



Synthesis and evaluation of chromate and arsenate anions extraction ability of a *N*-methylglucamine derivative of calix[4]arene immobilized onto magnetic nanoparticles

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ABSTRACT

In this study, 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. The calixarene derivative (**3**) was characterized by a combination of FTIR, ¹H NMR and elemental analyses. Following, using the macrocyclic building block, the compound **3** was immobilized by [3-(2,3-epoxypropoxy)propyl]trimethoxysilane-modified Fe₃O₄ magnetite nanoparticles (**EPPTMS-MN**). The prepared calix[4]arene immobilized material was characterized by a combination of Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM) and thermogravimetric analyses (TGA). Moreover, the studies regarding the removal of arsenate and dichromate ions from the aqueous solutions were also carried out by using the compound in solid–liquid extraction experiments. It was found that the calix[4]arene-based magnetic material has high extraction ability towards dichromate and arsenate anions in 66% (at pH 1.5) and in 86% (at pH 3.5), respectively.

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1. Introduction

Toxic oxyanions like arsenite, arsenate, chromate, and dichromate contamination of water are serious hazards. Apart from the industrial and other anthropogenic activities, they also interfere ground water from natural sources [1]. Arsenic is one of the most trace elements. It is well-documented that arsenic is a known carcinogenic causing various adverse health effects [2], such as skin, bladder, and lung cancer, as well as hyperkeratosis and hyper pigmentation of skin [3–5] even if the concentration of arsenic is as low as sub-ppm level [6,7]. Therefore, it needs to be determined in a variety of environmental samples.

Arsenic is found in soil and groundwater mainly in inorganic trivalent (arsenite, As(III)) and pentavalent (arsenate, As(V)) oxidation states [8,9]. The dominant species of arsenic depends on the pH of the solution; As(V) exists, as H₃AsO₄, H₂AsO₄⁻, HAsO₄²⁻, and AsO₄³⁻ in aqueous solution under oxidative conditions [10,11]. While H₂AsO₄⁻ is the dominant form at lower pH (<6.9), HAsO₄²⁻ is found to be the dominant form at higher pH [9].

Cr(VI) is also very toxic, carcinogenic and harmful [11] like As(V). Chromium and its compounds are widely used in plating, leather tanning, dying, cement production, and photographic industries in large quantities of toxic pollutants [12]. Although the chromium

can exist in several oxidation states, only the trivalent and hexavalent forms are environmentally important [13]. Chromium(III) has been reported to be biologically essential to mammals as it maintains effective glucose, lipid, and protein metabolisms. However, chromium(VI) can be very toxic as it can diffuse through cell membranes and oxidize biological molecules as Cr₂O₇²⁻ or HCr₂O₇⁻ [14].

The development of supramolecular chemistry has been dominated largely by the design and synthesis of macrocyclic compounds. Calix[*n*]arenes widely represent macrocyclic compounds used in third generation of supramolecular chemistry for the construction of variously receptors for the complexation of anion, cation and neutral molecules [15]. The complexation properties of calixarene derivatives appear to be highly dependent on the nature, number of donor atoms and the conformation of the calix[4]arene moiety [16–19]. Therefore, variety of sophisticated anion complexing ligands containing calix[4]arene backbones have been designed and synthesized to serve as selective anion extractants [15,20–22]. These molecules are generally calix[4]arene derivatives bearing amine or amide functions which are capable of interacting with anions by hydrogen bonds [23]. Recently, we have reported calix[4]arene-based receptors those effectively bind anions and used for laboratory, clinical, environmental, and industrial process analyses [24–27].

In the last decade, paramagnetic nanoparticles of iron oxides have been applied in many fields [28], including bioseparation [29,30], tumor hyperthermia [31], magnetic resonance imag-

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ing (MRI) diagnostic contrast agents [32], magnetically guided site-specific drug delivery agents [33] and immobilization of biomolecules [34,35]. In separation science, the application is generally based on the solid-phase magnetic feature which endows a rapid and easy separation with recovery of contaminants from the polluted environment by applying an external magnetic field.

In this paper, magnetic Fe₃O₄ nanoparticles were prepared by chemical co-precipitation of Fe³⁺ and Fe²⁺ ions. Following the nanoparticles were directly modified by [3-(2,3-epoxypropoxy)propyl]trimethoxysilane (**EPPTMS**) to introduce reactive groups onto the particles surface. The substituted calix[4]arene was immobilized onto the surface of modified nanoparticles. This strategy provides an efficient way to improve the separation capability of the calixarene composite silica carriers as well as those can easily be separated from reaction mixture due to its magnetism. Finally, extraction capability of functionalized magnetic particles for dichromate and arsenate anions in aqueous solution were investigated.

2. Experimental

2.1. Reagents

Analytical thin layer chromatography (TLC) was performed using Merck plates (Silica Gel 60 F₂₅₄ on aluminum). Flash chromatography separations were performed on a Merck Silica Gel 60 (230–400 mesh). All reactions, unless otherwise noted, were conducted under 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 followingly stored over molecular sieves. Anions were used as their sodium salts. The anhydrous MgSO₄ was used as drying agent. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

2.2. Instrumentation

Melting points were determined on a Gallenkamp apparatus in a sealed capillary and are uncorrected. Elemental analyses were performed by a Leco CHNS-932 analyzer. ¹H NMR spectra were recorded on a Varian 400 MHz spectrometer. Chemical shifts given in ppm are relative to an internal standard tetramethylsilane ($\delta = 0.0$). IR spectra were recorded with a PerkinElmer 1605 FTIR spectrometer using 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 (ContraAA 300) (Analytikjena). An Orion 410A+ pH meter was used for the pH measurements.

2.3. Synthesis

The synthesis of *p*-*tert*-butylcalix[4]arene (**1**) and calix[4]arene (**2**) were carried out according to the known procedures [36].

2.3.1. Synthesis of Fe₃O₄ nanoparticles

The preparation of Fe₃O₄ nanoparticles was followed by a chemical co-precipitation of Fe(III) and Fe(II) ions according to the procedure in Ref. [28]. With some modifications, 50.0 mL of each 1.0 M FeCl₂ and 1.75 M FeCl₃ solutions were prepared with deionized water in two separate beakers. They were transferred into a 250 mL three-necked flask and while stirring under nitrogen. The solution has been heated up to 60 °C, before NH₄OH (25 wt%) was added to the solution dropwise till pH reaches 10–11. After addition of base, the solution immediately became dark brown, which indicates iron oxide has been formed in the system. The solution

has been continued to heat until 80 °C and kept at that temperature for 1 h. The forming precipitate was isolated by magnetic decantation. It was repeatedly washed with deionized water until reaching neutral pH, and followingly dried under vacuum for 12 h at room temperature.

2.3.2. Preparation of

[3-(2,3-epoxypropoxy)propyl]trimethoxysilane

(**EPPTMS**)-modified Fe₃O₄ nanoparticles (**EPPTMS-MN**)

EPPTMS-modified magnetite nanoparticles were prepared by the reaction between **EPPTMS** and the hydroxyl groups on the surface of magnetite according to the reported procedure [37]. Typically, 2.0 g of Fe₃O₄ nanoparticles were suspended in 100 mL of distilled water. A mixture of 5.0 mL of **EPPTMS**, 15 mL of methanol and 5 mL of 1% NaF aqueous solution was stirred for 5 min. After that 30 mL of tetraethyl orthosilicate was dropped slowly into the flask and resulting solution was stirred for 48 h at room temperature. The forming products were collected by magnetic separation with permanent magnet and were thoroughly washed with ethanol and deionized water until reaching neutral pH. Final solution was dried under vacuum at room temperature. The IR spectral data of the **EPPTMS-MN** carriers (KBr disk) cm⁻¹: 3448, 1116, 1090, 955 and 789 (Si–O), 573 (Fe–O).

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

4 mL of glacial acetic acid, *N*-methylglucamine (26.085 mmol), and 37% aqueous formaldehyde (1.25 mL) were added into a solution of calix[4]arene (**2**) (4.7 mmol) in 150 mL of THF. The resulting solution was stirred for 20 days at room temperature while monitored by TLC. The solvent has been removed under vacuum before adding methanol. The remaining precipitate was filtered off and has been evaporated. Received product was washed with water and dried under vacuum. 39% yield: mp: >350 °C. ¹H NMR (400 MHz DMSO): δ 2.49 (s, 6H, –CH₃), 3.16–3.63 (br, 34H, –CH₂–N–, –CH–, –CH₂–, ArCH₂Ar, –OH, Ar–CH₂–N–), 4.23 (d, 4H, *J* = 19.6 Hz, ArCH₂Ar), 6.33–6.86 (br, 10H, ArH). Anal. Calcd. for C₄₄H₅₈N₂O₁₄: 62.99, C; 6.97, H; 3.34, N. Found: 63.02, C; 6.88, H; 3.32, N.

2.3.4. Preparation of magnetic calix[4]arene derivative (**Calix-MN**)

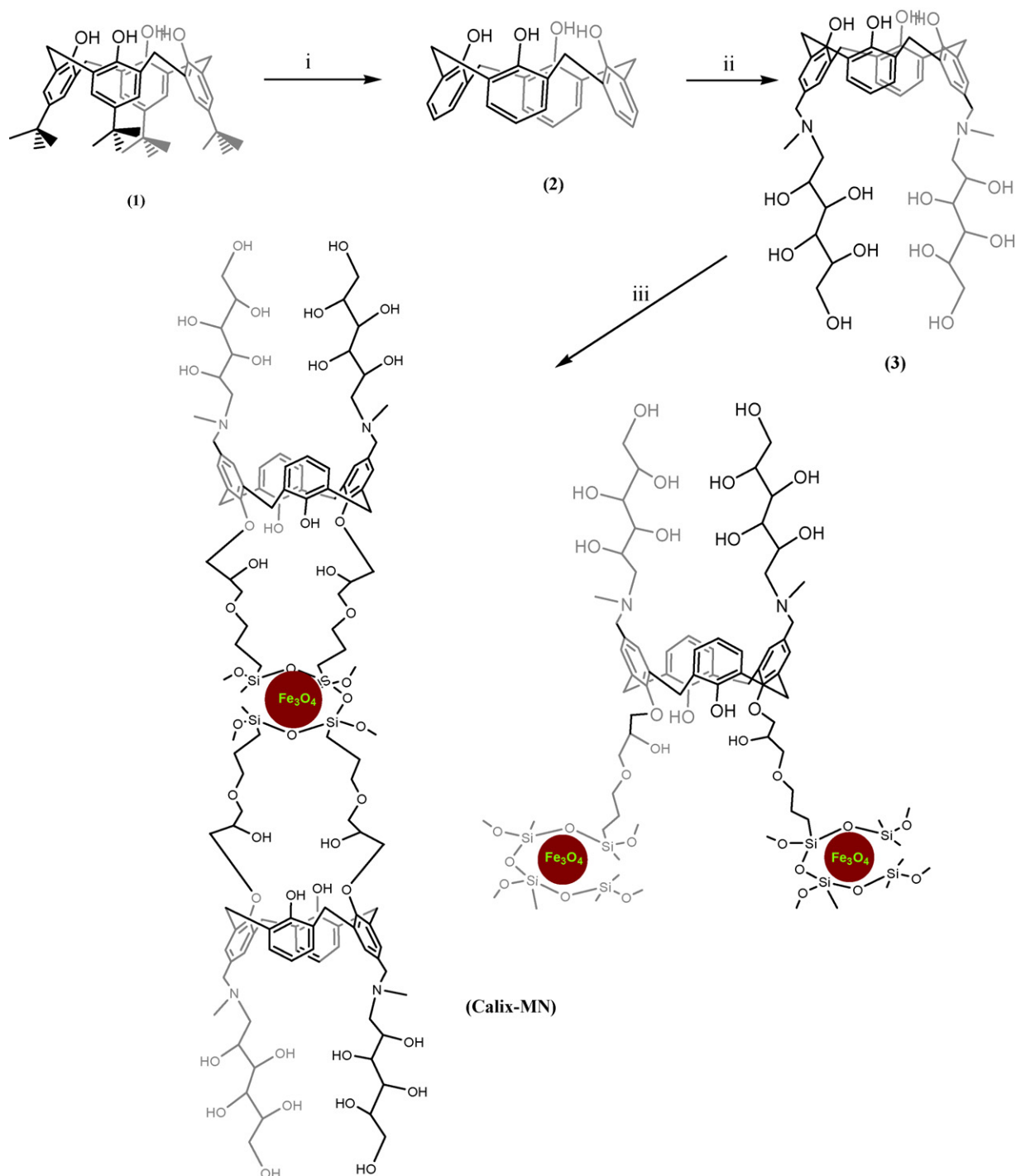
A mixture of the compound **3** (0.3 g), potassium carbonate (0.5 g) in acetonitrile (30 mL) was stirred for 30 min before adding 0.9 g of **EPPTMS-MN** and heated under reflux for 73 h. After magnetic separation, the resulted compound was washed with DMF (three times) to remove excess compound **3**, then washed with water and dried under vacuum. The IR spectral data of the **Calix-MN** is as (KBr disk) cm⁻¹: 1657 (amine), 1467, 1410 and 1385 (aromatic C=C), 1199, 1081, 958 and 796 (Si–O), 578 (Fe–O).

2.3.5. Synthesis of *p*-*tert*-butylcalix[4]arene grafted **EPPTMS-MN** (**4**)

To obtain compound **4**, above procedure for the synthesis of **Calix-MN** was adopted. The IR spectral data of the compound **4** is as (KBr disk) cm⁻¹: 3418, 1574 and 1477 (aromatic C=C), 1100, 1049 and 960 (Si–O).

2.3.6. Sorption procedure

The sorption capacities of the synthesized calix[4]arene derivatives (**Calix-MN** and **4**) was determined by the following technique [24]. Aqueous solution (10 mL) of Na₂Cr₂O₇ or Na₂HAsO₄ with 1.0 × 10⁻⁴ M (for dichromate) concentration and 1 × 10⁻⁵ M (for Na₂HAsO₄·7H₂O) and 25 mg of the sorbent were pipetted in a stoppered flask that was shaken at 175 rpm and 25 °C for 1 h. The sorbent



Scheme 1. The synthetic route for preparation of novel calix[4]arene derivatives (**3** and **Calix-MN**). Reaction conditions: (i) AlCl_3 , phenol, toluene; (ii) *N*-methylglucamine, formaldehyde, CH_3COOH , THF; (iii) EPPTMS-MN, K_2CO_3 , CH_3CN .

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 as well. The effect of pH was studied by adjusting the pH of aqueous solutions using diluted HCl and KOH solutions at 25 °C. The experiments were performed three times.

The percent sorption ($S\%$) was calculated according to Eq. (1):

$$S\% = \frac{A_0 - A}{A_0} \quad (1)$$

where A_0 and A are the initial and final concentrations of the dichromate ion before and after the sorption, respectively.

3. Results and discussion

3.1. Synthesis

The main goal of this study was to design and synthesize calix[4]arene immobilized magnetic nanoparticles and evaluate its sorption properties towards dichromate and arsenate anions.

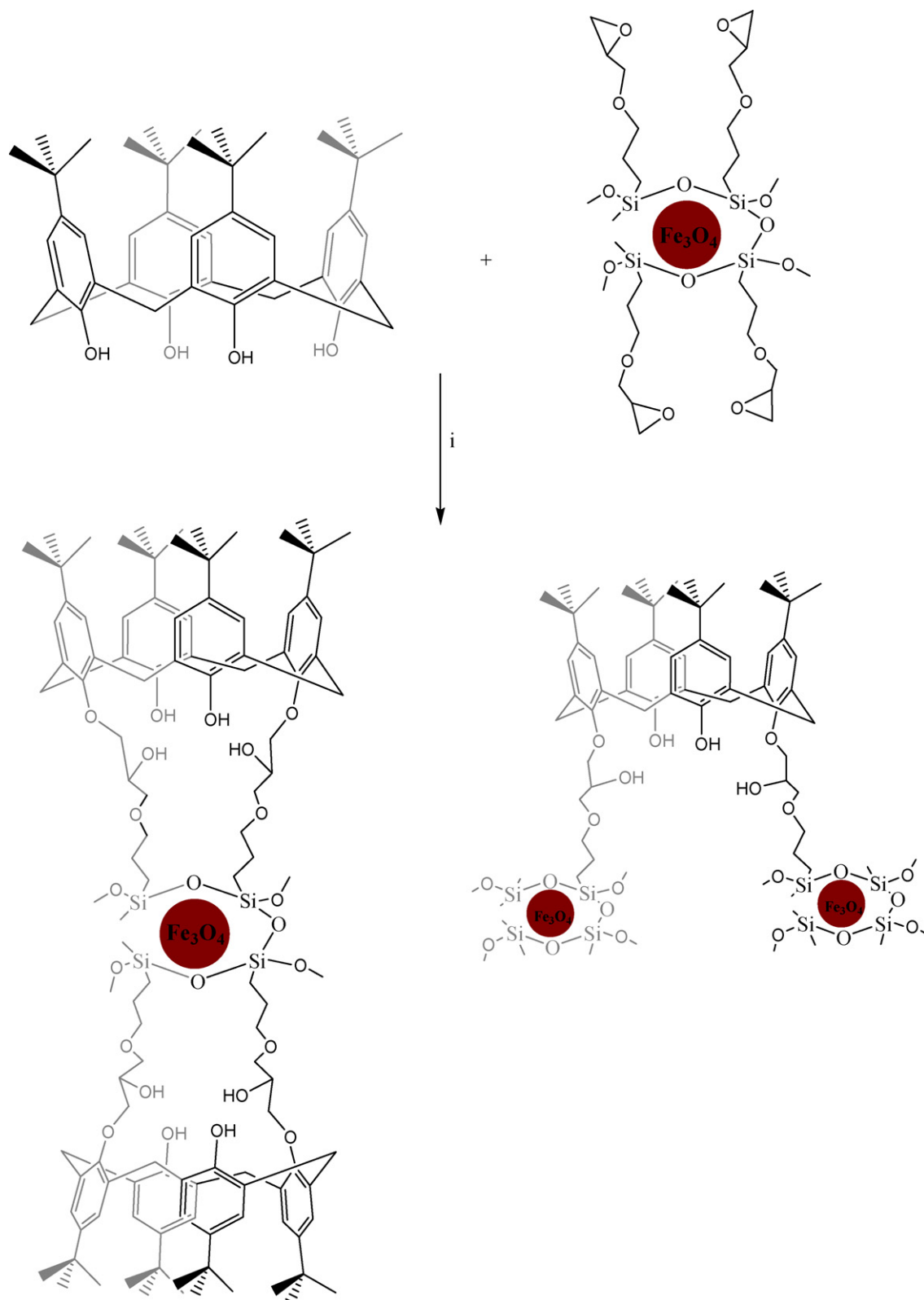


Fig. 1. Preparation of *p*-*tert*-butylcalix[4]arene-grafted EPPTMS-MN (4). Reaction conditions: (i) EPPTMS-MN, K_2CO_3 , CH_3CN , reflux, 3 days.

To obtain desired goal, *p*-*tert*-butylcalix[4]arene (1) and calix[4]arene (2) were prepared according to the known procedures [36]. 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 **3** at yield (39%). The ^1H NMR spectra of **3** has a typical AX pattern for the methylene bridge proton (ArCH_2Ar) of the calixarene moiety at 4.23 ppm ($J=19.6\text{Hz}$) which states that the compound does exist in the *cone* conformation [38]. The synthetic

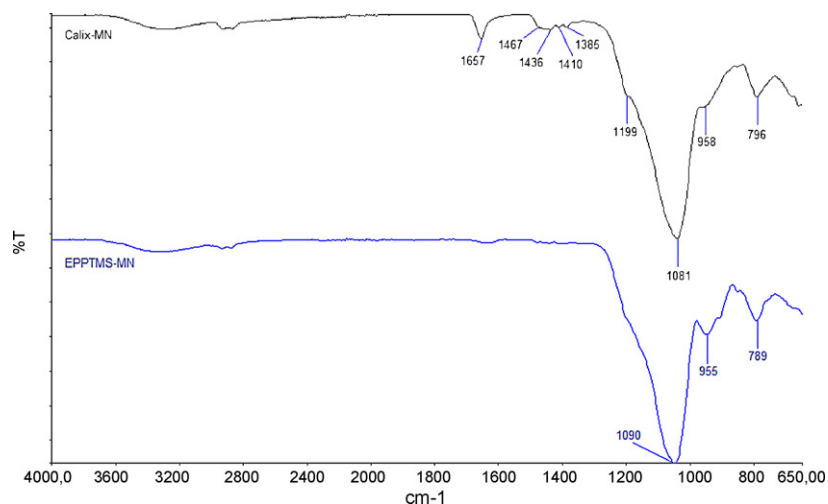


Fig. 2. FT-IR spectra of EPPTMS-MN and Calix-MN.

route for the preparation of calix[4]arene derivatives is given in Scheme 1.

According to the stated method, the preparation of magnetic Fe_3O_4 nanoparticles was held by the chemical co-precipitation of Fe^{3+} and Fe^{2+} ions in which their concentration ratio was selected by the stoichiometric ratio of 1:2, because Fe^{2+} is prone to the oxidation and thus changes to Fe^{3+} in solution. The Fe_3O_4 nanoparticles prepared by this method have a number of hydroxyl groups on the surface for contact with the aqueous phase. EPPTMS-modified Fe_3O_4 nanoparticles (EPPTMS-MN) were formed by the reaction between EPPTMS and the hydroxyl groups on the surface of magnetite.

Two respective reactions were involved in the process. First, the EPPTMS was hydrolyzed to the highly reactive silanol species in the solution phase under alkaline condition. Followingly, their condensation with surface free-OH groups of magnetite to render stable Fe–O–Si bonds takes place. Oligomerization of the silanols in solution also occurs as a competing reaction with their covalent binding to the surface. Afterwards, the nanoparticles were modified directly by [3-(2,3-epoxypropoxy)propyl]trimethoxysilane (EPPTMS) to introduce reactive groups onto the particles surface. Finally calix[4]arene derivative (3) was immobilized onto

modified nanoparticles by surface in the presence of K_2CO_3 in acetonitrile [39]. Same procedure was adopted to obtain *p*-tert-butylcalix[4]arene grafted modified Fe_3O_4 magnetite nanoparticles (EPPTMS-MN) (4) (see Fig. 1).

The new compound was characterized by a combination of IR, TGA TEM and elemental analyses.

FT-IR spectroscopy was used to elaborate the structure of Fe_3O_4 , EPPTMS-modified Fe_3O_4 , Calix-MN and compound 4. The IR peak at 568 cm^{-1} belongs to the stretching vibration mode of Fe–O bonds in Fe_3O_4 . Comparing with the IR spectrum of EPPTMS-modified Fe_3O_4 , calix[4]arene derivative (Calix-MN, 4) possessed peaks at 1657 cm^{-1} (for Calix-MN), which is stretching vibrations of amine band and at 1574 and 1477 (for 4), 1467 cm^{-1} (for Calix-MN), which is attributed to the bending vibration of aromatic C=C bonds of calix[4]arene. Additional peaks centered at 1100 , 1049 and 960 (for 4), 1199 , 1081 , 958 and 796 cm^{-1} (for Calix-MN) and 1116 , 1090 , 955 cm^{-1} (for EPPTMS-MN) were most probably due to the symmetric and asymmetric stretching vibration of framework and terminal Si–O–groups (Fig. 2).

In order to obtain more direct information on particle size and morphology, TEM micrographs of pure Fe_3O_4 nanoparticles and calix[4]arene-immobilized magnetic nanoparticles were provided

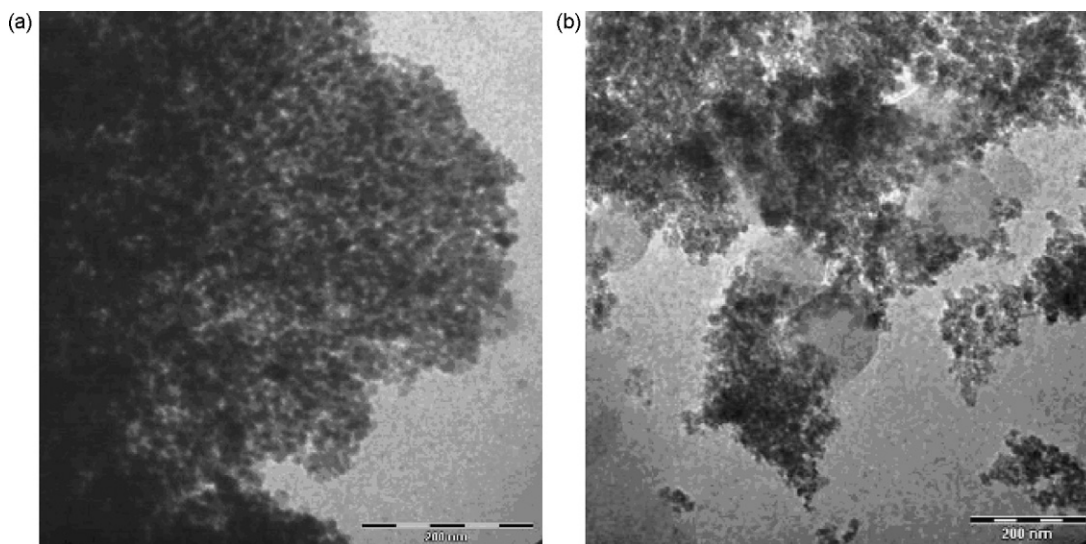


Fig. 3. TEM micrographs of (a) pure Fe_3O_4 nanoparticles, (b) magnetic calix[4]arene derivative (Calix-MN).

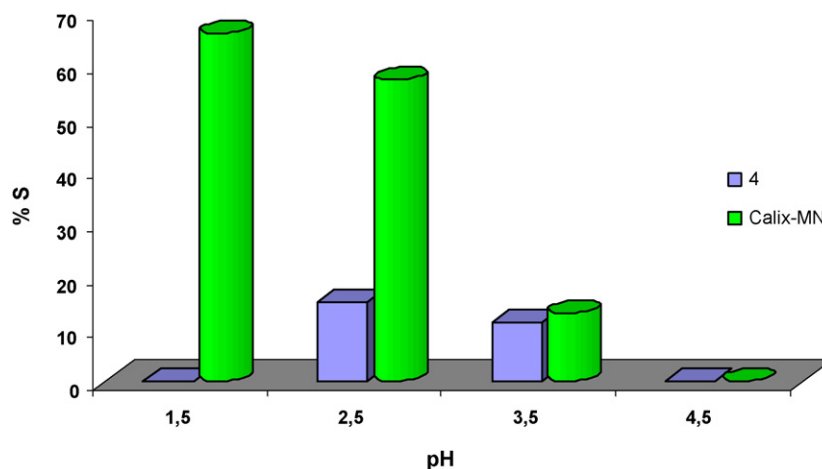


Fig. 4. Sorption percentages of dichromate anion with **Calix-MN** and **4** at pH 1.5–4.5 (solid phase, sorbent = 25 mg (**Calix-MN**, **4**), aqueous phase, $\text{Na}_2\text{Cr}_2\text{O}_7 = 1.0 \times 10^{-4}$ M (10 mL) at 25 °C for 1 h).

(Fig. 3a 1b). Observing the photograph (Fig. 3a), the nanoparticles are observed (Fig. 3a) as dense aggregates due to the lack of any repulsive force between the magnetite nanoparticles. This is mainly due to the nano-size of the **EPPTMS**-modified Fe_3O_4 , which is about 10 ± 2 nm. This may be considered as indirect evidence that the magnetic core of the **EPPTMS**-modified magnetite particles consisted of a single magnetite crystallite with a typical diameter of 8 ± 3 nm, and that difference corresponds the **EPPTMS** coating. After calix[4]arene immobilization, the dispersion of particles were improved greatly (Fig. 3b). It can easily be explained by the electrostatic repulsion force and steric hindrance between the calix[4]arene on the surface of Fe_3O_4 nanoparticles.

Thermal properties of **EPPTMS** modified Fe_3O_4 (**EPPTMS-MN**) and immobilized calix[4]arene magnetite nanoparticles were analyzed by thermogravimetric method. The indication of coating formation on the magnetite nanoparticles surface can be obtained from TGA measurement. Upon heating, the weight loss of **EPPTMS**-modified magnetite nanoparticles (**EPPTMS-MN**) were shown to be about 5% within a broad temperature range of 250 and 650 °C by decomposition of 3-(2,3-epoxypropoxy)-propyl groups. The weight loss of calix[4]arene immobilized magnetite nanoparticles indicated one-step thermal degradation between same temperature range similarly. The step arises from decomposition of both calix[4]arene units and 3-(2,3-epoxypropoxy)-propyl groups (26%).

3.2. Solvent extraction

3.2.1. Dichromate anion sorption studies

In this study, we were interested in synthesizing novel polymeric calix[4]arene derivatives including donor atoms having proton-switchable binding lobes for anions. We also examined the sorption properties for anions at the range of pH 1.5–4.5. Compound **3** was not evaluated due to its partial solubility in neutral water. Binding efficiencies of other hosts (**Calix-MN** and **4**) were carried out by solid-phase extraction system of HCr_2O_7^- from aqueous solution at different pH.

The extraction results of **4** and **Calix-MN** are summarized in Fig. 4. It is clear that the receptor (**Calix-MN**) is more effective than compound **4** which does not contain amine groups at the upper rim of calix[4]arene units for the removal of dichromate anions. Namely, the sorption data given in Fig. 4 indicated that magnetic calix[4]arene derivative (**Calix-MN**) has notably increased the anion extraction ability. This increase can be explained by the fact that magnetic calix[4]arene derivative (**Calix-MN**) is protonable in acidic conditions due to amine groups and it would easily form

complexes with dichromate anions by electrostatic interactions and hydrogen bonding.

The extraction results indicated that host **Calix-MN** is effective extractant at low pH between 1.5 and 3.5. The maximum percentage of extracted dichromate ions was found to be 66% when the pH of the aqueous solution was 1.5. The other side, minimum percentage of extracted ions was attained to be 13% when pH of the aqueous solution was increased 3.5. As a result, the extractant **Calix-MN** provided suitable binding affinity for dichromate anions at low pH, due to proton-switchable amine moiety.

In our previous study [27,40,41], we report the synthesis and extraction studies of polymers based on a calix[4]arene platform with cyclic amino groups on their upper rim. It was observed that the ionophores were very good adsorbents for dichromate from aqueous solution. This reflects the fact that calix[4]arene amine binding sites more strongly complex with dichromate in low pH medium. It is important to note that the conformation of the calix[4]arene unit and the cooperativity of the functionalities play important roles in the extraction systems.

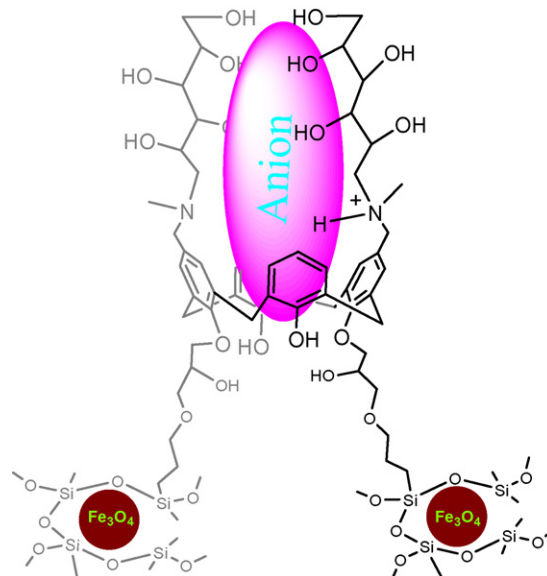
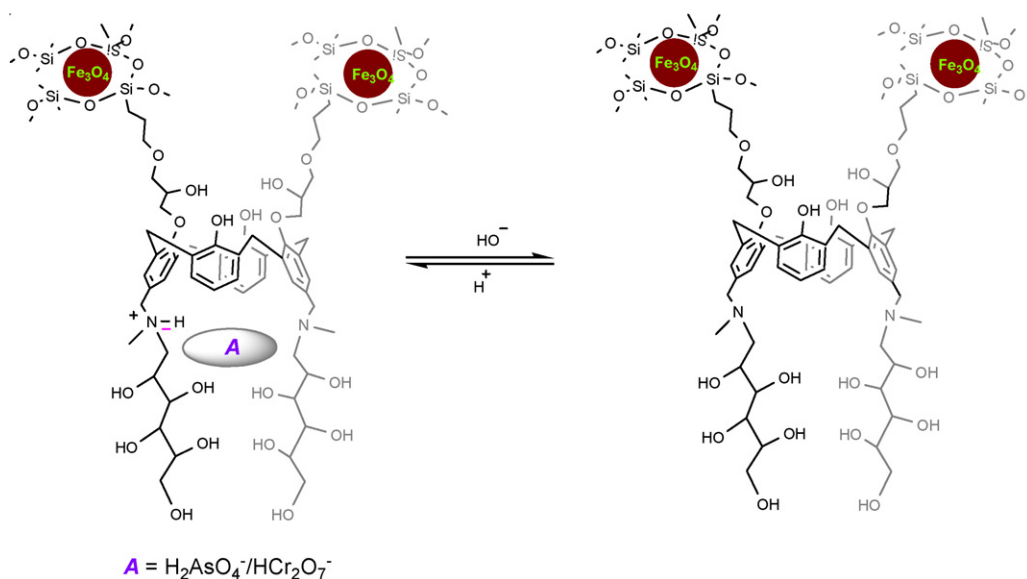


Fig. 5. Proposed interactions of magnetic calix[4]arene derivative (**Calix-MN**) with anions.



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

It is well known that under more acidic conditions $\text{Na}_2\text{Cr}_2\text{O}_7$ is converted into $\text{H}_2\text{Cr}_2\text{O}_7$ and after ionization in an aqueous solution it exists in the $\text{HCr}_2\text{O}_7^- / \text{Cr}_2\text{O}_7^{2-}$ form. At more strongly acidic conditions HCr_2O_7^- and $\text{Cr}_2\text{O}_7^{2-}$ dimers become the dominant Cr^{6+} form and $\text{p}K_{a1}$ and $\text{p}K_{a2}$ values of these equations are 0.74 and 6.49, respectively. It is clear that the magnetic calix[4]arene derivative (**Calix-MN**) form complex mostly with HCr_2O_7^- ions [42].

The proposed interaction for the extraction of anions with magnetic calix[4]arene derivative (**Calix-MN**) is given in Fig. 5 (Scheme 2).

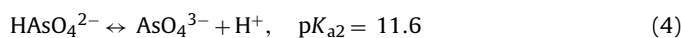
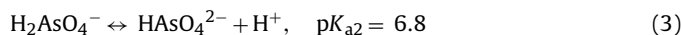
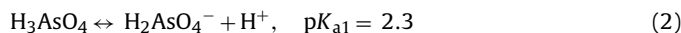
3.2.2. Arsenate anion sorption studies

Arsenic is a well known carcinogenic causing uncountable adverse health effects [2]. In this case, it is extremely important to remove arsenic from contaminated wastewater. The arsenate ($\text{H}_2\text{AsO}_4^- / \text{HAsO}_4^{2-}$) ions are dianions having oxide moieties at the periphery of the anions. These oxides alter potential sites for hydrogen bonding to the host molecule. In literature [43], immobilized *N*-methyl-*D*-glucamine on poly(vinylbenzyl chloride) beads shows high affinity towards arsenate ions. Hence, we designated a *N*-methyl-*D*-glucamine calix[4]arene derivative immobilized on magnetite Fe_3O_4 nanoparticles and examined its efficiency toward arsenate ion. Magnetic calix[4]arene derivative (**Calix-MN**) was

proved to be an effective extractant for the phase transfer of arsenate anions at pH 3.5–5.5 according to extraction data (Fig. 6).

The percentage of arsenate ions extracted was 86% for magnetic calix[4]arene derivative when the pH of the aqueous solution was 3.5 and attained minimum for the nanoparticles when pH of the aqueous solution increased to 7.0. It indicates that best interaction between ligand and arsenate ions occurs at this pH. These interactions include electrostatic interaction and hydrogen bonding between protonable amine and the oxygen of arsenate anions [44]. It is clear that role of polymeric ligand includes donor atom may be helped to increase of interaction capability, as well.

As(V) speciation is affected by the solution pH through the following equilibrium [11]:



From Eqs. (2)–(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 is depending on pH ranges. In higher acidic conditions (pH 1–3) the arsenate ions will be protonated in form H_3AsO_4 . Besides this, the monoanion (H_2AsO_4^-) will have a smaller free energy of hydration as compared to its dianionic form HAsO_4^{2-} [11].

4. Conclusion

In summary, we have prepared new magnetic nanoparticles containing calix[4]arene derivatives and one of them is believed to be an efficient way to improve the separation capability of the calixarene composite silica carriers as well as those may be helped for separation process due to magnetic properties. Then, prepared hosts have been used to remove toxic oxyanions like arsenate and dichromate in aqueous solution. The magnetic calix[4]arene derivative (**Calix-MN**) has notable increased the anion extraction ability at low pH by means of interactions include electrostatic interaction and hydrogen bonding between protonable amine and the oxygens of arsenate anions.

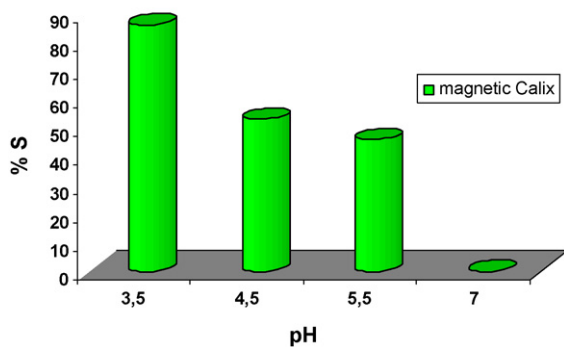


Fig. 6. Sorption percentages of arsenate anion with **Calix-MN** at pH 3.5–7.0 (solid phase, sorbent = 25 mg (**Calix-MN**), aqueous phase, $\text{Na}_2\text{HAsO}_4 = 1.0 \times 10^{-5}$ M (10 mL) at 25 °C for 1 h).

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