Novel Sn-doped Ammonium Phosphomolybdate: Preparation, Characterization and Adsorption Properties of Cs

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Abstract

With the development of nuclear power, a significant amount of radioactive waste liquid has been generated, among which cesium exhibits high radioactivity and a long half-life, necessitating its removal from waste liquids. In this study, a series of Sn-doped ammonium phosphomolybdate adsorbents were synthesized through chemical coprecipitation for the adsorption of cesium. The incorporation of stannum ions replaced one-third of the inert ammonium ions in ammonium phosphomolybdate, resulting in an increase in the volumetric charge density between molecules and enhanced adsorbent performance. Transmission electron microscopy, scanning electron microscopy, and energy dispersive spectroscopy analyses revealed that while the face-centered cubic crystal structure of the material remained unchanged, the morphology of the microparticles transitioned from cubic to spherical. Based on results from X-ray diffraction, Fourier transform infrared spectroscopy, and thermogravimetric analysis, as well as adsorption capacity and stability tests, the adsorbent SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe), which exhibited the best performance, was selected for further investigation. These investigations included X-ray photoelectron spectroscopy, adsorption selectivity, adsorption–desorption cycles, thermodynamics, isotherms, and kinetics experiments. The results indicated that SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) exhibited excellent selectivity for cesium, with the adsorption process characterized as an exothermic ion exchange reaction, achieving a saturated adsorption capacity of 115 mg/g and maintaining over 85% adsorption efficiency after three cycles. Additionally, density functional theory was employed to further analyze changes in the unit cell dimensions and energy of the material. The results demonstrated that this study successfully developed a novel adsorbent based on the ammonium phosphomolybdate matrix, capable of efficiently and rapidly extracting Cs from radioactive waste liquids. This study also provided new insights for the design and development of inorganic materials.

Full Text

Novel Sn-doped Ammonium Phosphomolybdate: Preparation, Characterization and Adsorption Properties of Cs

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Abstract

With the development of nuclear power, significant quantities of radioactive liquid waste have been generated, among which cesium exhibits high radioactivity and a long half-life, necessitating its removal from waste streams. In this study, a series of Sn-doped ammonium phosphomolybdate adsorbents were synthesized via chemical coprecipitation for cesium adsorption. The incorporation of tin ions replaced one-third of the inert ammonium ions in ammonium phosphomolybdate, resulting in increased volumetric charge density between molecules and enhanced adsorbent performance. Transmission electron microscopy, scanning electron microscopy, and energy dispersive spectroscopy analyses revealed that while the face-centered cubic crystal structure remained unchanged, the morphology of microparticles transitioned from cubic to spherical. Based on results from X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis, adsorption capacity, and stability tests, the adsorbent SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe), which exhibited the best performance, was selected for further investigation. This included X-ray photoelectron spectroscopy, adsorption selectivity, adsorption-desorption cycles, thermodynamics, isotherms, and kinetic experiments. The results indicated that SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) exhibited excellent selectivity for cesium, with the adsorption process characterized as an exothermic ion exchange reaction, achieving a saturated adsorption capacity of 115 mg/g and maintaining over 85% adsorption efficiency after three cycles. Additionally, density functional theory was employed to further analyze changes in unit cell dimensions and energy of the material.

The results demonstrated that this study successfully developed a novel adsorbent based on the ammonium phosphomolybdate matrix, capable of efficiently and rapidly extracting Cs from radioactive waste liquids. This work also provides new insights for the design and development of inorganic materials.

Keywords: Micronano scale, Hybrid, Coprecipitation, Heteropoly salt, Improved stability

1 Introduction

To address the global energy crisis and mitigate environmental pollution, advancements in clean energy technologies have driven continuous progress in the nuclear power industry worldwide [?]. However, the operation of nuclear power plants and the reprocessing of spent nuclear fuel generate substantial quantities of radioactive liquid waste. These wastes contain not only fissile materials such as uranium and plutonium but also significant quantities of fission products including cesium, strontium, palladium, and technetium, which remain highly radioactive [?, ?]. Ensuring the safe and effective treatment and disposal of these liquid wastes is critical for environmental protection, making the separation and recovery of radioactive nuclides a pressing global challenge [?]. Cesium-137 is particularly concerning due to its high radioactivity, significant heat generation, and long half-life [?, ?]. Its chemical properties are similar to those of sodium and potassium, and it exists primarily as cesium ions in aqueous solutions. Cesium exhibits high mobility and bioaccumulation, enabling it to readily enter various environments and eventually accumulate in human bones and muscle tissues [?]. This bioaccumulation can lead to inflammatory diseases and cancers in various organs and cause irreversible damage. Additionally, cesium-137 recovered from radioactive waste liquids can serve as a gamma radiation source for medical applications [?]. Therefore, it is crucial to efficiently and rapidly remove cesium-137 from radioactive wastewater to enable subsequent treatment, minimize environmental and societal harm, and ultimately benefit humanity.

Over the past few decades, various techniques have been developed for cesium separation, including chemical precipitation [?], solvent extraction [?], and ion exchange [?]. While precipitation methods are well-established, they face practical challenges such as difficulties in solid–liquid separation in high-radiation environments. Solvent extraction is currently the most widely used industrial method; however, it carries risks of radiation-induced degradation of solvents and diluents, which can cause severe equipment corrosion and generate substantial quantities of secondary liquid waste.

Ion exchange is an effective partitioning technology due to its high selectivity, large adsorption capacity, simple equipment requirements, and low cost. Various ion exchangers have been studied, including zeolites [?], heteropoly acids [?, ?], ferrocyanides [?], Prussian blue analogs [?], titanium silicates [?], metal sulfides [?], metal-organic frameworks (MOFs) [?], and covalent organic frameworks (COFs) [?]. Among these, ammonium phosphomolybdate (AMP), an inorganic ion exchanger with a Keggin structure composed of [P(Mo3O10)4]3− and ammonium ions, has garnered significant attention. The basic framework of AMP consists of 12 MoO6 octahedra, with $PO4^{3}-$ groups at the center of the crystal structure and ammonium ions occupying interstitial spaces (Fig. 1 [Figure 1: see original paper]) [?, ?]. Cesium adsorption occurs through an ion exchange reaction where ammonium ions in AMP are replaced by cesium ions. Cesium can then be eluted using concentrated NH4Cl solution, enabling its separation and recovery. Furthermore, compared with more expensive adsorbents such as COFs (20.0 USD/g), MOFs (47.2 USD/g), or titanium silicates (12.8 USD/g), AMP is highly economical, costing only 0.40 USD/g as a commercially available reagent.

Studies have demonstrated that synthesizing micro-nano-scale materials or incorporating metal ions into hybrid materials can significantly enhance their mechanical and adsorption properties [?]. Chattopadhyay et al. developed micronano zirconium phosphate, which improved both mechanical properties and cesium separation efficiency in 137Cs–137mBa mixtures [?]. Similarly, Taher Yousefi et al. incorporated cerium into phosphomolybdate, resulting in higher distribution coefficients for ions such as Tl+, Pb2+, Th4+, U4+, and Cs+ and achieving effective multinuclide separation and desorption [?]. Currently, the main methods for preparing micro-nano materials include chemical coprecipitation [?, ?], electrochemical deposition [?], vapor deposition [?], and sol-gel techniques [?].

Chemical co-precipitation is a simple and cost-effective method for efficiently producing large quantities of micro-nano materials. In this study, we synthesized micro-nano-scale metal-hybridized AMP via the chemical co-precipitation technique. During synthesis, various concentrations of Sn2+, Sn4+, and Fe3+ ions were introduced into the base material to achieve metal ion hybridization, resulting in the formation of SnIIxSnIVy(NH4)3-x-y[P(Mo3O10)4] adsorbents with enhanced chemical stability and mechanical properties. The incorporation of metal cations with differing sizes and charges into the Keggin structure of AMP, which replaced ammonium ions, altered the material' s surface lattice charge and channel size. These modifications in surface net charge and channel dimensions significantly influenced the selectivity and adsorption capacity of the adsorbent. Furthermore, variations in total surface charge altered the electrostatic forces (attractive or repulsive) between the adsorbent and target nuclides, resulting in contraction of the unit charge volume. This reduction in unit charge volume enhanced the stability of ion binding and desorption processes, leading to increased adsorption capacity and macroscopic stability [?]. The different valence states of tin ions selected for this study are expected to uniquely influence material performance. Sn4+, with its high charge, is anticipated to significantly enhance material properties, while Sn2+ and Fe3+ are expected to induce copolymerization effects during synthesis [?], promoting the formation of a stable crystal structure in the hybrid material.

Current research on AMP mainly focuses on modifications involving its loading onto various substrates such as silica or alginate beads. However, this approach may reduce adsorption capacity due to challenges such as limited loading efficiency. The objective of this study is to directly hybridize multivalent Sn ions into AMP via a chemical co-precipitation method. This approach aims to modify the microstructure of AMP by increasing charge density per unit volume, which preserves its high adsorption capacity while enhancing overall adsorption performance. The study involves microscopic characterization and adsorption behavior analysis of the synthesized materials to confirm successful preparation of Sn-doped AMP and identify the optimal material for further investigation. Additionally, we aim to analyze the fundamental factors contributing to the enhanced performance of the Sn-doped AMP series through experimental characterization and density functional theory (DFT) simulations. These simulations will model changes in energy structures during synthesis and adsorption processes and provide insight into the adsorption mechanism of cesium by Sn-doped AMP.

2.1 Materials

The chemical reagents used in this study included phosphomolybdic acid (H3[P(Mo3O10)4]), ammonium chloride (NH4Cl), tin dichloride (SnCl2), tin tetrachloride (SnCl4), ferric chloride (FeCl3), cesium nitrate (CsNO3), strontium nitrate (Sr(NO3)2), samarium trinitrate (Sm(NO3)3), lanthanum nitrate hexahydrate (La(NO3)3 · 6H2O), gadolinium nitrate hexahydrate (Gd(NO3)3 · 6H2O), cerium nitrate (Ce(NO3)4), europium nitrate (Eu(NO3)3), dysprosium nitrate hexahydrate (Dy(NO3)3 · 6H2O), holmium nitrate pentahydrate (Ho(NO3)3 · 5H2O), thulium nitrate pentahydrate (Tm(NO3)3 · 5H2O), ytterbium nitrate (Yb(NO3)3), lutetium nitrate pentahydrate (Lu(NO3)3 · 5H2O), potassium niobate (KNbO3), and nitric acid (HNO3). These reagents were procured from Macklin Biochemical Co., Ltd. All reagents had purity greater than 99.5%, except for SnCl4 (98%) and HNO3 (65.0%-68.0%).

2.2 Preparation of the Adsorbent

The SnIIxSnIVy(NH4)3-x-y[P(Mo3O10)4] adsorbents were synthesized via a chemical co-precipitation method, which involved the gradual addition of a hybrid solution containing various components into a soluble solution to ensure uniform mixing and controlled precipitation [**?**]. First, 100 mL of a 0.05 mol/L phosphomolybdic acid solution was prepared in a beaker. A magnetic stirrer was placed in the beaker, and the solution was stirred at 500 rpm. Appropriate amounts of SnCl4, FeCl3, and SnCl2 hybrid element solutions were then added dropwise to the phosphomolybdic acid solution while maintaining stirring for 30 min to ensure complete reaction between the hybrid elements and phosphomolybdic acid. Finally, an adequate amount of NH4Cl solution was added to enhance the crystallization performance of the material. The solid-liquid mixture was allowed to stand and age for 24 h to facilitate full development of the microcrystals of the hybrid material. After aging, the mixture was separated using a water aspirator and Buchner funnel to remove any undeveloped or damaged particles. The material was then washed with deionized water and centrifuged to remove insoluble impurities. Finally, the centrifuged material was dried in a constant-temperature vacuum oven. The resulting adsorbent materials contained various hybrid elements and different hybrid contents. Specific data for each formulation are presented in Table 1 , and undried samples are shown in Figure 2 [Figure 2: see original paper]. (In this study, x and y represent the number of ammonium ions replaced in each AMP molecule.)

2.3 Characterization

The surface morphology was examined using a scanning electron microscope (HITACHI, SU 8600, Japan) and a transmission electron microscope (JEOL, JEM-2100F, Japan). The composition and content of the adsorbent before and after adsorption were analyzed using an energy-dispersive spectroscope (FEI, NOVA NanoSEM 230, America). The unit cell size of the adsorbent was determined using a multifunctional X-ray diffractometer (BRUKER-AXS, D8 ADVANCE Da Vinci, Germany). The functional groups of the adsorbent were characterized using a Fourier transform infrared spectroscope (THERMO FISHER, Nicolet 6700, America). The thermal decomposition of the adsorbent was evaluated using a thermogravimetric analyzer (Perkin Elmer, TGA8000, America). The valence states and proportions of the main elements were investigated using an X-ray photoelectron spectroscope (AXIS Ultra DLD, Shimadzu, Japan).

2.4 Adsorption Experiments

Batch experiments were conducted to investigate the adsorption capacity and characteristics of the synthesized adsorbents for metal ions. First, the adsorption capacity for Cs and the stability of various materials were examined. The optimal hybrid material was then selected for studying multi-ion adsorption selectivity. Additionally, changes in isotherm models at different temperatures for this material were analyzed. Finally, the kinetics of various adsorbents were studied to assess the impact of hybridization on adsorption rates. A specified amount of adsorbent was added to a glass bottle, followed by the experimental solution (with varying metal ion compositions and concentrations). The bottle was sealed and placed in a pre-set temperature-controlled shaking bath for oscillation. After ensuring complete adsorption (except for kinetic tests), the bottle was removed. The mixture was then filtered to separate solid from liquid, and the concentration of target radionuclides in the solution was measured. Unless otherwise specified, experimental conditions were: $V/m = 100\ cm^3/g$, $T = 25°C$, $pH = 7$. The concentrations of Cs and other metal ions were measured using atomic absorption spectroscopy (Shimadzu, AA-660, Japan) and inductively coupled plasma atomic emission spectroscopy (Shimadzu, ICPS-7510, Japan).

2.5 DFT Calculations

Density functional theory is a powerful tool for accurately calculating and predicting the electronic properties of crystal structures. DFT avoids the need to solve complex multibody Schrödinger equations by assuming that the energy of the system can be expressed as a function of electron density, which significantly reduces computational load and saves time. In this study, DFT was employed to analyze the adsorption process and mechanism of the hybrid adsorbent for Cs. All calculations were performed using the Vienna Ab Initio Simulation Package (VASP 6.2) with plane-wave spin-polarized periodic DFT methods. The projector augmented wave method was used to describe electron–ion interactions, and electron exchange and correlation energies were treated using the Perdew-Burke-Ernzerhof generalized gradient approximation functional. A cutoff energy of 500 eV was applied, and the gamma grid was used for Brillouin zone sampling. First, the AMP model was optimized [**?**], with a force convergence threshold set to less than 0.05 eV/Å. Subsequently, single-point energies of the system were calculated, with total energy convergence set to less than 10^{-6} eV.

3.1 SEM, TEM, and EDS

The microstructure of AMP and the SnIIxSnIVy(NH4)3-x-y[P(Mo3O10)4] series was initially examined via scanning electron microscopy (SEM). According to the SEM results, the synthesized AMP predominantly exhibited a cubic structure (Fig. 3a1 [Figure 3: see original paper]), with most particles displaying surface defects that impair the mechanical properties of the material. After hybridizing with Sn(IV) alone (Fig. 3a2), the unit volume charge of the material increased, which enhanced the central attraction toward the outer surface and reduced surface defects on microscopic particles. When hybridized with Sn(II) alone (Fig. 3a3), the increase in unit volume charge was smaller, and due to the absence of Fe, complete particles did not form because of the lack of copolymerization effects. Therefore, further investigation of this material will not be pursued. When Sn(IV) and Sn(II) were added simultaneously but without Fe (Fig. 3a4), the material exhibited reduced defects, and microscopic particles transitioned from a cubic to a spherical structure under the high unit volume charge. Finally, when Fe was added alongside Sn(IV) and Sn(II) (SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] add Fe) (Fig. 3a5), the copolymerization effect between Sn(II) and Fe(III) enhanced the crystallinity of the material, resulting in well-formed spherical particles with intact surfaces and significantly improved mechanical properties. After adsorption of cesium ions, the microscopic spheres of SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) (Fig. 3a6) showed no significant changes, indicating that the material retained its stable fundamental structure throughout the adsorption process.

The SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) hybrid material, which featured spherical microparticles, was further analyzed via transmission electron microscopy (TEM). The TEM images revealed distinct lattice fringes with no noticeable disruptions or displacements, and the consistent spacing between parallel fringes confirmed a typical face-centered cubic unit cell structure. The lattice spacing within the unit cell was uniformly distributed. The lattice spacing of the sample was determined to be 2.55 Å by measuring and averaging the spacing between multiple sets of parallel fringes (Fig. 3b5). Additionally, Figure 3b4 displays uniform reflection rings produced by the numerous brightened nanoscale grains of SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe), as observed through selected area electron diffraction.

Energy dispersive spectroscopy (EDS) analysis was conducted on SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) to examine the elemental composition and proportions before and after adsorption. Surface scanning results (Figure 3c1 and Figure 3c2) confirmed the presence of Sn both before and after adsorption, while Cs was detected only post-adsorption. These findings suggested that Sn was successfully hybridized into AMP and that the hybridized adsorbent retained its Cs adsorption capacity. In addition, there was no significant change in Sn content or energy relative to Mo, indicating that Sn does not directly react with Cs. Line scan results (Figures 3c3 and 3c4) revealed good overlap of characteristic peaks for Sn and Cs after adsorption and demonstrated that both elements coexisted in a similar form within the material and that a substitution reaction with ammonium ions occurred [**?**].

3.2 Sn-doped-AMP

To identify the optimal hybrid adsorbent, a series of microstructural characterizations and batch adsorption experiments were performed on the Sn-doped AMP materials.

The crystalline structure of AMP and Sn-doped AMP was analyzed using X-ray diffraction (XRD). The relative intensity and distinct peaks confirmed good crystallinity of the products (Fig. 4a1 [Figure 4: see original paper]). For Sn-doped AMP, the diffraction peaks shifted to the right compared with those of AMP in the order of Sn(II) > Sn(II) + Sn(IV) > Sn(IV). This shift indicated a reduction in lattice constants, attributed to the smaller ionic radii of the hybrid elements compared with ammonium ions (ionic radii: $NH4^+$, 0.143 nm; Sn^{2+}, 0.093 nm; Sn^{4+}, 0.069 nm). Additionally, the higher ionic charge of the hybrid elements further reduced the unit cell volume. The formation of Sn(II)-O-Sn(IV) bonds might also contribute to the peak shift and contraction of the unit cell volume. As shown in Figure 4a1, the sample containing added Fe exhibited sharper diffraction peaks, highlighting improved crystallinity due to the copolymerization effect of Fe(III) and Sn(II).

Furthermore, the effect of various hybrid concentrations ($NH4^+$ substitution ratios) on the structure of Sn-doped AMP was analyzed. Figure 4a2 demonstrates that within a specific range of hybrid concentrations, the peak intensity of the samples increased with rising concentrations, indicating that the hybrid elements promote crystal growth. According to the width and intensity of the diffraction peaks, the Scherrer equation was applied to calculate the average grain size of the samples [**?**]:

$$D = \frac{0.89\lambda}{\beta \cos\theta}$$

where D represents the average grain size, λ denotes the wavelength of the incident X-rays, β refers to the full width at half maximum of the diffraction peak, and θ indicates the diffraction angle. According to the Scherrer equation, AMP samples exhibited an average particle size of 73.5 nm, while hybridized samples showed a reduced average particle size ranging from 55 nm to 65 nm, indicating a noticeable decrease in particle size due to hybridization.

Figure 4b shows the Fourier transform infrared spectroscopy (FT-IR) analysis results for AMP and Sn-doped-AMP samples. Both AMP and Sn-doped-AMP exhibited characteristic peaks at 1063 cm^{-1} (O=P-OH groups), 965 cm^{-1} (Mo-O absorption), 868 cm^{-1} (Mo-O-Mo absorption), and 765 cm^{-1} (antisymmetric stretching vibration of $PO4^{3-}$), confirming that the Keggin structure of the hybridized samples remained intact. Some samples displayed a bending vibration peak of H-O-H at 1630 cm^{-1} and a stretching vibration peak of H-O-H at 3210 cm^{-1}, attributed to insufficient drying and the presence of crystallization water. Additionally, the N-H bending vibration peak at 1385 cm^{-1} confirmed the presence of ammonium ions in the samples, which contributed to enhanced material crystallinity. Notably, after adsorption, the intensity of the N-H bending vibration peak decreased relative to the characteristic O=P-OH group peak and the Keggin structure peak of $[PMo12O40]^{3-}$ in the infrared spectra. This decrease indicated a reduction in ammonium ion content, suggesting their involvement in the adsorption process.

In the infrared spectra of the Sn-doped-AMP samples, a characteristic peak for Sn at 2976 cm^{-1} was observed. This peak remained detectable after adsorption, confirming the successful hybridization and stability of metal ions within the material as they did not detach during adsorption. Lastly, although the functional groups of the samples were similar, Sn-doped-AMP exhibited a shift toward lower wavenumbers, attributed to structural changes induced by hybridization and consistent with the XRD results.

Figure 4c and Table 2 present the thermogravimetric analysis (TGA) results for AMP and Sn-doped-AMP, which showed that all four materials underwent three stages of decomposition. The first stage involved weight loss due to release of crystalline water from the material. The second stage corresponded to decomposition of ammonium ions into NH3 gas. In this stage, AMP exhibited a weight loss of 2.58%, while Sn-doped-AMP showed a weight loss of approximately 1.6%, which aligned with theoretical values of 2.79% and 1.76%, respectively. The final weight loss stage resulted from decomposition of phosphomolybdic acid into phosphorus and molybdenum compounds, leading to destruction of the Keggin structure and loss of cesium adsorption capability. Despite similar pyrolysis processes, the thermal stability of the materials improved following hybridization. Notably, the SnIV1(NH4)2[P(Mo3O10)4] sample began releasing ammonia only at 765°C, whereas AMP initiated ammonia release at 710°C.

A comparison of adsorption capacities of various adsorbents was conducted. Adsorption capacity experiments involved using 50 mg of each hybridized material with a 1200 ppm Cs aqueous solution (Fig. 4d). At low $NH4^{+}$ substitution ratios, the main components of the samples from various hybrid formulations still showed a high degree of similarity to AMP, resulting in adsorption capacities comparable to those of AMP. However, the adsorption capacity of all materials increased with doping amount, except for those hybridized with Sn(II) alone. Linking this with the SEM results, the increase in adsorption capacity can be attributed to the transition of the material' s microstructure from cubes to polyhedra and eventually to spheres, leading to an increase in specific surface area. Compared with AMP, SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) exhibited the highest adsorption capacity of 106.8 mg/g, representing an increase of approximately 10%. In contrast, the decreased adsorption capacity of Sn(II)-doped AMP could be attributed to the presence of Sn(II) alone, which lacked the high charge of Sn(IV) to enhance material performance and did not form a stable crystal configuration through copolymerization with Fe(III).

Stability is a crucial factor for practical material applications. To assess this, chemical stability experiments were conducted on several hybrid materials with good adsorption capacities by immersing the materials in distilled water and measuring the Mo leaching rate at various time intervals. SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) demonstrated excellent stability, with Mo leaching rates of 0.69% and 1.18% after 1 and 3 days, respectively (Fig. 4e). These values were significantly lower than those of AMP, indicating that the copolymerization effect of Sn^{2+} and Fe^{3+} during synthesis enhanced crystallization of the hybrid material. Additionally, the high charge and small volume of Sn^{4+} reduced the unit charge volume and further improved material stability. This improvement in stability also reduced leakage of metal ions during practical application, which is beneficial for environmental protection.

Based on these experimental results, SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe), which retained the effective Keggin structure and exhibited good thermal stability, demonstrated the highest adsorption capacity and excellent chemical stability among the various Sn-doped-AMP materials. Therefore, it was selected as the hybrid material for subsequent in-depth research.

3.3 SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) Hybridized Material

X-ray photoelectron spectroscopy (XPS) analysis was conducted to investigate the adsorption mechanism of Cs on SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe). Figure 5a1 [Figure 5: see original paper] shows the full spectrum of SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) before and after Cs adsorption. Distinct Cs 3d peaks were observed, confirming successful adsorption of Cs onto the hybrid material. Additionally, no Fe-related peaks were detected in the full spectra before or after adsorption. This absence was attributed to the small ionic radius of Fe(III), which might prevent it from forming stable products with the Keggin structure of AMP. Further peak deconvolution of the main elements revealed no significant changes in their binding energies.

Figures 5a2 and 5a3 present the high-resolution Mo 3d spectra. Before adsorption, the binding energies for Mo were 233.11 eV and 236.26 eV (Mo^{6+}), as well as 232.19 eV and 235.27 eV (Mo^{5+}), with corresponding proportions of 51.17%, 35.30% (Mo^{6+}) and 8.00%, 5.52% (Mo^{5+}), respectively. After adsorption, the binding energies shifted to 232.72 eV and 235.87 eV (Mo^{6+}), and 231.53 eV and 234.76 eV (Mo^{5+}), with proportions of 53.27%, 36.72% (Mo^{6+}), and 5.93%, 4.09% (Mo^{5+}), respectively. The binding energies and peak area proportions for the various valence states of Mo showed no significant changes, indicating that no redox reactions involving Mo occurred during the adsorption process.

Figures 5a4 and 5a5 present the high-resolution Sn 3d spectra. Before adsorption, the binding energies for Sn were 487.25 eV and 495.66 eV (Sn^{2+}) and 487.49 eV and 496.10 eV (Sn^{4+}), with proportions of 28.23%, 19.55% (Sn^{2+}) and 31.33%, 20.89% (Sn^{4+}), respectively. After adsorption, the binding energies shifted to 486.85 eV and 495.25 eV (Sn^{2+}) and 487.39 eV and 495.79 eV (Sn^{4+}), with proportions of 23.77%, 16.46% (Sn^{2+}) and 35.69%, 24.08% (Sn^{4+}), respectively. Similar to the Mo results, the binding energies and peak area proportions of the various valence states of Sn showed no significant changes, confirming the absence of redox reactions involving Sn during the adsorption process. Combined with the IR spectroscopy results, it can be concluded that the adsorption mechanism of Cs on SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) primarily involved an ion-exchange reaction.

Radioactive wastewater contains various metal ions that often interfere with each other during industrial processes, leading to reduced adsorption capacity of the adsorbent for target radionuclides [**?**]. Therefore, it is essential to assess the adsorption selectivity of SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe). This material was introduced to mixed ion solutions at different pH values, and adsorption capacity curves for various ions were plotted (Fig. 5b1 [Figure 5: see original paper]). In mixed solutions at different pH values, SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) demonstrated high adsorption capacity for Cs, with almost no adsorption of other metal elements in the solution (e.g., Sr, Eu). This result indicated that SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) retained good adsorption selectivity for cesium under various conditions. Additionally, as pH decreased, the adsorption capacity of SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) decreased, mainly due to competition between H^+ and Cs^+ during the adsorption process.

The point of zero charge (PZC) pH value of SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) was measured via the mass titration method [**?**]. As shown in Figure 5b2 [Figure 5: see original paper], the PZC of SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) is 4.91. When the solution pH was lower than 4.91, a large amount of H^+ ions accumulated on the adsorbent surface. These high concentrations of H^+ ions could electrostatically interact with metal cations and reduce the adsorption capacity of the material [**?**, **?**].

To evaluate the effect of temperature on the adsorption process, the thermodynamic parameters of the adsorption reaction were calculated using the Van ' t Hoff equation:

$$\ln K_d = \Delta G = \Delta H - T\Delta S$$

As shown in Figure 6a [Figure 6: see original paper], the K_d values at different temperatures were fitted to the Van ' t Hoff equation, yielding a correlation coefficient (R^2) of 0.9623. Further analysis of the fitted equation provided the thermodynamic parameters—standard enthalpy (ΔH), standard entropy (ΔS), and Gibbs free energy (ΔG)—for this adsorption experiment, as presented in Table 3 .

Table 3 The thermodynamic parameters of SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe)

Temperature	ΔH (kJ/mol)	ΔS (kJ/mol · K)	ΔG (kJ/mol)

From the table, it can be observed that the ΔH value is negative, indicating that the reaction is exothermic. The negative ΔS value suggested that the driving force of the reaction decreased with increasing temperature, meaning the K_d value decreased as temperature rose [**?**]. Additionally, calculations revealed that the ΔG values for the adsorption reaction remained negative up to 215.48°C.

Adsorption isotherms illustrate the relationship between the amount of adsorbate adsorbed by the adsorbent at equilibrium and the concentration of the target radionuclide in solution. These isotherms can be used to identify specific adsorption mechanisms and calculate the saturated adsorption capacity of the adsorbent.

The Langmuir model assumes that the adsorption reaction is a monolayer adsorption process with constant adsorption energy. The fitting equation is:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$$

where Q_e is the adsorption capacity, Q_m is the maximum adsorption capacity, C_e is the equilibrium concentration of Cs in the solution, and K_L is the Langmuir constant.

The Freundlich model assumes that adsorption occurs on a heterogeneous adsorbent surface with multiple layers. The fitting formula is:

$$Q_e = K_F C_e^{1/n}$$

where K_F is the Freundlich constant, and $1/n$ is the Freundlich isotherm coefficient.

The Temkin model accounts for adsorbate-adsorbate interactions and assumes that adsorption energy decreases linearly as surface coverage increases. The fitting formula is:

$$Q_e = \frac{RT}{b_T} \ln(K_T C_e)$$

where R is the gas constant, T is the absolute temperature, K_T is the Temkin isotherm equilibrium binding constant, and b_T is the Temkin isotherm constant related to the heat of sorption.

The Dubinin-Radushkevich (D-R) model assumes that the adsorption process follows a porous filling mechanism with a Gaussian distribution of adsorption energies. The fitting equation is:

$$\ln Q_e = \ln Q_m - K_D \varepsilon^2$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right)$$

$$E = (2K_D)^{-1/2}$$

where K_D is the Dubinin-Radushkevich constant, ε is the Polanyi potential, and E is the adsorption energy.

Table 4 The parameters of Adsorption Isotherms of SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe)

Experimental Temperature	Isotherm Model	Estimated Isotherm Parameters (H_2O, pH=7)

The nonlinear Langmuir and Freundlich fitting results for the hybrid materials at different temperatures are shown in Figure 6b1 [Figure 6: see original paper], with estimated isotherm parameters listed in Table 4. For all temperature conditions, the Langmuir model consistently provided better fits, with correlation coefficients (R^2) exceeding 0.975. This suggested that the adsorption process of SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) followed a monolayer adsorption mechanism. According to the Langmuir isotherm model fitting, the maximum adsorption capacities of SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) at 25°C, 35°C, and 45°C were 115.00 mg/g, 108.78 mg/g, and 102.06 mg/g, respectively. These values indicated that SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) possessed significant adsorption capacity over a wide temperature range, demonstrating its effectiveness in purifying Cs from radioactive wastewater. Moreover, the maximum adsorption capacities obtained from the model fit at different temperatures were in close agreement with experimental results, further validating the suitability of the Langmuir isotherm model.

However, in some cases, the best-fit model for adsorption materials cannot be determined solely by R^2, which might introduce ambiguity [**?**]. The Langmuir isotherm model suggested that monolayer, uniform adsorption dominated under non-competitive equilibrium conditions. In contrast, the Freundlich isotherm model mainly examined the adsorption mechanism through the K_F and $1/n$ values, which helped infer the favorability of metal ion adsorption onto the adsorbent [**?**]. The Freundlich model fitting results indicated that the $1/n$ values for SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) at different temperatures fell within the range of 0.1–1.0, specifically 0.21 (25°C), 0.20 (35°C), and 0.20 (45°C), which are considered favorable for adsorption.

For the Temkin model (Fig. 6b2 [Figure 6: see original paper]), the correlation coefficient for SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) at different temperatures was greater than 0.97, indicating a high level of accuracy for this model. The value of b_T was greater than 1, suggesting that the reaction was endothermic and aligned with the thermodynamic results [**?**]. In the D-R model (Fig. 6b3 [Figure 6: see original paper]), the average adsorption energy (E) for SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) was approximately 1000 kJ/mol, which is significantly higher than 8 kJ/mol and indicates that the adsorption of Cs involved the breaking and reorganization of molecular bonds, characteristic of a chemisorption process [**?**].

The surface characteristics of the adsorbent directly influence the adsorption rate, primarily due to the significant effect of diffusion resistance on ion transport during adsorption. To describe the change in adsorption of the target nuclide over time, we selected the pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models, which correspond to physical and chemical adsorption, respectively.

The PFO kinetic model is based on membrane diffusion theory and a physical adsorption model. The expressions for the nonlinear and linear PFO kinetic models are as follows:

$$q_t = q_e(1 - e^{-k_1 t})$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

where k_1 is the adsorption rate constant for the PFO kinetic model, and q_t and q_e are the adsorption capacities of the adsorbent for the target nuclide at time t and equilibrium, respectively.

The PSO kinetic model represents a chemical adsorption process where electrons are shared or transferred between the adsorbate and adsorbent. The expressions for the two forms of the PSO kinetic model are as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where k_2 is the adsorption rate constant for the PSO kinetic model, and q_t and q_e represent the adsorption capacities of the adsorbent for the target nuclide at time t and equilibrium, respectively.

Figures 6c1 and 6c2 [Figure 6: see original paper] show the adsorption rates of AMP and SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe), along with fitted curves for the PFO and PSO models. As observed, the adsorption of AMP and SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) achieved uptake ratios of over 96% within 1 minute and reached equilibrium quickly. This indicates that after hybridization, SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) retains the extremely high adsorption rate of AMP while improving its adsorption capacity. Table 5 presents the parameters of the fitted curves for AMP and SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe). Both materials were best described by the PSO kinetic model, with correlation coefficients greater than 0.99. This suggested that the adsorption process of the hybrid materials was chemical in nature, which aligned with the XPS measurement results. Additionally, the PSO kinetic parameters of the hybrid materials were similar to those of AMP, indicating that hybridization did not alter the kinetic properties of the material, which still retained a high adsorption rate. According to the fitting results, the equilibrium adsorption capacities of AMP and SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) under these conditions were in close agreement with experimentally measured values, confirming the accuracy of the model.

Furthermore, this study investigated particle diffusion during the adsorption process of SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) using the intraparticle diffusion model (IPD). The equation for the intraparticle diffusion model is as follows:

$$q_t = K_I t^{1/2} + C$$

where K_I is the IPD constant and C is the constant associated with the IPD, which is proportional to the boundary layer thickness.

Table 5 The parameters of Kinetic Models of AMP and SnIIxSnIVy(NH4)3-x-y[P(Mo3O10)4] series

Sample	Kinetic Models	Estimated Kinetic Parameters (25°C, H_2O, 1500 ppm Cs)

As shown in Figure 6c3 [Figure 6: see original paper], the adsorption processes of SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) and AMP for Cs can be mainly divided into two stages. The first stage is the relatively steep surface diffusion stage, during which Cs rapidly adsorbed onto the surface of SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe). However, it is noteworthy that the curve does not pass through the origin, indicating that internal diffusion is not the sole factor controlling the adsorption process [**?**]. The second stage is the more gradual internal diffusion stage, where, due to occupation of a large number of adsorption sites on the surface and within the pores of SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe), the adsorption process transitions to diffusion within the particles, resulting in a significant decrease in adsorption rate and ultimately reaching equilibrium [**?**, **?**].

Desorption performance and reusability are crucial parameters for evaluating the effectiveness of adsorbents. In this experiment, a 500 ppm Cs solution was used for adsorption, and 3M NH4Cl was employed as the desorbent. The adsorption–desorption experiments were conducted at pH 7. After each adsorption, the adsorbent was immersed in 3M NH4Cl for desorption, followed by a new adsorption cycle. This process was repeated for a total of four cycles.

As shown in Figure 6d [Figure 6: see original paper], the desorption rate did not reach 100% after each cycle, leading to a gradual decline in adsorption efficiency of SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe). However, both the desorption rate in the third cycle and the adsorption rate in the fourth cycle remained above 85%, indicating that SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) exhibited good reusability and could meet the demands of practical industrial applications.

3.4 DFT Analysis

DFT simulations were performed to model the molecular structure of the synthesized hybrid materials and calculate their energy changes. First, the adsorption process was simulated by systematically replacing ammonium ion sites in AMP with other ions. When Fe atoms were introduced as substitutes, the model results failed to converge, indicating that Fe could not directly react with AMP. This finding aligned with microscopic characterization results obtained from EDS and XPS. A series of initial model structures for the hybrid materials were obtained by substituting ammonium ions with Sn atoms (Fig. 7 [Figure 7: see original paper]). Table 6 lists the crystal structural parameters of AMP and SnIIxSnIVy(NH4)3-x-y[P(Mo3O10)4] after optimization. Calculations were performed to determine the cell parameters of each material, energy changes during synthesis, and energy changes during the adsorption process. Static calculations were conducted on energy changes to obtain the total free energy changes for each system.

Table 6 Calculation of cell parameters by DFT

Number of Sn	AMP-Sn1	AMP-Sn2	AMP-Sn3	V(Å^3)

Table 7 Calculation of energy by DFT

System	Atom Energy	Free Energy	Binding Energy	Adsorption Energy
AMP-Sn1				
AMP-Sn2				
AMP-Sn1-Cs1				
AMP-Sn1-Cs2				
AMP-Sn2-Cs1				

The energy calculation formulas are as follows:

$$E_{\text{binding}} = E_{\text{free}} - E_{\text{atom}}$$

$$E_{\text{adsorption}} = E_{\text{binding}} + xE_{\text{binding}}(\text{NH}_4^+) - E_{\text{binding}}(\text{AMP}) - xE_{\text{atom}}(\text{Cs})$$

According to the DFT calculation results, when Sn ions replaced ammonium ions, the cell size of the crystals decreased, with simulation results aligning with experimental findings. Additionally, based on the energy calculation results in Table 7, the substitution of Sn was a spontaneous exothermic reaction. The binding energy was lowest when only one Sn ion was substituted, indicating that this configuration was the most stable. However, during subsequent adsorption processes, if two ammonium ions were replaced by Sn ions during synthesis, the reaction became endothermic and could not proceed spontaneously. Therefore, it was crucial to strictly control the Sn concentration and solution drop rate during synthesis of hybrid materials to ensure optimal hybridization conditions. According to previous research conducted by our group, two-thirds of the active ammonium ions in AMP underwent ion exchange reactions [**?**]. The hybrid material demonstrated optimal adsorption performance when one-third of the ammonium ions were substituted. This suggested that the non-active ammonium ions in AMP could be replaced by the hybrid element, which enhanced the stability and mechanical properties of the material while maintaining its adsorption capacity.

4 Conclusion

In this study, a series of Sn-doped AMP adsorbents were successfully prepared via the chemical co-precipitation method for efficient removal of cesium from radioactive waste solutions. Through various characterizations, the best-performing adsorbent, SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe), was selected, and its adsorption mechanisms and performance were further investigated in detail. The SnII0.5SnIV0.5(NH4)2[P(Mo3O10)4] (add Fe) exhibited excellent chemical stability, adsorption selectivity, and reusability for Cs. The adsorption of Cs follows an exothermic, monolayer chemisorption process, with a saturated adsorption capacity of 115 mg/g. DFT simulations revealed that following hybridization, Sn replaced an inactive ammonium ion in AMP and enhanced the performance of the remaining two active ammonium ions and hybrid molecules. This process improved both the stability and adsorption performance of the material. This work provides an effective approach for designing high-performance adsorbents for Cs separation. In addition, to meet the requirements of the hybrid material, more stringent synthesis control is needed, such as types of hybridizing agent, reaction rate, aging time, and so on.

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