



Adsorption of metal and metalloid ions onto nanoporous microparticles functionalized by atomic layer deposition



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ABSTRACT

A novel material was prepared by depositing ultrathin TiO₂ films on nanoporous micron-sized silica gel particles by atomic layer deposition (ALD). Silica gel particles were coated with 20 and 40 cycles of TiO₂ films by ALD. Half samples were heated at 500 °C to change the crystal structure of TiO₂. Their adsorption ability for a mixture of 19 trace elements of heavy metals and other toxic elements, including As(V), Se (IV), Be(II), Al(III), V(V), Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Ba(II), Tl(I), Sb(III), Cd(II), Ag(I), Sr(II), Mo (VI), and Pb(II), from aqueous solutions was investigated. The removal efficiencies of As(V), Se(IV), V(V), Mo(VI), and Pb(II) were higher than 75% simultaneously in the mixed solution at pH 3 for 20 and 40 cycles of TiO₂ coated silica gel particles without heat treatment. In contrast, the uncoated silica gel particles did not adsorb any ions under this pH condition. At pH 5, the 20 cycles of TiO₂ coated samples without heat treatment removed 95% As(V), 95% Se(IV), 86% V(V), 94% Mo(VI), 60% Pb(II), 40% Sb(III), 73% Ag(I), 72% Cu (II), and 49% Ba(II) simultaneously. Before heat treatment, the TiO₂ coated samples showed better adsorption performance than the samples with heat treatment due to the fact that the TiO₂ surface area decreased and thereby the amount of adsorption sites reduced after heat treatment. The micron-sized adsorbent particles were separated easily from water due to their large particle size, making it practically suitable for trace contaminant remediation in water.

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1. Introduction

Heavy metal and metalloid pollution has become one of the most important environmental concerns. When present in water, toxic heavy metal and metalloid ions, such as lead (Pb), manganese (Mn), chromium (Cr), and arsenic (As), can directly affect the environment and human health [1,2]. For example, Cr, Pb and Mn can cause brain and bone damage, As can cause cancer, and Cr can cause liver and kidney damage [3]. Hence, it is important to remove these ions from contaminated waste water to an acceptable, non-toxic level before being discharged to receiving water or being consumed as drinking water. Toxic heavy metal ions and metalloids can be removed by many techniques, such as ion exchange

[4], membrane filtration [5], reverse osmosis [6], chemical precipitation [7], evaporation [8], and sorption [2,9–17]. Among these methods, adsorption is one of the most effective and economical methods for the removal of heavy metal and metalloid ions from contaminated water, especially at low concentrations due to its high efficiency, simple operation, and low cost [2,18]. Numerous studies focused on adsorbent preparation and adsorption process, such as using TiO₂ and Al₂O₃ nanoparticles (NPs) as adsorbents [2,9–15]. TiO₂ was proven to have a high removal capability because of its promising properties, such as biological and chemical inertness, high adsorption capacity, photoactivity, and environment-friendly [19–21].

TiO₂ NPs have shown excellent adsorption ability for heavy metal and metalloid ions from aqueous solutions due to their high surface area. Li et al. [2] and Qian et al. [9] prepared TiO₂-graphene oxide core-shell microspheres and C/TiO₂ NPs with a maximum adsorption capacity for Cr(III) of 117.9 and 18.1 mg/g, respectively. Wu et al. [10] synthesized a chitosan-xylan-TiO₂ hybrid with highly

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porous structures with maximum adsorption capacities for Cu(II), Ni(II), Cd(II) and Hg(II) of 158.7, 96.2, 78.1 and 76.3 mg/g, respectively. Abbasizadeh et al. [14] reported the adsorption of Cd(II), Ni(II) and U(VI) separately by a cast polyvinyl alcohol/TiO₂/APTES (aminopropyltriethoxysilane) nanohybrid, with maximum sorption capacities of 49.0 (at pH=5.5), 13.1 (at pH=5.0) and 36.1 mg/g (at pH=4.5) for Cd(II), Ni(II) and U(VI) ions, respectively. Andjelkovic et al. [15] reported Fe doped TiO₂ adsorbent for As contaminated natural water treatment, and they demonstrated that this material could be used for the removal of As to the level of drinking water recommended by World Health Organization (WHO) without pretreatment.

While high adsorption ability was demonstrated by these studies, these adsorbents were nanosized. These materials are difficult and costly to remove from water after the adsorption process, which may cause a secondary pollution from TiO₂ NPs themselves, or even result in increased toxicity [22,23]. In addition, these reports focused on single element removal, which is not practical in real applications. Herein, we report a novel process to prepare nanoporous, micro-sized TiO₂/SiO₂ particle adsorbent. Briefly, an ultrathin TiO₂ film was conformally coated on the surface of micro-sized silica gel particles by atomic layer deposition (ALD). As a proof of concept, micro-sized silica gel particles (35–70 μm) with an average pore size of 15 nm was chosen as the support. The nanoporous structure of silica gel can provide large surface area of TiO₂ for metal ion adsorption, and the large particle size of silica gel can allow them being easily separated from water. ALD is very suitable for this application, since it is a surface controlled layer-by-layer coating process based on self-limiting surface reactions, and it has been utilized to deposit metal oxide films with nanometer-sized control of film thickness and well controlled film compositions [24–26]. It is an enabling technology for highly conformal coating over complex 3D topography structures with excellent control over stoichiometry and properties.

2. Experimental section

2.1. Preparation of TiO₂/SiO₂

TiO₂ films were deposited on porous silica gel particles by ALD using titanium tetrachloride (TiCl₄) (99%, Alfa Aesar) and concentrated H₂O₂ (50 wt.% in H₂O) as precursors in a fluidized bed reactor, as described in detail elsewhere [27]. All of the chemicals were used as received without any treatment. The silica gel particles were 35–70 μm in diameter, their average pore size was 15 nm, their pore volume was 1.04 cm³/g, and their Brunauer-Emmett-Teller (BET) surface area was 268.7 m²/g. For a typical run, 5 g of silica gel particles were loaded into the reactor. The reaction temperature was 100 °C. The minimum fluidization superficial gas velocity was determined by measuring the pressure drop across the particle bed versus the superficial gas velocity of purge gas. During the ALD reaction, TiCl₄ and H₂O₂ were fed separately through the distributor plate of the reactor using the driving force of their room-temperature vapor pressures. Two needle valves were used to adjust the TiCl₄ and H₂O₂ flow rates and to ensure that the pressures were high enough to promote particle fluidization. The reactor was also subjected to vibration via vibrators to improve the quality of particle fluidization during the ALD coating process [28]. N₂ was used as flush gas to remove unreacted precursors and any byproducts during the ALD coating process. A typical coating cycle used the following steps: TiCl₄ dose, N₂ purge, evacuation; concentrated H₂O₂ dose, N₂ purge, evacuation. 20 and 40 cycles of TiO₂ ALD films were deposited on silica gel particles. After the ALD coating, half amount of each sample was heated in air at 500 °C for 4 h.

2.2. Characterization

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used to measure Ti mass fraction in TiO₂/SiO₂ particles with different thicknesses of TiO₂ films. TiO₂ mass fraction was calculated based on the ICP results. The crystal structure of TiO₂ was detected by X-ray diffraction (XRD) with filtered Cu Kα radiation (λ=1.5406 Å). The scanning range was 2θ from 20° to 80°, with a scanning rate of 0.025 °/s. Scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX) was applied to observe the morphology and to analyze the surface composition of 40 cycles of TiO₂ coated silica gel samples before heat treatment. A Quantachrome Autosorb-1 was used to obtain nitrogen adsorption and desorption isotherms of the uncoated and the TiO₂ ALD coated particles at −196 °C. The surface area of the particles was calculated using the BET method in a relative pressure range of 0.05–0.25. The total pore volumes were calculated from the adsorption quantity at a relative pressure of P/P₀=0.99. The pore size distribution curves were derived from the adsorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) method.

2.3. Metal and metalloid ions removal studies

In a typical competitive adsorption experiment, a solution containing As(V), Se(IV), Be(II), Al(III), V(V), Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Ba(II), Tl(I), Sb(III), Cd(II), Ag(I), Sr(II), Mo(VI), and Pb(II) in ultra-pure water was adjusted to pH 3 or 5 in a 125 mL polypropylene bottle pre-cleaned with diluted HNO₃. The concentration of every element ion was 500 μg/L in the solution. pH was adjusted by 0.1 M HNO₃ or 0.1 M NaOH solutions as measured by a calibrated pH meter. Samples were prepared in 19 mL polypropylene vials pre-cleaned with HNO₃ by adding adsorbent (500 mg/L final concentration) to the pH adjusted solution with above-mentioned 19 elements. Samples were rotated at a low speed for 2 h before centrifugation at 1000 × g for 10 min. The supernatant was transferred to another pre-cleaned 19 mL polypropylene vial and diluted with 1% HNO₃ for inductively coupled plasma – mass spectrometry (ICP-MS) analysis. The uptake amount Q_e (mg/g) and removal efficiency of elements at equilibrium can be calculated by Eqs. (1) and (2):

$$Q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

$$\% \text{removal} = \frac{100(C_i - C_e)}{C_i} \quad (2)$$

where C_i is the initial metal or metalloid ion concentration (mg/mL), C_e is the equilibrium concentration of metal or metalloid ion (mg/mL), V is the volume of the solution (mL) and m is the mass of adsorbent (g). Single adsorption experiments of Sb(III), Cr(III), and Pb(II) ions were also carried out following the identical procedures. The initial concentrations of metal ions and adsorbents were 500 μg/L and 500 mg/L, respectively. This was the same as that in competitive adsorption experiments.

The competitive adsorption experiments were also carried out at pH 7 to evaluate adsorption property of the prepared adsorbents. The original concentration of each element was around 500 μg/L before the pH was adjusted to 7. However, there were severe precipitation of Al, V, Cr, Cu, As, and Pb ions in the standard solution without adsorbent when the pH was adjusted to 7, as shown in Table S1. The serious precipitation affected the adsorption results, so the adsorption experiments were carried out at pH 3 and 5 in this study.

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