



# Development of a new simultaneous separation of cesium and strontium by extraction chromatograph utilization of a hybridized macroporous silica-based functional material



Anyun Zhang\*, Jinying Li, Ying Dai, Lei Xu

Department of Chemical and Biological Engineering, Zhejiang University, 38 Zheda Road, Hangzhou 310027, PR China

## ARTICLE INFO

### Article history:

Received 29 September 2013

Received in revised form 13 February 2014

Accepted 15 February 2014

Available online 1 March 2014

### Keywords:

Adsorption

Separation

Supramolecular recognition material

Heat generator

Extraction chromatography

## ABSTRACT

Based on the intermolecular modification of 1,3-[(2,4-diethylheptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]) with 4,4',5'-di(*t*-butylcyclohexano)-18-crown-6 (DBC), a hybridized macroporous silica-based supramolecular recognition material, Calix[4]@DBC/SiO<sub>2</sub>-P, was prepared. The agents were impregnated and immobilized into the pores of the SiO<sub>2</sub>-P particles support. The adsorption of Cs(I), Sr(II), and some typical coexistent metals onto Calix[4]@DBC/SiO<sub>2</sub>-P was investigated. The influence of contact time and HNO<sub>3</sub> concentration in the range of 0.4–6.0 M was studied. Calix[4]@DBC/SiO<sub>2</sub>-P exhibited high adsorption ability and selectivity for Sr(II) and Cs(I) except for Rb(I) and Ba(II). The simultaneous partitioning of Cs(I) and Sr(II) from a simulated highly active liquid waste was performed by Calix[4]@DBC/SiO<sub>2</sub>-P packed column. They were effectively eluted with water and flowed into effluent along with Rb(I) and Ba(II), while others showed no adverse impact. A new separation process, GPSC (Group Partitioning of Strontium and Cesium by Extraction Chromatography), for the separation of Cs(I) and Sr(II) was proposed.

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## 1. Introduction

Cs(I) and Sr(II) are called heat generators. The isotopes of Cs(I), Cs-137 with a half-life of 30-year and Sr-90 with a half-life of 28.5-year contained in highly active liquid waste (HLW), are harmful for the vitrified-HLW in final geological disposal. Another isotopes, Cs-135 with a half-life of  $2 \times 10^6$ -year, has the long-termed potential risk on environment due to its mobility in final repository. They are considered to be one of the most contributors of the radioactivity in HLW. It is reported that they can pose a serious radiation hazard to health and environment. To significantly decrease the adverse impact, the effective separation of Cs(I) and Sr(II) from HLW to a great extent is necessary. However, the most of the investigations on the HLW treatment have been focused on the separation of the long-lived minor actinides MAs(III) [1–8], while a little of attention to Sr(II) and Cs(I). The partitioning and recovery of Sr(II) and Cs(I) have always been one of the most challenging works these decades.

The liquid–liquid solvent extraction is one of the main technologies for the Sr(II) and Cs(I) separation [9–18]. A few partitioning processes such as the universal solvent extraction [9–11], fission

product extraction [12,13], strontium extraction [14–16], and cesium separation with calixcrown extraction [17,18] have been reported. As an alternative pathway, extraction chromatography has not been used in the separation of Sr(II) and Cs(I) from HLW. In fact, it is known that the quantity of heat generators in HLW is lower than those of other metals in HLW. This made it possible that the effective separation of heat generators by means of extraction chromatography is better than that of solvent extraction, a conventional separation technology.

The derivative of calix[4]arene-crown is a kind of the macrocyclic organic agent with a special molecular structure. It is composed of a calix[4]arene and a crown ether moiety bonded together by means of the phenolic oxygens of the calix[4]arene and a polyether chain [19,20]. It usually combines the excellent supramolecular recognition ability of the calix[4]arene with the simplicity and high selectivity character of the crown ether. Especially, one of the most effective conformations, 1,3-alternate calix[4]arene-crown shows high selectivity for Cs(I) and forms to a 1:1 type of the mononuclear complex formation [21,22]. It was reported that in liquid–liquid solvent extraction, the selectivity ratios of Cs(I) to Na(I) and K(I) for some of these calix[4]arene-crown exceed 10,000 and 100. Application of the derivative of calix[4]arene-crown is suitable for the separation of Cs(I) from highly active liquid waste.

\* Corresponding author. Tel./fax: +86 571 8795 3919.

E-mail address: [zhangay@zju.edu.cn](mailto:zhangay@zju.edu.cn) (A. Zhang).

A new kind of the macroporous silica-based calix[4]arene-crown supramolecular recognition material (SSRM) was developed recently. It had better recognition property and high selectivity for Cs(I) or Sr(II) [23,24]. The preliminary results showed that in HNO<sub>3</sub> medium, Cs(I) or Sr(II) was promising to separate alone from an acidic highly active liquid waste by the macroporous SSRM. However, the simultaneous separation of Sr(II) and Cs(I) from HLW has not been archived yet. The investigations on the adsorption/separation of Sr(II) and Cs(I) together by the macroporous SSRM has not been reported. Because the alkali metals and the alkaline earths are difficult comparatively to form the stable complex, it is promising to separate Cs(I) or Sr(II) from waste water, respectively.

To separate Cs(I) and Sr(II) simultaneously, the object of the present work is focused on (1) vacuum preparation of a new macroporous silica-based 1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]) and 4,4', (5')-di(*tert*-butylcyclohexano)-18-crown-6 (DBC) supramolecular recognition material, Calix[4]@DBC/SiO<sub>2</sub>-P, through impregnation and immobilization of both Calix[4] and DBC into the pores of the SiO<sub>2</sub>-P particles. (2) Evaluating the impact of contact time and the HNO<sub>3</sub> concentration on the adsorption of some typical fission and non-fission products such as Pd(II), Ru(III), Mo(VI), Ba(II), Sr(II), Zr(IV), La(III), Na(I), K(I), Rb(I), Cs(I), and Y(III) onto Calix[4]@DBC/SiO<sub>2</sub>-P. The optimum HNO<sub>3</sub> concentration in the Cs(I) and Sr(II) adsorption was determined, and (3) simultaneous partitioning of Cs(I) and Sr(II) from a simulated HLW was performed by Calix[4]@DBC/SiO<sub>2</sub>-P packed column. An advanced separation process entitled GPSC (Group Partitioning of Strontium and Cesium by Extraction Chromatography) was developed.

## 2. Experimental

### 2.1. Reagents

Alkali metals nitrates M<sup>I</sup>NO<sub>3</sub> (M<sup>I</sup> = Na, K, Rb, and Cs), alkaline earths nitrates M<sup>II</sup>(NO<sub>3</sub>)<sub>2</sub> (M<sup>II</sup> = Sr and Ba), ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, RE(NO<sub>3</sub>)<sub>3</sub>·*n*H<sub>2</sub>O (RE = Y and La, *n* = 3 or 6) were of analytical grade. Ruthenium nitrosyl nitrate solution with 1.5 wt% of Ru(III) and palladium nitrate solution with 4.5 wt% of Pd(II) were provided by the Strem Chemicals, USA and the Tanaka Noble Metal Co. Inc., Japan, respectively. Trivalent La(III) and Y(III) were used to understand the adsorption behavior of all rare earths REs(III), Am(III), and Cm(III). The concentrations of all the tested metals were about 5.0 × 10<sup>-3</sup> M. The HNO<sub>3</sub> solutions of different concentrations in batch and column experiments were prepared temporarily.

1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]) was synthesized quantitatively by a complicated technical route as shown in Fig. 1. Its purity was greater than 98.5%, which was determined through a high performance liquid chromatography (HPLC). 4,4', (5')-Di(*tert*-butylcyclohexano)-18-crown-6 (DBC) with a purity more than 97% was provided by the Eichrom Technologies Inc., USA. 1-Octanol was an available commercial product, which was used as the molecular modifier being capable of improving significantly the affinity of Calix[4] and DBC through intermolecular interaction force.

### 2.2. Preparation of the macroporous silica-based materials

Calix[4]@DBC/SiO<sub>2</sub>-P was prepared through impregnating and immobilizing Calix[4] and DBC into the macroporous SiO<sub>2</sub>-P particles. It was based on the intermolecular interaction between Calix[4], DBC and co-polymer contained in the SiO<sub>2</sub>-P particles. Calix[4] is composed of a hydrophobic calix[4]arene and a

hydrophilic crown ether, while DBC is a hydrophilic compound containing oxygen atoms. The united use of them in the synthesis of the materials might be beneficial to increasing the hydrophilicity of calix[4]crown while decreasing the hydrophobicity of DBC. As a result, the quantity of 1-octanol, a molecular modifier, used in the synthesis of SSRM would be decrease. On the other hand, prior to synthesis of SSRM the macroporous SiO<sub>2</sub>-P particles were pretreated actively using methanol and acetone at room temperature. The synthesis of Calix[4]@DBC/SiO<sub>2</sub>-P was described as follows: Calix[4], DBC, and the modifier dissolved with an organic solvent and the activated SiO<sub>2</sub>-P particles were mixed into a 250 cm<sup>3</sup> of conical flask. After it was shaken for 90 min, it was then stirred in a silicon-oil bath for 180 min. The impregnation of Calix[4], DBC, and the modifier into the pores of the SiO<sub>2</sub>-P particles was not continued until the solvent was evaporated. The purpose was to effectively impregnate and immobilize the agents inside the SiO<sub>2</sub>-P particles at 323 K. Following drying the product at 318 K overnight, the novel material, Calix[4]@DBC/SiO<sub>2</sub>-P, was got. It was characterized by XRD, <sup>29</sup>Si CP/MAS NMR, TG-DSC, and BET. The appearance of the SiO<sub>2</sub>-P particles support and the Calix[4]@DBC/SiO<sub>2</sub>-P material are shown in Fig. 2.

### 2.3. Adsorption of the tested metals onto SSRMs

The adsorption of the tested elements towards Calix[4]@DBC/SiO<sub>2</sub>-P was performed at 298 K, which was controlled using a TAI-TEC MM-10 Model thermostated water bath.

As the designed volume of HNO<sub>3</sub> solution containing the tested metals Mo(VI), Na(I), K(I), La(III), Zr(IV), Pd(II), Rb(I), Cs(I), Ru(III), Ba(II), Sr(II), and Y(III) and the given amount of Calix[4]@DBC/SiO<sub>2</sub>-P were mixed into a 50 cm<sup>3</sup> of ground glass-stopped flask, it was shaken mechanically at 120 rpm. The HNO<sub>3</sub> concentration in aqueous phase was in the range of 0.4–6.0 M. The concentrations of the tested metals and the ratio of solid phase to aqueous one were around 5.0 × 10<sup>-3</sup> M and 0.25 g/5 cm<sup>3</sup>. Following the phase separation through a membrane filter, the concentrations of the tested metals in aqueous phase were then measured using a Varian 700-ES Model simultaneous inductively coupled plasma-optical emission spectrometer (ICP-OES, Varian Inc., USA) or by a Varian AA 240 FS Model atomic adsorption spectroscopy (Varian Inc., USA). The distribution coefficients (*K<sub>d</sub>*) of the tested metals onto Calix[4]@DBC/SiO<sub>2</sub>-P was calculated as follows:

$$K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{W} \quad (\text{cm}^3/\text{g}) \quad (1)$$

In Eq. (1), the symbols *C<sub>o</sub>* and *C<sub>e</sub>* present the initial and equilibrium concentrations of the tested metals in aqueous phase, respectively. The symbols *W* and *V* denote the weight of dry Calix[4]@DBC/SiO<sub>2</sub>-P and the volume of aqueous phase used in the experiments.

### 2.4. Simultaneous separation of Cs(I) and Sr(II) by extraction chromatography

The partitioning of Cs(I) and Sr(II) by the macroporous SSRM Calix[4]@DBC/SiO<sub>2</sub>-P was performed using a Pyrex-glass column as shown in Fig. 3. Prior to separation performance the Calix[4]@DBC/SiO<sub>2</sub>-P packed column was fully equilibrated with 3.0 M HNO<sub>3</sub>. The operation temperature in the loading and elution cycles was maintained at 298 K. It was kept by the circulation of the thermostated water using an EYELA NTT-1200 Model water jacket (Tokyo Rikakikai Co. Ltd., Japan). The flow rate in the column operation was 1.0 cm<sup>3</sup>/min controlled by a metering pump. The concentration of HNO<sub>3</sub> in feed solution was 3.0 M HNO<sub>3</sub>, which is the same with that of in genuine HLW. The tested metals were composed of 5.0 × 10<sup>-3</sup> M of Na(I), K(I), Rb(I), Ru(III), Mo(VI), Cs(I), Ba(II), Sr(II), La(III), Pd(II), and Y(III).

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