Application of Hydroxamic Modified Calix[6]arene for Selective Extraction of Uranium (VI)

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Abstract. Calix[6]arene hydroxamic derivatives were synthesized by two steps using calix[6]arene, ethyl bromoacetate and hydroxylamine hydrochloride as the main raw materials, and were characterized by infrared spectroscopy. The extraction of U(VI) by calix[6]arene and its hydroxamic derivatives on various experimental conditions were studied. The extraction results showed that pH played an important role in the extraction system. Maximum extraction was observed at a pH of 5.0 within 20 min, and the dynamic extraction model corresponded to a pseudo-second order model.

Introduction

In the last decade, an increasing amount of attention has been paid to calixarenes and their derivatives due to their unique molecular structure and simple one-pot synthesis for supramolecular chemistry[1]. Calixarene is a unique macromolecular compound with a cavity structure[2], and many studies have investigated the modification of its upper and lower edge with functional groups[3]. The calixarene derivatives have been applied in many areas, including molecular recognition, enzyme mimics, chemical sensors, and molecular assembly as well as optoelectronic and nanomaterials.

The application of calixarenes modified by heteroatom-containing groups for the extraction of heavy metals and transitional metals has been extensively studied due to their high complexation and recognition abilities[4]. Recent studies have indicated that functional groups containing nitrogen efficiently improve the ability of calixarene for the selective recognition of metal ions. Such functional groups include amidogen, acylamino, pyridine and Schiff base. The larger cavity in calix[6]arenes and calix[8]arenes with six and eight aromatic rings are more suitable for anchoring binding groups than calix[4]arenes. Uranium is an important radioactive element, and excessive amounts of uranium are released into the environment through activities associated with the nuclear industry and mining. Our main objective in this paper was to investigate the extraction of U(VI) by calix[6]arene hydroxamic derivative from an aqueous solution.

Experimental

Main Instruments and Chemicals

A PHS-3C precision pH meter, an electronic balance, a 2000 ultraviolet spectrophotometer, an EQUINOX 55 Fourier transform infrared (FTIR) spectrometer, a JJ-1 electric mixer, an HZP-C air bath oscillator, a DF205 electrothermal blowing dry box and an H.H.S11-4R Electro Thermostatic Water Bath were used in this study. U₃O₈ was provided by the Key Discipline Laboratory of National Defense for Biotechnology in Uranium Mining and Hydrometallurgy at the University of South China.
Synthesis of Calix[6]arene and Calix[6]arene Hydroxamic Derivatives

Calix[6]arene was synthesized according to a previously published protocol[5,6]. The structure of calix[6]arene is shown in Fig. 1. The calix[6]arene hydroxamic derivatives were synthesized based on previously reported procedures[7,8]. And the structure of calix[6]arene hydroxamic derivatives is shown in Fig. 2.

![Fig. 1 Structure of calix[6]arene.](image1)

![Fig. 2 Structure of the calix[6]arene hydroxamic derivative.](image2)

Extraction of Uranium by Calix[6]arene Hydroxamic Derivatives

20 mL of an aqueous solution of U(VI) ions at different original concentrations (i.e., 0.021 mmol•L\(^{-1}\), 0.042 mmol•L\(^{-1}\) and 0.084 mmol•L\(^{-1}\)) and 20 mL of a calix[6]arene hydroxamic derivative chloroform bulk solution at different original concentrations (i.e., 0.21 mmol•L\(^{-1}\), 0.42 mmol•L\(^{-1}\), 0.84 mmol•L\(^{-1}\) and 1.68 mmol•L\(^{-1}\)) was added to Erlenmeyer flasks, respectively. The results of the solution pH, calix[6]arene hydroxamic derivative concentration and contact time on the extraction capacity of the calix[6]arene hydroxamic derivatives for U(VI) were investigated. After the flasks were agitated on an orbital shaker (220 rpm) for a certain period of time, the concentration of U(VI) in aqueous phase was determined as previously described[9].

The percent removal was calculated using the following equations:

\[
\text{Percentage removal} (%) = \left( \frac{C_0 - C}{C_0} \right) \times 100
\]

where \(C_0\) and \(C\) are the concentrations of the uranium(VI) in the original solution (mg•L\(^{-1}\)) before and after extraction, respectively.

Results and Discussion

Infrared Spectra Analysis

The infrared spectra of calix[6]arene and its acetic ether and hydroxamic derivatives are shown in Fig. 3. In the IR spectra of calix[6]arene, the C-O of the phenol was seen at 1217.08 cm\(^{-1}\), and the vibrational peaks at 1602.85 cm\(^{-1}\), 1485.19 cm\(^{-1}\) and 1460.11 cm\(^{-1}\) were due to the aromatic skeleton. The C-H of the methyl group (CH\(_3\)-) was observed at 2962.66 cm\(^{-1}\) and 2870.08 cm\(^{-1}\). The CH\(_2\)- is observed at 1485.19 cm\(^{-1}\). The bending vibration peak at 1396.07 cm\(^{-1}\) and 1361.74 cm\(^{-1}\) are due to the C-H of symmetrical. The infrared spectra corresponding to the benzene ring, phenolic hydroxyl group and symmetrical confirmed the existence of calix[6]arene. In comparison to the IR spectra of calix[6]arene, the ethyl acetate derivatives exhibited a new vibrational peak at 1300 cm\(^{-1}\), which corresponds to the C-O-C vibrational peak from the aromatic ester. In comparison to the acetic ether derivatives, the hydroxamic derivatives exhibited -OH of hydroxamic at 3300 cm\(^{-1}\) and a C=N of
hydroxamic at 1620 cm\(^{-1}\) in the infrared spectra. The infrared spectra confirmed the structure of the calix[6]arene hydroxamic derivatives.

![IR spectra of calix[6]arene and its acetic ether and hydroxamic derivatives](image)

**Fig. 3** IR spectra of calix[6]arene and its acetic ether and hydroxamic derivatives.

**Effect of the Solution pH**

The solution pH plays an important role in the extraction of U(VI) from an aqueous solution. Both the speciation of U(VI) in an aqueous solution and the binding sites present on the surface of the calix[6]arene hydroxamic derivatives are influenced by pH. Experiments were performed at different pH values (2.0-6.0) at 25°C. Extracted U(VI) (%) as a function of pH is shown in Fig. 4.

![Extraction of U(VI) at different pH values](image)

**Fig. 4** Extraction of U(VI) at different pH values. Conditions: initial U (VI) concentration, 0.021 mmol L\(^{-1}\), 0.042 mmol L\(^{-1}\), 0.084 mmol L\(^{-1}\); contact time, 20 min; temperature, 25°C; calix[6]arene hydroxamic derivatives concentration, 0.42 mmol L\(^{-1}\).

The maximum percent removal of U(VI) was obtained at a pH of 5.0, and the minimum percent removal of U(VI) was observed at a pH of 2.0. The removal of U(VI) increased as the pH increased in the range of 2.0-4.0 but nearly remained constant in the range of 4.0-5.0. The observed decrease in the extraction capacity at pH>6.0 is attributed to the precipitation of uranium. When the solution pH is less than 2.0, U(VI) exists predominately in the form of UO\(_2\)\(^{2+}\). A high concentration of H\(^+\) and H\(_3\)O\(^+\) compete with U(VI) for the coordination site, which results in a decrease in the extraction of U(VI) at low pH values. Optimum extraction at pH 5.0 may due to the presence of ligands, such as carboxyl and hydroxyl groups on the calix[6]arene hydroxamic derivatives. The decrease in the uptake of U(VI) at higher pH values may be due to the formation of uranyl complexes, such as UO\(_2\)OH\(^+\), (UO\(_2\))\(_2\)(OH)\(^{2+}\) and (UO\(_2\))\(_3\)(OH)\(_5\)^\(^+\). The optimum pH was determined to be 5.0, and all of the subsequent experiments were conducted at this pH value.

**Effect of Original Concentration of Calix[6]arene Hydroxamic Derivatives**

The experiments were performed by varying the concentration of the calix[6]arene hydroxamic derivatives from 0.21 mmol•L\(^{-1}\) to 0.42 mmol•L\(^{-1}\), 0.84 mmol•L\(^{-1}\) and 1.26 mmol•L\(^{-1}\). The percent removal and extraction capacity of the calix[6]arene hydroxamic derivatives for U(VI) at different extractant concentrations are presented in Fig. 5.
The percent removal increased as the extractant concentrations increased for concentrations less than 0.84 mmol•L⁻¹. The maximum removal efficiency was obtained at a calix[6]arene hydroxamic derivative concentration of 0.84 mmol•L⁻¹ and remained constant at higher concentrations. This trend is due to the partial aggregation of the extractant at higher concentrations, which results in fewer binding sites for U(VI) ions during the extraction. In addition, the results indicated that the percent removal of U(VI) at an original U(VI) concentration 0.021 mmol•L⁻¹ was higher than that at an original U(VI) concentration of 0.042 mmol•L⁻¹ and 0.084 mmol•L⁻¹. Therefore, as the concentration of U(VI) increased, fewer coordination sites were available to the extractant.

**Effect of Contact Time**

The percent removal and extraction capacity of the calix[6]arene hydroxamic derivatives for U(VI) at different contact times is shown in Fig. 6. The results indicated that the percent removal of U(VI) by calix[6]arene hydroxamic derivatives increased from 30.7% to 99.7% when the contact time was varied from 5 min to 30 min. The extraction process was very fast after 15 min. In addition, extraction equilibrium was established within 20 min. It was also observed that the extraction slowed down in the later stages because the available surface vacant sites decreased over time.

**Extraction Kinetics**

The linear form of the pseudo-first order model and the pseudo-second order model for the extraction of U(VI) at various original U(VI) concentrations were used to investigate the extraction characteristic. The correlation coefficients (R²) for the linear plots using the pseudo-first order model ranged from 0.936 to 0.943. While the correlation coefficients for the linear plots from the
pseudo-second order model ranged from 0.990 to 0.994. This result suggests that the pseudo-second order model could be adapted to describe this process because it fitted more accurately to the experimental data. The kinetic constants of this model are shown in (Table 1).

Tab. 1. Kinetic parameters obtained from the Lagrangian models for the extraction of U(VI) by calix[6]arene hydroxamic derivatives. (initial U(VI) concentration, 0.021 mmol•L\(^{-1}\) (5 mg•L\(^{-1}\)), 0.042 mmol•L\(^{-1}\) (10 mg•L\(^{-1}\)), 0.084 mmol•L\(^{-1}\) (20 mg•L\(^{-1}\)); pH value, 5.0; contact time, 0, 5, 10, 15, 20, 25, and 30 min; temperature, 25°C; calix[6]arene hydroxamic derivative concentration, 0.42 mmol•L\(^{-1}\))

| C\(_0\) (mg•L\(^{-1}\)) | k\(_1\) (min\(^{-1}\)) | q\(_e\) (mg•g\(^{-1}\)) | R\(^2\) | k\(_2\) (g•mg\(^{-1}\) min\(^{-1}\)) | q\(_e\) (mg•g\(^{-1}\)) | R\(^2\) |
|--------------------------|-----------------|-----------------|--------|-----------------|-----------------|--------|
| 5                        | 0.2475          | 10.4682         | 0.936  | 0.1801          | 10.2987         | 0.994  |
| 10                       | 0.1394          | 18.2839         | 0.940  | 0.1118          | 21.6920         | 0.993  |
| 20                       | 0.2159          | 61.6950         | 0.943  | 0.0943          | 47.3934         | 0.990  |

Summary
These results indicate that U(VI) ions can be efficiently extracted by calix[6]arene hydroxamic derivatives. Extraction of U(VI) was determined to be more effective at pH 4.0~6.0, and the optimal extraction was observed at an original pH of 5.0. The results from the kinetic study indicated that the pseudo-second order model was more appropriate for describing the extraction process.

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References
[1] Z. Asfari, V. Bohmer, J. Harrowfield, J. Vicens, and M. Saadioui, Calixarenes 2001, Dordrecht, Springer Netherlands, 2002.
[2] M Tabakci and M Yilmaz, Sorption characteristics of Cu(II) ions onto silica gel-immobilized calix[4]arene polymer in aqueous solutions: Batch and column studies, J. Hazard. Mater. 151(2008) 331-338.
[3] S. Sayin and M. Yilmaz, Preparation and uranyl ion extraction studies of calix[4]arene-based magnetite nanoparticles, Desalination. 276(2011) 328-335.
[4] P. D. Beer, J. P. Martin, and M. G. Drew, Calix[4]arene cryptand and new 1,3-bis-pyridyl-, bipyridyl and -alkythioether calix[4]arenes designed to coordinate transition metal cations, Tetrahedron. 48 (1992) 9917-9928.
[5] D. A. Casteel, and S. P. Peri, Steric and electronic effects in the aryl phosphate to arylphosphonate rearrangement, Synthesis. 09(1991) 691-693.
[6] C. D. Gutsche, B. Dhawan, K. H. No, and R. Muthukrishnan, Calixarenes. 4. The synthesis, characterization, and properties of the calixarenes from p-tert-butylphenol, J. Chem. Soc. Am. 103(1981) 3782-3792.
[7] E. A. Shokova, and V. V. Kovalev, Thiacalixarenes-A new class of synthetic receptors, J. Org. Chem. Russ. 39(2003) 1-28.

[8] Y. Jiang, B. Zhao, X. Zhou, and L. Zhou, Flotation of diaspore and aluminosilicate minerals applying novel carboxyl hydroxamic acids as collector, Hydrometallurgy. 104(2010) 112-118.

[9] J. Wang, X. Hu, J. Wang, Z. Bao, S. Xie, and J. Yang, The tolerance of Rhizopus arrhizus to U(VI) and biosorption behavior of U(VI) onto R. Arrhizus, J. Biochem. Eng. 51(2010)19-23.