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The efficient removal of Sr²⁺ using two thiostannates *via* ion exchange

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 90 Sr is one of the most hazardous radionuclides in spent fuel, as it releases high energy eta radiation accompanied by the release of a large amount of heat. Its easy environmental mobility and calcium-like bioconcentration properties pose a serious threat to the ecological environment and human health. Therefore, the efficient removal of ⁹⁰Sr from complex aqueous environments is of great significance. Herein, two new isomorphic thiostannates K₂Sn₂S₅·H₂O and K_{1.1}Rb_{0.9}Sn₂S₅·H₂O, namely FJSM-KSnS and FJSM-KRbSnS, respectively, were prepared by the solvothermal method. Their structures feature a twodimensional (2D) wavy anionic layer of $[Sn_2S_5]_n^{2n-}$ with big windows of ten-membered rings. Alkali metal cations (K^+/Rb^+) as charge balancers as well as H_2O molecules are located in the interlayer spaces. They exhibit efficient Sr^{2+} removal performance with high adsorption capacities ($q_m^{Sr} = 59.88 \text{ mg g}^{-1}$ for FJSM-KSnS, $q_m^{Sr} = 62.82 \text{ mg g}^{-1}$ for FJSM-KRbSnS). FJSM-KSnS as a representative exhibits fast kinetics (equilibrium within 10 minutes) and good selectivity for Sr²⁺ removal in the presence of excessive Na⁺, and even in actual environmental water samples. In addition, the Sr²⁺ capture mechanism is revealed by energy-dispersive X-ray spectroscopy, elemental distribution mapping, and X-ray photoelectron spectroscopy characterization. The efficient capture of Sr²⁺ is attributed to the ion exchange between Sr²⁺ and interlayered alkali metal ions of thiostannates. This work expands the structural types of thiostannates and provides new efficient ion exchange materials for radiostrontium remediation.

Introduction

⁹⁰Sr (a half-life of 28.6 years) emitting β radiation (maximum energy of 0.546 MeV) is one of the most hazardous radionuclides produced by the nuclear fission process. ^{1,2} It is highly water-soluble (usually in the form of ⁹⁰Sr²⁺ ions in nuclear waste liquids) and environmentally mobile, which significantly increases the risk of ecological hazards if it diffuses in water systems. ³ In addition, due to its chemical similarity to calcium, it is easily absorbed by organisms through the food chain and preferentially accumulates in bones and teeth, posing a threat to human health. ^{4,5} On the other hand, ⁹⁰Sr can be used as a β radiation source in a variety of medical and industrial applications, such as radiation therapy, densitometry, and radioisotope thermoelectric generators. ⁶⁻⁸ Therefore, the efficient capture of ⁹⁰Sr from complex radioactive liquid

wastes is of vital significance for ecological protection, human health, and resource utilization. However, the strong water solubility and high mobility of ⁹⁰Sr, as well as the complex composition of radioactive waste liquids, pose a great challenge for its efficient capture.⁹

Currently, mainstream techniques for capturing Sr2+ include chemical precipitation, 10,11 solvent extraction, 12-14 and adsorption/ion exchange.15-17 However, the chemical precipitation method generally suffers from low adsorption capacity and poor selectivity. 18 Although the solvent extraction method can improve the separation efficiency, it faces the problems of high cost limitations and secondary waste liquid. 19 By contrast, the ion exchange method is regarded as a more desirable solution for Sr²⁺ capture due to its ease of operation, efficient treatment capacity, and low secondary waste generation. 20-22 To date, a variety of ion exchange materials have been developed for Sr²⁺ removal, including zeolites, ²³ clays, ²⁴ titanates, ²⁵ silica-based materials,26 and so on. Nevertheless, these reported materials still have limitations such as slow dynamics, low adsorption capacity, and insufficient selectivity.²⁷

Metal sulfide ion exchangers (MSIEs) are a class of highly promising ion exchange materials developed in recent years,

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where cations residing in the interlayer spaces or channels to balance the charge of thiometallate can be exchanged by radionuclide ions (such as $^{90}\mathrm{Sr^{2+}}$, $^{137}\mathrm{Cs^{+}}$, and $\mathrm{UO_2}^{2^{+}}$) in the water body to achieve the removal of radionuclides. 28-32 Notably, the anionic framework of MSIEs contains Lewis soft base S2-, exhibiting strong affinity for relatively soft Lewis acidic metal ions.³³ The high polarizability of the soft base S²⁻ promotes the deformation of the metal sulfide bonds (M-S), resulting in a relatively flexible metal sulfide framework that can usually exhibit "breathing action" to effectively trap and anchor the target ions in the structure.34 Therefore, the softly basic and flexible framework of MSIEs facilitates the efficient removal of target radioactive ions. Most of the reported MSIEs including $K_{2x}Mn_xSn_{3-x}S_6$ (x = 0.5-0.95, KMS-1), $K_{2x}Mg_xSn_{3-x}S_6$ (x = 0.5-1, KMS-2), ³⁶ and $K_{2x}Sn_{4-x}S_{8-x}$ (x = 0.65-1, KTS-3)³⁷ exhibit excellent capture ability for Cs⁺. KMS-1 and KTS-3 can quickly capture Cs⁺ within 5 minutes, ^{35,37} and the adsorption capacity $(q_{\rm m}^{\rm Sr})$ of KMS-2 for Cs⁺ reaches astonishing 531 mg g⁻¹.³⁶ However, even if some MSIEs can trap both Cs⁺ and Sr²⁺, their Sr²⁺ capture performance is not outstanding, usually suffering from the disadvantages of low adsorption capacity and slow kinetics. 36,38-43 For example, the maximum Sr2+ adsorption capacity of $K_{1.87}ZnSn_{1.68}S_{5.30}$ (KZTS) is only 19.3 mg g^{-1} , 40 and Na₅Zn_{3.5}Sn_{3.5}S₁₃·6H₂O (ZnSn-1) requires 1440 min to reach saturation adsorption of Sr²⁺. ⁴¹ Therefore, it is urgent to develop new MSIEs that can efficiently capture Sr²⁺.

Herein, two new two-dimensional (2D) layered thiostan-(FJSM-KSnS) nates, namely $K_2Sn_2S_5 \cdot H_2O$ K_{1.1}Rb_{0.9}Sn₂S₅⋅H₂O (FJSM-KRbSnS), were prepared by a simple one-pot solvothermal method. Their structures feature a wavy anionic layer of $[Sn_2S_5]_n^{2n-}$ with big windows of ten-membered rings composed of four [SnS₄] and six [SnS₅] polyhedra. Alkali metal cations (K⁺/Rb⁺) as well as H₂O molecules are located in the interlayer spaces. Both compounds show excellent removal ability for Sr²⁺ from aqueous solutions. Batch adsorption experiments show that the maximum Sr2+ adsorption capacities are 59.88 mg g⁻¹ for FJSM-KSnS and 62.82 mg g⁻¹ for FJSM-KRbSnS, respectively. FJSM-KSnS has the rapid kinetics for Sr²⁺ capture. It can reach adsorption equilibrium within 10 min with the removal rate of more than 99%. And it can maintain efficient adsorption of Sr²⁺ in a wide pH range of 4.14 to 10.05. Notably, it has good selectivity for Sr²⁺ in the presence of excessive Na⁺ and even in actual environmental water samples. This work not only enriches the structural types of the thiostannate family, but also shows their great potential in the field of radiostrontium remediation.

Experimental

Materials

K₂CO₃ (AR, General-Reagent), Rb₂CO₃ (99.8%, damas-beta), S (CP, Kermel), Sn (99%, damas-beta), HNO₃ (65%-68%, China Pharmaceutical Chemical Reagents Co., Ltd), NaOH (98.00%, Greagent Reagent Co., Ltd), CsCl (99.99%, Shanghai Longjin Metal Materials Co., Ltd), NaCl (AR, Sinopharm Chemical

Reagent Co., Ltd), CaCl₂·2H₂O (74%, Shanghai Sili Chemical Plant), MgCl₂ (AR, Adamas Reagent Co., Ltd), and SrCl₂·6H₂O (AR, Tianjin Guangfu Reagent Co., Ltd). All the chemicals were used without further purification.

Synthetic procedures

FJSM-KSnS and FJSM-KRbSnS were synthesized by the solvothermal method. A mixture of K₂CO₃ (5.0 mmol, 0.6912 g), Sn (5.0 mmol, 0.5937 g), S (15.0 mmol, 0.4808 g), and hydrazine hydrate (0.8 mL) was placed in a 28 mL stainless steel autoclave lined with polytetrafluoroethylene (PTFE). The sealed autoclave was heated to 220 °C for 2 h and held for 3 days, which was slowly cooled down to room temperature (RT) in 12 h. The resultant solid products were isolated and then washed with water and ethanol and naturally dried to obtain pale-yellow needle-like crystals of FJSM-KSnS (yield: 0.0795 g, 6.44%, based on Sn). Additionally, K₂CO₃ (3.0 mmol, 0.4145 g), Rb₂CO₃ (2.0 mmol, 0.4620 g), Sn (5.0 mmol, 0.5937 g), S (15.0 mmol, 0.4807 g), and hydrazine hydrate (0.8 mL) were mixed. Following the same temperature control procedure and washing method as those used for FJSM-KSnS, bright-yellow needle-like FJSM-KRbSnS crystals were obtained (yield: 0.0530 g, 3.97%, based on Sn). Energy-dispersive X-ray spectroscopy (EDS) results show that the atomic ratio of the elements in FJSM-KSnS is K, 22.5%; Sn, 22.9%; and S, 54.6%. The atomic ratio of the elements in FJSM-KRbSnS is K, 12.2%; Rb, 9.5%; Sn, 23.3%; and S, 55.0%.

Characterization techniques

Single-crystal X-ray diffraction (SC-XRD) analysis was performed on a Rigaku XtaLAB Synergy-R diffractometer equipped with a graphene-monochromated microfocus MoK_{α} radiation source ($\lambda = 0.71073$ Å) at 100 K. Powder X-ray diffraction (PXRD) patterns were obtained using a Miniflex II diffractometer using CuK_{α} radiation ($\lambda = 1.5418 \text{ Å}$) operated at 30 kV and 15 mA over the 2θ range of 5–65° at RT. EDS and elemental distribution mapping analysis were performed by a JEOL JSM-6700F scanning electron microscope. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere with a NETZSCH STA449C instrument at a heating rate of 10 °C min⁻¹. Solid-state UV-vis optical diffuse reflectance spectra in the range of 800-200 nm were recorded using a Shimadzu 2600 UV-vis spectrometer at RT. X-ray photoelectron spectroscopy (XPS) analysis was performed using an ESCALAB 250Xi spectrometer with AlK_{α} radiation; all peaks were corrected to the C 1s peak binding energy of adventitious carbon at 284.80 eV. Inductively coupled plasma-mass spectroscopy (ICP-MS) or inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to test the concentration of ions in solution. ICP-MS and ICP-OES detection were performed using XSerise II and Thermo 7400, respectively.

Batch adsorption experiments

Typical batch adsorption experiments were carried out in 20 mL plastic bottles. 5 mg of FJSM-KSnS or FJSM-KRbSnS crystalline samples were added into 5 mL of Sr2+ aqueous solution ($V/m=1000~{\rm mL~g^{-1}}$). After adsorption at RT for a period of time, the upper clarified solution was filtered through a 0.22 μm microporous membrane, diluted with 2% HNO₃ at different multiplicities, and then analyzed by ICP-MS or ICP-OES. Meanwhile, the samples precipitated at the bottom of the bottle were filtered and washed several times with deionized water and ethanol, and dried naturally for characterization, such as PXRD.

Isothermal adsorption. The solutions with Sr^{2+} concentrations from 10.39 to 1275.06 mg L^{-1} were prepared. 5 mg of FJSM-KSnS and FJSM-KRbSnS crystalline samples were added into 5 mL solution with different concentrations of Sr^{2+} , and shaken for 3 h at RT, respectively. The concentration of Sr^{2+} in the supernatant after filtration was determined by ICP-MS. Langmuir, Freundlich, and Langmuir–Freundlich models were used to fit the adsorption data and calculate the maximum adsorption capacity.

Kinetics. 20 mg of FJSM-KSnS crystalline samples were added to 20 mL of 5.32 mg L⁻¹ Sr²⁺ solution and magnetically stirred at RT. About 0.3 mL of the mixture was sampled at regular intervals (2, 5, 10, 30, 60, 90, 150, 210, 300, 390, and 510 minutes), and the concentration of Sr²⁺ was determined by ICP-MS after filtration.

pH effect on adsorption. Solutions with initial Sr^{2+} concentrations of 5.36–5.51 mg L^{-1} at different acidities (pH = 2.07–12.13) were prepared by HNO₃ solution and NaOH solution. 5 mg of crystalline samples for FJSM-KSnS were added to 5 mL of Sr^{2+} solution with different pH values and shaken for 3 h at RT. The concentration of Sr^{2+} and the leaching rate of Sn^{4+} in the solutions were determined by ICP-MS. The solid samples were washed with water and ethanol, and the PXRD test was performed after natural drying.

Competitive ion effect. Mixed Na⁺/Sr²⁺, Cs⁺/Sr²⁺, Ca²⁺/Sr²⁺, and Mg²⁺/Sr²⁺ solutions were prepared. In addition, Sr²⁺ ions were added to tap water, river water (Wulong River, Fujian, Fuzhou, China), lake water (Qishan Lake, Fujian, Fuzhou, China), and sea water (Dongshan Island, Fujian, Zhangzhou, China) to simulate contaminated actual environmental water samples. 5 mg of FJSM-KSnS crystalline samples were added to 5 mL of the above solutions and the mixtures were shaken for 3 h at RT. After filtration, the ion concentration in the solutions was determined by ICP-MS and ICP-OES.

Results and discussion

Crystal structure

Single crystal X-ray diffraction (SC-XRD) analysis confirms that both $K_2Sn_2S_5\cdot H_2O$ (FJSM-KSnS) and $K_{1.1}Rb_{0.9}Sn_2S_5\cdot H_2O$ (FJSM-KRbSnS) crystallize in the space group *Pbcn* and they are isostructural (Tables S1–S6). Therefore, only the structure of FJSM-KSnS as a representative is described in detail. The asymmetric unit of FJSM-KSnS contains atoms of one formula unit (Fig. S1). Sn(1) coordinates with four S atoms to form the [Sn (1)S₄] tetrahedron, and two [Sn(1)S₄] tetrahedra share the edge to form a [Sn(1)₂S₆] unit (Fig. S2a). Sn(2) coordinates with five

S atoms to form a $[Sn(2)S_5]$ trigonal bipyramid. Then $[Sn(2)S_5]$ trigonal bipyramids are connected together by sharing edges to generate an infinite chain along the a-axis (Fig. S2b). The chains are further linked by $[Sn(1)_2S_6]$ units via sharing S(3)atoms resulting in a 2D wavy anionic layer of $[Sn_2S_5]_n^{2n-1}$ (Fig. 1a) that contains big windows. It is found that the big window of the ten-membered ring is composed of four [SnS₄] and six [SnS₅] polyhedra in the 2D anionic layer and its size is about $13.30 \times 4.36 \text{ Å}^2$ (Fig. 1b). The interlayer distance is 4.2449 Å (Fig. 1d and Fig. S4). K^+ ions and the lattice H_2O molecules reside in the interlayer spaces (Fig. 1c and Fig. S3). FISM-KRbSnS has the same anionic layer as that of FJSM-KSnS, except that its interlayer spaces are filled with cooccupied K⁺ and Rb⁺ ions. In addition, due to the entry of Rb⁺ into FJSM-KRbSnS, the interlayer distance in FJSM-KRbSnS slightly expands to 4.3783 Å (Fig. 1d).

At present, many thiostannates and selenostannates containing alkali metal have been reported, and they exhibit rich structural types, such as zero-dimensional 0D-Na₄SnS₄ with $[SnS_4]$ structural units,44 one-dimensional isolated 1D-K₂SnS₃·2H₂O containing one-dimensional thiostannate chains, 45 layered 2D-Na₂SnS₃ and 2D-Rb₂Sn₄Se₉, 47 threedimensional $3D-K_2Sn_2S_5^{48-50}$ microporous 3D-K₄Sn₄Se₁₀·4.5H₂O.⁵¹ Among them, 2D layered thiostannates and selenostannates are attractive due to various layered frameworks. For example, a series of 2D-ASnS2 (A = Li, Na, K, and Rb) compounds have dense $[SnS_2]_n^{n-}$ anionic layers composed of [SnS₆] octahedra by sharing edges,⁵² in which there is no window. In addition, although some thiostannates and selenostannates containing alkali metals have windows in the 2D-Cs₂Sn₃Se₇,⁵⁶ $2D-Cs_4Sn_5S_{12}\cdot 2H_2O_{,}^{57}$ 2D-Cs₄Sn₄Se₁₀·3.2H₂O (Fig. S5),⁵¹ the wavy anionic layer of

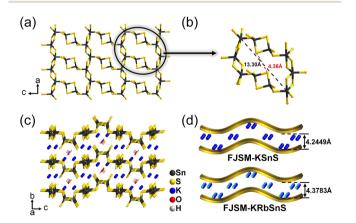


Fig. 1 (a) A 2D anionic layer of $[Sn_2S_5]_n^{2n-}$ parallel to the ac plane in the structure of FJSM-KSnS. (b) A big window of a ten-membered ring with the size of 13.30 \times 4.36 Å 2 in the structure of FJSM-KSnS. (c) Packing of layers in FJSM-KSnS in a perspective view along the a-axis. (d) The schematic representation of the interlayer distances of FJSM-KSnS and FJSM-KRbSnS. The blue balls represent K atoms. The blue and green bicolored balls represent co-occupied K and Rb atoms.

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 $[Sn_2S_5]_n^{2n-}$ with a big window of ten-membered ring in the current thiostannates is distinct from that of these reported $2D-K_2Sn_2S_8,^{49}$ compounds. The anionic layers of $2D-Rb_2Sn_4S_9$, 53 $2D-Na_2Sn_2Se_5$, 54 $2D-Rb_2Sn_3S_7 \cdot 2H_2O$, 55 and $2D\text{-}Cs_2Sn_2S_6^{\ 49}$ contain relatively small windows. There are obviously big windows in the anionic layers of 2D-Cs₂Sn₃Se₇,⁵⁶ $2D-Cs_4Sn_5S_{12}\cdot 2H_2O_5^{57}$ and $2D-Cs_4Sn_4Se_{10}\cdot 3.2H_2O_5^{51}$ The anionic layers of 2D-Cs₂Sn₃Se₇⁵⁶ and 2D-Cs₄Sn₅S₁₂·2H₂O⁵⁷ are constructed from $[Sn_3Q_{10}]$ (Q = S, Se) units with a $[Sn_3Q_4]$ semicubane-like core. Specifically, in the anionic layer of Cs₂Sn₃Se₇ twelve [SnS₅] trigonal bipyramids, form a big window of a twelve-membered ring (Fig. S5g). 56 In Cs₄Sn₅S₁₂·2H₂O the window of ten-membered ring is formed by ten [SnS₅] trigonal bipyramids (Fig. S5h).⁵⁷ Cs₄Sn₄Se₁₀·3.2H₂O contains [SnSe₄] tetrahedra and [SnSe₅] trigonal bipyramids, and the window of a ten-membered ring in its anionic layer consists of four [SnSe₄] and six [SnSe₅] (Fig. S5i),⁵¹ which is similar to that of FJSM-KSnS. However, their anionic layers are still different. In Cs₄Sn₄Se₁₀·3.2H₂O, [Sn₂Se₆] units and the chain composed of [SnSe₅] are connected by "trans" sharing Se(3) atoms on different sides of [Sn₂Se₆] (Fig. S6a), while [Sn₂S₆] units and the chain are interconnected by "cis" sharing S(3) atoms on the same side of [Sn₂S₆] in FJSM-KSnS (Fig. S6b). The new connection mode leads to the formation of a new unique wavy anionic layer in FJSM-KSnS, whereas the anionic layer in Cs₄Sn₄Se₁₀·3.2H₂O is relatively flat (Fig. S6c and S6d). Beyond doubt, the current thiostannates are new members of the thiostannate family.

Characterization and adsorption mechanism

The PXRD patterns of FJSM-KSnS and FJSM-KRbSnS are in agreement with the simulated PXRD patterns calculated from single-crystal X-ray data (Fig. S7), indicating that pure phases of FJSM-KSnS and FJSM-KRbSnS could be synthesized by a simple one-pot solvothermal method. 50 mg of crystalline samples for FJSM-KSnS and FJSM-KRbSnS were immersed in 50 mL of 500 mg L⁻¹ Sr²⁺ aqueous solutions, respectively. The mixtures were shaken for 3 h at RT, respectively. The Sr²⁺exchanged products (denoted as FJSM-KSnS-Sr FJSM-KRbSnS-Sr, respectively) could be obtained after washing with water and ethanol and drying naturally. According to the PXRD results, it is confirmed that FJSM-KSnS-Sr and FJSM-KRbSnS-Sr maintain the pristine layered structure (Fig. S8). The crystal photographs confirm that FJSM-KSnS-Sr and FJSM-KRbSnS-Sr remain in their original morphology (Fig. 2a and S9). Elemental distribution maps and EDS analyses show the uniform elemental distributions and the entry of Sr²⁺ and the disappearance of some K⁺ or Rb⁺ (Fig. 2a, S9 and S10).

Furthermore, XPS analysis indicates that the K 2p_{3/2} and K 2p_{1/2} characteristic peaks of FJSM-KSnS are located at binding energies of 292.90 eV and 295.69 eV, respectively. By contrast, the characteristic peaks of K 2p in FJSM-KSnS-Sr disappear, whereas the peaks of Sr $3d_{5/2}$ and Sr $3d_{3/2}$ are observed at 133.74 eV and 135.45 eV (Fig. 2b-d and Table S7). Similarly, the characteristic peaks of K 2p and Rb 3d disappear in the

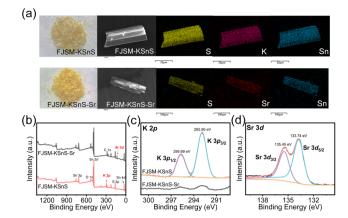


Fig. 2 (a) Photographs of crystal samples, morphologic maps, and elemental distribution mapping of FJSM-KSnS and FJSM-KSnS-Sr. (b) XPS spectra of FJSM-KSnS and FJSM-KSnS-Sr; narrow scan XPS spectra of K 2p (c) of FJSM-KSnS, and Sr 3d (d) of FJSM-KSnS-Sr.

XPS spectra of FJSM-KRbSnS, while the characteristic peaks of Sr 3d appear in those of FJSM-KRbSnS-Sr (Fig. S11 and Table S7). In summary, elemental distribution maps, EDS, and XPS results collectively demonstrate that the efficient capture of Sr²⁺ is attributed to the ion exchange between Sr²⁺ and interlayered alkali metal ions in title thiostannates. In addition, combined with SC-XRD analysis, the compound has unobstructed and wide interlayer spaces along the a-axis direction (Fig. 1c), which allows Sr²⁺ to enter the interlayer spaces from this direction. Therefore, the ion exchange pathway likely occurs along the a-axis.

In addition, the UV-vis absorption spectra show that the optical absorption edges of FJSM-KSnS and FJSM-KRbSnS are at 490.25 nm and 473.22 nm, respectively (Fig. S12a and S12c). After Sr²⁺ adsorption, the optical absorption edges of FJSM-KSnS-Sr and FJSM-KRbSnS-Sr are red-shifted to 546.29 nm and 544.70 nm, respectively (Fig. S12b and S12d). This is consistent with the deepening of the crystal color of FJSM-KSnS and FJSM-KRbSnS compared with that of the pristine compounds (Fig. 2a and S9). TGA and DTG results showed that the weight loss percentages of FJSM-KSnS and FJSM-KRbSnS were 4.85% and 3.28%, respectively, in the range of 96-270 °C, corresponding to the loss of lattice water in FJSM-KSnS and FJSM-KRbSnS. However, it can be clearly seen that the weight loss of FJSM-KSnS-Sr and FJSM-KRbSnS-Sr increased significantly before 270 °C. This is attributed to the entering to the crystal structure of hydrated ions of Sr²⁺ ions during the ion exchange process, which carries the adsorbed H2O to cause a significant increase in weight loss in TGA (Fig. S13).

Adsorption isotherm study

The maximum adsorption capacities of FJSM-KSnS and FJSM-KRbSnS at room temperature were determined through static batch experiments (Tables S8, S9 and eqn (S1)). The experimentally obtained Sr2+ adsorption data are fitted using

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the Langmuir (eqn (S2)), Freundlich (eqn (S3)) and Langmuir-Freundlich (eqn (S4)) models. The results show that the adsorption data of both FJSM-KSnS and FJSM-KRbSnS can be well fitted with the Langmuir-Freundlich model with correlation coefficients of 0.9881 and 0.9884, respectively (Tables S10 and S11). Based on the Langmuir-Freundlich model, the maximum Sr2+ adsorption capacities of FJSM-KSnS and FISM-KRbSnS are 59.88 mg g^{-1} and 62.82 mg g^{-1} (Fig. 3a and b), respectively. In addition, the maximum adsorption capacity of FJSM-KRbSnS is slightly higher than that of FJSM-KSnS. This may be due to the slightly larger interlayer spacing of FISM-KRbSnS, and thus it is more conducive to the entry of Sr²⁺. The adsorption capacity of FJSM-KSnS and FJSM-KRbSnS has exceeded that of some common adsorbents for Sr²⁺, such as metal sulfides KZTS (19.3 mg g $^{-1}$), 40 NaZTS (32.3 mg g $^{-1}$), 42 metal oxysalt TaSb (26.37 mg g $^{-1}$), 58 KNb $_3$ O $_8$ (45.6 mg g $^{-1}$) 59 and so on. In addition, although the adsorption capacity of FJSM-KSnS is slightly lower, it is easier to synthesize. Therefore, the following adsorption experiments using FJSM-KSnS as a representative are performed.

Adsorption kinetics studies

Adsorption kinetics is an important parameter to evaluate the adsorption performance of an adsorbent. Therefore, the kinetic experiments of FJSM-KSnS capturing Sr2+ were carried out at room temperature (Table S12). According to the experimental results, the removal rate (RSr) of Sr2+ by FJSM-KSnS rapidly reaches 84.21% within 5 min (eqn (S5)). Finally, the adsorption reaches equilibrium at 10 min with a RSr value of about 99% (Fig. 3c). The pseudo-first-order (eqn (S6)) and pseudo-second-order (eqn (S7)) models are used to fit the kinetic data (Fig. S14). The latter has a high correlation coefficient ($R^2 = 0.9999$) (Table S13). FJSM-KSnS exhibits faster adsorption kinetics for Sr2+ than that of many reported adsor-

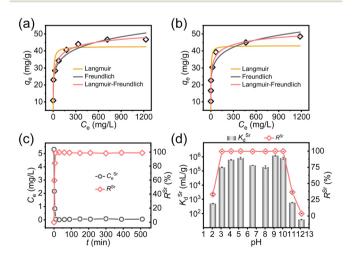


Fig. 3 Isothermal adsorption equilibrium curves of FJSM-KSnS (a) and FJSM-KRbSnS (b). (c) Kinetic curve of Sr^{2+} removal by FJSM-KSnS. (d) K_{cl}^{Sr} and R^{Sr} values of FJSM-KSnS in solutions with different initial pH values.

bents, such as KMS-2 (equilibrium time of 120 min)³⁶ and NaTS-2 (equilibrium time of 60 min).⁴³

pH effect on Sr²⁺ adsorption

Generally, the pH values of the solution will affect the adsorption performance of the adsorbent. Therefore, the ability of FJSM-KSnS to adsorb Sr2+ in solutions with pH values of 2.07-12.13 was systematically investigated (Table S14). The experimental result shows that Sr2+ can be effectively removed over a wide pH range of 3.10 to 10.05 with an RSr value greater than 99% and the distribution coefficient (K_{-}^{Sr}) consistently greater than 10^5 mL g^{-1} (eqn (S8)). The high K_d^{Sr} value of FJSM-KSnS exceeds that reported for ZnSnS-1 (Fig. 3d).⁴¹

Furthermore, the leaching percentages of Sn and PXRD patterns of solid products after adsorbing Sr2+ in solutions with pH of 2.07-12.13 were systematically studied to confirm the stability of the current material. The leaching percentages of Sn are less than 1.1% in the pH range of 2.07 to 10.05 (Fig. S15). PXRD results confirm that the framework of FJSM-KSnS can be maintained within the pH range of 4.14 to 10.05 (Fig. S16). Therefore, FJSM-KSnS can maintain good Sr²⁺ removal ability as well as framework stability in the pH range of 4.14 to 10.05.

Competitive adsorption study

In radioactive waste liquids, a large number of competing ions usually cause a great interference to the adsorption performance of the adsorbent. Therefore, the adsorption capacity of FJSM-KSnS for Sr²⁺ in the presence of competing ions was studied (Tables S15 and S16). The experimental results show that FJSM-KSnS has excellent adsorption performance for Sr²⁺ in the presence of individual monovalent ions (e.g. Na⁺). When Na/Sr molar ratios are between 14.20 and 402.65, the K_d^{Sr} values of FJSM-KSnS are consistently greater than 1.58×10^3 mL g^{-1} , and the R^{Sr} values are greater than 61.22%. Notably, when the Na/Sr molar ratio is 14.02, the separation factor (SF_{Sr/Na}, eqn (S9)) of FJSM-KSnS can reach a surprising value of 1943.1. Even when the Na/Sr molar ratio increases to 402.65, the $SF_{Sr/Na}$ value is still greater than 200, whereas the R^{Na} value is less than 1% (Fig. 4a). This indicates that FJSM-KSnS has high selectivity for Sr2+ and good separation ability for Sr2+ and Na⁺.

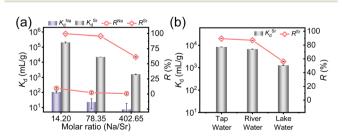


Fig. 4 (a) The K_d and R values of Sr^{2+} and Na^+ removed by FJSM-KSnS in solutions with different Na/Sr molar ratios. (b) K_d^{Sr} and R^{Sr} of FJSM-KSnS in actual water samples.

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In addition, in the solution containing coexisting Cs⁺ and Sr²⁺, the selectivity of FJSM-KSnS for Sr²⁺ was explored. When the Cs/ Sr molar ratio is 0.62, the K_d^{Sr} value reaches 2.43 \times 10⁵ mL g⁻¹ with an R^{Sr} value of 99.59%, and the $SF_{Sr/Cs}$ value is 129.9 (Fig. S17a). The removal ability of FJSM-KSnS for Sr²⁺ gradually decreases with an increase of Cs/Sr molar ratio. When divalent ions (Ca²⁺ and Mg²⁺) coexist with Sr²⁺, FJSM-KSnS can remove Sr²⁺ in solutions containing lower concentrations of competing divalent ions. When the Ca/Sr molar ratio is 10.13, the K_d^{Sr} value is greater than 10³ mL g⁻¹, and at the Mg/Sr molar ratio of 3.87, the R^{Sr} value is 88.40% (Fig. S17b and S17c).

Furthermore, low concentrations of Sr^{2+} (5.61–7.43 mg L⁻¹) were artificially added to tap water, river water (Wulong River), lake water (Qishan Lake), and sea water (Dongshan Island) to simulate polluted environmental water samples, which were used to evaluate the ability of FJSM-KSnS to capture Sr²⁺ in more complex aqueous solutions (Table S17). The results show that the R^{Sr} values of FJSM-KSnS are greater than 56% and the K_d^{Sr} values are greater than 10^3 mL g^{-1} , respectively, in simulated polluted tap water, river water, and lake water. In particular in tap water and river water, the RSr values of FISM-KSnS can even reach 89.46% and 87.10% (Fig. 4b), respectively. In addition, the R^{Sr} value of FJSM-KSnS is 43.51% in high-salinity sea water. Therefore, FJSM-KSnS can effectively remove Sr²⁺ from actual water samples contaminated with low concentrations of Sr²⁺.

Conclusions

In conclusion, two isomorphic alkali metal-containing thiostannates, $K_2Sn_2S_5\cdot H_2O$ (FJSM-KSnS) and $K_{1.1}Rb_{0.9}Sn_2S_5\cdot H_2O$ (FJSM-KRbSnS), have been synthesized by a simple one-step solvothermal method. They present wavy anionic layers with charge-balanced alkali metal cations (K⁺/Rb⁺) as well as H₂O molecules located in the interlayer spaces. FJSM-KSnS and FJSM-KRbSnS exhibit good Sr2+ capture capability with high adsorption capacity and fast kinetics. Moreover, FJSM-KSnS could maintain efficient adsorption of Sr^{2+} ($K_d^{Sr} > 10^5 \text{ mL g}^{-1}$) and good framework stability over a wide pH range of 4.14 to 10.05. FJSM-KSnS has good selectivity for the removal of Sr²⁺ from actual environmental water samples. In addition, the adsorption mechanism is revealed and the efficient Sr2+ capture derives from ion exchange between Sr²⁺ and interlayer alkali metal ions. This study endows the thiostannate family with new members. More importantly, it further highlights the value and great potential of MSIEs, especially thiostannates, as scavengers for radionuclides.

Author contributions

Y. W. Ren: data curation, writing - reviewing and editing, validation, formal analysis, investigation, and software. J. H. Luo: structural analysis. Z. H. Chen: validation and review. S. Z. Liu: formal analysis. X. P. Guo: formal analysis. G. Y. Chen: formal analysis. M. L. Feng: conceptualization, writing - reviewing and

editing, funding acquisition, resources, visualization, supervision, and project administration. X. Y. Huang: reviewing and editing, resources, visualization, and project administration.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of the study are included in the main text and SI files. Supplementary information: characterization techniques, crystal structure details, ion exchange experiments, ICP-MS (ICP-OES) data, PXRD, TGA, EDS, etc. See DOI: https://doi.org/10.1039/d5dt01904d.

Raw data can be obtained from the corresponding author upon request.

CCDC 2473640 and 2473641 (FISM-KSnS and FJSM-KRbSnS) contain the supplementary crystallographic data for this paper. 60a,b

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