

Sorption materials for sequestration Eu(III) modified with functionalized thiacalixarenes

M. Lukashova¹, K. Belikov¹, E. Bryleva¹,
S. Kharchenko²

1. State Scientific Institution "Institute for Single Crystals"
of NAS of Ukraine, UKRAINE, Kharkov, Lenin Avenue 60,
E-mail: lukashova@isc.kharkov.com

2. Institute of Organic Chemistry, NAS of Ukraine, UKRAINE,
Kiev, Murmanskaya street 5

Abstract – The effective solid extractants for the removal of Eu(III) ions from aqueous solutions were obtained. A number of modified thiacalix[4]arenes with phosphoryl groups on upper rim were used as impregnation agents. The obtained materials give sorption capacity of 8-14 mg/g and allow Eu(III) recovery up to 99% from aqueous solutions with average mineralization level.

Key words – thiacalix[4]arenes, europium, solid extractants,

I. Introduction

Currently, development of new materials for selective and effective extraction of actinides and lanthanides from solutions is a challenging issue. The growing activity of nuclear power plants, experimental laboratories and medical institutions poses significant environment contamination hazard. Actinide and lanthanide nuclides possess high migration capacity and can be easily accumulated in living tissues. The long-lived isotopes, e.g. americium 241, are of special concern in the view of long-term irradiation risk.

There are a number of techniques proposed for actinide and lanthanide sequestration from aqueous solutions. The use of selective sorption materials has many advantages over conventional extraction routes. It allows one-stage radionuclide extraction from the wastes of different chemical composition, thus simplifying extraction technology and reducing the amount of the organic solvents used. Also, sorption materials may be used in several decontamination cycles. However, most of sorbents are not sufficiently selective towards target ions. This drawback can be overwhelmed by modification of substrate with specific extracting agents, including thiacalixarene [1, 2].

Combination of sulfur atoms in the macrocycle backbone and phosphoryl groups on an upper rim along with grafting of thiacalixarene onto solid carrier provides efficient selective materials for extraction of radionuclides from nuclear wastes and contaminated natural waters. The selectivity of the calixarenes used towards actinide and lanthanide ions is achieved by modification of the macrocycle core with organophosphate functional groups. The presence of the bridged sulfur atoms in thiacalixarene structure leads to fixation of "cone" configuration of the macrocycle and facilitates metal ion binding via interaction between unshared electron pairs and vacant 3-d orbitals [3–6].

The present work is focused on the study of sorption materials obtained by impregnation of silica gel with a number of thiacalix[4]arenes. In the study, removal performance of the sorbents obtained was investigated using Eu (III) as Am (III) chemical analogue. The influence of bulk phase pH, contact time, calixarene content as well as Eu (III) and coexisting ions concentration on sorption efficiency was discussed. It was shown that Eu (III) removal percentage is strongly affected by the structure of functional groups on an upper rim of calixarene molecule.

II. Apparatus and material

The concentration of metal ions in solutions was determined by ICP-AES method using Trace Scan Advantage spectrometer (Thermo Jarrell Ash, USA). Bulk phase pH was adjusted using pH-150 pH-meter (Republican Unitary Enterprise "Gomel Measuring Instruments Plant", Belarus). The amount of thiacalix[4]arenes immobilized on the surface of the silica gel was determined using an EA-3000 CHNS elemental analyzer (EuroVector, Italy).

The thiacalix[4]arenes were synthesized at the Institute of Organic Chemistry, National Academy of Sciences of Ukraine. Thiacalix[4]arenes 1-4 were synthesized in accordance with scheme 1 using the procedures described in [3, 7]. The calixarenes used are denoted as follows:

p-Tert-Butylthiacalix[4]arene (1); thiacalix[4]arene (2); 5,11,17,23-tetrakis-(diethoxyphosphorylmethyl)-25,26,27,28-tetrahydroxythiacalix[4]arene (cone conformer) (4a); 5,11,17,23-tetrakis-(diisopropoxyphosphorylmethyl)-25,26, 27,28-tetrahydroxythiacalix[4]arene (cone conformer) (4b); 5,11,17,23-tetrakis-(dibutoxyphosphorylmethyl)-25,26, 27,28-tetrahydroxythiacalix[4]arene (cone conformer) (4c)

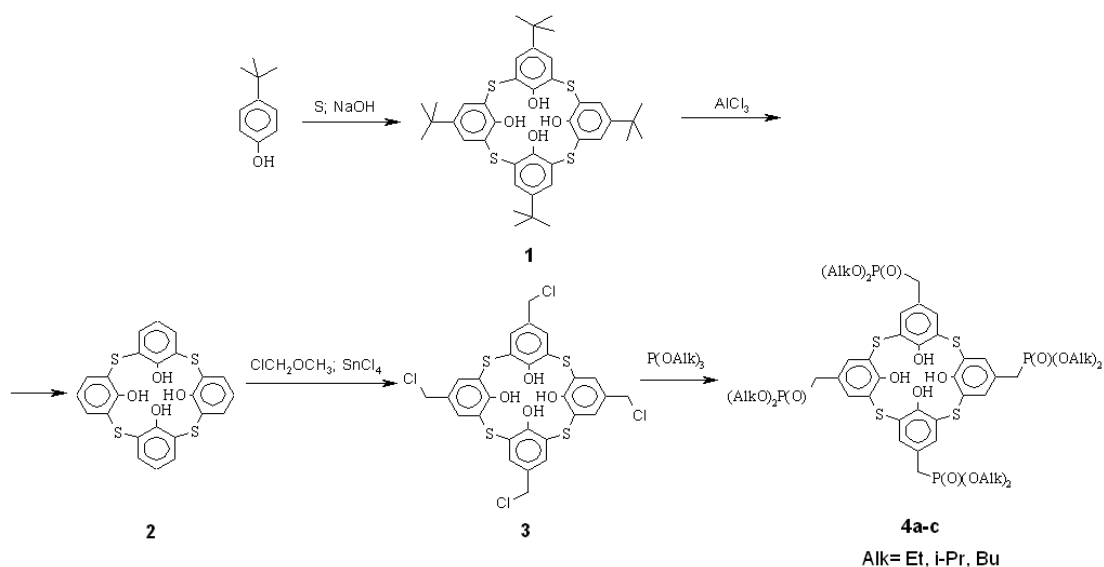
A standard solution of Eu (III) was prepared by dissolving appropriate amount of Eu₂O₃ in nitric acid. Multicomponent standards were prepared by diluting stock solutions materials of Na, Ca, Sr, Fe, Al at concentrations of 1 mg/mL; c.p. grade ammonia, special-purity grade nitric acid, special-purity grade hydrochloric acid, special-purity grade hexamethyldisilazane, c.p. grade toluene, pharmaceutical grade chloroform, silica gel 60 (surface area 500 ± 50 m²/g, ROCC, Belgium) were used as received.

Separate experiments were done for single-component model solutions and for natural groundwater of the following composition: Ca²⁺ 100 mg/L; Mg²⁺ 30 mg/L; Na⁺ 120 mg/L; K⁺ 11 mg/L; Sr²⁺ 1 mg/L; Fe(total) 0.1 mg/L; Cl⁻ 44 mg/L; NO₃⁻ 12 mg/L; SO₄²⁻ 144 mg/L, HCO₃⁻ 420 mg/L.

III. Sorption studies

As the support, silanized silica gel was used. The surface of the silica gel was impregnated with the calixarenes according to the following scheme [8].

The sorption properties were studied under static conditions.



Scheme 1

For the series of sorbents obtained, the optimal pH for sorption both in the model solutions and in the natural water was chosen. The concentration of Eu (III) ions was 5 mg/L; sorption time 3 h. maximum extraction of Eu (III) ions is achieved at pH 5.5-6 and remains at the same level both for the model solutions and for Eu (III) spiked natural water.

Previously, we have shown that in case of calixarene-impregnated materials Eu (III) sorption kinetics is described by pseudo-second order model [8]. The sorption process is suggested to occur in two steps. First, a rapid interaction between europium ions and calixarene molecules takes place and monolayer is formed. Further, a slow process of ion diffusion into the pores of the sorbent and sorption by substrate occurs. Obviously, the contributions of complexation and diffusion cannot be separated and kinetic data reflect overall process.

Sorption capacity of the materials obtained was studied under static conditions in model solutions and in natural waters according to the following procedure: the concentration of Eu(III) ions was varied in the range from 5 to 150 mg/L, sorption time 2 h, pH 5.5-6. The experimental data from the adsorption isotherm study were treated using the equation for a Langmuir monomolecular adsorption isotherm in linerized form.

Conclusion

The obtained materials were shown to reveal the maximum Eu (III) uptake percentage within the pH range of 5.5 – 6. The sorption kinetics follows the pseudo-second order model. The maximum sorption capacity increases in the order of $2 < 1 < 4a < 4c < 4b$; it was calculated to be 7 – 10 mg/g in model solutions and 8 – 14 mg/g in Eu(III)-spiked natural waters. It was shown that initial silanized silica has sorption capacity of 4 mg/g.

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