Preparation and uranyl ion extraction studies of calix[4]arene-based magnetite nanoparticles

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ABSTRACT

The article describes both syntheses of diamide derivatives of p-tert-butylcalix[4]arene (**3a** and **3b**) and their immobilization onto [3-(2,3-epoxypropoxy)-propyl]-trimethoxysilane-modified Fe_3O_4 magnetic nanoparticles to obtain calixarene-based magnetic nanoparticles (CB-MNs). All prepared magnetic nanoparticles (CB-MNs) were characterized by a combination of elemental analysis, FTIR, transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). The studies regarding the removal of uranyl ion from the aqueous solutions have been carried out both in liquid–liquid and in solid–liquid extraction studies. The results show that the prepared magnetic nanoparticles (**4a** and **4b**) are better removing uranyl ion than the precursor calix[4]arene derivatives (**3a** and **3b**).

1. Introduction

Uranium is most commonly used as nuclear fuel in fission reactors. Uranium exists commonly in aqueous solutions in the form of its oxide ion, uranyl ($U^{VI}O_2^{2+}$), which exhibits high stability in natural environments such as seawater [1]. Crystallographic X-ray studies have shown that the uranyl ion has a linear structure, and is capable of forming complexes of coordinative bonds with host molecules containing five or six ligand groups, primarily oxygen atoms [2,3]. These characteristics serve an important role in specific molecular recognition toward uranyl, as only certain molecules are found suitable for chelation of uranyl.

Out of the 4.58 billion tons of uranium present in the upper 100 m or the well-mixed surface layer of the oceans, nearly 2×10^9 t should be considered accessible for recovery [4]. Freshwater rivers in the world contribute approximately 9000 t/y of uranium to the sea. If trapped from the feed seawater for the nuclear desalination plant or from the rejected brine, this uranium may contribute to the fuel of the nuclear reactor and therefore the energy required for desalination processes may be met partly from the uranium recovered from the desalination process [4]. Therefore, it is worthwhile to tap this resource of uranium. It has been used for this purpose in various methods such as ion exchange, membrane-related processes, biological processes, electrochemical and adsorption techniques in particular [5–7], because adsorption represents an efficient and convenient

technique usually applied for removing and recovering of important elements such as uranium [8].

The hexavalent uranyl cation (UO_2^{2+}) was the most stable form in both aqueous solutions and in vivo [9,10]. In the case of nuclear accidents, uranium is the origin of severe internal contaminations by ingestion or inhalation. In mammals, uranyl ion is mainly complexed by blood transferring and by low molecular weight complexing agents such as citrates, bicarbonates and phosphates [11,12].

Calixarenes have attracted the interest of chemists for more than three decades [13–15]. Chemical modification from the upper or lower rim has made this class of synthetic ionophores as effective extractants for transferring anionic and cationic ions or neutral molecules from aqueous solution into an organic layer [16–20]. Extraction mechanism can be explained in terms of 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 [21].

In the last decade, superparamagnetic nanoparticles of iron oxide have found potential applications in biological fields such as bioseparation [22,23], tumor hyperthermia [22], magnetic resonance imaging (MRI), diagnostic contrast agents [23], magnetically guided site-specific drug delivery agents [24], and biomolecules immobilization [25,26]. In addition to these applications, these particles have been used recently to remove toxic oxyanions such as arsenic and dichromate [27,28]. In case of separation science, the application is generally based on the solid-phase magnetic feature that endows a rapid, easy separation and recovery of contaminants from the polluted environment by applying an external magnetic field.

In our previous work [28], alkyl amine derivative of calix[4]arene was immobilized onto the surface of modified-Fe_3O_4 nanoparticles.

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The immobilization results indicated that the calix[4]arene units were effectively immobilized onto the surface of Fe_3O_4 nanoparticles. That magnetic calixarene derivative was used for removal of toxic oxyanions such as arsenate and dichromate ions in the solid–liquid extraction studies. The extraction results showed that amine groups containing calix[4]arene modified-Fe_3O_4 nanoparticles were more efficient receptors for $HCr_2O_7^-$ and $H_2AsO_4^-$ ions at low pH.

Herein, magnetic Fe_3O_4 nanoparticles were prepared by the chemical co-precipitation of Fe^{3+} and Fe^{2+} ions and were directly modified by [3-(2,3-epoxypropoxy)propyl]trimethoxysilane (EPPTMS) to introduce reactive groups onto the particles surface according to the our previous procedures [27,28]. Then, dipyridyl-substituted calix[4]arenes were grafted onto the surface of modified magnetic nanoparticles. The functionalized magnetic particles also have been used for extraction studies for removing of uranyl ion from aqueous solution at various pH.

2. Experimental

2.1. Apparatus

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

2.2. Materials

TLC analyses were carried out on 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 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. Arsenazo III, uranyl acetate dihydrate were purchased from Fluka. 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 reagent. The pH values of the working solutions were adjusted by using 5 M (2 mL) of sodium acetate buffer to allow determination of UO_2^{2+} in aqueous solution.

2.3. Synthesis

The compounds **1**, **2**, Fe_3O_4 nanoparticles, EPPTMS-MN, **3a** and **3b** were synthesized according to the literature procedures [16,27,29–31]. The syntheses of the magnetic *p-tert*-butylcalix[4]arene derivatives (**4a** and **4b**) is herein reported firstly.

2.3.1. Synthesis of p-tert-butylcalix[4]arene diamide derivative 3a

White powder 65.8% yield-m.p.: 239–242 °C. The IR spectral data is as (KBr disk) cm^{-1}: 3454, 3358, 1681; ^1H NMR (400 MHz $CDCl_3$): δ 0.98 (s, 18H, ^tBu), 1.22 (s, 18H, ^tBu), 3.27 (d, 4H, $ArCH_2Ar$, $J = 13.3$ Hz), 3.90 (d, 4H, $ArCH_2Ar$, $J = 13.3$ Hz), 4.46–4.49 (m, 8H, OCH_2, Ar–CH_2–NH), 6.85 (s, 4H, ArH), 7.00 (s, 4H, ArH), 7.06–7.10 (m, 2H, PyH), 7.18 (s, 2H, OH), 7.61 (d, 2H, PyH, $J = 7.8$ Hz), 8.45 (d, 2H, PyH, $J = 4.5$ Hz),

8.62 (d, 2H, PyH) 9.21(t, 2H, NH). Anal. Calcd. For $C_{60}H_{72}O_6N_4$: C, 76.24; H, 7.68; N, 5.93. Found: C, 76.31; H, 7.73; N, 5.84%.

2.3.2. Synthesis of p-tert-Butylcalix[4]arene diamide derivative 3b

White powder 65.0% yield-m.p.: 259–262 °C. The IR spectral data is as (KBr disk) cm^{-1}: 3454, 3358, 1676 cm^{-1}; ^1H NMR (400 MHz $CDCl_3$): δ 0.98 (s, 18H, ^tBu), 1.22 (s, 18H, ^tBu), 3.31 (d, 4H, $ArCH_2Ar$, $J = 13.3$ Hz), 4.02 (d, 4H, $ArCH_2Ar$, $J = 13.3$ Hz), 4.50–4.55 (m, 8H, OCH_2, Ar–CH_2–NH), 6.85 (s, 4H, ArH), 7.00 (s, 4H, ArH), 7.06–7.10 (m, 2H, PyH), 7.18 (s, 2H, OH), 7.61 (d, 2H, PyH, $J = 7.8$ Hz), 8.45 (d, 2H, PyH, $J = 4.5$ Hz), 8.62 (d, 2H, PyH), 9.21(t, 2H, NH). Anal. Calcd. For $C_{60}H_{72}O_6N_4$: C, 76.24; H, 7.68; N, 5.93. Found: C, 76.31; H, 7.73; N, 5.84%.

2.3.3. General procedure of the preparation of CB-MNs

A mixture of diamide derivative of *p-tert*-butylcalix[4]arene (**3a** or **3b**) (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 74 h. After magnetic separation, the resulting compound was washed with dichloromethane three times to remove excess diamide derivative of *p-tert*-butylcalix[4] arene, then washed with water and dried under vacuum.

For **4a**: The IR spectral data is as (KBr disk) cm^{-1}: 3428, 1657 (amide C=O), 1556, 1456 (aromatic C=C), 1193, 1087, 953, 802 (Si–O) and 572 (Fe–O). For **4b**: The IR spectral data is as (KBr disk) cm^{-1}: 1648 (amide C=O), 1461, 1411 (aromatic C=C), 1195, 1087, 953, 796 (Si–O) and 578 (Fe–O).

2.3.4. Preparation of p-tert-butylcalix[4]arene grafted EPPTMS-MN (5)

A mixture of *p-tert*-butylcalix[4]arene (0.25 g), potassium carbonate (0.1 g) in acetonitrile (25 mL) was stirred for 30 min. then 0.75 g of EPPTMS-MN was added to that solution and heated under reflux for 3 days. After magnetic separation, the resulted compound was washed with dichloromethane for three times to remove excess compound **1**, then washed with water and dried under vacuum. The IR spectral data of the compound **5** is as (KBr disk) cm^{-1}: 3418, 1574 and 1477 (aromatic C=C), 1100, 1049 and 960 (Si–O).

2.3.5. Extraction studies

Into a vial was pipetted an aqueous solution (10 mL) containing $UO_2(AcO)_2 \cdot 2H_2O$ at a concentration of 1.15×10^{-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 1×10^{-3} M solution of **3a** or **3b** in CH_2Cl_2 for liquid–liquid extraction, 25 mg of CB-MNs for solid–liquid extraction). The mixture was vigorously agitated in a stoppered glass vial with a mechanical shaker for 2 min, then was shaken at 175 rpm, 25 °C for 1 h. The sorbents were separated before measurements. The residual uranyl concentration of aqueous solute was determined spectrophotometrically [32].

Blank experiments showed that no uranyl extraction occurred in the absence of calixarene. Uranyl cation in aqueous phase measured at 652 nm (for pH 5.5–8.5). The percent sorption (E %) was calculated as equation [33];

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

where C_0 and C are initial and final concentrations of uranyl ion before and after extraction, respectively.

2.3.6. Selectivity studies

Selectivity studies of **3a** were performed in the presence of Fe^{3+}, Ca^{2+}, K^+ and Na^+ cations since they are co-present with uranyl cation in aqueous solutions, with a higher concentration. Therefore, one