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Cesium Removal from High Level Liquid Waste Utilizing a Macroporous Silica-based Calix[4]arene-R14 Adsorbent Modified with Surfactants

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1,3-[(2,4-diethylheptylethoxy)oxy]-2,4-crown-6-Calix[4]arene(Calix[4]arene-R14) modified with dodecanol and dodecyl benzenesulfonic acid (DBS) was impregnated into the pores of macroporous silica-based polymer support (SiO₂-P). The adsorbent was used to uptake Cs(I), Na(I), K(I), Sr(II), Pd(II), Ru(III), Y(III), La(III), Eu(III), Ce(III), Rh(III), Zr(IV), and Mo(VI) from HNO₃ solution by batch technique. The leakage of total organic carbon (TOC) and dodecyl benzenesulfonic acid from the adsorbent into aqueous phase were below 60 ppm and 0.51 wt% at 298 K, 75 ppm and 1 wt% at 318 K in the range of 0.5 ~ 5 M HNO₃, respectively. The adsorbent containing DBS presented a higher selectivity for Cs(I) compared to the DBS-free one. The K_d value of Cs(I) was about 3×10^3 cm³/g at 0.5 M HNO₃. The adsorbent had almost no uptake for other tested metals in the range of 0.5 ~ 7 M HNO₃.

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Keywords: cesium; silica-based support; calix[4]arene-R14; dodecyl benzenesulfonic acid; adsorption

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Nomenclature

K_d	distribution coefficient (cm^3 / g)
Q	adsorption capacity (mmol / g)
C_o	initial concentration in aqueous phase (ppm)
C_e	equilibrium concentration in aqueous phase (ppm)
M	weight of adsorbents (g)
V	volume of liquid phase (cm^3)
M	molecular weight of metal elements (g / mol)

1. Introduction

The safe management of radioactive waste is one of the pre-requisites for reprocessing of spent nuclear fuel, especially the high level liquid waste (HLLW) from the PUREX (Plutonium and Uranium Recovery by Extraction) reprocessing process. It is known that ^{137}Cs , a heat-generated nuclide, with half-life about 30 years [1], is produced by uranium fission occurring in nuclear reactors. The removal of cesium from HLLW is an important issue for the safe management of radioactive waste, which will allow the long-term storage of it for geological repository. The removal of Cs(I) may facilitate the safer management of spent nuclear fuel, and the recovered ^{137}Cs may also be used as a valuable radiation source. Therefore, it is very important to develop highly efficient method to selectively remove Cs(I) from HLLW.

Some techniques such as solvent extraction [1, 2], ion exchange [3], ion-selective electrodes (ISEs) [4], and ionic liquids methods [5], have been reported for the separation of Cs(I). In contrast to other methods, solvent extraction method has shown great promise for selective separation of Cs(I) from acidic waste solutions. In solvent extraction method, the calixarene was widely studied specifically for its stronger extraction and complexing ability to Cs(I). 1,3-[(2,4-diethylheptylethoxy)oxy]-2,4-crown-6-Calix[4]arene (Calix[4]arene-R14) has been found to be the most promising extractant based on highly efficient separation for Cs(I) due to the cavity of its ligand match well with the ionic radius of Cs(I) [1, 6]. However, the traditional liquid-liquid solvent extraction process has many problems, such as the radiolytic degradation, the use of large scale equipment and generation of abundant organic waste. These problems can be solved by extraction chromatography [7], which has advantages over liquid-liquid method such as no or very limited organic diluents utilization, compact equipment and less waste accumulation. Recently, the novel macroporous silica-based ($\text{SiO}_2\text{-P}$) adsorbents for extraction chromatography have been investigated. The $\text{SiO}_2\text{-P}$ support is prepared by combing silica particles with organic copolymer. The kind of inorganic-organic hybrid materials was widely used in stationary chromatography due to good mechanical strength and interfacial stability [8]. Therefore, there is no denying the trend for immobilization of the organic extractants into $\text{SiO}_2\text{-P}$ to recovery metal ions from aqueous solution [9].

In our previous work, the Calix[4]arene-R14 and 1-dodecanol impregnated on $\text{SiO}_2\text{-P}$ for adsorption of Cs(I) has been studied [10]. The results showed that the addition of 1-dodecanol was capable of improving the chemical stability of Calix[4]arene-R14 in acidic solution. In order to utilize Calix[4]arene-R14 having higher affinity to Cs(I), in this work, we have prepared (Calix[4] + dodecanol + DBS)/ $\text{SiO}_2\text{-P}$ by immobilization of Calix[4]arene-R14, dodecanol and dodecyl benzenesulfonic acid into the pores of

the SiO₂-P particles. Here, dodecanol and anionic surfactant, dodecyl benzenesulfonic acid, were simultaneously used as molecule modifier. The uptake behaviour of (Calix[4] + dodecanol + DBS)/SiO₂-P adsorbent towards Cs(I), Na(I), K(I), Sr(II), Pd(II), Ru(III), Y(III), La(III), Eu(III), Ce(III), Rh(III), Zr(IV), and Mo(VI) was investigated.

2. Experimental

2.1. Materials

A macrocyclic supramolecular recognition agent, 1,3-[(2,4-diethylheptylethoxy)oxy]-2,4-crown-6-Calix[4]arene(Calix[4]arene-R14) with the purity greater than 98.7%, was used without any further purification. The structure of Calix[4]arene-R14 is shown in Fig. 1(a). Dodecyl benzenesulfonic acid, an anionic surfactant, as a molecular modifier of Calix[4]arene-R14, was purchased from Aladdin Chemistry Co., Ltd. Its chemical structure is presented in Fig. 1(b). 1-Dodecanol with the purity of 99% is the other modifier by hydrogen bonding to improve chemical stability of adsorbents, and was purchased from J&K Scientific Ltd. Fig. 1(c) is the structure of 1-dodecanol.

Alkali metal nitrate MNO₃ (M = Na, K, Cs), alkaline Sr(NO₃)₂, rare earth nitrate RE(NO₃)₃ · nH₂O (RE = La, Ce, Eu, Y), ZrO(NO₃)₂ · 2 H₂O, (NH₄)₆Mo₇O₂₄ · 4H₂O, Rh(NO₃)₃ · nH₂O, Palladium nitrate solution (4.5 wt%), and Ruthenium nitrosyl nitrate solution (1.5 wt%) were reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd.

The SiO₂-P particles with particle size range of 40 ~ 60 μm were used as the support material. The synthesis method of SiO₂-P was reported in the literature [11]. The composition of SiO₂-P was 83.1 wt% of SiO₂ and 16.9 wt% of copolymer.

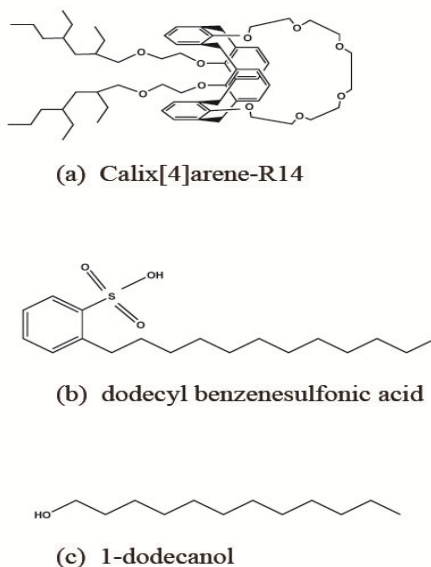


Fig. 1. Structure formula of (a) Calix[4]arene-R14 adsorbent, (b) dodecyl benzenesulfonic acid, and (c) dodecanol

2.2. Preparation of silca-based adsorbents

The synthesis procedure of (Calix[4] + dodecanol + DBS)/SiO₂-P was performed as follows [12]. Firstly, SiO₂-P particles were treated with methanol to improve the affinity between copolymer and Calix[4]arene-R14. Secondly, the Calix[4]arene-R14, 1-dodecanol and dodecyl benzenesulfonic acid were dissolved in dichloromethane in glass conical flash. Then the quantity of SiO₂-P was added. Thirdly, the mixture was stirred mechanically by a rotary evaporator (EYELA N-1100) for 60 min at 25 °C. Subsequently, the mixture was stirred for 240 min at 40 °C to impregnate the Calix[4]arene-R14, 1-dodecanol and dodecyl benzenesulfonic acid into the pores of the SiO₂-P particles by evaporation and immobilization. Finally, adsorbents were dried in vacuum for 24 h at 40 °C. The synthesis method for (Calix[4] + dodecanol)/SiO₂-P is identical as (Calix[4] + dodecanol + DBS)/SiO₂-P.

2.3. Measurements

The concentration of Cs(I) in solution was analyzed by atomic absorption spectrophotometer (AAS, Hitachi Z-2000). The concentrations of other tested metals and sulphur (S) were performed by the inductively coupled plasma-optical emission spectrometer (ICPS, Shimadzu 7510). The measurement of TOC was carried out using a total organic carbon analyzer (TOC, Shimadzu V_{CPH}).

2.4. Batch experiments

The adsorption experiments of the adsorbents for the tested metal ions were performed. For distribution studies, an aqueous phase (10 ml), containing varying concentrations of nitric acid (0.5 – 6M) and the tested metals (10 ppm), was equilibrated with 0.05 g adsorbents in stoppered glass tubes in a thermostated water bath (Tokyo RIKAKIKA Co., LTD) at 298 K. It was shaken mechanically at 120 rpm. After the adsorbents were separated from aqueous solution by filtering, the concentrations of the tested metals in aqueous phase were measured by AAS or ICP. The distribution coefficients (K_d) and the adsorption amount (Q) of the tested metals were calculated as follows:

$$K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{m} \quad (1)$$

$$Q = \frac{V}{m} \times \frac{(C_o - C_e)}{M} \quad (2)$$

3. 3. Results and discussion

3.1. Chemical stability

In order to understand the chemical stability of the (Calix[4] + dodecanol + DBS)/SiO₂-P against HNO₃ solution, some experiments were performed by treating (Calix[4] + dodecanol + DBS)/SiO₂-P with HNO₃. The amount of TOC and S concentration of aqueous phase was measured. Fig. 2 depicts the bleeding of TOC from (Calix[4] + dodecanol + DBS)/SiO₂-P in the range of 0.5 ~ 5 M HNO₃ at 298 K and 318 K, respectively. It can be seen that the quantity of TOC in aqueous phase slowly increases with increasing of HNO₃ concentration. It is reported that the Calix[4]arene-R14 compound is composed of

chemical bonding of a Calix[4]arene and an 18-crown-6 by phenolic oxygen and polyether chain [12]. The composition of crown ether has high affinity for aqueous phase especially in HNO_3 solution [13], so the gradual increase in TOC with increase of HNO_3 concentration may result from the bleeding of the Calix[4]arene-R14 in the adsorbent. The maximum concentration of TOC is about 60 ppm at 298 K. However, the temperature also effects the chemical stability of (Calix[4] + dodecanol + DBS)/ SiO_2 -P in nitric acid. At 318K, the maximum leakage of TOC with 75 ppm increased by nearly 25 % than 298 K. The bleeding DBS from (Calix[4] + dodecanol + DBS)/ SiO_2 -P was further examined. The leakage of S from (Calix[4] + dodecanol + DBS)/ SiO_2 -P in the range of 0.5 – 5 M HNO_3 at 298 K and 318 K is shown in Fig. 3. According to Fig. 3, the leakage of DBS has almost no dependence on HNO_3 concentration. The average leakage percentage of DBS was calculated as 0.5 wt% at 298 K and 1 wt% at 318 K, respectively.

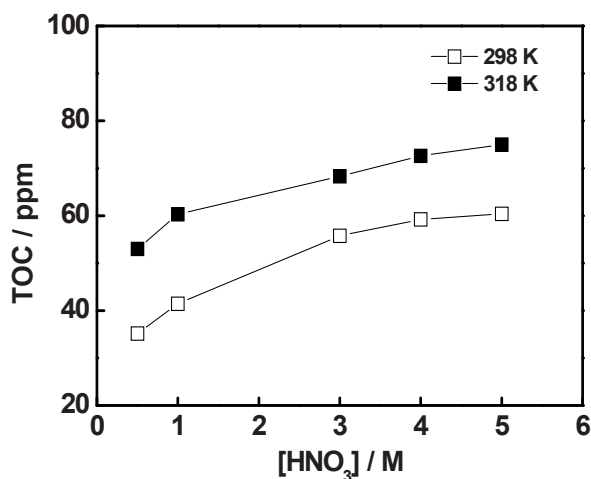


Fig.2. The leakage of TOC from (Calix[4] + dodecanol + DBS)/ SiO_2 -P . Contact time: 24 h; Phase ratio: 0.1 g / 5 cm^3 .

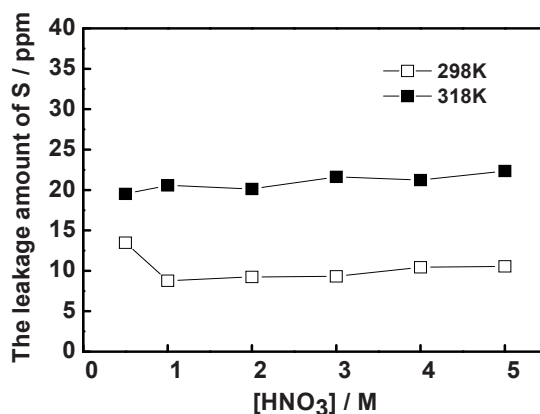


Fig. 3. The leakage of S from (Calix[4] + dodecanol + DBS)/ SiO_2 -P. Contact time: 24 h; Phase ratio: 0.1 g / 5 cm^3 .

3.2. Effect of HNO_3 concentration on adsorption

To compare the adsorption properties of two kinds of the macroporous silica-based adsorbents in partitioning of HLLW, the adsorption of Cs(I), Na(I), K(I), Sr(II), Pd(II), Ru(III), Y(III), La(III), Eu(III), Ce(III), Rh(III), Zr(IV) and Mo(VI) on two adsorbents was examined at different concentrations of HNO_3 up to 7 M by batch method. As for (Calix[4] + dodecanol)/ SiO_2 -P (Fig. 4), the K_d value of Cs(I) is getting gradually increase with the increasing of the HNO_3 concentration range from 0.5 to 3 M. The maximum K_d value is obtained at 3 M HNO_3 about $300 \text{ cm}^3 \text{ g}^{-1}$. On the other hand, the K_d of Cs(I) is getting gradually decrease above 3 M HNO_3 . The uptake of Cs(I) was probably due to the effective capture of Calix[4]arene-R14 towards Cs(I) through ionic size fitting effect (Eq. 3). The reason of decreasing K_d of Cs(I) with HNO_3 concentration was mainly resulted from the interaction between Calix[4]arene-R14 and HNO_3 molecules (Eq. 4) [13]. In contrast, the K_d values for Na(I), K(I), Sr(II), Pd(II), Ru(III), Y(III), La(III), Eu(III), Ce(III), Rh(III), Zr(IV) and Mo(VI) were considerably low in the range of 0.5 ~ 7 M HNO_3 . So, (Calix[4] + dodecanol)/ SiO_2 -P had almost no adsorption for these metal ions. The cavity size of the Calix[4]arene is about 0.162 nm, which is very close to the radius of Cs(I), 0.167 nm. However, the ionic radius of REs(III) and other FPs such as Mo(VI), Pd(II), Ru(III), and Zr(IV) are in the range of 0.0848 ~ 0.106 nm and 0.065 ~ 0.086 nm [14]. This may be due to the unmatched size for combination of these metals with Calix[4]arene-R14.

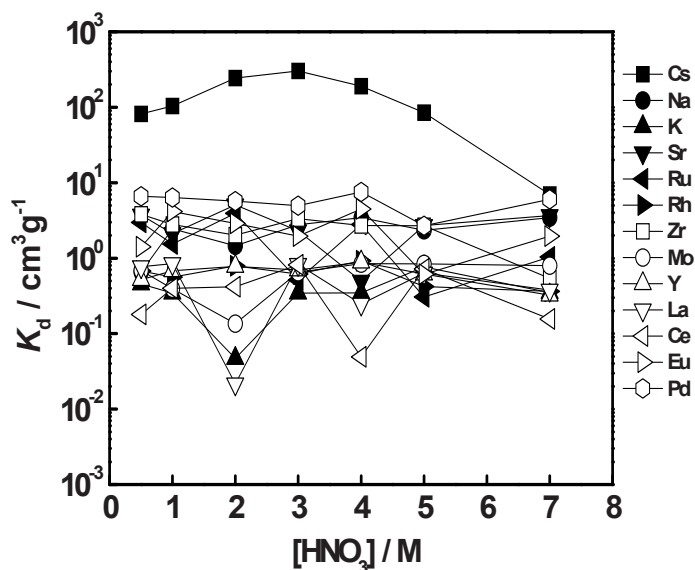


Fig. 4. Dependence of K_d of tested metals on (Calix[4] + dodecanol)/ SiO_2 -P. [metal] = 10 ppm; Temperature: 298 K; Phase ratio: 0.05 g / 10 cm^3 .

Fig. 5 shows the K_d values of the tested metal ions on (Calix[4] + dodecanol + DBS)/ SiO_2 -P with the HNO_3 concentration from 0.5 M ~ 7 M. The K_d value of Cs(I) decreased with increasing of HNO_3

concentration up to 7 M. A highest K_d of Cs(I) for (Calix[4] + dodecanol + DBS)/SiO₂-P was obtained at around 0.5 M HNO₃. It can be seen that the K_d of Cs(I) was $3.3 \times 10^3 \text{ cm}^3\text{g}^{-1}$ at 0.5 M HNO₃, $1.4 \times 10^3 \text{ cm}^3\text{g}^{-1}$ at 1 M HNO₃, $6.1 \times 10^2 \text{ cm}^3\text{g}^{-1}$ at 2 M HNO₃, and $5.8 \times 10^2 \text{ cm}^3\text{g}^{-1}$ at 3 M HNO₃, respectively. The (Calix[4] + dodecanol + DBS)/SiO₂-P exhibited the higher K_d value for Cs(I) compared to (Calix[4] + dodecanol)/SiO₂-P in 0.5 ~ 3 M HNO₃. However, the K_d values of Cs(I) for (Calix[4] + dodecanol + DBS)/SiO₂-P adsorbent were similar to (Calix[4] + dodecanol)/SiO₂-P in the range of 4 ~ 7 M HNO₃. At the same time, (Calix[4] + dodecanol + DBS)/SiO₂-P adsorbent had also almost no adsorption for the tested metal ions except for Cs(I) in the HNO₃ concentration from 0.5 M ~ 7 M. These results suggested that the modification of Calix[4]arene-R14 with DBS could make an efficient extraction system of Cs(I).

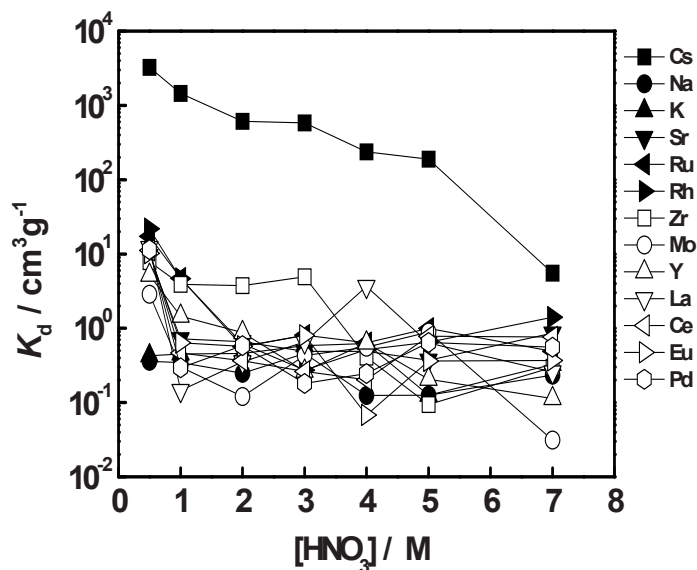


Fig. 5. Dependence of K_d of tested metals on (Calix[4] + dodecanol + DBS)/SiO₂-P. [metal] = 10 ppm; Temperature: 298 K; Phase ratio: 0.05 g / 10 cm³.

In order to understand the adsorption mechanism of (Calix[4] + dodecanol + DBS)/SiO₂-P, only dodecanol and dodecyl benzenesulfonic acid were impregnated into the SiO₂-P particles support for examining the adsorption ability of Cs(I), Na(I), K(I), Sr(II), Pd(II), Ru(III), Y(III), La(III), Eu(III), Ce(III), Rh(III), Zr(IV) and Mo(VI). In this experiment, it was found that (dodecanol + DBS)/SiO₂-P had almost no adsorption for all tested metal ions in the HNO₃ concentration range of 0.5 ~ 7 M. The comparison of K_d for Cs(I) on two adsorbents without other coexisting metal ions in the range of 0.5 ~ 7 M HNO₃ is given in Fig. 6. From above results, the relatively large K_d value of Cs(I) on (Calix[4] + dodecanol + DBS)/SiO₂-P in 0.5 ~ 3 M HNO₃ may be due to the promotion of Cs(I) adsorption by DBS which acted as a counter anion as shown in Eq. 5 [15]. The decreasing K_d of Cs(I) with the increasing of HNO₃ concentration may be explained by the protonation of Calix[4]arene-R14 with the increasing H⁺ concentration and the hydrogen bonding becomes dominant in this adsorption process.



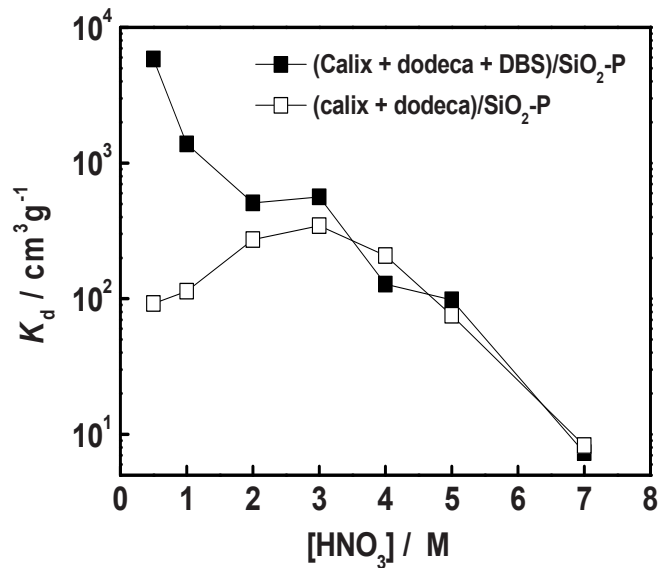


Fig.6. The comparison of K_d for Cs(I) on two adsorbents. [Cs] = 10 ppm; Temperature: 298 K; Phase ratio: 0.05 g / 10 cm³.

4. Conclusions

A macroporous silica-based (Calix[4] + dodecanol + DBS)/SiO₂-P adsorbent was successfully prepared and characterized by TOC. The adsorption of (Calix[4] + dodecanol + DBS)/SiO₂-P for Cs(I), Na(I), K(I), Sr(II), Pd(II), Ru(III), Y(III), La(III), Eu(III), Ce(III), Rh(III), Zr(IV) and Mo(VI) was investigated in 0.5 ~ 7 M HNO₃. It was found that (Calix[4] + dodecanol + DBS)/SiO₂-P showed a high adsorption ability to Cs(I) in 0.5 ~ 3 M HNO₃, and had almost no adsorption for other tested metal ions. The adsorption mechanism of (Calix[4] + dodecanol + DBS)/SiO₂-P was discussed, and dodecyl benzenesulfonic acid is presumed to act as a counter ion for the adsorption of Cs(I) with Calix[4]arene-R14. As for (Calix[4] + dodecanol + DBS)/SiO₂-P treated with 0.5 – 5 M HNO₃ at 298K and 318K, the leakage amount of TOC into aqueous phase was gradually increased with increasing HNO₃ and temperature. The TOC concentration was below 75 ppm and less than 1wt% of DBS leaked from adsorbent in 5 M HNO₃ within 24h at 318K. Thus, the (Calix[4] + dodecanol + DBS)/SiO₂-P are effective for the selective adsorption of Cs(I) from HLLWs in a broad range of HNO₃ concentration.

Acknowledgements

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