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Adsorption of cesium on silica gel containing embedded phosphotungstic acid

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ABSTRACT

Mesoporous silica gel containing embedded phosphotungstic acid (PTA) was synthesized by sol-gel co-condensation of tetraethoxysilane with PTA in acidic media. The obtained material had high BET surface area and pore volume. A characteristic band of the Keggin structure of PTA was present in its FT-IR spectrum while its XRD patterns were absent. This proved the embedding of PTA on a sub-molecular level. The material demonstrated high adsorption capacity of Cs. Unexpectedly, porosity of the adsorbent increased after substitution of most protons by cesium cations. Cation exchange also favored agglomeration of the material particles. Kinetic studies showed that the adsorption data correlates strongly with the pseudo-second order model. The adsorbent had two types of adsorption sites: heteropolyacid anions and silanol groups. However, adsorption on silanol groups was very sensitive to the temperature. At the increased temperature, the nature of adsorption fit the Langmuir model extremely well. The obtained results can be used in the development of an effective adsorbent for clean-up of water contaminated by radioactive cesium-137.

1. Introduction

Radioactive isotopes of cesium are among the most hazardous contaminants that can be released into the environment at nuclear disasters (e.g. the Fukushima accident [1]) or small incidents, which may occur during fissile materials processing [2]. This contaminant is easily introduced to food and potable water because of the unique mobility of the Cs^+ ion in the environment.

Currently, the development of materials that can adsorb Cs^+ selectively in the presence of Na^+ and K^+ is a challenging problem. While other radionuclides, e.g., ^{60}Co or ^{90}Sr, can be separated easily due to their ability to form insoluble products with many anions, most compounds of ^{137}Cs and ^{134}Cs are soluble and, therefore, highly mobile in aqueous media.

Existing technologies and current research for removing ^{137}Cs from soil and water fall into five general categories: solvent extraction [3], phytoextraction [4], precipitation [5], ion exchange [6], and adsorption [7]. However, the first four approaches have insufficient effectiveness due to low selectivity and high cost. The adsorption method has attracted a great deal of attention due to rapid separation, high thermal and radiation stabilities of the adsorbents, and reduced volumes of wastes.

One of the groups of inorganic materials studied extensively with respect to Cs^+ adsorption is natural and synthetic aluminosilicates. Abusafa and Yucel demonstrated the possibility of Cs^+ removal from radioactive wastes on natural clinoptilolite [8]. Further, Smičiklas et al. studied the adsorption of Cs^+, Co^{2+}, and Sr^{2+} on this material [9]. Synthetic zeolites are also able to adsorb cations of various metals [10]. Other natural minerals tested in this process are clays [11]. However, Iijima et al. showed that the adsorption on these materials is reversible [12], making them inefficient.

Cesium forms stable insoluble salts with some complex acids. One group of such compounds is hexacyanoferrates [13]. Zhang et al. used $K_2Zn_3[Fe(CN)_6]_2$ for adsorption of Cs^+ from liquid waste water [14]. They achieved removal of 99.44% Cs^+. Nilchi et al. prepared $Cu[Fe(CN)_6]$–polyacrylonitrile composite for Cs separation [15]. Recently Mimura et al. developed an ion exchanger for Cs^+ uptake using hexacyanoferrates [16]. However, the efficiency of this ion exchanger appeared sensitive to K^+ concentration. In addition,

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it was unstable in acidic and alkaline media. The most significant disadvantage of cyanoferrates is their instability in presence of UV light. As it was shown, hydrolytic degradation of cyanoferrates under irradiation at $\lambda < 480$ nm results in the formation of highly toxic HCN [17]. Broderius and Smith proved that photodegradation of cyanoferrates in natural water under sunlight is relatively fast and may be of toxicological importance [18].

Another group of Cs-binding compounds are heteropolyacids. Sheha and El-Khouly developed a zirconium iodomolybdate exchanger [19]. Its adsorption capacity strongly depended on the ionic strength of the solution and decreased in presence of organic acids. Other similar ion exchangers are zirconium molybdoarsenate [20], $(NH_4)_3PW_{12}O_{40}$ [21], and $(NH_4)_3PMo_{12}O_{40}$ [22]. Arnal et al. successfully used $(NH_4)_3PMo_{12}O_{40}$ for the decontamination of radioactive wastes formed at the incident that occurred in the steel factory of Acerinox in Cádiz (Spain) in 1998 [23]. Around 98% of ^{137}Cs was removed from contaminated acidic solution.

Some other materials were also studied as potential adsorbents for ^{137}Cs uptake. Iron oxide [24], silica gel [25], cement mortar [26], polymer composites [27], and humic acids [28] are among them. A review of different technologies for decontamination of liquid nuclear wastes was published by Bellenger and Staunton [29].

However, the selectivity of known adsorbents in the presence of competing ions is insufficient while some of these materials are too expensive. Some of the adsorbents are not stable in acidic media. In spite of significant achievements in the field of porous composite materials, none of them were developed for selective ^{137}Cs uptake from solutions.

The objective of this work is the synthesis of a mesoporous material containing embedded phosphotungstic acid and its study in the selective adsorption of cesium.

2. Materials and methods

2.1. Reagents

Tetraethoxysilane (TEOS) and phosphotungstic acid hydrate (PTA) (Acros Organics, Morris Plains, NJ) were precursors in the syntheses. Pluronic P123 with M.W. = 5800 (Sigma-Aldrich) was used as a pore-forming agent. Adsorption studies were conducted with CsCl (Acros Organics), $CoCl_2 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$, KCl, and NaCl (Fisher Scientific, Pittsburg, PA).

2.2. Synthetic procedures

The adsorbent H-PTA/SiO_2 was synthesized using a slightly modified procedure published earlier [30]. Two solutions were prepared. Pluronic P123 (50 g) was dissolved in 150 mL of ethanol, and TEOS (72 g) and PTA (18 g) were dissolved separately in 50 mL of ethanol. The initial contents of the reagents were chosen from the data obtained in [30] for providing the highest effectiveness of the adsorbent. Then solutions of TEOS/PTA and 20% HCl (150 mL) were simultaneously added dropwise to the solution of the surfactant under stirring. The reaction mixture was refluxed for 24 h. The obtained gel was filtered, washed with deionized water until complete removal of the acid, rinsed with acetone, then air-dried overnight. The sample was calcined at 500 °C for 5 h. Literature had shown that this temperature is sufficient for full removal of the template [31] while the Keggin structure is still stable at these conditions [32].

Cs-exchanged material Cs-PTA/SiO_2 was prepared by mixing 8.2 g of H-PTA/SiO_2 with 100 mL of 0.13 M solution of CsCl. The mixture was stirred overnight, washed by deionized water, and dried on air overnight.

2.3. Chemical analysis

Contents of Cs and W in the samples were determined on a Shimadzu AA-6300 atomic absorption spectrometer (Kioto, Japan). The samples for measurement were prepared by dissolution of the materials in 48% HF (VWR International, Radnor, PA) followed by neutralization to pH = 7. Concentrations of Cs^+, Sr^{2+} and Co^{2+} in solutions after adsorption were measured on the same instrument.

Chemical stability of adsorbed Cs^+ in acidic and basic media was examined by the treatment of Cs-PTA/SiO_2 samples (0.1 g each) with 10 mL of 11.6 M HCl and 2.3 M Na_2CO_3 solutions for 2 h. Then the contents of leached Cs^+ were analyzed by AAS.

Surface acidity of the samples was determined by reversed titration. Keggin units are unstable in aqueous media at high pH, thus the neutralization of acidic sites on the samples was conducted in anhydrous THF. The samples were dried overnight at 140 °C to remove physically adsorbed water molecules. Then 0.1 g of each sample was dispersed in 6 mL of 0.01 M solution of pyridine or diphenylamine in dry THF. The mixture was allowed to equilibrate for 18 h at 23 °C. After equilibration, the solution was decanted from the solid, diluted by 100 mL of DI water, and titrated by 0.01 M HCl until pH = 3. Obtained data were compared to the blank solution prepared without the solids. The data were recorded on an Orion 350 pH meter (Thermo Scientific, Pittsburg, PA). The volumes occupied by pyridine and diphenylamine molecules were calculated using Spartan software and found 93 and 196 Å^3, respectively.

2.4. Instrumental characterization

FT-IR spectra were recorded in KBr pellets on a Vertex 70/80 FT-IR spectrometer (Bruker Optics, Inc., Billerica, MA).

All solid state NMR spectra were acquired on a Bruker AVANCE 400 spectrometer (Rheinstetten, Germany). ^{29}Si spectra were recorded at 79.49 MHz, pulse length: 6 μs, delay time: 15 s, number of scans: 50,000. Relative intensities of the signals were calculated by deconvolution of the spectra using the Gaussian function on Origin 2016 software. ^{1}H NMR spectra were recorded at 400.13 MHz, pulse length: 12 μs, delay time: 2 s. The number of scans was 128. Chemical shifts were referenced to external TMS. For recording ^{31}P spectra, the experiments were conducted at 162 MHz, pulse length: 14 μs, delay time: 10 s, number of scans: 1024. Chemical shift was measured in respect to 85% H_3PO_4. ^{133}Cs spectrum was recorded at 52.48 MHz, pulse length: 12 μs, delay time: 0.5 s, number of scans: 1024. The standard was CsCl solution in D_2O. Before measurements, samples were dried at room temperature in vacuum until the weight was constant.

Transmission electron microscopy (TEM) images were obtained on a JEOL 1230 electron microscope (Tokyo, Japan) at 80 kV. Before imaging, samples were dispersed in a 50% ethanol solution using a W-385 sonicator (Heat Systems Ultrasonic, Newtown, CT) for 2 min.

Porous characteristics were measured on a Quantachrome Nova 2200e porosimeter (Boynton Beach, FL). Prior to measurements, the samples were degassed at 300 °C in vacuum for 2 h. Adsorption/desorption isotherms were recorded at −196 °C using N_2 as an adsorbate. The Brunauer–Emmett–Teller (BET) surface areas were calculated from the adsorption branch of isotherms to be in the range of P/Po = 0.2–0.4. Total pore volumes, average pore diameters, and pore size distributions were obtained using Density Functional Theory (DFT) method. Micropore volumes and average diameters were calculated by Saito–Foley (SF) method. All calculations were performed using NovaWin v.11.02 software.

Particle sizes were determined by dynamic light scattering on a Zetasizer Nano ZS90 (Malvern, UK). The samples were dispersed in water at sonication.