Unexpected ultrafast and high adsorption of U(VI) and Eu(III) from solution using porous Al₂O₃ microspheres derived from MIL-53

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HIGHLIGHTS

- Novel porous Al₂O₃ microspheres were fabricated by calcination of MIL-53(Al).
- Porous P-Al₂O₃ microspheres showed homogeneous porosity and high specific surface area.
- Porous P-Al₂O₃ microspheres exhibited excellent adsorption capacity for U(VI) and Eu(III).
- Hydroxy groups played an important role for U(VI) and Eu(III) binding to P-Al₂O₃.

GRAPHICAL ABSTRACT

The P-Al₂O₃ microspheres showed high elimination of U(VI) and Eu(III) through the formation of strong surface complexes in environmental pollution cleanup.
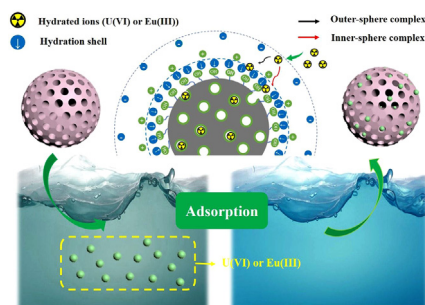
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ABSTRACT

Uranium, a kind of strategic resource for nuclear energy, is inevitably released into environment because of nuclear fuel fabrication and ore mining. Although numerous traditional materials have been applied for the removal of radionuclides, the integrating advantages of ultrafast adsorption kinetics and high adsorption capacity are still an extreme challenge. Herein we reported a facile strategy for fabricating a novel porous Al₂O₃ microsphere (P-Al₂O₃ MSs) by the calcination of metal–organic frameworks (MIL-53(Al)) and applied it to immobilize radionuclides from wastewater. The resulting P-Al₂O₃ MSs inherited the morphology of MIL-53(Al) and manifested a mesoporous structure with high specific area ($\sim$248.57 m²·g⁻¹). Kinetic analyses denoted that U(VI)/Eu(III) adsorption onto P-Al₂O₃ MSs achieved equilibrium within 25 min, much shorter than the commercial γ-Al₂O₃ nanomaterials. The calculated maximum adsorption amounts of P-Al₂O₃ MSs at 298 K reached 316.87 mg·g⁻¹ for U(VI) (pH = 5.0) and achieved 223.37 mg·g⁻¹ for Eu(III) (pH = 6.0), much higher than γ-Al₂O₃ and most of other functionalized metal oxides. XPS analysis indicated that the hydroxy groups played a necessary part role for the binding of U(VI) and Eu(III) to P-Al₂O₃ MSs. Moreover, the excellent adsorption capabilities for U(VI) and Eu(III) in natural or synthetic waters further confirmed the practical application of P-Al₂O₃ MSs in real wastewater treatment.

1. Introduction

Over the last decade, civilian and military nuclear programs resulted in a substantial legacy of intermediate level radioactive wastes [1], which are worryingly released into nature due to the mining operations and nuclear cycles unavoidably. Because of its long-term storage and carcinogenic effects, the nuclear waste could pose serious health risk to local residents and cause detrimental disease, for instance, liver and kidney damage, lung function insufficiency, cancers even death [2]. Thus, the elimination of radionuclides from solutions is crucial to decrease the risk of radionuclides [3]. Various methods, such as ion-exchange [4,5], chemical/biochemical reductive precipitation [6–8], liquid–liquid extraction [9], filtration [10] and adsorption [11,12], are employed for radionuclides' removal and enrichment from radioactive wastewater. Notably, adsorption technology is of particular interest to preconcentrate radionuclides from wastewater due to its easy operation in large scale. Therefore, the investigation of advanced adsorbents with enhanced decontamination rates and capacities is a clear direction for radionuclides immobilization in nuclear wastewater.

Generally, the materials offer either numerous functional groups within their framework (*e.g.*, graphene oxides and other active carbon materials), or lattice vacancies (*e.g.*, metal oxides) can efficiently eliminate radionuclides from wastewater [13]. The commendable materials for radionuclides enrichment in wastewater should meet three characteristics: i) fast removal rate and high capabilities for radionuclides; ii) environmental friendly and low cost; iii) high stability to radiation and stable mechanical structure and reusability. Hierarchically structured metal oxides can inherit these features, and various metal oxides have been applied for radionuclides' elimination from wastewater due to their mechanical robustness against wear and tear. Drisko et al. [14] found that different macropore dimensions and morphology of hierarchically structured zirconium titanium oxides could greatly impact the surface accessibility, and thereby affect the diffusion rate and the spatial capacity for U(VI) ions. For the purpose of improving the adsorption rate and capacity of materials, novel synthesis methods are expected to simultaneously control the micro/macropore characteristics (*i.e.*, pore volume and specific surface area). In view of this point, metal oxides synthesized from metal-organic frameworks (MOFs) could offer great possibilities for synthesizing tailored functional materials in a simple and controllable fashion way [15–17]. MOFs, which comprise of clusters or chains of metal ions bonded with organic ligands, represent an emerging class of materials that have extraordinary high surface area and tunability of the pore size [18]. Thermal calcination of MOFs can produce hierarchically structured metal oxides with homogeneous porosity and high specific surface area. The metal oxides derived from MOFs have shown their promising applications in electrocatalysis [16] and energy storage/conversion [19]. However, the application for the contaminants immobilization from wastewater is still scarce [20].

In this work, a kind of porous Al_2O_3 was synthesized from MIL-53(Al) and applied for the removal of radionuclides from radioactive liquid waste. Europium and Uranium were chosen as representative radionuclides of trivalent lanthanides and hexavalent actinides in this study. The purposes included: (1) fabricate P-Al_2O_3 and investigate the P-Al_2O_3 using TEM, SEM, FT-IR, N_2-BET and XPS characterized techniques; (2) study the adsorption performance of P-Al_2O_3 towards U(VI) and Eu(III) across multifarious conditions (such as reaction time, ionic strength, pH, coexisting electrolytes (*i.e.*, anions: NO_3^-, ClO_4^-, Cl^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, and cations: Na^+, K^+, Mg^{2+}, Ca^{2+}) and different water systems); (3) elucidate the interaction mechanism between radionuclides and P-Al_2O_3 using XPS analysis. The current paper highlights the P-Al_2O_3 as a high-efficiency and rapidly sequestrated adsorbent for the immobilization of radionuclides from aqueous solution.

2. Macroscopy experiments

2.1. Chemical reagents

All the chemicals we used were purchased in analytical grade. Nitric acid (70%) was bought from Alfa Aesar Company. Terephthalic acid (H_2BDC, 99%, Aldrich), aluminum chloride hexahydrate ($AlCl_3·6H_2O$, Cl., Ltd, Beijing, China) and the solvent of N, N-dimethylformamide (DMF, Aesar) were used without any further purification.

2.2. Synthesis and characterization of P-Al_2O_3 microspheres

Typically, $AlCl_3·6H_2O$ (3.16 g) was dissolved in DMF (100 mL) under stirring for 20 min, followed by adding H_2BDC (3.5 g, 21.0 mmol). The mixed solution was transferred into Teflon autoclave and then heated under 220 °C for 3 days. The collected powder was purified by ultrasonic vibration and rinsed with DMF and Milli-Q water for several times. After drying overnight at 65 °C, the light-yellow material was obtained and then calcined at 800 °C for 4 h to get white P-Al_2O_3 powder. The as-prepared P-Al_2O_3 was characterized with analytical techniques and more detailed descriptions for the different characterization was presented in Supporting information (SI).

2.3. Characterization of P-Al_2O_3 nanospheres

The as-prepared P-Al_2O_3 was characterized using SEM, TEM, FTIR, XRD, N_2-BET and XPS techniques. More detailed description for the different characterization was presented in Supporting information (SI).

2.4. Adsorption experiments

The uptake of radionuclides from natural or synthetic water was carried out by batch technique. Solid P-Al_2O_3, the stock electrolyte solution ($NaNO_3$, NaCl, $NaClO_4$, Na_2SO_4, Na_3PO_4, KNO_3 etc.) and the stock solution of U(VI) or Eu(III) were added into polyethylene tubes (10 mL) to achieve the target concentrations. The batch experiments were carried out with $0.1\,g\,L^{-1}$ P-Al_2O_3, which was obtained by preliminary experiment as shown in Fig. S1. The pH was adjusted by adding 0.1 or 0.01 M HNO_3 or NaOH. After sorption equilibration, membrane filters ($\Phi = 22\,\mu m$) were employed to split the liquid and solid phase of the suspension. The supernatant concentrations of U(VI)/Eu(III) were confirmed by UV–vis adsorption spectrometer at the wavelengths of 650 and 654 nm (Shimadzu UV-2550 spectroscopy, Japan), respectively. The detailed information about the composition of different types of synthetic water was described in *SI*. Real seawater (Liuheng Island, Zhejiang, China) was also applied to study the U(VI)/Eu(III) elimination behaviors from contaminated water. The amounts of target ions on the surface of P-Al_2O_3 were calculated by initial concentration (C_o, $mg·L^{-1}$) and the equilibrium one (C_e, $mg·L^{-1}$):

$$Adsorption(\%) = \frac{(C_0-C_e)}{C_0} \times 100\% \tag{1}$$

$$q_e = \frac{V \times (C_0-C_e)}{m} \tag{2}$$

where m (mg) and V (mL) represented the P-Al_2O_3 dosage and suspension volume.

3. Results and discussion

3.1. Properties of porous Al_2O_3 microspheres

The morphology and microstructure of the MIL-53(Al) and P-Al_2O_3 samples were characterized by SEM-EDS analyses and TEM images. The obtained MIL-53(Al) product exhibited uneven microspheres structure with rough surface and an average particle size of 0.74 μm confirmed by