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

Nanoporous microparticles for metal and metalloid ions adsorption

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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), 69% 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.

Keywords: atomic layer deposition (ALD), water treatment, trace element, nanoporous silica particle, TiO₂

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 TiO_2 and Al_2O_3 nanoparticles (NPs) as adsorbents [2, 9-15]. TiO_2 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].

TiO_2 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 TiO_2 -graphene oxide core-shell microspheres and C/ TiO_2 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- TiO_2 hybrid with highly 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/ TiO_2 /APTES (aminopropyltriethoxyl silane) 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 TiO_2 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 cm^3/g , and their Brunauer-Emmett-Teller (BET) surface area was 268.7 m^2/g . For a typical run, 5 g of silica gel particles were loaded into the reactor. The reaction temperature was 100 $^{\circ}\text{C}$. 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, TiCl_4 and H_2O_2 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 TiCl_4 and H_2O_2 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]. N_2 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: TiCl_4 dose, N_2 purge, evacuation; concentrated H_2O_2 dose, N_2 purge, evacuation. 20 and 40 cycles of TiO_2 ALD films were deposited on silica gel particles. After the ALD coating, half amount of each sample was heated in air at 500 $^{\circ}\text{C}$ for 4 hr.

2.2. Characterization

Inductively coupled plasma - atomic emission spectroscopy (ICP-AES) was used to measure Ti mass fraction in $\text{TiO}_2/\text{SiO}_2$ particles with different thicknesses of TiO_2 films. TiO_2 mass fraction was calculated based on the ICP results. The crystal structure of TiO_2 was detected by

X-ray diffraction (XRD) with filtered Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The scanning range was 2θ from 20° to 80° , with a scanning rate of $0.025^\circ/\text{s}$. 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 $P/P_0 = 0.99$. 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 $\mu\text{g/L}$ 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 hr 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 the Table S1. The serious precipitation affected the adsorption results, so the adsorption experiments were carried out at pH 3 and 5 in this study.

To verify the hypothesis that TiO₂ coated porous silica gel particles can be easily separated from water, the sedimentation rate of the samples was evaluated, and commercial TiO₂ NPs (P25, 21±5 nm, Degussa) were used as a reference. Briefly, 50 mg of 40 cycles of TiO₂ coated SiO₂ samples without heat treatment and P25 NPs were added into 1 mL of methylene blue (MB, 10

mg/L) separately. The sedimentation rate of the particles was evaluated.

3. Results and discussion

3.1. Adsorbent characterization

Figure 1 shows that the TiO_2 content of the particles without heat treatment increased fast with the increase in the number of ALD coating cycles, from 0 to 22 wt.% with the TiO_2 ALD coating cycles less than 20 cycles, then increased slowly to 32% with the number of ALD cycles further increased. The high loading rate of TiO_2 before 20 cycles of ALD coating was due to the nanoporous structure of silica gel particles. A lot of sub-nanoscale pores could be filled with TiO_2 , which would result in the reduction of particle surface area and pore volume, as shown in Figure 2b. TiO_2 films were deposited throughout both the internal and external surfaces of silica gel particles. After 20 cycles of ALD, most of the sub-nanoscale pores were completely filled with TiO_2 , which resulted in a reduced growth rate of TiO_2 content. Since the growth rate of TiO_2 is very slow at this reaction condition [27], larger pores would not be filled with further increase of the ALD coating cycles, less than 40 cycles in this study.

Figure 1. TiO₂ content of TiO₂ coated porous silica gel particles versus the number of ALD coating cycles.

Figure 2. (a) Nitrogen adsorption and desorption isotherms, (b) surface area and pore volume, and (c) pore size distributions of uncoated and as-deposited silica gel particles coated with different thicknesses of TiO₂ ALD films.

The nitrogen adsorption and desorption isotherms, surface area, pore volume, and pore size distributions of silica gel particles coated with different thicknesses of TiO₂ ALD films are shown in Figure 2. Hysteresis loop was seen at high relative pressure in all isotherms, suggesting that these materials had porous structures. The trend of surface area of these particles versus the number of ALD coating cycles is consistent with that of TiO₂ content versus the number of ALD coating cycles. As shown in Figure 2b, the pore volume of samples decreased rapidly with the increase in the number of ALD coating cycles, from 1.04 to 0.66 cm³/g after 20 cycles of TiO₂ coating, then it decreased to 0.53 cm³/g after additional 20 cycles of TiO₂ coating. As mentioned above, since initially most of the sub-nanoscale pores were filled with TiO₂, the pore volume of the particles decreased quickly during the first 20 cycles of ALD coating. As shown in Figure 2c, the pore size distribution did not shift before 20 cycles of TiO₂ ALD coating, but the pore volume decreased a lot, indicating that many nanoscale pores were filled with TiO₂ after the ALD coating. Then the pore size distribution shifted to the left with the increase in the number of ALD coating cycles after 20 cycles of TiO₂ ALD coating, indicating a decrease of pore size. This is mainly due to the reduction of pore size and segmentation of nanoscale pores to sub-nanoscale pores by ultrathin TiO₂ films inside the porous structure of the particles.

The XRD patterns of 40 cycles of TiO₂ coated particles before and after heat treatment are presented in Figure 3. All broad reflections of the sample without heat treatment reflected the

crystal structure of silica gel, so apparently the TiO₂ ALD films on the samples should be amorphous totally. In contrast, the sharp reflections located at the positions $2\theta = 25.3^\circ$, 37.8° , 48.1° , 53.9° , 55.2° , 62.8° , and 75.2° correspond to the reflections from (101), (004), (200), (105), (211), (204), and (215) planes of TiO₂ in the anatase phase, respectively, which has a tetragonal structure for the sample after heat treatment. Peak assignments were made according to JCPDS (Cards No. 21-1276 and No. 21-1272). No rutile phase was detected. It indicates that the structure of TiO₂ transferred from amorphous to tetragonal after heat treatment. The TiO₂ crystal size was 11.0 nm after heat treatment according to the XRD analysis. However, the TiO₂ film thickness should be less than 4 nm after 40 cycles of TiO₂ ALD. Thus, it indicates that the thin TiO₂ film aggregated and became large TiO₂ particles with the formation of a tetragonal structure during the heat treatment, and thereby the surface area of TiO₂ decreased. Carbon (C), oxygen (O), silica (Si) and titanium (Ti) were detected on the surface of 40 cycles TiO₂ coated silica gel particles without heat treatment (Figure S1). EDX analysis showed that TiO₂ content on the particle surface was 34.6 wt.%, which is very close to the value measured by ICP-AES (31.7 wt.%). This implies that TiO₂ films were coated uniformly on the external surface and internal surface of the silica gel particles.

Figure 3. XRD pattern of 40 cycles of TiO_2 coated silica gel particles before and after heat treatment.

3.2. Adsorption performance

It has been an important objective to prepare a proper adsorbent with high adsorption capability and large particle size for easy separation from water after the removal of heavy metal and metalloid ions. Due to their high porosity and micrometer scale, TiO_2 coated silica gel particles with and without heat treatment were used in this study to adsorb the toxic ions. The simultaneous removal efficiency of the mixture ions of 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), Pb(II), and Mo(VI) by the uncoated and TiO_2 coated silica gel particles was evaluated at different pH values, as shown in Tables 1 and 2. Obviously, the uncoated silica gel particles were ineffective for all ions removal at pH 3. In contrast, the 20 cycles TiO_2 coated adsorbent without heat

treatment removed 99% As(V), 98% Se(IV), 75% V(V), 93% Mo(VI), 94% Pb(II), 40% Sb(III), and 42% Ag(I) from the solution at pH 3. The 40 cycles of TiO₂ coated particles without heat treatment showed similar adsorption performance. After heat treatment, the 20 and 40 cycles TiO₂ coated particles showed high removal efficiencies for As(V), Se(IV), V(V), Mo(VI) and Pb(II), but did not adsorb any Sb(III) and Ag(I) ions at pH 3. At pH 5, the simultaneous removal efficiencies of As (V), Se(IV), V(V), Mo(VI), Pb(II), Sb(III), Ag(I), Cu(II), and Ba(II) were higher than 40% for the 20 and 40 cycles of TiO₂ coated particles without heat treatment. After heat treatment, the removal efficiencies decreased for some elements and increased for some other elements, and no significant change for some elements. For example, there is almost no adsorption of Sb(III) for the 20 and 40 cycles TiO₂ coated silica gel particles. Instead, they removed about 45% Cr(III) and 40% Tl(I) simultaneously from the solution. The uncoated silica gel particles also removed 75% V(V), 99% Pb(II), 83% Ag(I), and 57% Cr(III) simultaneously under this pH condition. The point of zero charge (PZC) of amorphous TiO₂, anatase TiO₂, and SiO₂ was around 6.5, 7.2, and 3.5, respectively [29, 30]. When the pH value is below the PZC, TiO₂ and silica gel surface is positively charged. Otherwise, it will be negatively charged. Generally, the physisorption is driven by electrostatic force between oppositely charged adsorbates and adsorbents, but for chemisorption, like charged ions can interact by chemical bond [31].

Table 1. Removal efficiency of metal and metalloid ions by uncoated, 20 cycles, and 40 cycles of TiO₂ coated silica gel particles with/without heat treatment at pH 3.

	Uncoated	20 cycles TiO ₂	40 cycles TiO ₂	20 cycles TiO ₂ , 500 °C	40 cycles TiO ₂ , 500 °C
As	0%	99%	99%	82%	92%
Se	0%	98%	98%	74%	85%
Be	0%	0%	0%	0%	1%
Al	0%	0%	0%	0%	0%
V	0%	75%	79%	57%	60%
Cr	0%	4%	1%	18%	20%
Mn	0%	0%	4%	7%	4%
Co	0%	1%	3%	7%	4%
Ni	0%	0%	0%	0%	0%
Cu	0%	4%	4%	0%	2%
Zn	0%	0%	0%	0%	0%
Sr	0%	0%	2%	1%	0%
Mo	0%	93%	91%	99%	99%
Ag	0%	42%	40%	0%	11%
Cd	0%	1%	2%	1%	4%
Sb	0%	40%	56%	0%	2%
Ba	0%	12%	6%	0%	5%
TI	0%	6%	7%	22%	27%
Pb	0%	94%	94%	92%	94%

Table 2. Removal efficiency of metal and metalloid ions by uncoated, 20 cycles, and 40 cycles of TiO₂ coated silica gel particles with/without heat treatment at pH 5.

	Uncoated	20 cycles TiO ₂	40 cycles TiO ₂	20 cycles TiO ₂ , 500 °C	40 cycles TiO ₂ , 500 °C
As	60%	95%	95%	71%	73%
Se	21%	95%	97%	47%	55%
Be	11%	0%	0%	0%	0%
Al	28%	0%	0%	26%	18%
V	75%	86%	81%	93%	89%
Cr	57%	0%	0%	46%	45%
Mn	12%	0%	0%	2%	2%
Co	11%	4%	1%	7%	7%
Ni	11%	0%	0%	3%	1%
Cu	18%	72%	71%	64%	70%
Zn	12%	9%	7%	11%	6%
Sr	4%	1%	2%	5%	3%
Mo	10%	94%	91%	97%	97%
Ag	83%	73%	66%	30%	21%
Cd	13%	2%	0%	22%	19%
Sb	0%	40%	52%	3%	1%
Ba	4%	49%	38%	41%	43%
TI	5%	12%	10%	43%	41%
Pb	99%	60%	57%	73%	70%

As shown in Table 1, for all TiO₂ coated particles at pH 3, the removal efficiencies of As(V) and Se(IV) were high. In contrast, there is no obvious removal efficiency for the uncoated particles. When pH changed to 5, the removal efficiencies of As(V) and Se(IV) almost kept constant for the TiO₂ coated samples without heat treatment ($\geq 95\%$), but the removal efficiencies decreased for the TiO₂ coated samples with heat treatment (Figure S2). The uncoated particles removed 60% As(V) and 21% Se(IV) simultaneously at pH 5. At pH 3 and 5, the surface of the TiO₂ coated samples was positively charged, since the PZC of amorphism TiO₂ and anatase TiO₂ was higher than 5. As(V) and Se(IV) are commonly found in water in the form of inorganic

species. H_2AsO_4^- and HSeO_3^- are the dominant species in the pH range of 3.0-7.0 [32, 33]. The strong adsorption of As(V) and Se(IV) at pH 3 might suggest that H_2AsO_4^- and HSeO_3^- were adsorbed on TiO_2 through electrostatic interactions for the TiO_2 coated samples. At pH 3, the removal efficiencies of As(V) and Se(IV) for the samples with heat treatment were lower than that for the samples without heat treatment. This fact could be attributed to the reduced TiO_2 surface area of the particles after heat treatment. At pH 5, the removal efficiencies of As(V) and Se(IV) decreased for the TiO_2 coated samples with heat treatment. The single adsorption studies of As(V) and Se(IV) indicated that the adsorption performance was almost the same in the pH range between 3 and 5 for TiO_2 [32, 33]. In this study, the decrease of removal efficiencies could be mainly due to the fact that more other ions were adsorbed by the samples and there was not much space left for the As(V) and Se(IV) adsorption.

For the uncoated silica gel particles, though its surface was positive charged and could attract H_2AsO_4^- and HSeO_3^- , the PZC of the uncoated silica gel might be too low and thereby the interaction between metalloid ions and the particles was not strong enough to attract As(V) and Se(IV) at pH 3. At pH 5, the uncoated particles was negatively charged and adsorbed certain amount of metal ions. The As(V) and Se(IV) adsorption could result from electrostatic effect. Thus, the adsorption of As(V) increased from 0% at pH 3 to 60% at pH 5 (Figure S2).

Normally As(V) and Se(IV) occur as different species (e.g., H_2AsO_4^- , HAsO_4^{2-} and HSeO_3^- , SeO_3^{2-}) in water, which are affected by many factors (e.g., pH). The unstable nature of As(V) and Se(IV) compounds makes it difficult to treat, resulting in treated wastes with changing toxicity and mobility according to environmental conditions [34]. In this study, the TiO_2 coated samples,

especially the ones before heat treatment, could adsorb all kinds of As(V) and Se(IV) species and showed high removal efficiencies at different pH values (pH 3 and 5). Thus, it is a potential and promising adsorbent for the removal of As(V) and Se(IV).

At pH 3 and 5, the surface of the TiO₂ coated samples was positively charged, thereby these samples mainly adsorbed metal ions through chemisorption since both the surface of the samples and metal ions (except Mo(VI)) were positively charged and cannot attract each other by physisorption. Xie et al. [29] reported that Pb(II) ions could be adsorbed through the bond between Pb²⁺ and Ti-O- (chemisorption). The species of V(V), Sb(III) and Ag(I) were VO₂⁺, Sb³⁺ and Ag⁺, respectively, and they could be adsorbed by TiO₂ coated silica gel particles through the similar process. The dominate species of Mo(VI) are HMoO₄⁻ and MoO₄²⁻ at pH 3 and 5, respectively. Thus, the adsorption of molybdates could be through another process, as shown in the following reactions [35],

The single inner-sphere surface complexes [35], TiHMoO₄ and TiMoO₄⁻, were the dominant adsorbed molybdates species for the TiO₂ coated samples. For the uncoated silica gel particles, at pH 3 both metal ions (except Mo(VI)) and the surface of the silica gel particles were positively charged and cannot be attracted. After the pH was adjusted to 5, the silica gel surface changed to be negatively charged. So the sorption of V(V), Pb(II), Ag(I), and Cr(III) increased due to electrostatic attraction between the metal ions and silica gel (Figure S3). For Mo(VI) ions, though molybdates species was negatively charged and could be attracted, the PZC of the SiO₂

(3.5) was so low that the surface charge of the particles might not offer enough electrostatic force between molybdates species and particles at pH 3. It resulted in the low adsorption of Mo(VI) for the uncoated silica gel (Figure S3). **Beside the electrostatic attraction, the hydrolysis of metal ions was also an important factor in the adsorption process. With the increase in pH, the hydrolysis of metal cations increased. Hydroxyl–metal complexes (e.g., $\text{Cu}(\text{OH})^+$) are known to adsorb with a higher affinity than the unhydrolyzed metal cations (e.g., Cu^{2+}), and thereby the hydroxyl–metal complexes are easier to be adsorbed onto adsorbents [36-38]. In this study, the hydrolysis products of some metal ions formed, when pH increased to 5, and consequently the efficiency of some metal removal increased (e.g., Cu(II)).**

Before heat treatment, both 20 and 40 cycles of TiO_2 coated silica gel particles had amorphous TiO_2 structure, and the surface area and pores size of the TiO_2 coated samples reduced after additional 20 cycles of TiO_2 ALD coating. In comparison with the adsorption results for the 20 cycles of TiO_2 coated particles at pH 5, the simultaneous removal efficiencies of V(V), Mo(VI), Pb(II), Ag(I), Cu(II), and Ba(II) for the 40 cycles of TiO_2 coated silica gel particles decreased slightly. This could be attributed to the surface area decrease of silica gel particles, which led to the reduction of adsorption sites. At pH 3, more adsorption sites might be occupied by H_3O^+ for both of these two samples, so they did not show obvious difference of removal efficiency. After heat treatment, the crystal structure of TiO_2 changed to anatase and the crystal size of TiO_2 particles on the silica gel particles was much larger than that before heat treatment. The 20 and 40 cycles of TiO_2 coated silica gel particles with heat treatment showed similar adsorption performance. It may indicate that the TiO_2 surface area of these two samples

were similar after heat treatment.

Compared to the TiO_2 coated samples without heat treatment, the removal efficiencies of Sb(III) and Ag(I) (especially Sb(III)) were low for the TiO_2 coated silica gel particles with heat treatment at pH 3 and 5, which could be attributed to the hypothesis that Sb(III) and Ag(I) ions were much easier to be absorbed by amorphous TiO_2 than anatase TiO_2 . Thus, the removal efficiency of Sb(III) was less than 5% for the TiO_2 coated silica gel particles with heat treatment (anatase TiO_2). To verify this hypothesis, single adsorption experiments using Sb(III) ions only were performed. At pH 5, both the 20 and 40 cycles of TiO_2 coated samples with heat treatment removed 29% of Sb(III) from the solutions (Table 3). This proved that anatase TiO_2 could adsorb Sb(III) , but compared with amorphous TiO_2 , the uptake amount of Sb(III) was low for anatase TiO_2 . It is also noted that the TiO_2 coated samples after heat treatment removed much more Ti(I) and Cr(III) than the samples before heat treatment. This could be attributed to the relative high uptake amount of Ti(I) and Cr(III) for the TiO_2 coated silica gel particles with heat treatment. As shown in Table 3, the results of Cr(III) single adsorption experiments showed that the removal efficiencies were 21% and 17% for the 20 and 40 cycles of TiO_2 coated silica gel particles without heat treatment at pH 5, respectively. It indicated that the amorphous TiO_2 could adsorb Cr(III) ions, but the uptake amount was not high. The results also showed that the competitive adsorption was real occurring in the experiments and it affected the removal efficiencies of different ions partly. Similar phenomenon was observed in the study on competitive adsorption of Pb(II) , Cd(II) , Cu(II) and Cr(III) ions onto titanate nanotubes by Liu et al. [39].

Table 3. Results of single adsorption experiments of Sb(III), Cr(III), and Pb(II) ions by the 20 cycles and 40 cycles of TiO₂ coated silica gel particles with/without heat treatment at pH 5.

	20 cycles	40 cycles	20 cycles, 500 °C	40 cycles, 500 °C
Sb(III)	-	-	29%	29%
Cr(III)	21%	17%	-	-
Pb(II)	71%	76%	100%	100%

For all samples, the removal efficiency of Pb(II) reduced as pH increased from 3 to 5 (Figure S4), which is probably due to the fact that other metal ions occupied more adsorption sites at pH 5 and less sites were available for Pb(II). Pb(II) single adsorption experiments were carried out to verify this assumption. The results showed that more than 70% and 90% of Pb(II) was removed from the solution for the TiO₂ coated samples without and with heat treatment at pH 5, respectively (Table 3). The removal efficiency was higher than that in competitive adsorption case. Thus, in the experiment with mixed ions, the decrease of Pb(II) removal efficiency at pH 5 should be due to the competitive adsorption between Pb(II) and other ions.

The simultaneous uptake amounts of As(V), Se(IV), V(V), Pb(II), and Mo(VI) were 0.99, 0.98, 0.79, 0.91 and 0.91 mg/g at pH 3 for the the 40 cycles of TiO₂ coated particles without heat treatment, respectively. At pH 5, the uptake amounts of As(V), Se(IV), V(V), Sb(III), Ag(I), and Cu(II) increased to 0.95, 0.97, 0.81, 0.52, 0.66 and 0.71 mg/g, respectively. Compared to other studies, the uptake amounts in this work were not high. This can be explained by the following two reasons. First, the surface area of our adsorbent is low due to the relative low surface area of the silica gel particles used in this study. Thus, the adsorbents only offered relative limited

adsorption sites. Second, there were 19 different metal and metalloid ions in the solution and they could competitively occupy the limited adsorption sites of TiO_2 , which affected the sorption performance of each other. This phenomenon has also been mentioned by Youssef and Malhat [13]. In their study, TiO_2 nanowires were used to remove Pb(II) , Cu(II) , Zn(II) , Cd(II) , and Fe(III) in a solution simultaneously and the adsorption capacities of Pb(II) , Cu(II) , Zn(II) , Cd(II) , and Fe(III) were only 0.48, 0.38, 0.17, 0.32, and 0.40 mg/g, respectively [13]. In our current study, 19 different ions were simultaneously involved in the adsorption process, and the uptake amounts were still much higher.

Generally, it is more difficult to remove metal and metalloid ions from acidic solutions than from neutral and basic solutions, since some elements are easy to precipitate in the neutral and basic solutions, as shown in Table S1. In this study, the 20 and 40 cycles of TiO_2 coated silica gel particles without heat treatment showed good adsorption performance for V(V) , Mo(VI) , Pb(II) , Sb(III) , Ag(I) , Cu(II) , Ba(II) , As(V) , and Se(IV) ions in acidic and even highly acidic medium. It is a highly practical adsorbent because none of wastewater contains only one element ion at neutral pH in industry. Moreover, the desorption and regeneration of $\text{TiO}_2/\text{SiO}_2$ samples are easy to carry out using HNO_3 solution [40] or ethylenediaminetetraacetic acid (EDTA) [41]. This regeneration process is adopted widely and thereby it could save the cost and reduce waste production since both TiO_2 and SiO_2 are stable in acidic condition. Compared to the $\text{TiO}_2/\text{SiO}_2$ samples, the regeneration of activated carbon, a conventional adsorbent, is difficult under common conditions [41]. Thus, this is a big advantage to be a practical adsorbent for $\text{TiO}_2/\text{SiO}_2$ samples in the future.

In summary, the performance of the novel TiO₂ coated adsorbent on the removal of heavy metal ions is quite promising, especially for the adsorption of V(V), Pb(II), and Mo(VI) in acidic solution. Unsaturated oxygen bond and high chemisorption ability of TiO₂ could be the key reason for the difference of sorption capability between the uncoated and the TiO₂ coated particles [29]. Compared to the uncoated silica gel particles, TiO₂ coating brought unsaturated oxygen bond, which can interact with metal ions by chemical bond and then improve the sorption capability greatly in acidic solution [29]. The strategy of TiO₂ ALD coating is a universal and effective method to prepare different adsorbents for water treatment. TiO₂ can be coated on various substrates besides silica gel particles through ALD, such as high surface area active carbon and Al₂O₃ substrates. Compared to other preparation methods, TiO₂ can be coated on substrates over complex 3D topography structures uniformly, which can take full advantage of the high surface area of substrates.

3.3. Sedimentation experiments

Since TiO₂ particles are white and difficult to be observed in water, so methyl blue (MB) solution was chosen in the following experiments. As we know, TiO₂ can adsorb MB [42] and the particles would change to blue, then the sedimentation of particles can be observed easily. As shown in Figure 4a, after the silica gel particles coated with 40 cycles of TiO₂ (without heat treatment) were added in the MB solution for 2 min, all particles settled down and the solution changed to clear completely. In contrast, for the case of P25, the solution was still turbid after 60 min, as shown in Figure 4b. This proved that most P25 NPs did not settle down. Thus, the

prepared nanoporous microparticles are much faster and easier to be separated from solutions.

Figure 4. Sedimentation of (a) 40 cycles of TiO_2 coated silica gel particles without heat treatment and (b) P25 NPs in MB solution.

4. Conclusion

Ultrathin TiO_2 films were deposited on nanoporous, micron-sized silica gel particles by ALD in a fluidized bed reactor. At pH 3 and 5, the 20 and 40 cycles of TiO_2 coated particles without heat treatment could efficiently remove As(V), Se(IV), V(V), Mo(VI), Pb(II), Sb(III), Ag(I), Cu(II), and Ba(II) ions simultaneously. The heat treatment of the TiO_2 coated particles affected their adsorption performance a lot. This might be due to the decreased TiO_2 surface area during

the heat treatment. Compared to other adsorbents, the TiO₂ coated particles showed good performance in acidic medium and could remove different metal and metalloid ions at the same time. In addition, this novel micro-sized adsorbent (30-75 μm particle size) is very easy to be separated and will not cause a second pollution. This is a big advantage, as compared to the TiO₂ NPs adsorbent.

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