Adsorption Properties of Sulfonylcalix[4] arenetetrasulfonate-loaded Resin towards Strontium(II) from Aqueous Solutions

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Abstract. Sulfonylcalix[4]arenetetrasulfonate-loaded D201 composite (SCAS-D201) was prepared by a simple method and used as an adsorbent for removal of Sr(II) from aqueous solutions. The adsorption of the Sr(II) onto SCAS-D201 composite as a function of contact time, pH, Sr(II), temperature concentration was investigated. Results show that the adsorption capacities of SCAS-D201 composite towards Sr(II) reached a maximum at pH values of ~7. The adsorption has reached equilibrium within 120 min and the kinetics can be well fitted by a pseudo-second-model. The adsorption isotherm was well fitted by the Langmuir model, and the maximum value of adsorption capacity of the adsorbent was 76.43 mg g⁻¹. Possible adsorption mechanisms are also analysed.

1. Introduction
A large amount of radioactive wastes are generated each year from nuclear power plants, nuclear fuel reprocessing and radioisotopes production facilities due to extensive industrial activities. However, these radionuclides have versatile advanced industrial and medical applications if they are purified [1]. Thus, removal of radionuclides from aqueous solutions has become an important topic for sustainable development recently [2].

Various techniques to remove radionuclides are available, such as adsorption, solvent extraction, and ion exchange. Among those techniques, adsorption has been considered to be a favorable technique for its high efficiency, easy operation, and flexibility. It is imperative to have an advanced adsorbent which possesses high adsorption capacity, chemical stability and low cost for radionuclides treatment.

Calixarenes, third-generation supramolecular host compounds, have been regarded as molecular platforms for the construction of metal ion carriers [3, 4]. The thiacalix[4]arenes represent a class of receptor compounds. They were widely studied in the treatment of heavy metals [5, 6]. Hu et al. prepared thiacalix[4]arenetetrasulfonate (TCAS) modified 717 anion exchange resin and pointed out that the selective adsorption property of the adsorbent is attributed to complexation of the TCAS with heavy metals [7]. Also, sulfonylcalix[4]arene, as a thiacalix[4]arenes derivative, has been investigated to remove of radionuclides in recent years [8-9]. Morohashi et al. described that the excellent complexation ability of octylsulfonylcalix[4]arenes towards quite a few metals such as Sr(II) and Eu(III) [10].

The adsorption kinetics and isotherms of radionuclides adsorptions are particularly significant to the practical application. However, the data with respect to the adsorption of sulfonylcalix[4]arenes-loaded resin towards Sr(II) is barely reported. In order to obtain systematic information on the adsorption kinetics and thermodynamics, sulfonylcalix[4]arenetetrasulfonate-loaded D201 resin (SCAS-D201) was prepared by using a simple method and used as adsorbent for Sr(II) removal.

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2. Experimental section

2.1 Reagents
The main materials are as follows: elemental sulfur, diphenyl ether, p-tert-butylphenol, sulfuric acid (98%), nitric acid, sodium hydroxide, chloroform, sodium chloride, ethanol, hydrogen peroxide (30%), trifluoroacetic acid, acetone, Sr(NO₃)₂. The above reagents used in the experiment were purchased from Klamar and Aladdin. The D201 resin was purchased from the Beijing Mancang technology Ltd.

2.2 Preparation of SCAS-D201 composite.
The TCA, TCAS, and SCAS were synthesized referring to the documents [11-13]. In the general preparation procedure of SCAS-D201, pretreated D201 resin (3 g) was immersed in a 50 mL of SCAS aqueous solution (14.42 mmol·L⁻¹) with slowly stir for 24 h. Subsequently, the SCAS-D201 composite was filtered off and washed 3 times with ultrapure water. It dried in an oven at 45 °C for overnight. Fig. 1 shows the schematic of preparation of SCAS-D201.

2.3 Characterization of SCAS-D201 composite.
The SEM was observed by a Quanta 250 scanning electron microscopy instrument (FEI, USA) at 25 kV. 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 weighed quantities of materials were subjected to TGA on a TG/DTA6200 instrument (Seiko instruments inc, Japan) in nitrogen atmosphere at a heating rate of 10 °C·min⁻¹ from 40 to 800 °C.

2.4 Batch adsorption experiments.
Generally, 20 mL aqueous phase and 10 mg SCAS-D201 composite were mixed in a lot of flasks and horizontally shaken at 150 rpm for 3 h maintained at temperatures between 25 and 40 °C unless otherwise stated. Then the liquid was filtered through 0.22 μm filter membranes. The concentration of the cations was measured using a MP-AES atomic emission spectrometer (Agilent, USA). Adsorption isotherms were determined by mixing 10 mg SCAS-D201 adsorbent with 20 mL of varying concentration solutions (10-150 mg·L⁻¹). Adsorption percent (E %) and adsorption capacity (qₑ, mg·g⁻¹) was calculated according to the equations (1-2), respectively:

\[ E = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1) \]
\[ q_e = \left( \frac{C_0 - C_e}{V} \right) m \quad (2) \]

where \( C_0 \) represents the initial concentrations of the cations in the flasks, \( C_e \) (mg·L⁻¹) represents the equilibrium concentrations of the cations, \( V \) (L) is the volume of the solution, and \( m \) (g) is the mass of adsorbent.
3. Results and discussion

3.1 Characterization.

SEM images, which were shown in Fig. 2, provide the morphologies of D201 resin, SCAS, and SCAS-D201 composite. As demonstrated in Fig. 2a, the spherical D201 resin exhibited rich pores, which can afford abundant space for loading the molecular modifier. From Fig. 2b, SCAS showed irregular shape that can be ascribed to its growth characteristic. It is important to note that the appearance of the SCAS-D201 (Fig. 2c) remained in spherical shape which indicated that the original structure of D201 resin was retained before and after the impregnation synthesis except a few minor cracks appeared, which was due to the external forces effect on the D201 resin in the immobility process. Due to the impregnation of the SCAS molecules, the surface of the SCAS-D201 was covered by the white layer. (Fig. 2d).

The FTIR spectra of pure D201 resin, SCAS and SCAS-D201 composite are presented in Fig. 2e. In the FTIR spectrum of SCAS, the absorption bands at 1198 and 1044 cm\(^{-1}\) corresponding to the -SO\(_3\) peaks, while the absorption bands at 1326 cm\(^{-1}\) corresponding to the asymmetrical sulfonyl stretching vibrations of SCAS. The IR spectrum of SCAS-D201 composite is similar to that of pure D201 resin. The obvious difference between the spectra is that new absorption peaks appeared near 1326, 1198 and 1044 cm\(^{-1}\), which can also be observed in the spectrum of SCAS, confirming the immobilization of SCAS onto D201 resin.

Figure 2f reveals the TGA curves of blank D201 resin, SCAS and SCAS-D201 composite. For SCAS, there was 12 % weight loss within 40–100 °C due to the evaporation of water. From 325 to 800 °C, the main stage on thermal degradation curves was assigned to the decomposion of SCAS molecular skeleton. Over the range of 325 to 450 °C, the weight loss of 18.1 % for SCAS-D201 was greater than that of 16.6 % for D201 resin, which is attributed to the decomposion of the loaded SCAS of the SCAS-D201 composite. The weight loss rate of SCAS-D201 and SCAS was apparently greater than that of D201 resin between 450 and 800 °C, indicating SCAS was introduced into the D201 resin.

![Fig. 2. SEM images of (a) D201 resin, (b) SCAS, (c) SCAS-D201 (×100) and (d) SCAS-D201 (×160000), (e) FTIR and (f) TGA of D201 resin, SCAS, and SCAS-D201 composite](image)

3.2 Effect of pH.

As can be seen in Fig. 3a, the adsorption percentage of Sr(II) (\(E_{Sr}\)) via SCAS-D201 composite increased with increasing pH, and reached the maximum at approximately pH values of 7 for Sr(II). However, the \(E_{Sr}\) with D201 resin was less than 20% under the experimental conditions, indicating poor adsorption with D201 resin. It can be inferred that the observed adsorption ability is essential contributed to the loaded SCAS of the SCAS-D201 composite. The complex of loaded SCAS with Sr(II) can be explained by the Hard and Soft Acids and Bases (HSAB) theory [14]. The bridging sulfonyl group (O=S=O) of the SCAS categorized as borderline acid which is sensitive to Sr(II), leading to excellent adsorption ability of the SCAS-D201 composite for the selected metals. Since the adsorption of Sr(II) with SCAS-D201 composite is pH dependent, it also appears that the phenolic hydroxyl groups of the loaded SCAS had contribution to the complex of SCAS-D201 composite with Sr(II). It is reported that the complex of SCAS with metal ions is accomplished by coordination of the O=S=O group and phenolic oxygen [15]. It can be confirmed in the FTIR spectra of SCAS-D201 composite before and after the adsorption of Sr(II) (Fig. 3b). The SCAS-D201-Sr(II) complexes were obtained by air drying after the adsorption at pH 7.
As can be seen in Fig. 3b, the characteristic adsorptions at 3455 cm$^{-1}$ in the FTIR spectrum of SCAS-D201 composite are attributed to OH stretching, while that of the SCAS-D201-Sr(II) complexes were observed at 3421 cm$^{-1}$. The OH stretching vibrations of the adsorbed species were shifted to lower frequencies, which indicated that -OH were coordinated with tested metals. Previously investigated complexes of $p$-tert-butylcalix[5]arene hexacarboxylic acid ligand with Cu(II) showing that C=O stretching vibration of ligand-Cu(II) changed positively and intensely [16]. In our experiment, the band due to the O=S=O stretching of SCAS-D201 at 1326 cm$^{-1}$ shifted to 1329 cm$^{-1}$ after adsorption of Sr(II). This higher frequencies compared to the free SCAS-D201 denoting the complexation of the O=S=O groups of SCAC with Sr(II). Obviously, the decreased relative intensities (green lines) of the asymmetrical sulfonyl vibration stretching to the -SO$_3$ peaks imply that the bridging O=S=O groups were coordinated with the metal ions as well. However, the sulfonate groups (-SO$_3$) of the SCAS are extensively regarded as poor ligands that can hardly participate in the metals adsorption [17]. Therefore, it is quite obvious that the typical coordination pattern of SCAS-D201 composite to the Sr(II) is mainly depend on the O=S=O groups and hydroxy groups of the loaded SCAS.

Thus, the changes of $E_{Sr}$ with increasing pH can be explained by the fact that the ionization of -OH of SCAS was inhibited at lower pH value, which is adverse to the coordination of O=S=O group and phenolic oxygen, resulting in poor adsorption of the SCAS-D201 composite towards radionuclides in strong acidic solution.

![Fig. 3. (a) Effect of pH on the adsorption of the Sr(II) onto SCAS-D201 and D201. (b) FTIR spectra of the SCAS-D201 composite before and after the adsorption of Sr(II) Conditions: T = 298 K, m/ V = 0.5 gꞏL$^{-1}$, [Metal] = 10 mg ꞏ L$^{-1}$, contact time = 4 h, shaking speed: 150 rpm.]

3.3 Adsorption Kinetics.
The adsorption kinetics were studied at different contact time and temperature. As can be seen in Fig. 4, the adsorption capacity increased rapidly in the first 30 min, which can be attributed to the effective complexation of the loaded SCAS with Sr(II). Then, it reached equilibrium at approximately 65 min for. However, it needs less time to reach equilibrium with the increase of temperature, which can be explained by the phenomenon that increasing temperature leads to an improved diffusion rate of ions across the external boundary layer.

In order to clarify the kinetic mechanism on the adsorption of SCAS-D201 composite towards Sr(II), the obtained data was fit to the pseudo-first-order, pseudo-second-order and intraparticle diffusion models to evaluate the time-dependent adsorption process. The pseudo-first-order, pseudo-second-order and intraparticle diffusion rate expressions are given in equations (3-5), respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$  
$$q_t = \frac{1}{t} = k_2 q_e^2 t$$  
$$q_t = k_i t^{0.5} C$$

where $q_e$ is the adsorption capacities at equilibrium time, $q_t$ (mgꞏg$^{-1}$) is the adsorption capacities at given time $t$, $k_1$ (min$^{-1}$) is the rate constant of the pseudo-first-order adsorption, $k_2$ (gꞏmg$^{-1}$ꞏmin$^{-1}$) is the rate constant of the pseudo-second-order adsorption, $k_i$ (mgꞏg$^{-1}$ꞏmin$^{0.5}$) is the rate constant of the
intraparticle diffusion model adsorption, and $C$ (mg·g$^{-1}$) is the constant proportional to the boundary layer thickness.

Plots of these models for the adsorption of SCAS-D201 composite towards Sr(II) are shown in Fig.5. The relative parameters are summarized in Table 1. The results illustrate that the adsorption kinetics of Sr(II) are fitted better by the pseudo-second-order kinetic model ($R^2 > 0.99$) than the pseudo-first-order model. The pseudo-second-order model is based on the assumption that the chemisorption between binding sites of the adsorbent and metal ions is the rate-limiting step of the adsorption [18]. Thus, it can be concluded that the chemical interaction between SCAS-D201 composite and tested ions is the primary adsorption manner in the adsorption process.

![Fig. 4. Adsorption kinetics of Sr(II). Conditions: m/ V = 0.5 g·L$^{-1}$, [Metal] = 10 mg·L$^{-1}$, pH = 7, shaking speed: 150 rpm.](image1)

![Fig. 5. plots of (a) pseudo-first-order, (b) pseudo-second-order, and (c) intraparticle diffusion kinetics models for Sr(II). Conditions: m/ V = 0.5 g·L$^{-1}$, [Metal] = 10 mg·L$^{-1}$, pH = 7, shaking speed: 150 rpm.](image2)

| Table 1. Parameters Obtained from Adsorption Kinetics Studies |
|---------------------------------------------------------------|
| model                  | parameter             | Absolute temperature (K) |
| pseudo-first-order    | $q_e$(mg·g$^{-1}$)    | 298     | 303     | 308     | 313     |
|                       |                       | 15.14   | 14.17   | 14.54   | 12.23   |
|                       | $k_1$(min$^{-1}$)     | $6.19 \times 10^{-2}$ | $5.90 \times 10^{-2}$ | $5.75 \times 10^{-2}$ | $6.07 \times 10^{-2}$ |
|                       | $R^2$                 | 0.94271 | 0.96740 | 0.99449 | 0.94247 |
| pseudo-second-order   | $q_e$(mg·g$^{-1}$)    | 18.64   | 18.80   | 18.93   | 19.04   |
|                       | $k_2$(g·mg$^{-1}$·min$^{-1}$) | $8.49 \times 10^{-3}$ | $9.03 \times 10^{-3}$ | $9.79 \times 10^{-3}$ | $11.06 \times 10^{-3}$ |
|                       | $R^2$                 | 0.99862 | 0.99876 | 0.99779 | 0.99889 |
| Intraparticle diffusion| $C$(mg·g$^{-1}$)      | 9.06    | 9.36    | 9.67    | 10.24   |
|                       | $k_i$(mg·g$^{-1}$·min$^{-0.5}$) | $7.84 \times 10^{-1}$ | $7.79 \times 10^{-1}$ | $7.72 \times 10^{-1}$ | $7.41 \times 10^{-1}$ |
|                       | $R^2$                 | 0.66589 | 0.7065  | 0.71562 | 0.64656 |

Conditions: m/ V = 0.5 g·L$^{-1}$, [Metal] = 10 mg·L$^{-1}$, pH = 7, shaking speed: 150 rpm.

3.4 Adsorption Isotherm Models.

The adsorption isotherms were studied by changing the initial concentrations of the metal ions at pH 7, for an adsorbent dosage of 0.5 g·L$^{-1}$, a contact time 3 h, and a temperature of 298 K. As presented in Table 2, the adsorption capacity increased with increasing initial ion concentration, which is due to the
higher cations concentration, the more active adsorption sites of SCAS-D201 composite involved, and thus the larger the adsorption capacity. Although the adsorption capacity increased with increasing initial cations concentration, the ions removal demonstrated a downward trend. The distribution coefficient, $K_d$ ($K_d = q_e / C_e$, mL·g$^{-1}$), is a significant parameter to evaluate the adsorption performance. In this experiment, $K_d$ is greater than $1 \times 10^4$ mL·g$^{-1}$ in low initial ions concentration ([Sr(II)] $<$ 20 mg·L$^{-1}$), indicating that the SCAS-D201 composite is an excellent adsorbent [19].

To understand the mode of interaction between tested cations and SCAS-D201 composite, the adsorption equilibrium was also investigated using Langmuir and Freundlich isotherm models, which can be defined by equations (6-7) in their respective order:

$$ C_e q_e = C_e q_m 1 (q_m k_L) $$

$$ \ln q_e = n \ln C_e \ln k_F $$

where $C_e$ (mg·L$^{-1}$) is the final equilibrium concentration, $q_e$ (mg·g$^{-1}$) and $q_m$ (mg·g$^{-1}$) are the adsorption capacity at equilibrium and the maximum adsorption capacity at monolayer coverage, respectively. $k_L$ (L·mg$^{-1}$) is the Langmuir constant, $k_F$ (mg·g$^{-1}$) is the Freundlich constant, $n$ is related to energetic heterogeneity.

The fitted curves are presented in Fig.6, and the relative parameters $q_m$, $k_L$, and $k_F$ can be determined from the slope and intercept. The values of these relative parameters are listed in Table 3. The correlation coefficients clearly indicate that the Langmuir model ($R^2 > 0.99$) is appropriate for representing the adsorption process. The adsorption capacity $q_m$ (76.43 mg·g$^{-1}$) is consistent with the experimental saturation amount $q_e$ (76.36 mg·g$^{-1}$), indicating that the porous surface of SCAS-D201 composite is homogeneous and that the adsorption can be described as monolayer adsorption.

![Fig. 6. Adsorption isotherms and plots of (a) Langmuir and (b) Freundlich isotherm models for Sr(II). Conditions: T = 298 K, $m/V$ = 0.5 g·L$^{-1}$, contact time = 3 h, pH = 7, shaking speed: 150 rpm.](image)

Table 2. Effect of Initial Ion Concentration on Adsorption of Sr(II) by SCAS-D201

| $C_0$ (mg·L$^{-1}$) | $C_e$ (mg·L$^{-1}$) | $q_e$ (mg·g$^{-1}$) | $E$ (%) | $K_d$ (mL·g$^{-1}$) | RSD (%) |
|---------------------|---------------------|--------------------|---------|---------------------|--------|
| 10.11               | 1.03                | 18.16              | 89.81   | 1.76×10$^4$        | 1.16   |
| 19.98               | 2.53                | 34.9               | 87.34   | 1.38×10$^4$        | 0.89   |
| 30.62               | 7.12                | 47                 | 76.75   | 6.6×10$^3$         | 1.6    |
| 40.03               | 14.36               | 51.34              | 64.13   | 3.58×10$^3$        | 0.37   |
| 51.12               | 20.65               | 60.94              | 59.6    | 2.95×10$^3$        | 1.36   |
| 74.25               | 42.47               | 63.56              | 42.8    | 1.5×10$^3$         | 2.04   |
| 99.87               | 65.1                | 69.54              | 34.82   | 1.07×10$^3$        | 0.53   |
| 123.66              | 88.96               | 69.4               | 28.06   | 0.78×10$^3$        | 1.02   |
| 150.37              | 112.19              | 76.36              | 25.39   | 0.68×10$^3$        | 1.43   |

Conditions: T = 298 K, $m/V$ = 0.5 g·L$^{-1}$, contact time = 3 h, pH = 7, shaking speed: 150 rpm
Table 3. Langmuir, Freundlich, Temkin, and D-R Model Fitting Parameters for Adsorption on SCAS-D201 composite.

| model   | parameter | $q_m$ (mg·g$^{-1}$) | $k_L$ (L·mg$^{-1}$) | $R^2$ |
|---------|-----------|----------------------|---------------------|-------|
| Langmuir|           | 76.43                | 0.19                | 0.99435 |
| Freundlich |          | 23.77                | 3.79                | 0.88407 |

Conditions: $T = 298$ K, $m/ V = 0.5$ g·L$^{-1}$, contact time = 3 h, pH = 7, shaking speed: 150 rpm.

4. Conclusions
In this work, SCAS-D201 was prepared by using a simple method. Characterization results confirmed that SCAS was immobilized onto the D201 resin successfully. The SCAS-D201 composite showed excellent Sr(II) removal capability under neutral conditions. The adsorption capacities of SCAS-D201 composite reached maximum at pH values of ~7 for Sr(II). The adsorption capacities increased rapidly with time, and the equilibrium was reached within 2 h. The equilibrium adsorption data fit the Langmuir isotherm model best, and the maximum adsorption capacity of the SCAS-D201 composite for Sr(II) was 76.43 mg·g$^{-1}$. The adsorption kinetics of Sr(II) are fit to the pseudo-second-order model. This research exhibits potential of the SCAS-D201 composite to be a superior adsorbent for removing radionuclides from aqueous solutions.

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