Preparation of Sulfonylecalix[4]arene-loaded XAD-7 Resin for Strontium(II) Adsorption

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Abstract. Sulfonylecalix[4]arene-loaded XAD-7 Resin was prepared and used as an adsorbent for removal of Strontium(II) from aqueous solutions. The adsorption of the metal ions onto SCA-XAD-7 as a function of pH, contact time, metal ions concentration, temperature, and reuses was investigated. The adsorption capacity of SCA-XAD-7 composite towards tested ions reached a maximum at pH values of ~6. The adsorption has reached equilibrium within 7 h. The adsorption isotherms were well fitted by the Langmuir model, and the maximum values of adsorption capacity of the adsorbent were 28.87 mg·g⁻¹. Thermodynamic studies imply the adsorption was a spontaneous and exothermic process in nature.

1. Introduction
Substantial amounts of radioactive wastes are generated each year from radioisotopes production facilities, nuclear fuel reprocessing and nuclear power plants due to massive industrial activities. It is known that radioactive ⁹⁰strontium (⁹⁰Sr), with half-lives of 28.9 years, can be introduced into the food chain, which seriously threatens human health [1]. Therefore, removal and recovery of these elements from aqueous solutions has become a crucial topic for sustainable development in recent years.

Adsorption has been widely considered to be an attractive technique for its easy operation, high efficiency and flexibility. Lots of adsorbents such as zeolites, nanomaterials and clay minerals have been applied to radionuclides adsorption [2]. The low adsorption capacity and inconvenience procedures may hinder their practical applications. Therefore, it is significant to develop new adsorbents possessing chemical stability, high adsorption capacity, and low cost for radionuclides treatment.

A number of chelating ligands and supports have been utilized for the design of advanced adsorbents. Interestingly, XAD-7 resin with the incorporation of calixarenes has shown excellent adsorption property for the pollutants removal. Calixarenes, third-generation supramolecular host compounds, are regarded as molecular platforms for the construction of metal ion carriers [3]. Horwitz et al. developed a kind of polymer-based resin by impregnating DtBuCH18C6 in 1-octanol into XAD-7 resin for solid phase extraction of Sr(II) [4]. Xiao et al. synthesized a BiPCalix[4]C6/XAD-7 adsorbent by vacuum immobilization of BiPCalix[4]C6 into the pores of the macroporous XAD-7 particles and studied its adsorption of cesium(I) and Sr(II) [5]. Although there are many reports on the synthesis of calixarene-modified resins, the XAD-7 resin with the incorporation of p-tertsulfonylecalix[4]arene (SCA-XAD-7) for radionuclides removal is scarcely reported.
To obtain systematic information on the adsorption property, SCA-XAD-7 adsorbent was prepared and used as adsorbent for the removal of Sr(II). The adsorbent was characterized by Fourier transform infrared spectra (FTIR), thermal gravimetric analysis (TGA), and Scanning electron microscopy (SEM). Adsorption kinetics, thermodynamics, and isotherm of SCA-XAD-7 towards Sr(II) were researched to optimize the current adsorption technology.

2. Experimental section

2.1 Reagents
The main materials are as follows: p-tert-butylphenol, diphenyl ether, elemental sulfur, sodium hydroxide, nitric acid (65%), sulfuric acid (98%), chloroform, ethanol, toluene, methanol, anhydrous magnesium sulfate, sodium perborate, Sr(NO₃)₂. The above reagents were analytically pure grades and were used directly without further purification. The Amberlite XAD-7 resin (20-60 mesh, surface area > 380 m²·g⁻¹) was supplied by the Beijing Mancang technology Ltd.

2.2 Preparation of SCA-XAD-7 composite.
The p-tert-butylthiacalix[4]arene (TCA) and SCA were synthesized according to the procedure reported in the previous paper [6]. In the general impregnation procedure, SCA (0.6 g) was dissolved in chloroform (300 mL). Then, the pretreated XAD-7 resin (3 g) was immersed in the organic solution with stir for 24 h. After chloroform was removed by reduced pressure distillation, this procedure was repeated three times that the SCA was completely impregnated in the XAD-7 resin. The XAD-7 resin coated with SCA was filtered off, washed with ultrapure water and dried in a vacuum dry oven at 85 °C for overnight. The schematic of preparation of SCA-XAD-7 is demonstrated in Figure 1.

2.3 Characterization of SCA-XAD-7.
The FTIR spectra for samples were recorded by a Nicolet iS10 infrared spectrometer (Thermo Fisher, USA) in the frequency range of 4000-400 cm⁻¹. The SEM was observed by a JSM-7500F scanning electron microscopy instrument (JEOL, Japan) at 5 kV. The weighed quantities of materials were subjected to TGA on a Plus EVO instrument (Thermo Fisher, USA) in nitrogen atmosphere at a heating rate of 10 °C·min⁻¹ from 50 to 650 °C.

2.4 Batch adsorption experiments.
The pH was adjusted by injecting negligible volume of HNO₃ and NaOH. An IS128 pH meter was used to measure the adjusted pH. Generally, 10 mL aqueous phase containing the metal ions (≈ 20 mg·L⁻¹) and 10 mg SCA-XAD-7 composite were mixed in a series of flasks and horizontally shaken at 150 rpm for 8 h in a thermostated water bath maintained at required temperatures between 20 and 45 °C unless otherwise stated. Sequentially, the liquid was filtered through 0.22 μm filter membranes. Then, the concentration of the ions was measured using a MP-AES atomic emission spectrometer (Agilent, USA). Adsorption isotherms were determined by mixing 10 mg SCA-XAD-7 adsorbent with
10 mL of varying concentration solutions (10-70 mg·L⁻¹). The adsorption experiments were conducted three times, and the mean experimental value is reported. Adsorption capacity ($q_e$, mg·g⁻¹), adsorption percent ($E\%$) and distribution coefficient ($K_d$, mL·g⁻¹) was calculated according to the following equations (1-3), respectively:

$$q_e = \frac{(C_0 - C_e)V}{m}$$  

$$K_d = \frac{(C_0 - C_e)V}{mC_e}$$  

$$E\% = \frac{C_0 - C_e}{C_0} \times 100$$

where $C_0$ and $C_e$ (mg·L⁻¹) represent the initial and equilibrium concentrations of the cations in the flasks, respectively, $m$ (g) is the mass of adsorbent used, and $V$ (L) is the volume of the solution.

3. Results and discussion

3.1 Characterization.

The immobilization of SCA onto XAD-7 resin was characterized by FTIR spectroscopy. The FTIR spectra of blank XAD-7 resin, SCA and SCA-XAD-7 are presented in Figure 2. A broad band observed in the range of 3700 cm⁻¹ to 3300 cm⁻¹ was due to the hydroxyl stretching vibration caused by H₂O, indicating that some free water in air was adsorbed by these materials. In the FTIR spectrum of XAD-7, the characteristic absorption at 1152 and 1727 cm⁻¹ is attributed to the C-O-C and C=O stretching, which remained unchanged after immobilizing with SCA. In the case of SCA, the adsorption peaks at 3068 and 764 cm⁻¹ corresponding to the C-H stretching vibration in benzene ring, while the absorption bands at 1318 and 1132 cm⁻¹ corresponding to asymmetrical and symmetrical sulfonyl (O=S=O) stretching vibrations. These characteristic peaks of pure SCA can also be found in the spectrum of SCA-XAD-7 composite, reflecting that SCA was introduced into XAD-7 resin successfully. Obviously, adsorption peak of SCA-XAD-7 composite different from that of XAD-7 and SCA was not observed, indicating the immobilization of SCA onto XAD-7 resin depends on the intermolecular interaction rather than chemical reaction or grafting. After adsorption of Sr(II), the intensity of the characteristic peaks for O=S=O of the SCA-XAD-7 at 1319 and 1128 cm⁻¹ is especially decreased after the adsorption process, illustrating that the sulfonyl functional groups were coordinated with the metal ions.

The TGA was used to study the thermal stability of SCA-XAD-7 composite and to determine the content of SCA in the SCA-XAD-7 composite. Figure 3 demonstrates the thermal decomposition behaviors of SCA-XAD-7 composite, blank XAD-7 resin and SCA. From thermal degradation curves of XAD-7, the main steps on at 300-440 °C was due to the decomposition of the molecular skeleton of XAD-7 resin. For SCA, it can be found that at a temperature range of 50-120 °C, there was 3% weight loss due to evaporation of water. The main stage from 400 to 415 °C was ascribed to the loss of the p-tert-butyl functional groups and the sulfonyl groups. In this stage, the weight loss of the sample was about 60%, which was close to the theoretical value. The second stage from 415 to 550 °C was assigned to the thermal decomposition of the SCA rings. As to SCA-XAD-7 composite, it exhibited two weight losses in the temperature intervals of 290 to 390 °C and 390 to 460 °C. The first step of weight loss was due to the decompositon of the XAD-7 resin, and on the basis of the thermal decomposition of the SCA, the second step was ascribed to the decomposition of the loaded SCA and XAD-7. The results show that SCA-XAD-7 composite was prepared successfully and indicate that the sample has pleasurable thermal stability. On the other hand, the content of SCA in the SCA-XAD-7 composite was roughly calculated to be 12.92 % (0.15 mmol·g⁻¹) based on the fact that the weight loss of 100% for XAD-7 resin, 76% for SCA, and 96.9 % for SCA-XAD-7 composite at 650 °C.

Figure 4 provides the morphologies of the XAD-7 resin, pure SCA and prepared SCA-XAD-7. The XAD-7 resin exhibited spherical shape (Figure 4a) and its high magnification image (Figure 4b) shows
rich pores that can afford abundant space for impregnating the supramolecular modifier. From Figure 4c, the SCA showed irregular shape, which was attributed to its growth characteristic. It is critical to note that the surface of the SCA-XAD-7 sample (Figure 4d) was similarly constant that implied that the structure of XAD-7 was retained before and after the impregnation synthesis. It enables SCA-XAD-7 to be a suitable material for ions adsorption in aqueous solutions.

3.2 Effect of pH.

In order to evaluate the influence of pH on the removal of the target ions, the adsorption was investigated at various pH values as shown in Figure 5.

From Figure 5, the tested ions with the adsorption capacities less than 2 mg·g⁻¹ showed extremely poor or almost no adsorption with blank XAD-7 resin. Meanwhile, the adsorption capacities of Sr(II) via SCA-XAD-7 increased with increasing pH, and reached a maximum at pH values of 6~7. The observed adsorption ability of SCA-XAD-7 towards Sr(II), which is highly improved after the impregnation and immobilization process, is mainly contributed to the introduced SCA of the SCA-XAD-7 composite. Since the adsorption of Sr(II) with SCA-XAD-7 is pH dependent, it seems that the phenolic hydroxyl groups of the immobilized SCA had contribution to the complex of SCA-XAD-7 with these metal ions. The ionization of hydroxy groups of SCA is restrained at lower pH value that is not suitable for complexing these ions with phenolic oxygen. Thus, the adsorption ability of SCA-XAD-7 towards Sr(II) in neutral solution is better than that in acidic condition.
3.3 Effect of contact time.
For better understanding of the adsorption performance of the SCA-XAD-7 composite towards Sr(II), the adsorption kinetics were studied in contact time from 5 min to 8 h. As shown in Figure 6, the adsorption amounts of these ions increased rapidly and more than 60% of the ions was adsorbed in the first 60 min owing to the higher concentration ions solution at primary adsorption process. While after 120 min, the adsorption amounts increased slowly ascribed to the lack of adsorption sites on the external and internal surfaces of the sample in the process of complexing tested ions with the functional groups. After 420 min, the adsorption curves became very stable, indicating that the adsorption had reached equilibrium state. Based on the results, 480 min was selected to be the optimized contact time for the following experiments.

3.4 Effect of initial ions concentration.
Batch adsorption experiments were performed for initial ions concentration ranging from about 10 to 70 mg·L⁻¹. As shown in Table 1, the adsorption capacity increased with increasing initial ions concentration. The increase in the adsorption capacity of SCA-XAD-7 composite is attributed to the higher metal ions concentration, the more the amount of active adsorption sites of SCA-XAD-7 involved, and thus the larger the adsorption capacity. The ions removal reached high values of above 90% when the ions concentration was less than 10 mg·L⁻¹. Furthermore, the distribution coefficient $K_d$ is greater than $1 \times 10^4$ mL·g⁻¹ in low initial ion concentration ([Sr(II)] < 16 mg·L⁻¹), indicating that the SCA-XAD-7 is an excellent adsorbent for removal of Sr(II).

To estimate the adsorption capacity of SCA-XAD-7 for tested ions, the adsorption data at higher initial ions concentration were treated with Langmuir and Freundlich isotherm models, which can be described by equations (4-5) in their separately order:

$$
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}
$$

(4)

$$\ln q_e = -\frac{1}{n} \ln C_e + \ln K_F$$

(5)

where $C_e$ (mg·L⁻¹) represents the final equilibrium concentration, $q_e$ (mg·g⁻¹) is the adsorption capacity at equilibrium, $q_m$ (mg·g⁻¹) is the maximum adsorption capacity at monolayer coverage, and $K_L$ (L·mg⁻¹) is the Langmuir constant. The $K_F$ (mg·g⁻¹) represents the Freundlich constant, and $n$ is an empirical parameter related to energetic heterogeneity. The calculated parameters are listed in Table 2.
Table 1. Effect of Initial Ion Concentration on Adsorption of Sr(II) by SCA-XAD-7 Composite.

| ion    | $C_0$ (mg·L$^{-1}$) | $C_e$ (mg·L$^{-1}$) | $q_e$ (mg·g$^{-1}$) | $E$ (%) | $K_d$ (mL·g$^{-1}$) |
|--------|---------------------|---------------------|---------------------|---------|---------------------|
| Sr(II) | 8.95                | 0.82                | 8.13                | 90.84   | 9.91×10$^3$        |
|        | 16.47               | 1.49                | 14.98               | 90.95   | 1.01×10$^4$        |
|        | 23.48               | 3.44                | 20.04               | 85.35   | 5.83×10$^3$        |
|        | 30.81               | 7.59                | 23.22               | 75.37   | 3.06×10$^3$        |
|        | 39.89               | 14.02               | 25.87               | 64.85   | 1.85×10$^3$        |
|        | 47.99               | 21.87               | 26.12               | 54.43   | 1.19×10$^3$        |
|        | 56.46               | 28.87               | 27.59               | 48.87   | 0.96×10$^3$        |

Conditions: pH = 6, T = 298 K, $m/V = 1$ g·L$^{-1}$, contact time = 8 h, shaking speed: 150 rpm.

Table 2. Langmuir and Freundlich Model Fitting Parameters for Sr(II) Adsorption on SCA-XAD-7.

| ion     | Langmuir isotherm model | Freundlich isotherm model |
|---------|-------------------------|---------------------------|
|         | $q_m$ (mg·g$^{-1}$)     | $k_L$ (L·mg$^{-1}$)       | $R^2$   | $k_F$ (g·mg$^{-1}$) | n      | $R^2$   |
| Sr(II)  | 28.87                   | 0.58                      | 0.9986  | 3.38             | 11.43  | 0.8182  |

Conditions: pH = 6, T = 298 K, $m/V = 1$ g·L$^{-1}$, contact time = 8 h, shaking speed: 150 rpm.

The results clearly indicate that the Langmuir model ($R^2 > 0.99$) fit the adsorption isotherm well, which can be ascribed to the homogeneous distribution of SCA on the SCA-XAD-7 surface. The calculated $q_m$ (28.87 mg·g$^{-1}$) is consistent with the experimental adsorption capacity $q_e$ (27.59 mg·g$^{-1}$).

In an earlier investigation, many materials were used to adsorb radionuclides. All of them are summarized in Table 3. It reveals the potential of the SCA-XAD-7 to be a good adsorbent for removing Sr(II).

Table 3. Comparison of Adsorption Capacity of Sr(II) With Various Adsorbents.

| Adsorbents          | pH | T (K) | $q_{max}$ (mg·g$^{-1}$) | References |
|---------------------|----|-------|-------------------------|------------|
| GO-HAp              | 7  | 298   | 702.18                  | [7]        |
| PAN-zeolite         | 7  | 298   | 98.13                   | [8]        |
| GMZ bentonite       | 7  | 298   | 9.72                    | [9]        |
| Phosphate-modified Montmorillonite | 5  | 298   | 12.56                   | [10]       |
| MnO$_2$-ZrO$_2$     | > 5.5 | 298 | 16.95                   | [11]       |
| SCA-XAD-7           | 6  | 298   | 28.87                   | This work  |

3.3 Effect of temperature.

To investigate the influence of temperature on the adsorption of Sr(II) by SCA-XAD-7, the adsorption experiments were performed at the temperature of 293, 298, 303, 308 and 313 K. The effect of temperature on the adsorption of Sr(II) by SCA-XAD-7 composite is shown in Figure 7. The adsorption capacities decreased with increasing temperature, indicating that the adsorption is exothermic in nature. Besides, the adsorbent can keep high values of the distribution coefficient at 293 K in the adsorption process. Thus, decreasing the operation temperature is conducive to the adsorption process.

4. Conclusions

In this work, SCA-XAD-7 composite was prepared and characterized by FTIR, TGA and SEM. The material was found to have adsorption ability for Sr(II) due to the complex of the immobilized SCA and the target ions. The adsorption capacities of SCA-XAD-7 composite increased for the tested metals with increasing pH, and reached a maximum at pH values of ~6 for Sr(II). The adsorption capacities increased with time and equilibrium was reached in 7 h. The equilibrium adsorption data fit the Langmuir isotherm model best, and the maximum adsorption capacities of the SCA-XAD-7
composite for Sr(II) was 28.87 mg·g⁻¹. The adsorption reaction was a spontaneous and exothermic process.

Figure 7. Relationship between ln K_d and 1/ T. Conditions: pH = 6, [Metal] ≈ 20 mg·L⁻¹, m/ V = 1 g·L⁻¹, contact time = 8 h, shaking speed: 150 rpm.

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