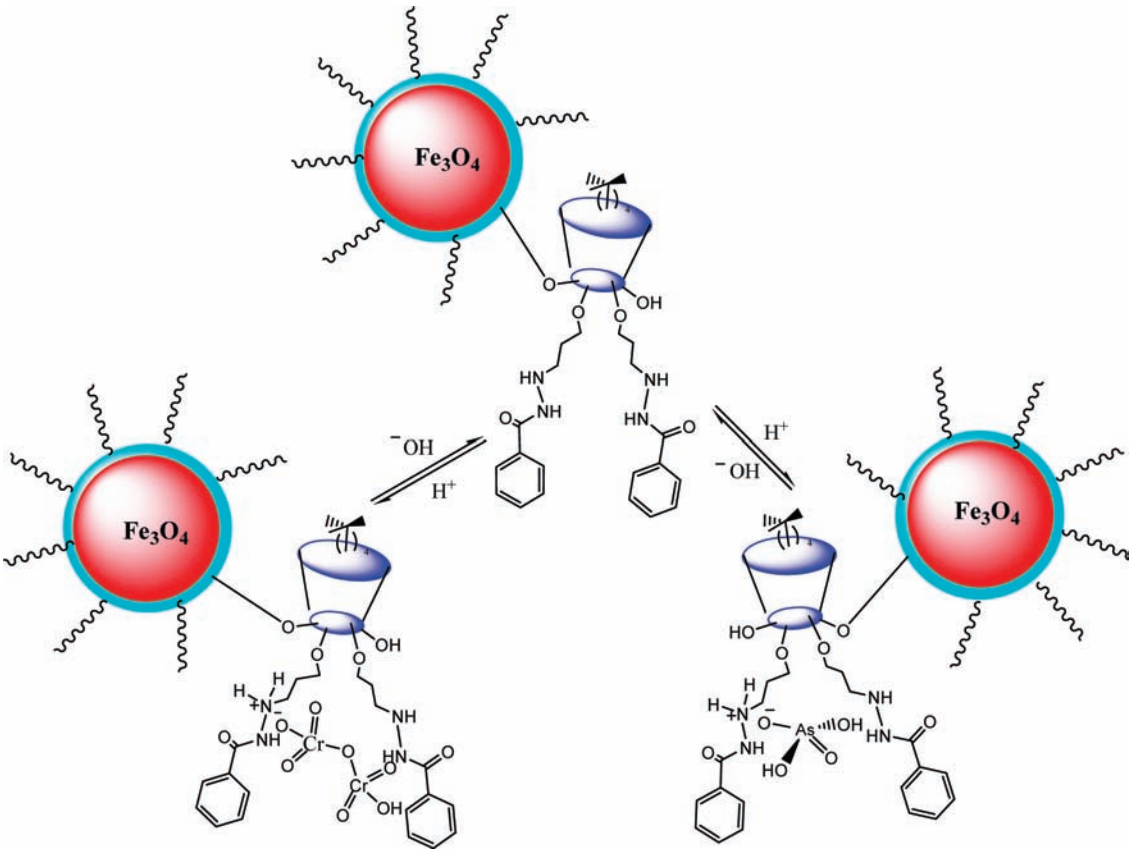


Figure 6. The suggested complexation phenomenon of arsenate and the dichromate ion with BHCB-MN.

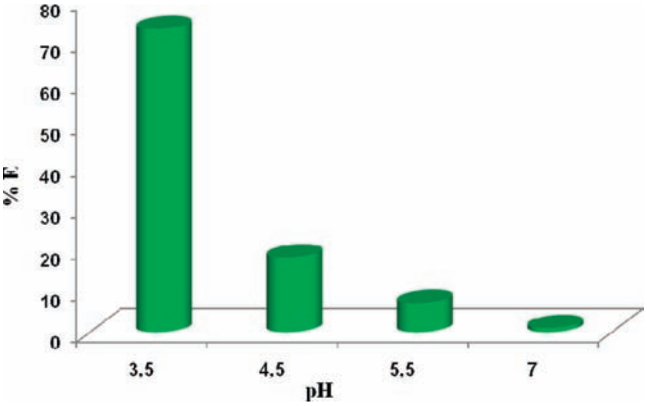


Figure 7. Extraction percentages of the arsenate anion with **3** at a pH of 3.5 to 7.0. H_2O/CH_2Cl_2, 10/10 (v/v); Na_2HAsO_4, $1 \cdot 10^{-5}$ M; ligand, 1.10^{-3} M; 1 h; 25 °C.

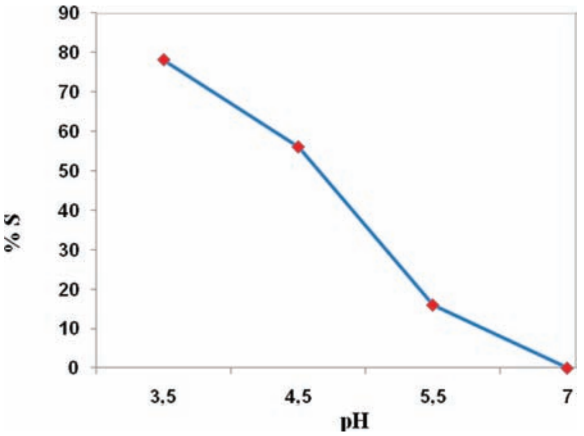


Figure 8. Sorption percentages of the arsenate anion with BHCB-MN at a pH of 3.5 to 7.0. Solid phase, sorbent = 25 mg, aqueous phase, $Na_2HAsO_4 = 1.0 \cdot 10^{-5}$ M (10 mL) at 25 °C for 1 h.

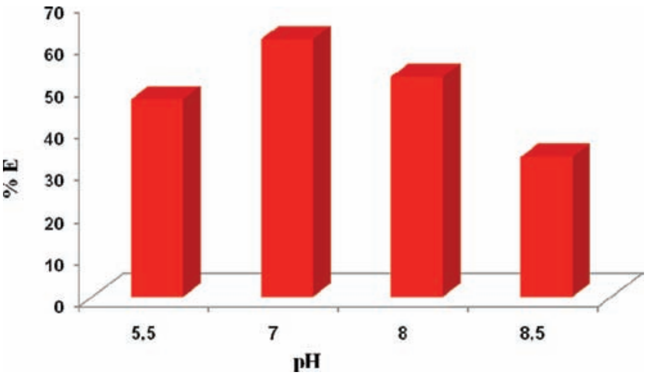
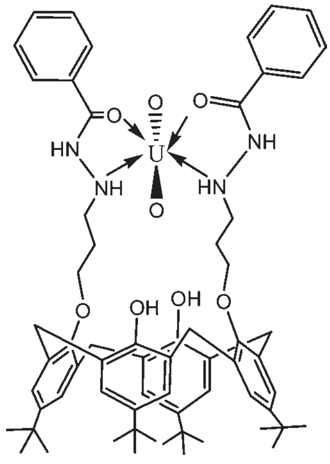


Figure 9. The extraction percentages of the uranyl cation with **3** at a pH of 5.5 to 8.5 (10 mL, $1.15 \cdot 10^{-5}$ M), $UO_2(AcO)_2 \cdot 2H_2O$, and calix[4]arene derivatives (10 mL of $1 \cdot 10^{-3}$ M solution of **3** in CH_2Cl_2) at 175 rpm and 25 °C for 1 h.



(3)

Figure 10. Suggested complexation phenomenon of the uranyl ion with **3**.

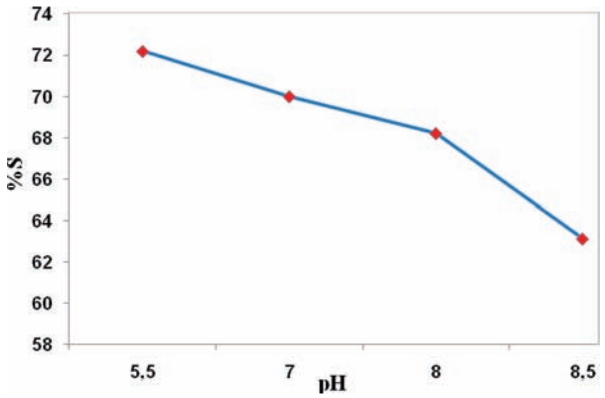


Figure 11. Sorption percentages of the uranyl cation with BHCB-MN at a pH of 5.5 to 8.5 (10 mL, $1.15 \cdot 10^{-5}$ M), $UO_2(AcO)_2 \cdot 2H_2O$, and magnetic calix[4]arene nanoparticles (25 mg) at 175 rpm and 25 °C for 1 h.

Table 3. Uranyl Retention Results of 3 (pH 7.0), in the Presence of Foreign Cations (Fe^{3+}, Ca^{2+}, Na^{+}, and K^{+})^{a}

	different cations				
	none	Fe^{3+}	Ca^{2+}	Na^{+}	K^{+}
3	61.3	0	12.1	60.7	61.1

[a] Uranyl acetate dihydrate = $1.15 \cdot 10^{-5}$ M; **3** = $1.0 \cdot 10^{-3}$ M at 25 °C. The concentration of different cations = $1.15 \cdot 10^{-3}$ M.

results indicate that the sorption process is most favorable at a pH of 7. When the acidity decreases, the sorption increases and reaches a maximum at a pH of 7 (61.3 %). At higher pH values (pH 8 to 11), the percentage removal of uranyl ions decreases, owing to the formation of insoluble $UO_2(OH)_2$ and the hydrolysis of uranyl ions forming complex hydroxy anions such as $UO_2(OH)_3^{-}$, $UO_2(OH)_4^{2-}$, $(UO_2)_3(OH)_7^{-}$, $(UO_2)_3(OH)_8^{2-}$, $(UO_2)_3(OH)_{10}^{4-}$, and $(UO_2)_3(OH)_{11}^{5-}$.[54,55]

The possible coordination mechanism for the interaction between uranyl ions and **3** may be illustrated by Figure 10. The prepared sorbent provides O-, S-, and N-donor ligands with which uranyl ions readily form complexes.[56,57]

The binding efficiency of another host (BHCB-MN) was carried out via solid-phase sorption of U(VI) from an aqueous solution at different pH's.

In the solid phase sorption for U(VI) ions, the pH value of the sample solution is an effective factor for quantitative sorption of BHCB-MN due to the competitive reactions with chelate forming groups in sorbent and hydrogen ions in solution. To find the optimum pH value of the sample, 25 mg of the sorbent was equilibrated with U(VI) ion solutions (10 mL, $1.15 \cdot 10^{-5}$ g mL^{-1}) with various pH's of 5.5 to 8.5 for 1 h. The U(VI) ion concentration was estimated from the amount of U(VI) ions remaining in the supernatant, which was analyzed spectrophotometrically by Arsenazo III. The results showed that the greatest uptake of U(VI) ions occurred in the pH range of 5.5 to 7.0 (Figure 11).

From sorption results given in Figure 11, it is clear that the receptor (BHCB-MN) is most effective for the removal of uranyl anions. Magnetic calixarene nanoparticles (**4**) that have a rigid structure have notably increased the U(VI) sorption capability. It could also be understood that the sorption behavior of U(VI) on **4** sorbents mainly depends on the sorts and structure types of selected chelating ligands, the preparation method (impregnation or grafting), and the supporting materials used.

The foreign cation effect on U(VI) retention of **3** in additional different metal cations (Fe^{3+}, Ca^{2+}, K^+, and Na^+) was examined. The results showed that the selective retention of U(VI) with **3** was effected by the presence of other cations (see Table 3). The extraction of U(VI) with **3** was affected by the presence of the Fe^{3+} and Ca^{2+} cations but not affected by the presence of the Na^+ and K^+ cations. In conclusion, all calixarene derivatives could be used selectively with some cations like Na^+ and K^+ ions.

CONCLUSION

In the present work, new Cr(VI)/As(V) and U(VI) selective extractants have been developed as excellent chelating ligands. The preparation method was simple, and the materials were commercially available. The ligands have excellent affinity and selectivity for Cr(VI) and As(V) as well as U(VI), even in the solution containing a great deal of competing foreign ions. They would be promising candidates both for liquid phase extraction and solid phase sorption of Cr(VI)/As(V) and U(VI) from (Cr or As or U)-contaminated wastewater. The proposed method based on 5,11,17,23-tetra-*tert*-butyl-25,27-di(benzhydrazidylmethoxy)-26,28-dihydroxy-calix[4]arene (**3**) and its immobilized derivative (**4**) provides a valuable reference for the removal of Cr(VI) and As(V) as well as U(VI). The important features of this study are that the work done in this context may help not only to recover the particular targeted anion/cation from industrial effluents for reuse but also to restore polluted sites to their original state. Another important point of this work is that the separation capability improved due to magnetism of the calixarene composite silica carriers.

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