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The novel composite mechanism of ammonium molybdophosphate loaded on silica matrix and its ion exchange breakthrough curves for cesium

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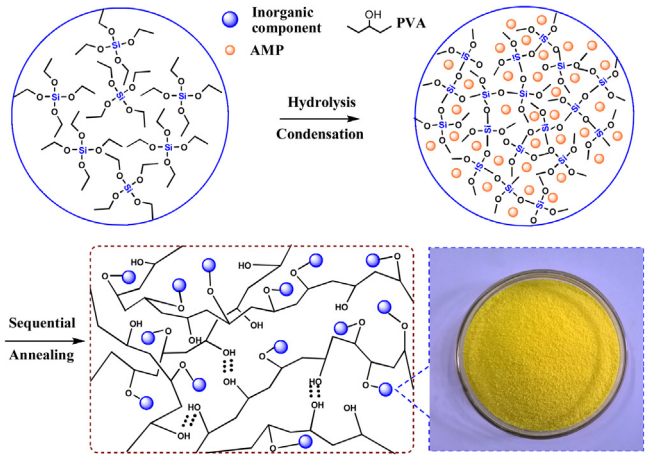
HIGHLIGHTS

- The granular composites were fabricated by the sequential annealing mechanism.
- The method controls the porous characteristics and stable structure of materials.
- The breakthrough curve of Cs^+ follows the Thomas model with a high removal rate.
- It is a probable for SM-AMP20 to recycle Cs^+ using an eluent of 2–3 mol/L NH_4NO_3.

GRAPHICAL ABSTRACT



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ABSTRACT

Long-lived ^{137}Cs (over 30 years), a byproduct of the spent fuel fission processes, comprises the majority of high-level and prolific heat-generating waste in downstream processing. This study reports a novel sequential annealing mechanism with cross-linked network of polyvinyl alcohol, fabricating the composite of ammonium molybdophosphate loaded on silica matrix (SM-AMP20, 20 wt% AMP) as an excellent granular ion exchanger for removal Cs^+. When the matrix is remarkably sequential annealed, well-dispersed SM-AMP20 particles are formed by firmly anchoring themselves on controlling the porous characteristics and stable structure. The material crystallizes in the complex cubic space group *Pn*-3*m* with cell parameters of crystalline AMP formation. The breakthrough curve of Cs^+ by SM-AMP20 follows the Thomas model with a high removal rate of 88.23% (~10 mg/L of Cs^+) and breakthrough time as high as 26 h (flow rate $Q \approx 2.5$ mL/min and bed height $Z \approx 11$ cm) at neutral pH. We also report on sorbents that could efficiently remove Cs^+ ions from complex solutions containing different competitive cations (Na^+,

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Al^{3+}, Fe^{3+}, and Ni^{2+}, respectively) in large excess. Furthermore, this study shows that there is a probability for SM-AMP20 to recycle cesium using an eluent of 2–3 mol/L NH_4NO_3 solution.

1. Introduction

Radioactive waste remediation, the safe disposal of spent fuel, has attracted wide attention from research institutions and governments around the world. High-level liquid waste (HLW) is an especially primary emission of radioactive waste in the well-known PUREX downstream processing, which accumulates the more than 95% radioactivity of the spent fuel and contains 0.5–0.25% of the remnants of U and Pu, minor actinides (Np, Am, Cm) and long-lived fission products (^{99}Tc, ^{129}I, ^{79}Se, ^{93}Zr, ^{137}Cs) [1].

Of the non-actinide fission products (such as the liquid waste after TRPO process of the remediation of HLW in China [2]), one of the most hazardous and prolific heat-generating is ^{137}Cs [3]. These radionuclides are the chief biohazard in nuclear waste, producing γ and high energy β particles [4]. ^{137}Cs of long half-life ($t_{1/2}$ = 30 years), nevertheless, could be also used as a radiation source for the corresponding possible application to industrial, agricultural and medical [5,6]. Thus, developing effective techniques for the separation and uptake of ^{137}Cs from radioactive liquid waste is indispensable for the sustainable development of nuclear power. In view of secondary waste volume and disposal costs of such waste solutions, the reversible ^{137}Cs uptake of inorganic ion exchanger has generally been considered more preferable to solvent extraction [7], organic ion exchange resins [8] and irreversible geological immobilization [9].

Among the previously developed inorganic ion exchangers, ammonium molybdophosphate (AMP) is used as an ion exchanger with excellent selectivity for monovalent cations in strong acidity [10]. But it does not directly apply to column operation because of its micro-crystalline structure and fine powder morphology [11]. SM-AMP was developed by several works [12–14] combining silica matrix (SM) with ammonium molybdophosphate (AMP). Several researchers have demonstrated that SM-AMP is an effective adsorbent for removing ^{137}Cs from acidic and high salted radioactive waste stream through both batch and column tests [12–15]. Younjin Park et al. [12] reported that the AMP at a loading of 50 wt% supported on SBA-15 showed a high ion exchange capacity (70.9 mg/g) with the negligible influence of coexisting cations (Na^+, K^+ and NH_4^+) and acidity (0–2.5 mol/L HNO_3) for Cs ion sorption in the batch tests. Chunyan Sun et al. [13] reported that the 30%AMP/Al-MCM-41 adsorbs up to 84% of the Cs^+ ions in the concentration range tested (50–100 mg/L). The regeneration of the adsorbent was achieved by using NH_4NO_3 (6 mol/L) as an eluent at room temperature. Hence, the flexibility of SM-AMP materials and their excellent selectivity and ion exchange capacity for strong acidity liquid make them attractive for possible remediation of Cs^+ from nuclear wastes [10,16]. However, studies on the SM-AMP are limited to the composite of combining ammonium molybdophosphate (AMP) with silica matrix (SM) from these expensive finished product matrixes such as SBA-15 or MCM-41, and application on the treatment of column operation was less investigated.

In previous work, we also described on porous silica matrix impregnated with ammonium molybdophosphate (SM-AMP), which could be used as an effective ion exchanger for Cs^+ static adsorption [15]. This fabrication allowed us to obtain better acidic stability and ion exchange properties of the SM-AMP. In fact, the interface reaction of SM-AMP was nevertheless reported to have a little flaw for the compatibility of SM and AMP. And the previous method could not rapidly create a considerably higher mechanical strength and stiffness of the matrix, which causes environmental and economic problems. Furthermore, granular properties of AMP were appropriately optimized using the reported silica matrix [15], which could not be well satisfied for column uptake of Cs^+. In this work, we extend the method class to developing the better controllable granular properties and understanding the mechanism of formation for the wide application.

Here, we report the synthesis and structure of SM-AMP20 rapidly possessing better granulating properties with a new sequential annealing mechanism for improving compatibility of SM and AMP. The challenge is to understand and develop the novel mechanism of composites formation according to our reported method, namely, whether the method could extensively apply to some corresponding fields of improving mechanical strength, especially the ion exchange process of radioactive waste remediation in the strong acidity. We, furthermore, also demonstrate the SM-AMP20 to be suitable for Cs^+ column operation experiment and its regeneration possibility.

2. Experimental section

2.1. Starting materials

$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (powder, ≥ 99%) was purchased from Jinhuada Chemical (Guangzhou, China). Tetraethyl orthosilioate (TEOS) (as SiO_2, ≥ 28%) obtained from United Chemical industry (Chengdu, China) was used for the preparation of silica matrix (SM). Nonradioactive Cs^+ (as $CsNO_3$) (powder, ≥ 99%) obtained from KeLong (Chengdu, China) was used as a surrogate for ^{137}Cs ion due to their similar chemical characteristics. All other chemical reagents were purchased from KeLong (Chengdu, China) unless otherwise noted.

2.2. Synthesis of SM-AMP20

The granulating SM-AMP20 of 20 wt% AMP content was prepared using a sequential annealing mechanism (Fig. 1A). In a short, the preparation processes were carried out in the following two comprehensive steps. Step 1. Firstly, a reagent of TEOS (11.437 g, 0.055 mol) was added to 10 mL anhydrous ethanol (EtOH, KeLong) and thoroughly mixed. Secondly, 10 mL of 5 wt% polyvinyl alcohol (PVA) (degree of polymerization, n ≈ 1700, KeLong) aqueous solution was added into the previous mixture slowly. The resultant mixture was left to react for 40 min under vigorous stirring (~500 r/min) using a JJ-1 electric blender (Jintan Medical Instrument Factory, China) at room temperature (25 °C). Once the first two steps were completed, the homogeneous mixture was repeatedly stirring to become the suspended matter at 96 °C. Step 2. The suspended matter was added to AMP suspended solution prepared in advance at 90 °C. The suspended particles of AMP were prepared by respectively mixing $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ aqueous solution (0.1 mol/L, 10 mL), NH_4NO_3 aqueous solution (0.1 mol/L, 2 mL) and H_3PO_4 aqueous solution (0.25 mol/L, 2 mL). The final mixed solutions were made at 6–7 mol/L with respect to HNO_3 aqueous solution, corresponding to the stoichiometry of the product. As the final step, these dried precipitates were centrifuged and finally drying at

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