



# Ammonium salt of heteropoly acid immobilized on mesoporous silica (SBA-15): An efficient ion exchanger for cesium ion



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## HIGHLIGHTS

- ▶ The ammonium salt of heteropoly acid deposited on mesoporous silica was synthesized.
- ▶ The ammonium salt of heteropoly acid was highly dispersed on a silica surface.
- ▶ 50 wt% ammonium salt of heteropoly acid supported on silica showed high Cs sorption.
- ▶ Sorption of Cs was dependent on other cations and nitric acid concentrations.
- ▶ The coexisting cations and acidity have negligible influence on Cs sorption.

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## ABSTRACT

The ammonium salt of heteropoly acid ( $\text{NH}_4\text{HPA}$ ) deposited on the surface of mesoporous silica (SBA-15) support was prepared and characterized using the following analytical techniques: X-ray diffraction (XRD), nitrogen adsorption–desorption, scanning electron microscopy (SEM), particle size analysis and infrared spectra. The spectroscopic results revealed that the  $\text{NH}_4\text{HPA}$  was well dispersed on the internal and external silica surfaces. The ion exchange capacity tests demonstrated that the insertion of the  $\text{NH}_4\text{-HPA}$  phase on the silica surface increased the specific activity for Cs removal. The ion exchange capacity of Cs increased with increasing the HPA loading. The  $\text{NH}_4\text{HPA}$  at a loading of 50 wt% supported on silica showed a high ion exchange capacity (70.9 mg/g) for Cs ion. The effects of co-existing cations, nitric acid and temperature on the Cs sorption efficiency onto the composites were investigated.

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## 1. Introduction

The Keggin anion is composed of a central tetrahedron ( $\text{XO}_4$ ; X is normally P, Si, or Ge) surrounded by 12 $\text{MO}_6$  octahedra (M usually being Mo, W, or V) arranged in four groups of three-edge-sharing  $\text{M}_3\text{O}_{13}$  units [1]. In the protonated form, they are known as heteropoly acids (HPAs). The most cited polyoxometalates are those with the Keggin structure, e.g., phosphomolybdic acid ( $\text{H}_3\text{-PMo}_{12}\text{O}_{40}$ ) and phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) [2]. These HPAs are applied to a broad range of utilities in industrial chemistry because of their intrinsic multi-functionality, strong acidity and tunable redox properties [3]. The importance of the heteropoly compounds has already been revealed in several applications such as selective catalysts, ion exchangers, solid electrolytes and precipitators [3–5]. Despite these advantages, HPAs have the drawbacks of high solubility in water and polar solvents, low surface area

and poor reproducibility of synthetic methods. Additionally, although the acid form itself is a useful solid acid, there are a few acidic sites on the surface because of the low surface area. Therefore, it is imperative to improve the number of surface acidic sites for the development of solid acids in industrial chemistry [3,6].

HPAs were applied to remove radionuclides released from nuclear power plants (NPPs) by precipitation method in the early research phase. Schultz and Bray [7] reported the precipitation of  $^{137}\text{Cs}$  using phosphotungstic acid to recover this isotope from PUREX process waste at the Hanford DOE site. However, the higher pH value typically associated with precipitation methods often results in the precipitation of macro-quantities of metals necessitating further separation or decontamination process steps [4]. To overcome these weaknesses in HPA applications, the salt form of HPAs, substituting proton with alkaline cations, was developed and found to show improved properties in terms of the surface area, pore structure, solubility and hydrophobicity [8]. Among those cations such as  $\text{NH}_4^+$ ,  $\text{Cs}^+$ ,  $\text{Rb}^+$  and  $\text{Ag}^+$ , the ammonium ion

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salt of HPAs is insoluble in water or other polar solvents and has increased thermal stability [3]. In particular, ammonium salts of HPAs such as ammonium molybdophosphate (AMP) and ammonium tungstophosphate (ATP) are well known to have high Cs selectivity and to be promising inorganic sorbents [9–12]. These sorbents have been widely used for the determination of cesium in environmental samples. The selectivity of AMP for cesium is considerably higher than conventional organic resins [10]. AMP and ATP also have an advantage in being easily prepared by direct precipitation through the addition of either a stoichiometric or a nonstoichiometric amount of a cation from a solution containing the dissolved acid [3].

However, the microcrystalline ammonium salt of HPAs ( $\text{NH}_4$ -HPAs) has not been applied as a sorbent on a large scale owing to its fine powder morphology ( $<0.5 \mu\text{m}$ ), which is unsuitable for efficient separation such as column operations [12]. In addition, its low specific surface area provides few active sites on their surface [5]. Therefore, the  $\text{NH}_4$ HPAs must be granulated or deposited on a ready-made granulated support. The deposited or incorporated  $\text{NH}_4$ HPAs shows better flow rates and performance of sorption–desorption cycles than bulk  $\text{NH}_4$ HPAs [13]. Many studies have investigated on the use of a supporting or binding material for the granulation of  $\text{NH}_4$ HPA. Both inorganic supporting matrices such as asbestos [9], silica gel [14], titanium phosphate [15], alumina [13,16], zirconium phosphate [17], silicon oxide and titanium oxide [5], and organic supporting matrices such as Amberlite XAD-7 [18], resorcinol formaldehyde polycondensate resin [19], calcium alginate [11,12] and polyacrylonitrile (PAN) [20–22] were applied. Organic supports for binding an inorganic sorbent are not suitable considering the aspects of regeneration, treatment and disposal of spent ion exchangers. On the other hand, inorganic supports for  $\text{NH}_4$ HPAs have several advantages such as radiation stability and disposal simplicity of radioactive wastes compared with organic matrices. In addition, acidic or neutral inorganic substances are suitable as supports since basic solids such as alumina tend to decompose HPA [23].

Among many inorganic matrices, ordered mesoporous materials such as MCM-41 and SBA-15 could be used as supports for immobilization. A new branch of research on the synthesis of mesoporous materials combined with functional groups has evolved and a powerful new class of sorbent materials has been designed for the removal of cesium contamination [24]. For the removal of radioactive ions, only mesoporous silicas functionalized with transition metal hexacyanoferrates have been studied [24–27]. In the field of catalysts, numerous attempts have been made to use mesoporous silicas as matrices for cesium salt of HPAs for the synthesis of heterogeneous catalysts [28–31]. In these studies, two-step impregnation method was used to synthesize the alkali metal salt of HPA immobilized on mesoporous silica.

The purpose of this research is firstly to develop  $\text{NH}_4$ HPA immobilized on the mesoporous silica (SBA-15) surface and secondly to evaluate the applicability of the efficient inorganic sorbent for the removal of radioactive ions in the low and intermediate liquid wastewater released from NPPs. The physicochemical properties including scanning electron microscopy (SEM), Fourier transform-infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) spectroscopy, pore structure and specific surface area analysis were conducted to evaluate the applicability of the inorganic sorbent in practice. In addition,  $\text{NH}_4$ HPA was immobilized on not only the mesoporous silica (SBA-15) surface with high surface area but also the silicon dioxide ( $\text{SiO}_2$ ) surface as the same silica substrate to evaluate the effect of the mesoporous matrix on Cs sorption. The selective removal of radioactive ions by the  $\text{NH}_4$ HPA immobilized on mesoporous silica ( $\text{NH}_4$ PMA/SBA-15) was also evaluated with various conditions (initial metal ion concentrations, presence of competing metal ion, nitric acid and temperature).

## 2. Experimental

### 2.1. Chemicals

All the chemicals used were of analytical grade and were used without further purification. Phosphomolybdic acid hydrate (PMA, average M.W. = 1825,  $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ ), tetraethyl orthosilicate (TEOS,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ), the block copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (average M.W. = 5800, designated  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ; Pluronic P-123), cesium nitrate ( $\text{CsNO}_3$ , 99+%), cobalt nitrate ( $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ , 98+%) and strontium nitrate ( $\text{Sr}(\text{NO}_3)_2$ , 99+%) were received from Sigma–Aldrich Chemical Co. (Milwaukee, WI, USA). Silicon dioxide ( $\text{SiO}_2$ , 10% ignition loss at  $950 \pm 50 \text{ }^\circ\text{C}$ ) that contains 1% hydrochloric acid-soluble matter, 2% non-volatile matter with hydrochloric acid, 0.01% chloride, 0.05% sulfate, 0.01% heavy metal as Pb and 0.01% iron was purchased from Junsei Chemical Co., Ltd., Japan. MES (2-[N-morpholino]ethanesulfonic acid hydrate, 99.5%) buffer was purchased from ACROS Organics (NJ, USA). Ammonium chloride ( $\text{NH}_4\text{Cl}$ , 98.5%), sodium nitrate ( $\text{NaNO}_3$ , 97%), ammonium nitrate ( $\text{NH}_4\text{NO}_3$ , 98%), potassium nitrate ( $\text{KNO}_3$ , 99%), 1-butanol ( $\text{C}_4\text{H}_9\text{OH}$ , 99%), hydrochloric acid (HCl, 35–37%), hydrofluoric acid (HF, 50%) and nitric acid ( $\text{HNO}_3$ , 64–66%) were purchased from Duksan Chemicals Co., Korea. All solutions were prepared by dissolving the chemicals in distilled and deionized (DI) water prepared by Barnstead E-pure Water Purification Systems (18.3 M $\Omega$  cm, Barnstead, D4641, USA).

### 2.2. Sorbent preparation

The SBA-15 was synthesized by following the procedure described by Yun et al. [32]. TEOS was introduced to an aqueous HCl solution containing P123 and hydrolyzed for 1 h under stirring at  $40 \text{ }^\circ\text{C}$ . Two grams of P123 was dissolved in 10 g of DI  $\text{H}_2\text{O}$ , 60 g of 2 M HCl and 4.25 g of TEOS with stirring for 24 h. The precipitated product was filtered, washed with DI water, dried at room temperature for 72 h, and then calcined at  $500 \text{ }^\circ\text{C}$  for 5 h in a muffle furnace to remove the P123 template.

The  $\text{NH}_4$ HPA was prepared by the precipitation method in aqueous solution according to the procedure developed by Alcañiz-Monge et al. [33]. For the synthesis of  $\text{NH}_4$ PMA, 3.27 mM of an aqueous solution of an ammonium salt ( $\text{NH}_4\text{Cl}$ ) was added dropwise to 1.09 mM of an aqueous solution of  $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$  (PMA) with continuous stirring. The  $[\text{NH}_4]^+ : [\text{PMo}_{12}\text{O}_{40}]^{3-}$  molar ratio was adjusted to 3:1, corresponding to the stoichiometry of the product. The obtained solid ( $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ ,  $\text{NH}_4$ PMA) was filtered, washed with slightly acidified water and dried in an oven at 333 K overnight. PMA was used as one of the HPAs and  $\text{NH}_4$ PMA denoted the ammonium salt of PMA.

Highly dispersed  $\text{NH}_4$ PMA on the mesoporous silica (SBA-15), denoted as  $\text{NH}_4$ PMA/SBA-15, was prepared following the two-step impregnation technique using the modified method proposed by Yadav and George [30]. A series of the sorbents having different  $\text{NH}_4$ PMA loadings (20–50 wt%) on SBA-15 were synthesized. Two grams of silica support (SBA-15) in aqueous solution of  $\text{NH}_4\text{Cl}$  was stirred overnight at room temperature. The mixture was then evaporated for drying at  $110 \text{ }^\circ\text{C}$  overnight to promote interactions between surface silanols and  $\text{NH}_4\text{Cl}$ . Following this, the desired amount of PMA was impregnated using 1-butanol as a solvent. The preformed material was dried in an oven at  $120 \text{ }^\circ\text{C}$  for 3 h and then calcined at  $300 \text{ }^\circ\text{C}$  for 3 h. Compared to the properties of the applied supports,  $\text{NH}_4$ PMA on silicon dioxide, denoted as  $\text{NH}_4$ PMA/ $\text{SiO}_2$  was also prepared by the same method as applied in the  $\text{NH}_4$ PMA/SBA-15 composites.

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