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# Efficient capture of $Sr^{2+}$ ions by a layered crystalline zirconium phosphate fluoride

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The effective remediation of radioactive strontium-90 ($^{90}Sr$) from complex aqueous environments remains challenging due to the inherent high solubility and migration propensity of $Sr^{2+}$ ions. Herein, we synthesized hydrothermally a new two-dimensional (2D) crystalline zirconium phosphate fluoride $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ featuring a layered anionic architecture of $[Zr(PO_4)F_2]_n^{n-}$ with intercalated $[(CH_3)_2NH_2]^+$ cations, which shows exceptional $Sr^{2+}$ remediation capability. It possesses a high maximum $Sr^{2+}$ adsorption capacity ($q_m^{Sr}$) of 161.48 mg $g^{-1}$ (higher than that of many inorganic crystalline adsorbents) and fast kinetics for $Sr^{2+}$ capture ($Sr^{2+}$ removal rate ($R^{Sr}$) of 94.89% within 1 min). Specifically, it maintains $Sr^{2+}$ removal efficiency in the presence of competing $Cs^+$, $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$ ions and in actual aqueous systems including seawater ($R^{Sr}$ = 79.06%). X-ray photoelectron spectroscopy (XPS) and thermodynamics confirm that spontaneous $Sr^{2+}$ capture occurs through ion exchange processes, where the interlayered $[(CH_3)_2NH_2]^+$ cations in $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ are exchanged with $Sr^{2+}$. The compound $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ represents the first crystalline inorganic zirconium phosphate fluoride ion exchange material for radionuclide capture. This work provides a high-performance ion exchanger as a candidate for radiostrontium capture.

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## Introduction

Strontium-90 ($^{90}Sr$), recognized as one of the most hazardous artificial radionuclides, predominantly exists as $^{90}Sr^{2+}$ ions in radioactive waste liquids. As a β-emitting radioisotope derived from the nuclear fission of $^{235}U/^{239}Pu$, $^{90}Sr$ exhibits a long half-life ($t_{1/2}$ = 28.6 years) and high β-particle energy (0.546 MeV),[1,2] posing severe environmental and health risks due to its high mobility, radiotoxicity, and biotoxicity.[3,4] Its chemical similarity to $Ca^{2+}$ facilitates bioaccumulation in human bone tissues, leading to bone cancer and leukemia.[5,6] On the other hand, $^{90}Sr$ has found significant implementation in therapeutic oncology as a radiation source for targeted bone cancer treatment.[7] Concurrently, its sustained decay heat generation enables essential roles in radioisotope thermoelectric generators (RTGs), particularly for powering deep-space probes and remote terrestrial monitoring systems under extreme environmental conditions.[7,8] Thus, the rapid separation and recovery of $^{90}Sr$ are critical for radioactive waste management, human health protection, environmental sustainability, and resource recycling.[7] However, $^{90}Sr$ waste liquids are extremely complex, typically containing abundant non-radioactive ions (*e.g.*, $Na^+$, $K^+$, and $Mg^{2+}$) and other fission products.[9] Therefore, highly selective capture of $Sr^{2+}$ from such complex radioactive matrices remains a significant challenge.

Current strategies for $Sr^{2+}$ removal include solvent extraction,[10,11] chemical precipitation,[12] and adsorption/ion exchange.[13] Among these, adsorption/ion exchange stands out for its cost-effectiveness, operational simplicity, and high efficiency.[14,15] Various ion exchange materials have been widely studied, such as zeolites,[16] layered clay minerals,[17] crystalline silicotitanates,[18] porous coordination polymers,[19] and metal chalcogenides.[20,21] Particularly, inorganic ion exchangers demonstrate potential for radionuclide remediation due to their structural robustness under extreme conditions.[22] Metal phosphate compounds have employed as ion exchange materials for $Sr^{2+}$ ion capture, attributed to their good thermostability, radiation resistance,[23] and inherent selective coordination capacity of phosphate groups toward multivalent cations.[23–25] Specifically, tetravalent metal orthophosphates exhibit superior ion exchange characteristics, particularly in nuclear waste treatment scenarios due to their thermal stability, radiation tolerance, and structural stability under acidic conditions.[23,25–29]

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Zirconium phosphate (ZrP) and its structural analogues have been extensively studied as classical materials for $Sr^{2+}$ capture.[25,30,31] However, most of them exhibit poor $Sr^{2+}$ selectivity in excessive competitive ions (such as $Na^+$, $K^+$, and $Ca^{2+}$), severely compromising strontium capture.[32–35] For instance, crystalline $\alpha$-$Zr(HPO_4)_2{\cdot}H_2O$ ($\alpha$-ZrP) exhibits adsorption capacities of 64.10 mg $g^{-1}$ for $Cs^+$ and 43.03 mg $g^{-1}$ for $Sr^{2+}$.[32,33] Meanwhile, $\gamma$-$Zr(PO_4)H_2PO_4{\cdot}2H_2O$ ($\gamma$-ZrP) demonstrates enhanced uptake for both $Rb^+$ (129.90 mg $g^{-1}$) and $Sr^{2+}$ (114.78 mg $g^{-1}$), though excessive $Na^+/Ca^{2+}$ ions severely compromise strontium capture.[34] Kinetic analyses reveal that $\gamma$-ZrP's ion exchange rates follow the hierarchy of $Cs^+ > K^+ > Rb^+ > Sr^{2+}$. Recently, potassium-incorporated zirconium phosphate ($K_2Zr(PO_4)_2$) shows the $Sr^{2+}$ capture property but with poor selectivity for $Sr^{2+}$ due to the effect of competitive ions ($Ca^{2+}$, $Na^+$, and $H^+$).[35] Additionally, introducing fluorine into phosphate structures facilitates the formation of highly stable Zr–F bonds, enhancing crystallinity and thermal stability and improving structural diversity and robustness.[36] Nevertheless, crystalline inorganic zirconium phosphate fluoride has never been studied for the removal of radioactive ions.

In this work, a new crystalline zirconium phosphate fluoride $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ is reported, which is characterized by a layered anionic framework of $[Zr(PO_4)F_2]_n^{n-}$ hosting intercalated $[(CH_3)_2NH_2]^+$ cations. It exhibits exceptional $Sr^{2+}$ capture across wide pH regimes (1.95–8.46). It has a high $Sr^{2+}$ adsorption capacity ($q_m^{Sr}$ = 161.48 mg $g^{-1}$) and rapid capture kinetics (removal rate $R^{Sr}$ = 94.89% within 1 min). Further, it maintains $Sr^{2+}$ removal efficiency in the presence of competing $Cs^+$, $K^+$, $Na^+$, $Ca^{2+}$, and $Mg^{2+}$ ions. It is also demonstrated that the material can efficiently capture $Sr^{2+}$ from actual aqueous systems (especially seawater), surpassing most reported solid sorbents. This study highlights the substantial potential of layered crystalline zirconium phosphate fluorides for radionuclide capture, while establishing a rational design paradigm for developing $Sr^{2+}$-selective ion-exchange materials of crystalline zirconium phosphate fluorides.

## Materials and methods

### Materials

$ZrOCl_2{\cdot}8H_2O$ (98.00%, Shanghai Adamas Reagent Co., Ltd.), *N*,*N*-dimethylacetamide (abbreviated as DMA, AR, Sinopharm Chemical Reagent Co., Ltd.), 2-hydroxyphosphonoacetic acid (abbreviated as HPAA, 50%, Shanghai Adamas Reagent Co., Ltd.), hydrofluoric acid (abbreviated as HF, AR, ≥40 nt, Shanghai Adamas Reagent Co., Ltd.), $HNO_3$ (65–68%, China Pharmaceutical Chemical Reagents Co., Ltd.), NaOH (98.00%, Greagent Reagent Co., Ltd.), $SrCl_2{\cdot}6H_2O$ (AR, Guangfu Co., Ltd.), CsCl (99.99%, Shanghai Longjin Metal Materials Co., Ltd.), KCl (AR, Shanghai Titan Co., Ltd.), NaCl (AR, Sinopharm Chemical Reagent Co., Ltd.), $CaCl_2{\cdot}2H_2O$ (74–78%, Shanghai Songjiang Silian Chemical Co., Ltd.), $MgCl_2{\cdot}6H_2O$ (AR, Kelong Co., Ltd.). Ultrapure water was supplied by a certified laboratory water purification system (Model WP-UP-LH-10, Sichuan Water Treatment Equipment Co., Ltd.). All reagents were purchased directly for use without further purification.

### Synthesis of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$

$[(CH_3)_2NH_2][Zr(PO_4)F_2]$ was synthesized through a solvothermal process using stoichiometric quantities of $ZrOCl_2{\cdot}8H_2O$ (2.4 mmol, 0.7735 g) and HPAA (2.4 mmol, 0.3745 g) in a mixed solvent system containing DMA (24 mL) and deionized water (5 mL). To modulate crystallization kinetics, HF (0.08 mL) was introduced as a mineralizer.[37] The reaction mixture was then acidified to pH 4 through precise addition of $HNO_3$ (1 mL), a critical parameter influencing layer assembly.

After homogenization *via* magnetic stirring at ambient temperature, the precursor solution was transferred to a 100 mL Teflon-lined autoclave and subjected to thermal treatment at 200 °C for 72 h under autogenous pressure. This prolonged aging period facilitated the formation of well-defined crystalline phases.

The resultant crystals were isolated by vacuum filtration, followed by sequential washing cycles with deionized water and ethanol (3 × 20 mL each) to remove residual organics. Subsequently, drying under ambient conditions yielded the target compound $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ (relative molecular mass ($M$) = 270.28 g $mol^{-1}$) as colorless plate-like crystals, where $[(CH_3)_2NH_2]^+$ was generated by the thermal decomposition of DMA as the starting material and $(PO_4)^{3-}$ was generated by the thermal decomposition of HPAA.[38] Yield: 20.13% (calculated based on Zr content). Elemental analysis (EA) validated phase purity: theoretical: C 9.02%, H 3.03%, N 5.26%. Experimental: C 8.97%, H 3.33%, N 4.83%.

### Batch adsorption experiment

The adsorption performance evaluation of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ was conducted in 25 mL polyethylene bottles with caps at room temperature. The experimental setup included: phase allocation, precise dosing of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ (solid–liquid ratio $m/V$ = 1 g $L^{-1}$) and $Sr^{2+}$ standard solution into bottles, followed by continuous agitation on a magnetic stirrer for 12 h at ambient temperature. Post-adsorption, aliquots of the supernatant were extracted *via* syringe, filtered through 0.22 μm membranes, and diluted with 2% $HNO_3$ prior to $Sr^{2+}$ concentration analysis by ICP-OES or ICP-MS. The post-adsorption solid phase was isolated from the aqueous medium *via* centrifugal separation at 8000 rpm for 10 min, followed by triple rinsing with deionized water to eliminate residual ions prior to subsequent analysis.

The $Sr^{2+}$-exchanged derivative of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ (designated as $[(CH_3)_2NH_2][Zr(PO_4)F_2]$-Sr) was synthesized *via* 12 h room-temperature agitation of 200 mg adsorbent in 200 mL of $Sr^{2+}$ solution. The resultant $[(CH_3)_2NH_2][Zr(PO_4)F_2]$-Sr underwent comprehensive characterization (PXRD, EDS,

 

SEM, and EA). Experimental particulars are described in the supplementary information (SI).

### Characterization techniques

Elemental composition (C, H, N) was quantified *via* high-precision combustion analysis using a Vario EL III EA. Single-crystal X-ray diffraction analysis of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ was performed on a Rigaku XtaLAB Synergy-R diffractometer equipped with a graphene-monochromated microfocus Mo $K_\alpha$ radiation source ($\lambda$ = 0.71073 Å) at 100 K. Powder X-ray diffraction (PXRD) patterns were acquired at room temperature on a Rigaku Miniflex II system equipped with Cu $K_\alpha$ radiation ($\lambda$ = 1.54178 Å), operating at 30 kV and 15 mA, with a $2\theta$ scanning range of 5–65°. Elemental composition and spatial distribution were analyzed by energy-dispersive X-ray spectroscopy (EDS) coupled with scanning electron microscopy (SEM, JEOL JSM-6700F). Surface chemical states were investigated *via* X-ray photoelectron spectroscopy (XPS) on a ThermoFisher ESCALAB 240 Xi spectrometer using monochromatic Al $K_\alpha$ excitation. Solution pH measurements were conducted with a Leimage E-201F digital pH meter (Shanghai, China). The concentration of $Sr^{2+}$ and other metal ions were quantificationally measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo iCAP 7400) and inductively coupled plasma mass spectrometry (ICP-MS, Thermo XSeries II), respectively. Liquid–solid separation was achieved *via* centrifugation using a G16-WS benchtop centrifuge.

## Results and discussion

### Crystal structures

Single-crystal X-ray diffraction (SC-XRD) analysis determines that $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ crystallizes in the monoclinic space group $P2_1/m$. The asymmetric unit comprises one Zr atom, one $PO_4$ group, two F atoms, and one $[(CH_3)_2NH_2]^+$ cation (Fig. S1). The Zr center adopts a distorted octahedral geometry, coordinated by four oxygen donors from distinct $PO_4$ groups (Zr–O: 2.054–2.079 Å) and two F atoms (Zr–F: 1.972–2.007 Å). The bond angles span 86.6(3)–93.5(3)° for O–Zr–F and 88.89(10)–91.11(10)° for O–Zr–O, reflecting minor octahedral distortion (Tables S1–S3).

Alternating arrangements of $ZrO_4F_2$ octahedra and $PO_4$ tetrahedra by corner-sharing mode generate a 2D anionic layer of $[Zr(PO_4)F_2]_n^{n-}$, in which each $ZrO_4F_2$ octahedron connects four $PO_4$ tetrahedra and each $PO_4$ tetrahedron links four $ZrO_4F_2$ octahedra (Fig. 1a). It is found that an eight-membered ring (8-MR) window with dimensions 4.63 × 5.04 Å is formed by two Zr atoms, two P atoms, and four O atoms in the anionic layer (Fig. 1b). Charge-balancing $[(CH_3)_2NH_2]^+$ cations are intercalated between adjacent layers (Fig. 1c and d), with an interlayer spacing of 7.60 Å (defined as the shortest perpendicular distance between Zr atom of adjacent anionic layers, as defined in Fig. S1).[39] The relatively big interlamellar spacing and the presence of exchangeable

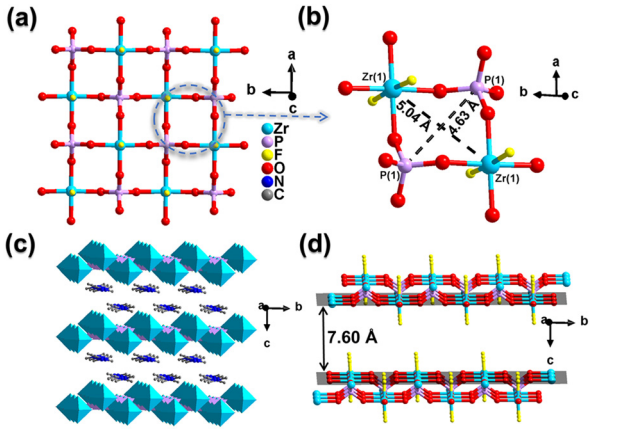


Fig. 1 Crystal structural diagrams for the compound $[(CH_3)_2NH_2][Zr(PO_4)F_2]$. (a) A 2D anionic layer of $[Zr(PO_4)F_2]_n^{n-}$ viewed along the *c*-axis. (b) Ball-and-stick representation of the eight-membered ring in the anionic layer. (c) View of the packing diagram of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ along the *a*-axis. (d) The anionic $[Zr(PO_4)F_2]_n^{n-}$ layers arrangement illustrating interlayer spacing (7.60 Å). Color scheme: Zr (cyan), P (purple), O (red), F (yellow), N (blue), C (grey).

$[(CH_3)_2NH_2]^+$ cations provide the prerequisite for the $Sr^{2+}$ capture *via* the ion exchange way.[40]

### Adsorption isotherms studies

Adsorption isotherm analysis serves as a fundamental methodology for characterizing the surface characteristics and binding affinity of adsorbents, while also determining their maximum adsorption capacity ($q_m^{Sr}$). The actual and theoretical (assuming that all available $[(CH_3)_2NH_2]^+$ is fully exchanged by $Sr^{2+}$) ion-exchange capacity is calculated by eqn (S1) and eqn (S2). The $Sr^{2+}$ ions adsorption capacity of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ was systematically evaluated through equilibrium isotherm studies. Experimental data were modeled using three classical adsorption isotherms: Langmuir (monolayer adsorption), Freundlich (heterogeneous surface), and Langmuir–Freundlich hybrid (multi-mechanism synergy).[41] Nonlinear regression analysis reveals superior correlation for the Langmuir–Freundlich model ($R^2$ = 0.9858) compared to the Langmuir ($R^2$ = 0.9699) and Freundlich ($R^2$ = 0.8467) models (Fig. 2a, Tables S4 and S5, and eqn (S3)–(S5)). This statistical dominance indicates a complex adsorption mechanism involving both monolayer coverage and heterogeneous surface interactions.[41] The derived $q_m^{Sr}$ from the Langmuir–Freundlich model reaches 161.48 mg $g^{-1}$, which is higher than that of some crystalline zirconium-based adsorbents such as zirconium fluorophosphonate $[(CH_3)_2NH_2]_2[ZrC_6H_4(CH_2PO_3)_2F_2]$ (SZ-7, 129.1 mg $g^{-1}$), $[(CH_3)_2NH_2][ZrCH_2(PO_3)_2F]$ (SZ-4, 121 mg $g^{-1}$),[42] and zirconium phosphates such as γ-ZrP (114.78 mg $g^{-1}$), $K_2Zr(PO_4)_2$ (52.83 mg $g^{-1}$), and α-ZrP (43.03 mg $g^{-1}$), as visually compared in Table S6 and Fig. 2b.[20,21,42–46] Furthermore, the title compound $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ also outperforms some other inorganic adsorbents

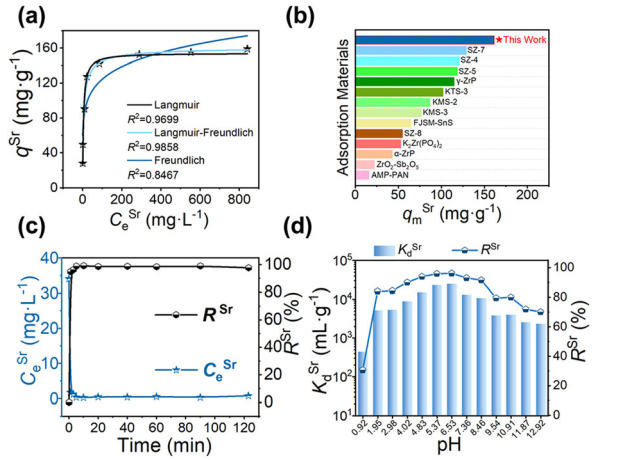


Fig. 2 Adsorption performance diagrams of the compound $[(CH_3)_2NH_2][Zr(PO_4)F_2]$. (a) $Sr^{2+}$ adsorption isotherms of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ fitted by the Langmuir (black line), Langmuir–Freundlich (azure line), and Freundlich (blue line) models. (b) Comparison of the adsorption capacities of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ with other reported inorganic adsorbents for $Sr^{2+}$. (c) The kinetic curves of $Sr^{2+}$ removal rate ($R$) by $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ plotted as the concentration ($C_e$) and $R^{Sr}$ of $Sr^{2+}$ ions *vs.* time (min). (d) Distribution coefficient ($K_d^{Sr}$, columns) and removal rate ($R^{Sr}$, line) at various solutions with different initial pH (0.92–12.92).

such as $K_{2x}Sn_{4-x}S_{8-x}$ ($x$ = 0.65–1) (KTS-3, 102.00 mg $g^{-1}$)[47] and commercial AMP–PAN (16 mg $g^{-1}$).[48]

## Adsorption kinetics studies

The rapid capture capability of an adsorption material for radioactive $Sr^{2+}$ ions is critical in nuclear emergency management. $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ demonstrated exceptional adsorption efficiency, achieving a $Sr^{2+}$ removal rate of 94.89% within 1 min in neutral aqueous solutions ($Sr^{2+}$ concentration: from 34.04 mg $L^{-1}$ to 1.74 mg $L^{-1}$, Fig. 2c, Table S7, eqn (S6)). The current compound approached adsorption equilibrium within a 5 min contact period, achieving remarkable $Sr^{2+}$ removal efficiency ($R^{Sr}$ = 98.88%). We systematically investigated the $Sr^{2+}$ adsorption mechanism of it using pseudo-first-order and pseudo-second-order kinetic models (Table S8, Fig. S2, eqn (S7) and (S8)).[49] Quantitative analysis demonstrated superior correlation with the pseudo-second-order kinetic model.

## pH effect on adsorption

The pH of aqueous solutions critically governs adsorption processes by mediating proton competition and material stability. To systematically evaluate these effects, the removal performance of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ was investigated across a pH range of 0.92–12.92 (Fig. 2d, Table S9, eqn (S9)). The title compound exhibited exceptional adsorption capacities across the pH range of 1.95–8.46, with distribution coefficients ($K_d^{Sr}$) consistently exceeding 5 × $10^3$ mL $g^{-1}$ and $R^{Sr}$ above 83.99%, accompanied by a moderate leaching of Zr (Fig. S3a). The leaching rates of Zr of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ after being immersed in different acidic (pH of 1.95) or alkaline (pH of 11.87) solutions for 12 h were less than 6.60% (Fig. S3a). At pH 1.95–12.92, the layered anionic architecture of $[Zr(PO_4)F_2]_n^{n-}$ is stable, as no phase transition observed by PXRD (Fig. S3b). This indicates that $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ has relatively wide acid–base stability. Under strongly acidic conditions (pH = 0.92), $K_d^{Sr}$ exhibits a substantial reduction to 4.4 × $10^2$ mL $g^{-1}$, possibly attributed to competitive proton exchange, where $H^+$ effectively displaces $Sr^{2+}$ at $[(CH_3)_2NH_2]^+$ sites. Under extreme acidity, concomitantly partially structural degradation of the anionic layers further diminished the ion-exchange capacity.[30] Subsequently, we employed the pH drift method for analysing the pH dependence of adsorption. The ΔpH (= $pH_0$ − $pH_f$) *vs.* $pH_0$ curve shows the $pH_{pzc}$ value of 5.0 (Fig. S3c). It indicates that the surface of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ is positively charged at pH < 5.0 and negatively charged at pH > 5.0. For low pH, the surface of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ favours electrostatic attraction of anions, while for high pH, it favours the attraction of cations.

## Competitive adsorption

The presence of high-concentration competing ions ($Na^+$, $K^+$, $Mg^{2+}$, and $Ca^{2+}$) poses significant challenges for selective $Sr^{2+}$ removal in nuclear wastewater treatment. Thus, we systematically evaluated the $Sr^{2+}$ selectivity of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ under competing ions ($Na^+$, $K^+$, $Cs^+$, $Mg^{2+}$, and $Ca^{2+}$) using separation factor (SF) and distribution coefficient ($K_d$) analyses. Notably, effective SF typically requires values exceeding 100.[50]

Competitive impacts of individual competitive $Na^+$, $K^+$, and $Mg^{2+}$ ions concentrations on $Sr^{2+}$ adsorption by $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ were quantified. At the $Na^+/Sr^{2+}$ molar ratio of 494.4 : 1, it maintains $Sr^{2+}$ removal efficiency of 99.37% ($K_d^{Sr}$ = 1.59 × $10^5$ mL $g^{-1}$, $SF_{Sr/Na}$ = 2219.95), confirming excellent $Na^+/Sr^{2+}$ separation (Fig. 3a, Table S10, eqn (S10)). At the $K^+/Sr^{2+}$ molar ratio of 45.6 : 1, $K_d^{Sr}$ reaches 3.96 × $10^4$ mL $g^{-1}$ with $R^{Sr}$ of 97.54% (Fig. 3b, Table S11). Even under extremely excessive $K^+$ ($C_0^{Sr}$ = 5.57 mg $L^{-1}$, $C_0^K$ = 294.91 mg $L^{-1}$, $K^+/Sr^{2+}$ molar ratio of 118.7 : 1), $K_d^{Sr}$ reaches 2.69 × $10^4$ mL $g^{-1}$ ($R^{Sr}$ = 96.41%). Notably, $SF_{Sr/K}$ surpasses 100, confirming exceptional selectivity for $Sr^{2+}$ over competing $K^+$ ions. At the $Mg^{2+}/Sr^{2+}$ molar ratio of 20.1 : 1, $K_d^{Sr}$ remains 1.17 × $10^5$ mL $g^{-1}$ ($R^{Sr}$ = 99.15%, $SF_{Sr/Mg}$ = 299.98), underscoring $[(CH_3)_2NH_2][Zr(PO_4)F_2]$'s resilience against the interference of alkaline earth metal ions (Fig. 3c, Table S12). However, when the $Mg^{2+}/Sr^{2+}$ molar ratios are more than 211.4 : 1, the $Sr^{2+}$ removal of the current compound is interfered.[51]

Simultaneously, $Sr^{2+}$ selectivity of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ was systematically evaluated in mixed $Na^+$, $K^+$, $Cs^+$, and $Sr^{2+}$ solution and mixed $Cs^+$, $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, and $Sr^{2+}$ solution (Fig. 3d and e, Tables S13 and S14), respectively. In the mixed $Na^+$, $K^+$, $Cs^+$, and $Sr^{2+}$ solution, the material exhibits exceptionally high separation factors ($SF_{Sr/M}$ > 100, M = $Na^+$

 

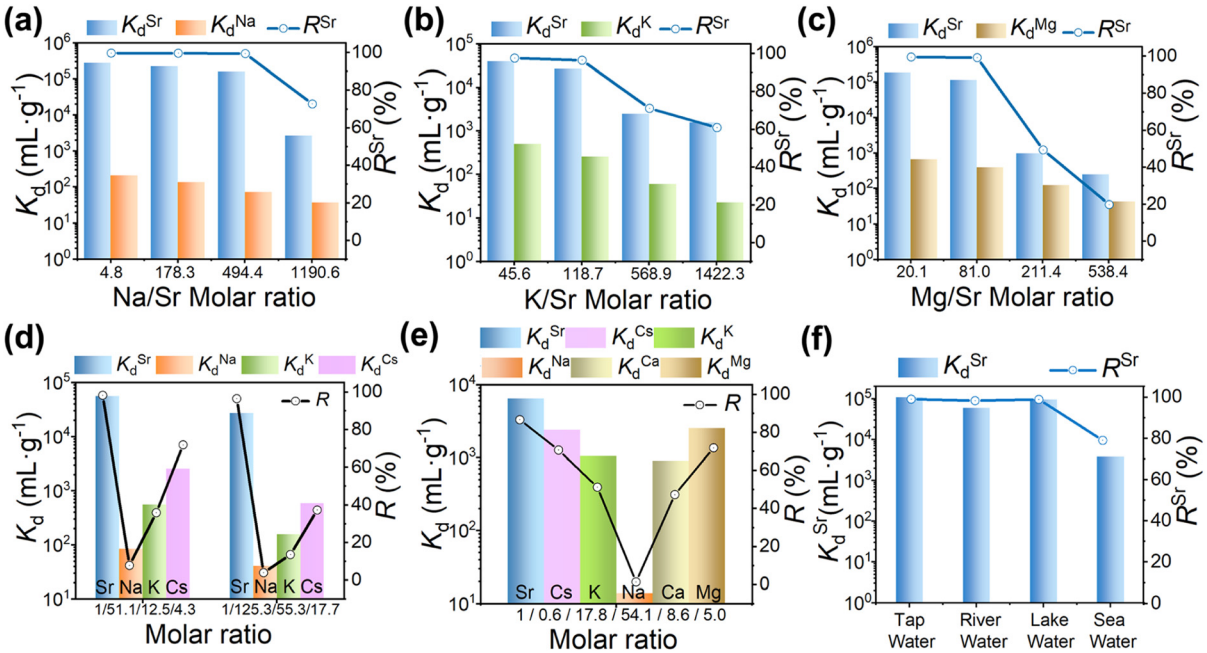


Fig. 3 Selectivity performance diagrams of the compound $[(CH_3)_2NH_2][Zr(PO_4)F_2]$. $K_d$ (columns) for $Sr^{2+}$, $K^+$, $Na^+$, $Mg^{2+}$ and $R^{Sr}$ (line plot) of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ at different molar ratios of Na/Sr (a), K/Sr (b), and Mg/Sr (c). (d) $K_d$ for $Sr^{2+}$, $K^+$, $Na^+$, $Cs^+$ and $R^{Sr}$ of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ in mixed $Na^+$, $K^+$, $Cs^+$, and $Sr^{2+}$ solution at different molar ratios. (e) $K_d$ for various metal ions and $R^{Sr}$ of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ in mixed $Cs^+$, $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, and $Sr^{2+}$ solution. (f) $K_d^{Sr}$ and $R^{Sr}$ of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ in tap water, river water, lake river, and sea water.

and $K^+$) for $Sr^{2+}$ under the presence of monovalent competing ions. $SF_{Sr/M}$ (M = $Na^+$, $K^+$) exceed 668.67 and 173.09 despite the presence of high concentrations for competing ions, whereas $SF_{Sr/Cs}$ is merely 45.66. Nevertheless, in the mixed $Cs^+$, $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, and $Sr^{2+}$ solution, significantly diminished selectivity ($SF_{Sr/M} < 100$, M = $K^+$, $Cs^+$, $Mg^{2+}$, and $Ca^{2+}$) was observed in monovalent and divalent cation matrices. Remarkably, $SF_{Sr/Na}$ values still remain elevated (464.99) with concurrent high distribution coefficient ($K_d^{Sr}$ = $6.44 \times 10^3$ mL $g^{-1}$) and removal efficiency ($R^{Sr}$ = 86.57%).

Significantly, further validation in actual aqueous environments including tap water, lake water, river water, and seawater demonstrates consistently high $R^{Sr}$ values of 99.09%, 98.34%, 98.97%, and 79.06%, respectively, while $K_d^{Sr}$ values exceed $3.78 \times 10^3$ mL $g^{-1}$ without exception (Fig. 3f, Table S15). The removal rate in actual seawater is higher than that of many reported adsorbents, such as $K_2SbPO_6$ ($R^{Sr}$ = 1.17%)[52] and K-HTNs ($R^{Sr}$ = 35%)[53] at $m/V$ = 1 g $L^{-1}$. These results unequivocally establish the maintenance of the removal capacity of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ in complex contaminated matrices.

## Adsorption and desorption

Reusability serves as a critical performance for ion exchange materials. Remarkably, the Sr-loaded phase $[(CH_3)_2NH_2][Zr(PO_4)F_2]$-Sr can be efficiently reused through elution with a 0.5 mol $L^{-1}$ KCl solution. The sample treated with KCl solution is named $[(CH_3)_2NH_2][Zr(PO_4)F_2]$-Sr-K. EDS analysis of the eluted material confirms near-complete substitution of $Sr^{2+}$ by $K^+$ ions (Fig. S4a and b). The eluted material still maintains exceptional $Sr^{2+}$ adsorption capacity ($R^{Sr}$ = 93.80%) over one adsorption–desorption cycle, with high desorption efficiencies ($E^{Sr}$ = 91.47%) (Table S16, eqn (S11)). Structural integrity preservation is verified through PXRD patterns in cycled samples (Fig. S4c). $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ demonstrates reusability capabilities for the sequential capture of $Sr^{2+}$ ions in radioactive waste management.

## Adsorption mechanism

PXRD analysis validates no detectable phase transitions observed upon $Sr^{2+}$ displacement (Fig. S5). Notably, the (002) diffraction peak of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$-Sr shifts toward higher Bragg angles ($\Delta 2\theta$ = 0.46°) according to the Bragg equation. Corresponding SEM characterization reveals well-defined $[(CH_3)_2NH_2][Zr(PO_4)F_2]$-Sr crystals exhibiting pristine morphological integrity, evidenced by defect-free planar facets (Fig. S6).

Based on the above evidences, we hypothesized that this follows the ion exchange mechanism, wherein $[(CH_3)_2NH_2]^+$ cations are displaced by $Sr^{2+}$ (Fig. 4a). To validate this hypothesis, high-resolution XPS analysis of the pristine and Sr-loaded phases was conducted. All XPS spectra were corrected to the C 1s peak of adventitious carbon at 284.8 eV. XPS spectra reveal Sr 3d and P 2p signals overlap at ~133.0 eV in $[(CH_3)_2NH_2][Zr(PO_4)F_2]$-Sr (Fig. 4b),[54] while emergent peaks at 360.0 eV (Sr 3s) and 270.0 eV (Sr 3p) provide unambiguous evidence of strontium integration, accompanied by definitive Sr 3d spectral signatures at

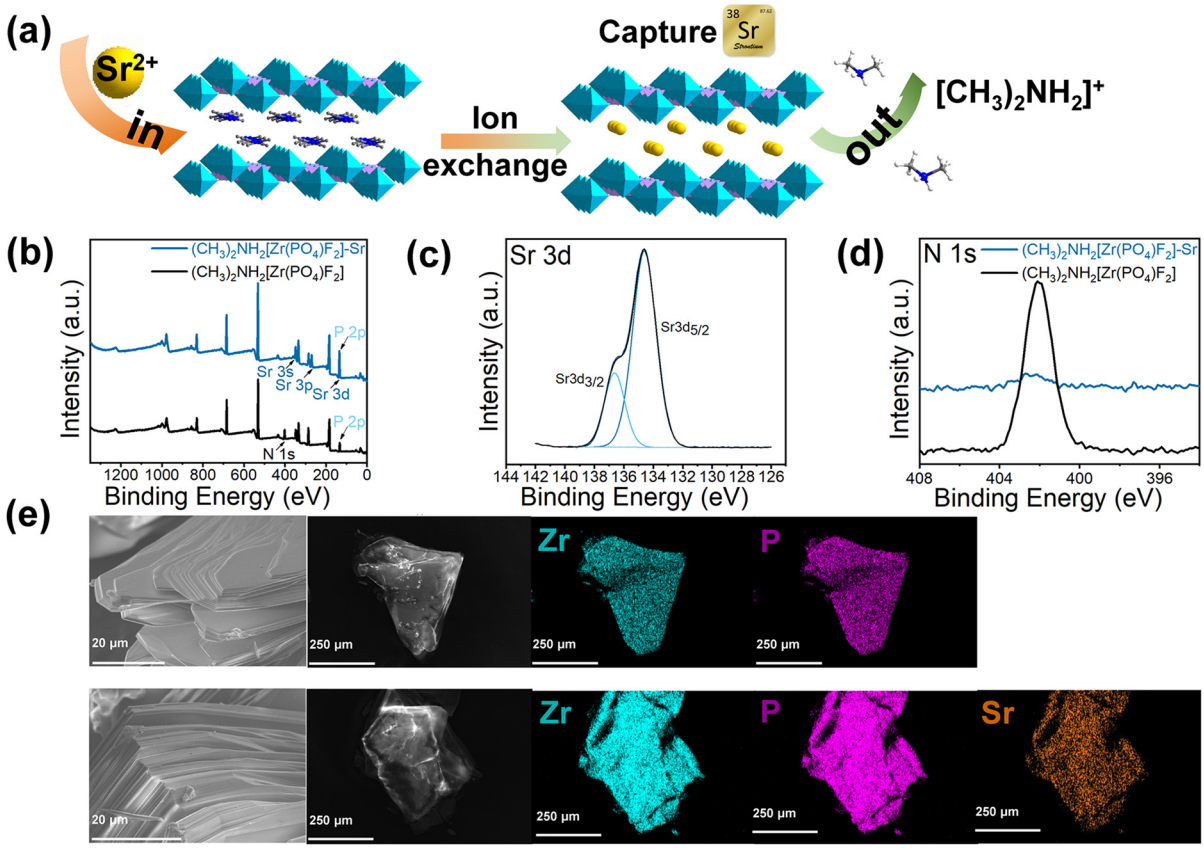


**Fig. 4** Adsorption mechanism diagrams of the compound $[(CH_3)_2NH_2][Zr(PO_4)F_2]$. (a) Mechanistic illustration of $Sr^{2+}$ exchange within the anionic layers of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$. (b) Comparative XPS survey spectra of pristine $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ (black) and $[(CH_3)_2NH_2][Zr(PO_4)F_2]$-Sr (blue). (c) Narrow scan XPS spectrum of Sr 3d of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$-Sr. (d) Narrow scan XPS spectra of N 1s in pristine $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ (black) *versus* $[(CH_3)_2NH_2][Zr(PO_4)F_2]$-Sr (blue). (e) SEM micrographs at magnification of 2.0k, complemented by corresponding elemental distribution profiles of pristine $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ and $[(CH_3)_2NH_2][Zr(PO_4)F_2]$-Sr.

binding energies of 134.6 eV (Sr $3d_{5/2}$), 136.6 eV (Sr $3d_{3/2}$) (Fig. 4c). At the same time, N 1s intensity attenuated at 402.1 eV after $Sr^{2+}$ capture (Fig. 4d). Collectively, these results confirm that $Sr^{2+}$ capture occurs *via* ion exchange between interlamellar $[(CH_3)_2NH_2]^+$ cations and $Sr^{2+}$.

EDS analysis (Fig. S6f) confirmed successful capture of $Sr^{2+}$ ions. Elemental mapping reveals a homogeneous distribution of $Sr^{2+}$ in $[(CH_3)_2NH_2][Zr(PO_4)F_2]$-Sr (Fig. 4e). EA further reveals a concomitant reduction in nitrogen content from 4.83% to 0.43% after $Sr^{2+}$ ion exchange (experimental: C 1.50%, H 2.11%, N 0.43%), quantitatively confirming that $[(CH_3)_2NH_2]^+$ ions have been exchanged during ion exchange. Furthermore, the theoretical ion exchange capacity of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ for $Sr^{2+}$ is calculated as 162.10 mg $g^{-1}$ (eqn (S2)), whereas by experimental measurements the adsorption capacity of $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ for $Sr^{2+}$ is 161.48 mg $g^{-1}$. This indicates that the interlamellar $[(CH_3)_2NH_2]^+$ cations are almost completely exchanged by $Sr^{2+}$ ions.

In simulated nuclear wastewater containing competing ions ($Na^+$, $K^+$, $Cs^+$, $Ca^{2+}$, and $Mg^{2+}$), $(CH_3)_2NH_2[Zr(PO_4)F_2]$ maintained $Sr^{2+}$ removal efficiency. Ion exchange constitutes a stoichiometrically constrained process wherein charge balance is preserved through equivalent substitution of exchanged cations.[55] The $Sr^{2+}$ selectivity of $(CH_3)_2NH_2[Zr(PO_4)F_2]$ may arise from the electrostatic valence-dependency rule: adsorbent affinity scales with cation charge density under constant selectivity coefficients and concentrations of competing cations.[56] Consequently, the $[Zr(PO_4)F_2]_n^{n-}$ anionic layers may exhibit preferential binding toward divalent $Sr^{2+}$ over monovalent $Na^+/K^+$. This material achieves $SF_{Sr/Mg}$ exceeding 100, possibly because the hydrated $Sr^{2+}$ diameter (8.24 Å) is smaller than competing cations ($Mg^{2+}$, 8.56 Å).[51]

Thermodynamics of $Sr^{2+}$ adsorption on $[(CH_3)_2NH_2][Zr(PO_4)F_2]$ was further investigated between 293–353 K (Table S17, Fig. S7). The $K_d$ values increased with temperature, indicating enhanced adsorption affinity at higher temperatures. The thermodynamic parameters were also calculated using the thermodynamic model (eqn (S13)–(S15)).[57,58] Thermodynamic parameters reveal positive $\Delta H^0$ (29.62 kJ $mol^{-1}$) and $\Delta S^0$ (0.18 kJ $mol^{-1}$ $K^{-1}$), confirming an entropy-driven process. Negative $\Delta G^0$ values (−22.10 to −32.55 kJ $mol^{-1}$) demonstrate spontaneous adsorption across the temperature range. The decreasing $\Delta G^0$ with rising temperature further support favourable

 

adsorption at elevated temperatures. Notably, operational expenditure increases at higher temperatures, necessitating balanced temperature selection.

## Conclusions

Here, a new layered zirconium phosphate fluoride ($[(CH_3)_2NH_2][Zr(PO_4)F_2]$) was synthesized hydrothermally. This material achieves a maximum $Sr^{2+}$ adsorption capacity of 161.48 mg $g^{-1}$ (higher than that of many inorganic crystalline adsorbents) and fast kinetics ($R^{Sr}$ = 94.89% within 1 min). It exhibits exceptional pH tolerance (operational range: 1.95–8.46). This material maintains $Sr^{2+}$ removal efficiency in the presence of competing $Cs^+$, $K^+$, $Na^+$, $Ca^{2+}$, and $Mg^{2+}$ ions. Particularly, it can maintain $R^{Sr}$ of 79.06% even in seawater. XPS and thermodynamics confirm that spontaneous $Sr^{2+}$ adsorption occurs through ion exchange with interlayered $[(CH_3)_2NH_2]^+$ cations in the current zirconium phosphate fluoride. This work provides a promising adsorbent for capture of radiostrontium in radioactive waste management.

## Author contributions

Z. Y. Chen: data curation, writing – reviewing and editing, validation, formal analysis, investigation, and software. S. Z. Liu: formal analysis and data curation. S. J. Li: formal analysis. Z. H. Chen: formal analysis and visualization. L. Yang: data curation. S. M. Zhang: data curation. H. Y. Sun: funding acquisition, reviewing and editing, supervision, and project administration. M. L. Feng: conceptualization, funding acquisition, review and editing, visualization, supervision, and project administration. X. Y. Huang: review and editing, and project administration. All authors have read and agreed to the published version of the manuscript.

## Conflicts of interest

The authors declare no conflict of interest.

## Data availability

Supplementary information: experimental section (batch adsorption experiments, equations, crystal structures section, and characterization section), and additional tables (Tables S1–S17) and figures (Fig. S1–S7). See DOI: **https://doi.org/10.1039/D5CE00784D**.

CCDC 2466544 contains the supplementary crystallographic data for this paper.[59]

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