



Removal of aqueous arsenite by simultaneous ultraviolet photocatalytic oxidation–coagulation of titanium salts: effect of precipitate particles size and solution chemistry

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ABSTRACT

This study explored the As(III) removal efficiency by simultaneous UVA ($\lambda = 365$ nm) photocatalytic oxidation–coagulation of $\text{Ti}(\text{SO}_4)_2$ (UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation) under the influence of solution chemistry and the size of $\text{Ti}(\text{SO}_4)_2$ precipitate particles. The results indicated that As(III) removal efficiency by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation was greater than 96% at pH 4–6, but experienced a large drop with increasing of solution pH from 7 to 10 at $\text{Ti}(\text{SO}_4)_2$ dose of 5 mg Ti/L and initial As(III) concentration of 200 $\mu\text{g/L}$. The As(III) removal behavior presented by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation was greatly different from $\text{Ti}(\text{SO}_4)_2$ coagulation, indicating the oxidation of As(III) during UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation. As(III) removal efficiency increased greatly with the improvement of ionic strength and decreased with the increase of precipitate particle size. Sulfate exhibited negligible influence on As(III) removal at pH 4–7, whereas made As(III) decreased by 20%–32% at pH 8–10. Sulfate mainly competes for the active adsorption sites with arsenic but exerted a slightly effect on the formation of Ti(IV) precipitates. Fluoride reduced As(III) removal efficiency by 9%–33% over the pH range of 4–10 mainly by both competing with arsenic for adsorption sites and increasing the solubility of Ti(IV), and the effect increased with the increase of fluoride concentration. In acid circumstance (pH 4–6), both Fe(II) and Mn(II) imposed little effect on As(III) removal by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation, while in alkaline circumstance (pH 7–10), the presence of Fe(II) made As(III) removal increase by different extent, the effect of Mn(II) varied with solution pH and Mn(II) concentration.

Keywords: As(III) removal; $\text{Ti}(\text{SO}_4)_2$; Ultraviolet photocatalytic oxidation; Coagulation; Solution chemistry

1. Introduction

Elevated arsenic (As) in groundwater has been a serious global health and environmental concern prevailing in several areas around the globe for the last several years [1]. Chronic arsenic exposure from drinking water is associated

with numerous human diseases and influences millions of people worldwide [2]. Due to the severe toxicity of arsenic to human health, a more strict drinking water allowance limit of 10 $\mu\text{g/L}$ was prescribed by the United States Environmental Protection Agency [3].

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The inorganic species of arsenite (As(III)) and arsenate (As(V)) are the dominating arsenic speciation in nature water. As(V) which mainly exists as H_2AsO_4^- and HAsO_4^{2-} at $\text{pH} > 2.3$ is the predominant As form under oxidized environments, while As(III) occurs predominantly in neutral molecular form of H_3AsO_3 in reduced conditions at $\text{pH} < 9.2$ [4,5]. The removal of As(III) is more challenging due to the fact that As(III) is more toxic, mobile, and soluble than As(V) [6]. Additionally, As(III) can account for up to 67%–99% of total arsenic in groundwater [7]. The oxidation of As(III) to As(V) not only decreases the toxicity of arsenic but also enhances arsenic removal from raw water by adsorption or co-precipitation.

Various oxidation methods have been studied for the oxidation of As(III), such as TiO_2 photocatalysis [8,9], chlorine, ozone [10], manganese-oxide [11], Fenton's reaction [12], Fe(VI) [13], UV irradiation [14,15], etc. Among those techniques, TiO_2 photocatalysis had been proved to be effective for As(III) pre-oxidation, and As(V) formed could be subsequently adsorbed by TiO_2 particles [9]. However, it is difficult to separate As(V)– TiO_2 particles from treated water by gravity owing to the small size of TiO_2 particles, coagulation or adsorption processes are still needed as a posttreatment to improve the removal of As(V)– TiO_2 particles [9,16]. A novel process, simultaneous ultraviolet photocatalytic oxidation–coagulation of titanium sulfate using UVC ($\lambda = 254 \text{ nm}$) as ultraviolet source, was developed in our previous research for the oxidation and removal of As(III). As(III) could be oxidized to As(V) during UVC/ $\text{Ti}(\text{SO}_4)_2$ coagulation in the whole pH range of 4–10, resulting in the highly efficient arsenic removal at pH 4–6 [17].

The wavelength of UV irradiation is a crucial factor for photocatalytic reactions. Whether As(III) could be oxidized and removed efficiently by photocatalytic oxidation–coagulation of titanium sulfate when UVA ($\lambda = 365 \text{ nm}$) was used as ultraviolet source (UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation) is unclear currently.

The precipitation of hydrolyzing metal salts include nucleation, crystal growth and aggregation [18,19], and the particles size, which was reported to highly affect the rate of the photocatalytic reaction and adsorption of arsenic [20], grew with time due to the aggregation of primary particle during coagulation. Hence, it is of great importance to investigate the role of the Ti(IV) precipitate particles size in the removal of As(III) by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation.

The removal of arsenic by coagulation or adsorption could be negatively affected by co-existing anions such as sulfate (SO_4^{2-}) [21] and fluoride (F^-) [22]. Moreover, the co-occurred Fe(II) and Mn(II) were reported to play a vital role in both the oxidation and removal of As(III) [23]. It is necessary to examine systematically the effect of the co-existing ions on As(III) removal by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation.

This study aims at investigating the As(III) removal efficiency by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation under the influence of solution pH and the size of Ti(IV) precipitate particles. The effect of co-existing ions such as SO_4^{2-} , F^- , Fe(II), and Mn(II) on the removal of As(III) by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation, which had not been conducted in our previous works [17], were also examined as functions of solution pH and co-existing ion concentration.

2. Materials and methods

2.1. Reagents

NaAsO_2 (AR) was purchased from Sigma-Aldrich (Bellefonte, PA, USA); Titanium sulfate ($\text{Ti}(\text{SO}_4)_2$, CP), Titanium tetrachloride (TiCl_4 , 98%), Na_2SO_4 (AR), NaF (AR), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (AR), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (AR), NaCl (AR) and NaHCO_3 (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China), and HCl (AR) and NaOH (AR) were purchased from Xi'an Chemicals Ltd., (Xi'an, China). A 0.5 mol/L $\text{Ti}(\text{SO}_4)_2$ stock solution was prepared weekly using 1 mol/L H_2SO_4 solution. The TiCl_4 stock solution was prepared used the method as follows: a desired amount of TiCl_4 was slowly dropped into ultrapure water in an ice-water (0°C – 4°C) bath to obtain 0.5 mol/L TiCl_4 stock solution. Fresh Fe(II) and Mn(II) stock solutions were prepared for each experiment and used within 5 min after preparation.

All solutions were prepared using ultrapure water (18.2 M Ω cm, TOC $\leq 1 \mu\text{g/L}$) produced by an Elga Purelab Ultra Analytic System (UK) and stored in a refrigerator at 4°C .

2.2. Experimental procedure

All the UV irradiation experiments were performed in a photochemical reactor (Bilang Instrument Co., Shanghai, China). A 500 W medium pressure mercury lamp (MPML, $\lambda = 365 \text{ nm}$) operating inside a recirculating cooling water system was used as UV light source and placed at a fixed position beside a 500 mL quartz beaker. The average UV fluence rate (I_s) was determined to be 0.59 mW/cm 2 using the same method reported in our previous research [17]. The mercury lamp was cooled by circulating tap water, and the working solution temperature was maintained at $20^\circ\text{C} \pm 1^\circ\text{C}$ during the irradiation reaction. Two hundred and fifty milliliters of working solution containing 200 $\mu\text{g/L}$ As(III), 1 mmol/L NaHCO_3 , and 1 mmol/L NaCl was transferred to a quartz beaker and stirred on a magnetic stirrer. To obtain a designated final pH, a predetermined amount of HCl or NaOH was added to the working solution firstly. The MPML was preheated at least 15 min before used and switched on immediately after the addition of $\text{Ti}(\text{SO}_4)_2$ coagulant (a fixed dosage of 5 mg/L as Ti). The solution was then rapid stirred for 60 s at 300 rpm followed by slow stirring at 150 rpm for 20 min. After the operation, the suspension was settled statically for 20 min. Then supernatant samples were filtered through 0.45 μm polyethersulfone (PES) membrane, and stored in a polyethylene bottle in a refrigerator at 4°C with acidification (67% HNO_3) for the determination of total concentration of arsenic and other metal. For comparison, As(III) removal by UVA/ TiCl_4 coagulation was performed following the same procedure as UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation. Solution pH was measured using a pH meter (PHS-3C, Dapu, China) and reported with errors $\leq \pm 0.05$. The zeta potential of the precipitates was measured using a Zetasizer (Nano ZS, Malvern, UK). All experiments were conducted at least in triplicate and the average values of results were reported.

To investigate the role of size of Ti(IV) precipitates in As(III) removal by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation, the experiments of As(III) removal kinetics were conducted in the following way: As(III) was added, respectively, at 0, 1, 5, and

10 min after the dosing of coagulant, 0 min meant that As(III) was added before $\text{Ti}(\text{SO}_4)_2$. The UV lamp was switched on immediately after the dosing of $\text{Ti}(\text{SO}_4)_2$. During photoreaction, sample aliquots were withdrawn at fixed time interval and filtered through 0.45 μm PES membrane for the analysis of arsenic species and total arsenic concentration. The time scale for arsenic removal by coagulation for all photoreaction was 21 min.

2.3. Analyses

The residual concentration of As(III) and As(V) after filtration were detected using high performance liquid chromatography hyphenated with inductively coupled plasma mass spectrometry (HPLC-ICP/MS) (ELAN DRC-e, Perkin Elmer SCIEX, Canada). A Hamilton PRP-X100 HPLC column (250 mm \times 4.1 mm, 10 μm , Switzerland) was used. The limit of quantitative detection was 0.5 μg As/L. The concentration of total arsenic, Ti(IV), iron, and manganese in filtrate were analyzed using ICP-MS.

3. Results and discussion

3.1. Effect of solution pH

The As(III) removal efficiency by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation was investigated as function of solution pH during the

range of 4–10, and compared with $\text{Ti}(\text{SO}_4)_2$ coagulation and UVA/ TiCl_4 coagulation. The results are presented in Fig. 1.

The As(III) removal efficiency of 99.6%, 99.2%, and 96.1% by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation, which was much higher than $\text{Ti}(\text{SO}_4)_2$ coagulation, could be achieved at solution pH of 4, 5, and 6, respectively (Fig. 1a). The arsenic remaining in solution was all below 10 $\mu\text{g/L}$. As pH increased from 7 to 10, As(III) removal efficiency declined significantly from 69.4% to 34.9%. As(III) removal by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation was highly dependent on solution pH. On the other hand, only 46.1%–68.7% of As(III) could be removed throughout the pH range of 4–10 by $\text{Ti}(\text{SO}_4)_2$ coagulation, and the removal efficiency varied slightly with solution pH. In agreement with our previous study on As(III) removal by UVC/ $\text{Ti}(\text{SO}_4)_2$ coagulation [17], the great difference in As(III) removal between UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation and $\text{Ti}(\text{SO}_4)_2$ coagulation was attributable to the oxidation of As(III) to As(V) during UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation. It had been confirmed that acid circumstance was more effective in As(V) removal by coagulation or adsorption, the removal efficiency decreased with the increase of pH [24,25].

The oxidation of As(III) to As(V) during UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation could also be verified by the results of HPLC-ICP/MS detection that the arsenic remaining in solution was all in the oxidized form of As(V) across the pH range of 4–10. The precipitates hydrolyzed from aqueous solutions of titanium sulfate were reported to consist of

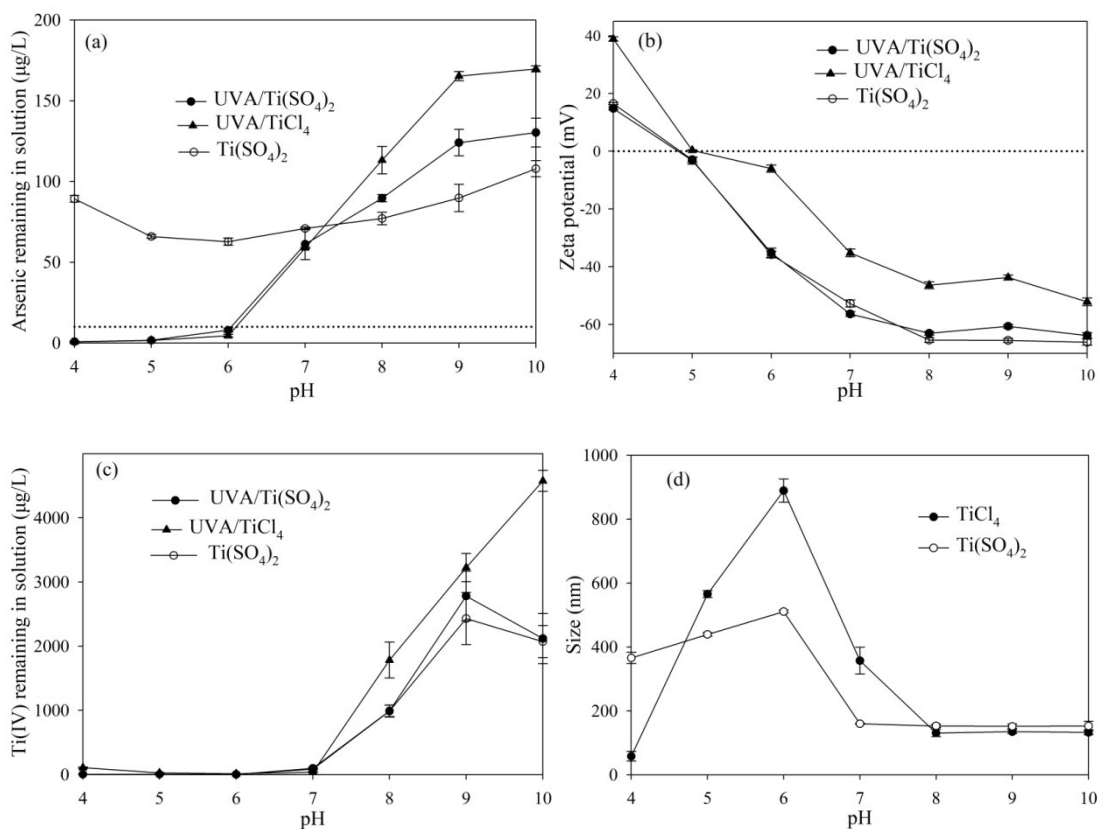


Fig. 1. Effect of solution pH on As(III) removal by UVA/ $\text{Ti}(\text{SO}_4)_2$, UVA/ TiCl_4 , and $\text{Ti}(\text{SO}_4)_2$ coagulation. Conditions: $C_{0,\text{As(III)}} = 200$ $\mu\text{g/L}$, $\text{Ti}(\text{SO}_4)_2$ or TiCl_4 dose = 5 mg/L (as Ti), $I_s = 0.59$ mW/cm². (a) As remaining in solution vs. pH, (b) zeta potentials of coagulated precipitates vs. pH, (c) Ti(IV) remaining in solution vs. pH, and (d) size of Ti(IV) precipitate particles of $\text{Ti}(\text{SO}_4)_2$ and TiCl_4 vs. pH.

nano-crystalline [26], which might catalyzed the oxidation of As(III) under UVA irradiation. The oxidized product As(V) was subsequently removed by Ti(IV) precipitates. It should be noted that the homogeneous photooxidation of As(III) by UVA photolysis alone was very slow and weak [14,15].

In the pH range of 4–5, zeta potential of $\text{Ti}(\text{SO}_4)_2$ precipitates was mainly positive (from 15 to -3 mV) (Fig. 1b), protonated active sites ($\text{I}-\text{OH}_2^+$) would predominate. As the result of oxidation, As(III) was converted to As(V) and existed mainly as H_2AsO_4^- at the same pH range. The electrostatic attraction promoted the diffusion and subsequent adsorption of negatively charged As(V) oxyanions onto positively charged precipitates during UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation. But the electrostatic interaction between neutral As(III) species (H_3AsO_3) and positively charged precipitates was relatively weak during $\text{Ti}(\text{SO}_4)_2$ coagulation, resulted in the higher arsenic removal efficiency by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation than that by $\text{Ti}(\text{SO}_4)_2$ coagulation. As pH increased from 6 to 10, zeta potential of $\text{Ti}(\text{SO}_4)_2$ precipitates became increasingly negative (from -35 to -64 mV) (Fig. 1b), the active sites of precipitates surface became deprotonated ($\text{I}-\text{O}^-$), the positively charged active sites ($\text{I}-\text{OH}_2^+$) decreased. The electrostatic repulsion between HAsO_4^{2-} , AsO_4^{3-} and the negatively charged precipitates would increase and be against the diffusion of the oxyanions onto the surface and further adsorption at higher solution pH value. As a results, As(III) removal efficiency by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation dropped greatly from pH 7 to 10. In addition, the electrostatic repulsion between the primary precipitate particles

prevented their aggregation to form large particles whose sizes were large enough to realize solid–liquid separation by MF (membrane filtration). Most precipitate particles passed through $0.45 \mu\text{m}$ pore size membrane when filtrated. As shown in Fig. 1c, the Ti(IV) remaining in filtrate increased greatly, indicating the reduce of precipitate solids for arsenic retention, this also resulted in the decrease of As(III) removal efficiency. While the electrostatic repulsion between neutral As(III) species (H_3AsO_3) and negatively charged precipitates was much weaker, the neutral H_3AsO_3 molecules might be able to diffuse onto precipitates surfaces regardless of the surface charge to engage an adsorption process during $\text{Ti}(\text{SO}_4)_2$ coagulation. Hence the As(III) removal efficiency by $\text{Ti}(\text{SO}_4)_2$ coagulation preceded that by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation at higher solution pH values.

At pH 8, when improving NaCl concentration from 1 to 10 and 100 mmol/L during UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation, the zeta potential of Ti(IV) precipitates increased from -63.09 to -5.5 and -15.90 mV (Fig. 2a) due to the double layer compression. The decrease of surface charge made the reduce of colloid stability of the primary colloidal precipitates, consequently the aggregation of colloidal precipitates and formation of larger precipitated flocs [24], particularly for NaCl concentration of 100 mmol/L. The size of $\text{Ti}(\text{SO}_4)_2$ precipitate particles increased from 153.0 to 912.3 nm at 100 mmol/L NaCl, which resulted in effective solid–liquid separation and consequently the removal of arsenic with precipitates by MF (as shown in Figs. 2b–d). Moreover, the reduce of negative surface charge decreased

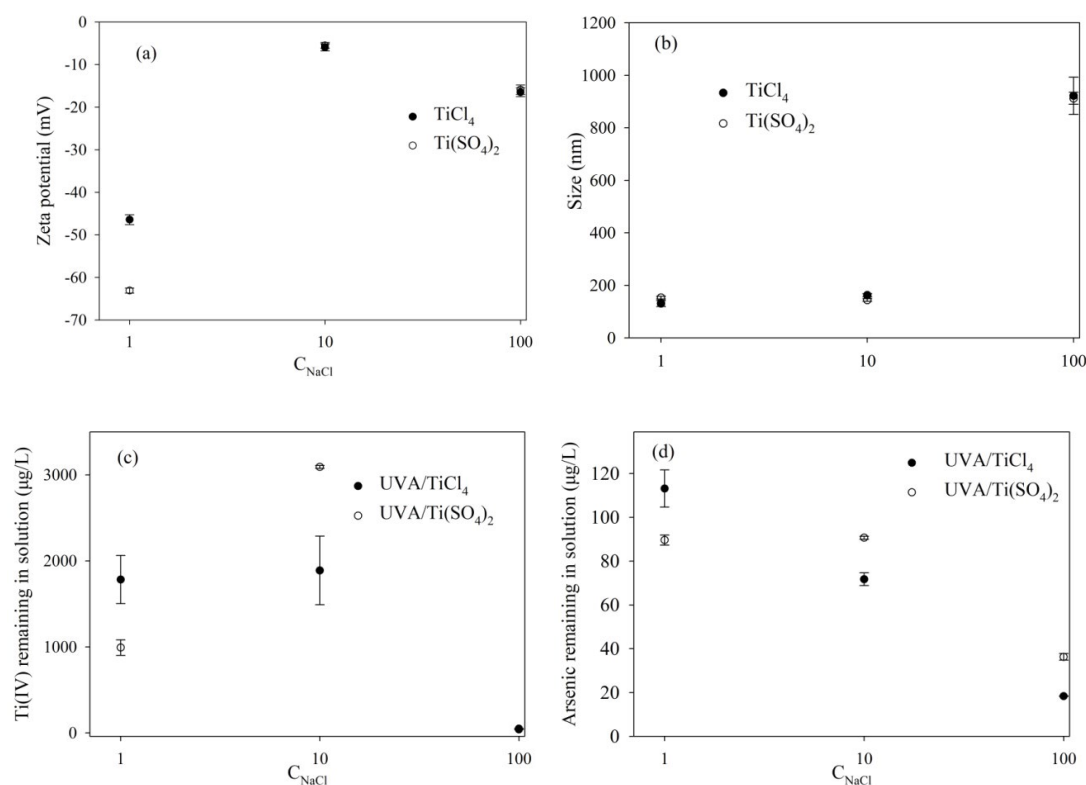


Fig. 2. Effect of NaCl concentration on the removal of As(III) by UVA/ $\text{Ti}(\text{SO}_4)_2$ and UVA/ TiCl_4 coagulation. Conditions: $C_{0,\text{As(III)}} = 200 \mu\text{g/L}$, $\text{Ti}(\text{SO}_4)_2$ or TiCl_4 dose = 5 mg Ti/L, solution pH = 8, $I_s = 0.59 \text{ mW/cm}^2$. (a) Zeta potentials of coagulated precipitates, (b) size of floc particles, (c) Ti(IV) remaining in solution vs. NaCl concentration, and (d) As remaining in solution vs. NaCl concentration.

the electrostatic repulsion between HAsO_4^{2-} , AsO_4^{3-} and the negatively charged hydrolyzed precipitates and promoted the adsorption of As(V). As a result, the As(III) removal efficiency by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation increased from 55.2% to 81.9% at 100 mmol/L NaCl (Fig. 2d). Arsenic removal efficiency had been reported to increase with increasing ionic strength resulted from an enhancement of the electrostatic interactions owing to the compression of the double layer thickness [27–29].

As(III) removal efficiency by UVA/ TiCl_4 coagulation was comparable to that by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation at pH 4–7 whereas lower by 12%, 21%, and 20% at pH 8, 9, and 10, respectively (Fig. 1a). The lower As(III) removal efficiency probably resulted from the reduce of precipitates retained by membrane filtration after UVA/ TiCl_4 coagulation at pH 8–10 (Fig. 1c). The average sizes of primary hydrolyzed precipitate particles at pH 8–10 were all below 200 nm for $\text{Ti}(\text{SO}_4)_2$ and TiCl_4 (Fig. 1d), and the particles sizes were very stable in the reaction time. Although the average size of $\text{Ti}(\text{SO}_4)_2$ precipitate particles was comparable for that of TiCl_4 , the size distribution of TiCl_4 precipitate particles might be less homogeneous than that of $\text{Ti}(\text{SO}_4)_2$. There might be more small precipitate particles, most likely well below the reported average size for UVA/ TiCl_4 coagulation. Those small particles containing a number of arsenic passed through the micro-membrane and resulting in the higher filtrated Ti(IV) concentration and finally the lower As(III) removal by UVA/ TiCl_4 coagulation. Similar to UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation, due to the double layer compression, the zeta potential of TiCl_4 precipitates increased from -46.4 to -6.0 and -16.5 mV when improved NaCl concentration to 10 and 100 mmol/L, respectively, resulting in the formation of larger particles (921.8 nm) at 100 mmol/L NaCl (Fig. 2b). Consequently the precipitates associated with arsenic could be effectively retained by MF, and a As(III) removal efficiency up to 90.8% could be achieved by UVA/ TiCl_4 coagulation (Fig. 2d). The slightly higher As(III) removal efficiency by UVA/ TiCl_4 coagulation than by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation at 100 mmol/L NaCl was probably resulted from the competitive adsorption of sulfate with arsenic.

3.2. Effect of precipitate particles size

The effect of size of precipitate particles on As(III) removal by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation at pH 5 is shown in Fig. 3.

The size of Ti(IV) precipitate particles at 1, 5, and 10 min was around 0.54, 3.5, and 5.4 μm in diameter, respectively. As revealed in Fig. 3, 61.7%, 55.9%, 42.0%, and 38.6% of As(III) could be removed after 1 min for the reaction that As(III) was added before $\text{Ti}(\text{SO}_4)_2$ coagulant and at 1, 5, and 10 min after $\text{Ti}(\text{SO}_4)_2$ coagulant, respectively. For the reaction As(III) was added before $\text{Ti}(\text{SO}_4)_2$ coagulant, arsenic concentration reduced from 200 $\mu\text{g/L}$ to lower than 4.71 $\mu\text{g/L}$ at the first measuring interval (10 min). However, it needed about 15 min to achieve the comparable arsenic removal efficiency for the reaction that As(III) was added at 5 and 10 min after $\text{Ti}(\text{SO}_4)_2$ dosing. The increase of particles size led to the decrease of As(III) removal rate. This was in line with the previous researches that particles size was a curial factor for both photocatalysis and adsorption. Lin et al. [30] reported that the photocatalytic

rate constants decreased exponentially with the increase of the primary particle size. The agglomeration of particles played an important role in the photocatalytic degradation rate [31]. The increase of particles size, which would lead to the decrease of particles specific surface area, resulted in greatly decrease of arsenic adsorption capacities of adsorbents [20,32]. The faster As(III) removal in the first few minutes suggested that the primary precipitates formed at the early stage of Ti(IV) hydrolysis, which provided a great number of reaction sites for photo-oxidation of As(III) and absorption of the oxidized As(V), might play an important role in the oxidation and removal of As(III).

3.3. Effect of sulfate

The influence of sulfate on As(III) removal by UVA/ $\text{Ti}(\text{SO}_4)_2$ coagulation as function of solution pH was conducted at sulfate concentration of 100 and 250 mg/L. The results are shown in Fig. 4.

The effect of sulfate was highly dependent on solution pH value. The presence of both of 100 and 250 mg/L sulfate had negligible effect on As(III) removal at pH 4–7, but made As(III) removal efficiency decrease by 20%–32% at pH 8–10 (Fig. 4a). There might be competitive adsorption between sulfate and arsenic at higher pH. As shown in Fig. 4b, the presence of sulfate increased the negative surface charge of Ti(IV) precipitates. The shift of the isoelectric point (IEP) of precipitates to more acid pH in the presence of 100 and 250 mg/L sulfate indicated that a fraction of SO_4^{2-} was chemically bonded to the metal hydroxide precipitates. The increase of sulfate concentration from 100 to 250 mg/L did not result in a larger reduction of As(III) removal, probably indicating the saturation of sites accessible to SO_4^{2-} .

There had been controversial reports about the effect of sulfate on arsenic removal. Guan et al. [21] reported that the presence of 50–100 mg/L SO_4^{2-} had negligible effect on As(III) removal at pH 4–5 while made As(III) removal decrease by 6.5%–36% over pH 6–9 in the KMnO_4 -Fe(II) process. Meng et al. [33] indicated that as high as 300 mg/L

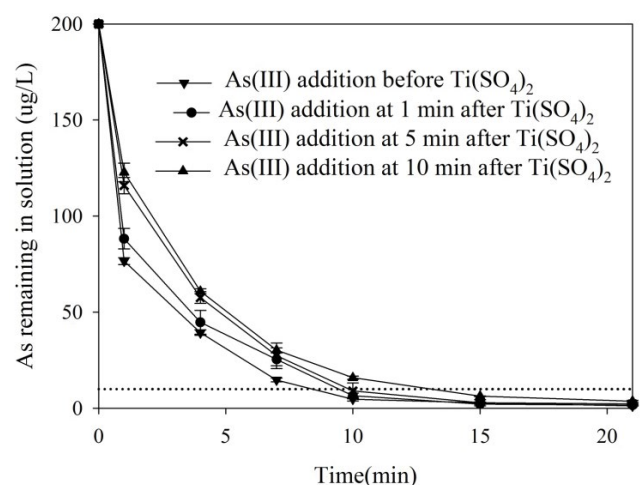


Fig. 3. As(III) remaining in solution vs. coagulation time. Conditions: $C_{0,\text{As(III)}} = 200 \mu\text{g/L}$, $\text{Ti}(\text{SO}_4)_2$ dose = 5 mg Ti/L, $I_s = 0.59 \text{ mW/cm}^2$, pH = 5.

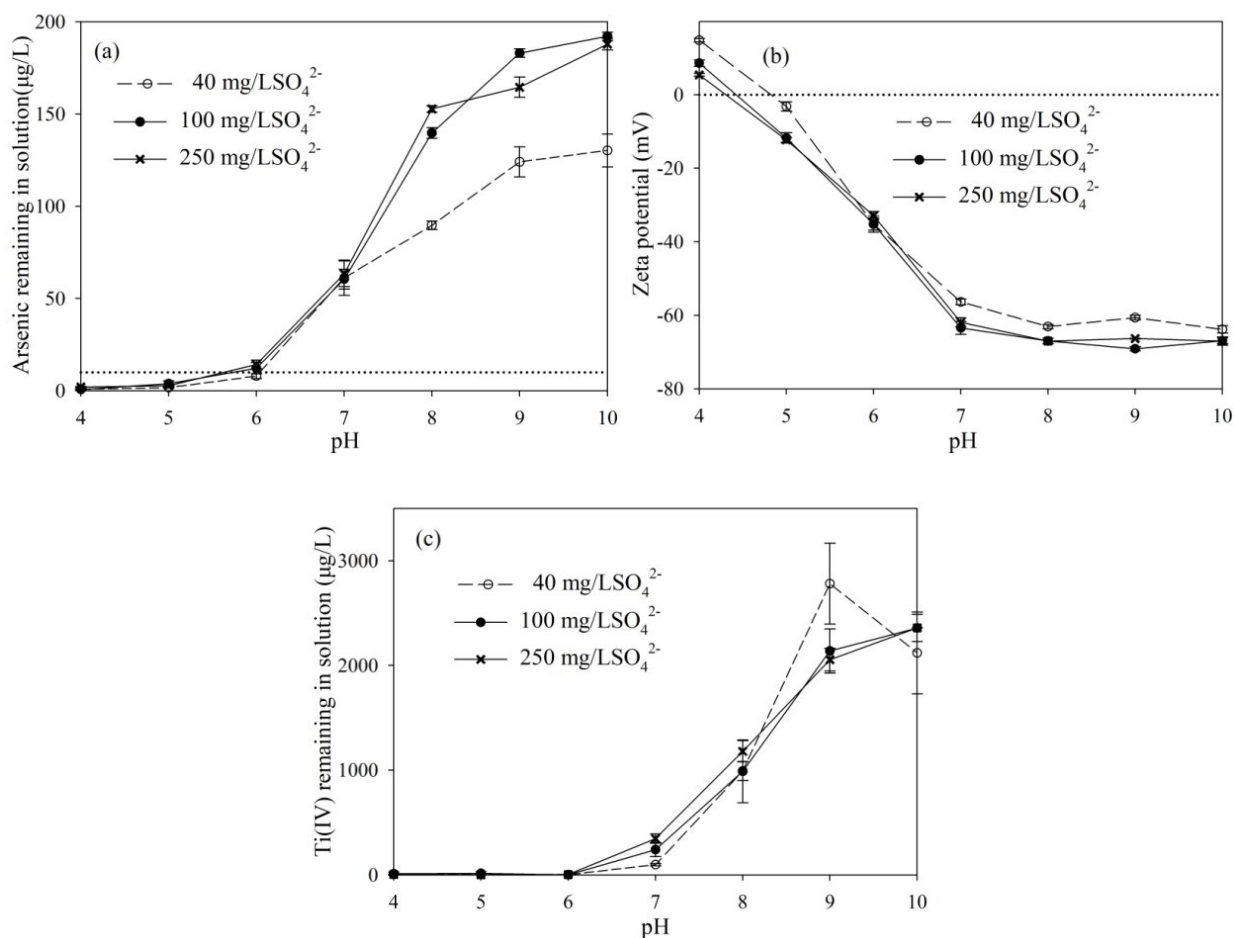


Fig. 4. Effect of sulfate on As(III) removal by UVA/Ti(SO₄)₂ coagulation. Conditions: $C_{0,As(III)} = 200 \mu\text{g/L}$, $\text{Ti}(\text{SO}_4)_2$ dose = 5 mg Ti/L, $I_s = 0.59 \text{ mW/cm}^2$, $C(\text{SO}_4^{2-}) = 100$ or 250 mg/L. (a) As remaining in solution vs. pH, (b) zeta potentials of coagulated precipitates vs. pH, and (c) Ti(IV) remaining in solution vs. pH.

sulfate almost had no influence on As(V) removal by coprecipitation with ferric chloride at pH 6.8, and indicated that sulfate binding affinity for ferric hydroxide was much weaker than As(V). It was reported in our previous study that sulfate had almost no effect on the As(V) removal at pH 5–7 and only marginal decreases in removal efficiencies were observed above the neutral pH value [24]. Though a drop occurred in As(III) removal efficiency in the presence of 100 and 250 mg/L sulfate at pH 8–10 in the present research, HPLC–ICP/MS detection revealed that the arsenic remaining in solution was all in the oxidized form of As(V). The presence of sulfate had little influence on As(III) oxidation.

As shown in Fig. 4c, the filtrated Ti(IV) concentration experienced a slight increase by 3%–5% at pH 7, 8, and 10, but a little decrease by 13%–15% at pH 9 in the presence of 100 and 250 mg/L sulfate, indicating that the effect of sulfate on the hydrolysis of Ti(IV) and formation of titanium hydroxide precipitates should not take major responsibility for the decrease of arsenic removal. The effect of sulfate on As(III) removal by UVA/Ti(SO₄)₂ coagulation was mainly attributable to the competitive adsorption between sulfate and arsenic for the active sites on the surface of titanium hydroxide precipitates at high sulfate concentration [21].

3.4. Effect of fluoride

Fig. 5 depicted the influence of fluoride on As(III) removal by UVA/Ti(SO₄)₂ coagulation as function of solution pH at F⁻ concentration of 5 and 10 mg/L.

As indicated in Fig. 5a, As(III) removal by UVA/Ti(SO₄)₂ coagulation was obviously inhibited by F⁻ across the pH range of 4–10. The removal efficiency reduced by 9%–18% at F⁻ concentration of 5 mg/L. The detrimental effect of F⁻ increased as F⁻ concentration increased to 10 mg/L. The presence of 10 mg/L F⁻ made As(III) removal efficiency decrease by 13%–33% at pH 4–10. The decrease of As(III) removal efficiency might be attributable to the reasons as follows: firstly, F⁻ led to a great drop of IEP (as shown in Fig. 5b), indicating the chemical bond of F⁻ to the titanium hydroxide precipitates. The increase of negative surface charge of Ti(IV) precipitates would consequently enhance electrostatic repulsion between oxidized As(V) species (HAsO₄²⁻, AsO₄³⁻) and charged Ti(SO₄)₂ precipitates, hence hinder the adsorption of As(V). This influence was more significantly at acid solution pH (pH 4–6). Secondly, Ti(IV) remaining in solution after membrane filtration was notably increased in the presence of F⁻ over the pH range of 4–10 (Fig. 5c), possibly

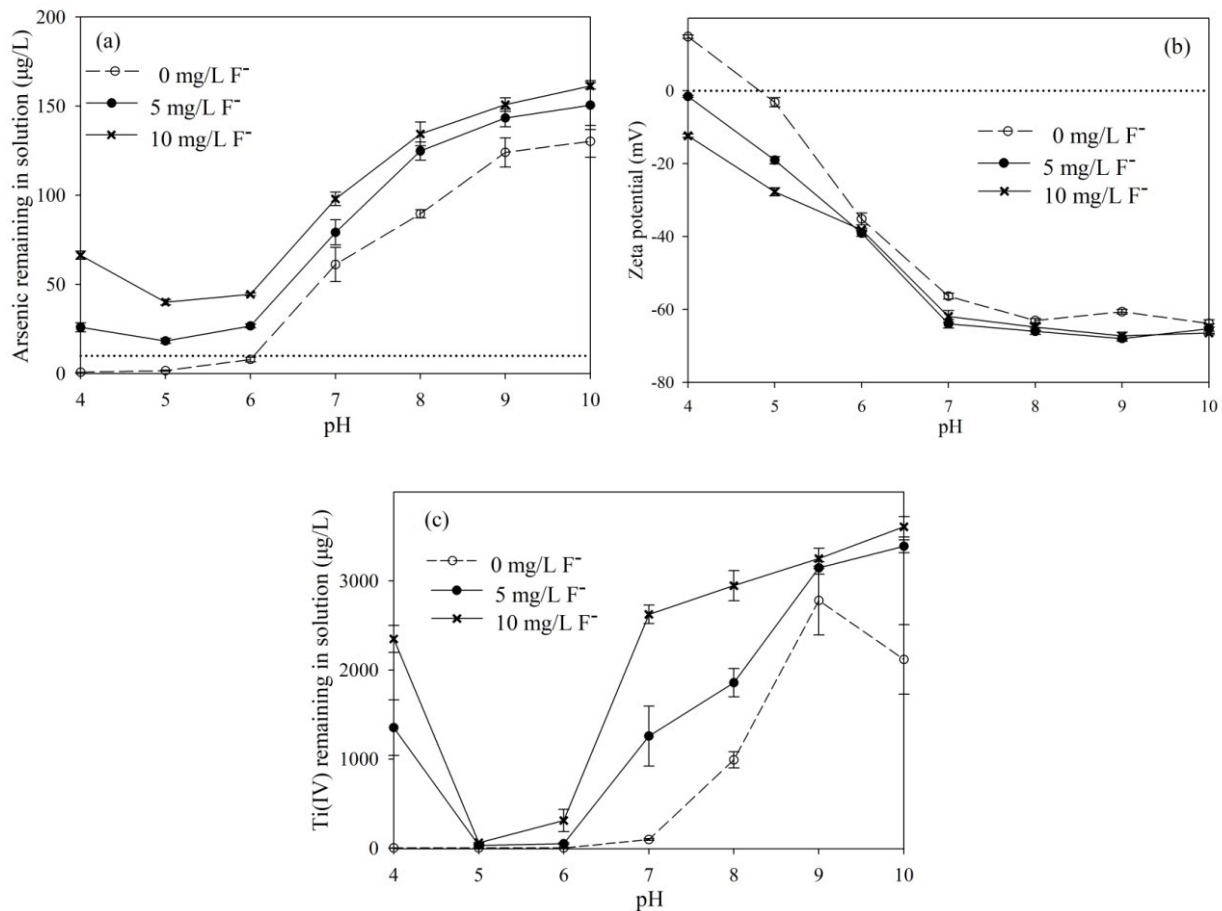


Fig. 5. Effect of fluoride on As(III) removal by UVA/Ti(SO₄)₂ coagulation. Conditions: $C_{0,As(III)} = 200 \mu\text{g/L}$, $\text{Ti(SO}_4)_2$ dose = 5 mg Ti/L, $I_s = 0.59 \text{ mW/cm}^2$, F^- concentration = 5 or 10 mg/L. (a) As remaining in solution vs. pH, (b) zeta potentials of coagulated precipitates vs. pH, and (c) Ti(IV) remaining in solution vs. pH.

due to the formation of soluble Ti(IV)–F complex, which would lead a great decrease of the surface active sites available for arsenic adsorption. Moreover, the increase of the surface negative charge of Ti(SO₄)₂ precipitates would consequently increase the electrostatic repulsion between the primary precipitate particles and make them not favorable to aggregate to form bigger precipitate particles, resulted in the penetration of precipitates associated with arsenic when filtrated, which finally made the arsenic removal efficiency decline greatly compared with the case without F⁻. Thirdly, there would be competition adsorption for active sites on the surface of Ti(IV) precipitates between F⁻ and arsenic. Note that arsenic remaining in solution was all in the oxidized form of As(V), indicating that F⁻ affected little on the oxidation of As(III).

The present results agreed well with previous reports about the influence of F⁻ on arsenic removal. Deng et al. [22] reported that F⁻ imposed detrimental effect on As(V) adsorption by Ce–Ti oxide adsorbent, and this effect was surpassed only by phosphate. Liu et al. [34] observed that due to the competitive adsorption effects, the removal of As(V) and F⁻ by iron and aluminum binary oxide in co-existing system was lower than that in single pollutant system. Ryu and Choi [35] reported that the amount of As(III) and

As(V) species adsorption on fluoride modification TiO₂ was much smaller than that on bare TiO₂, and the adsorption of fluoride hindered the inner-sphere complexation between arsenic and surface hydroxyl groups via replacing the surface hydroxyl groups.

3.5. Effect of Fe(II)

The role of Fe(II) in As(III) removal by UVA/Ti(SO₄)₂ coagulation was explored at Fe(II) concentration of 300 and 1,000 μg/L over the pH range 4–10. The results are shown in Fig. 6.

The presence of 300 and 1,000 μg/L Fe(II) had negligible effect on As(III) removal at pH 4–6 but made it increase by 0.3%–27% at pH 7–10, and the effect increased correspondingly with the increase of Fe(II) concentration from 300 to 1,000 μg/L (Fig. 6a). The effect of Fe(II) might be mainly associated with the increase of surface active sites for adsorption. The negligible effect of Fe(II) on arsenic removal at pH 4–6 might be ascribed to the fact that the almost complete precipitation of Ti(IV) could supply sufficient surface active sites for arsenic adsorption. With the increase of solution pH to neutrality and alkalinity (pH 7–10), the amount of Ti(IV) precipitates decreased significantly in the

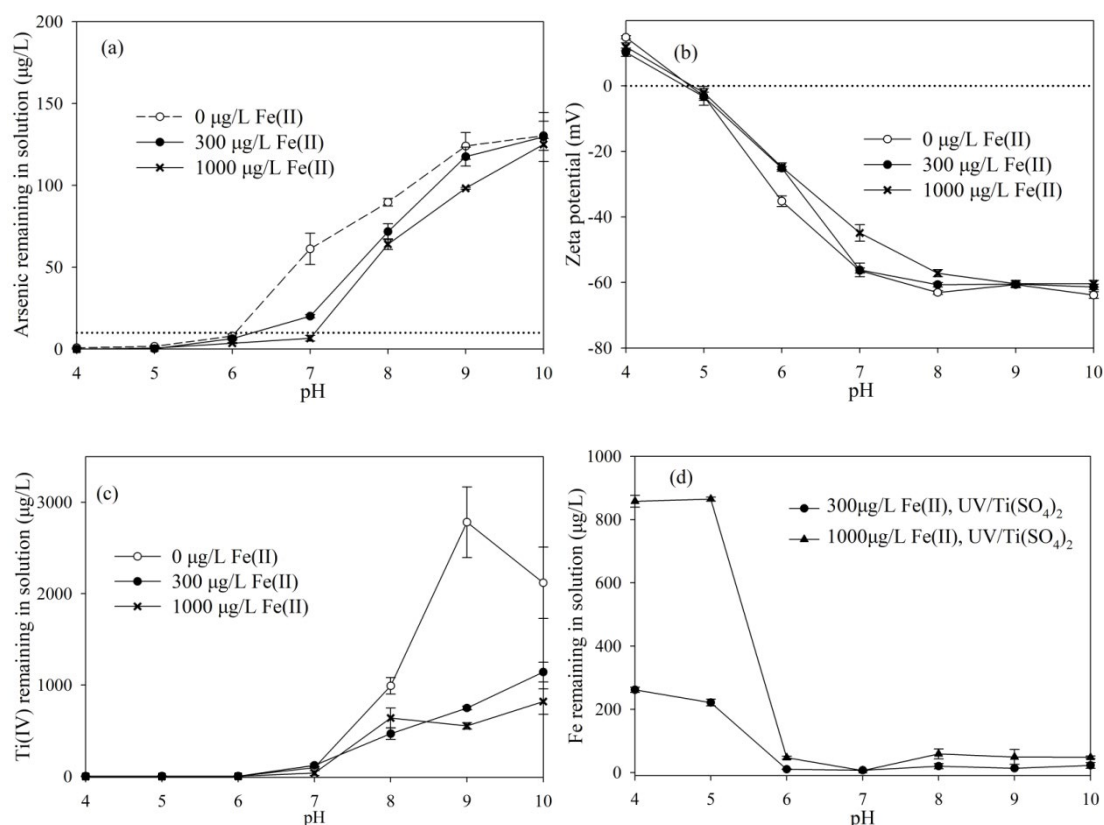


Fig. 6. Effect of Fe(II) on As(III) removal by UVA/Ti(SO₄)₂ coagulation. Conditions: $C_{0,As(III)} = 200 \mu\text{g/L}$, $Ti(SO_4)_2$ dose = 5 mg Ti/L, $I_s = 0.59 \text{ mW/cm}^2$, $C(Fe(II)) = 300$ or $100 \mu\text{g/L}$. (a) As remaining in solution vs. pH, (b) zeta potentials of coagulated precipitates vs. pH, (c) Ti(IV) remaining in solution vs. pH, and (d) Fe remaining in solution vs. pH.

absence of Fe(II), consequently the active sites decreased and As(III) removal was inhibited. However, the amount of Ti(IV) remaining in solution decreased apparently in the presence of Fe(II) (Fig. 6c) at pH 8–10, indicating that the precipitation of Ti(IV) was facilitated and more active sites were supplied for arsenic adsorption. As a result, As(III) removal efficiency increased clearly. The enhanced formation of Ti(IV) precipitates could be associated with the oxidation of Fe(II) and further formation of ferric hydroxide precipitates in neutral and alkaline pH, which could entrap the tiny titanium hydroxide precipitates during the grow of ferric hydroxide precipitates and make the Ti(IV) precipitates retained by MF increase. This could be verified by the fact that the filtrated ferric concentration was evidently low at 6–10 (Fig. 6d). Meanwhile, Arsenic could also be removed partly by adsorption or co-precipitation with HFO derived from Fe(II) [36]. Moreover, the surface negative charge of Ti(SO₄)₂ precipitates decreased slightly in the presence of Fe(II) at pH 6–8 (Fig. 6b). This would consequently reduce the electrostatic repulsion between negatively charged precipitates and oxidized As(V) species (HAsO₄²⁻, AsO₄³⁻) and increase arsenic removal by UVA/Ti(SO₄)₂ coagulation to some extent.

Although it was reported that the presence of Fe(II) reduced the adsorption of As(III) on zero-valent iron by forming complexes with arsenite and hence suppressing the degree of deprotonation/dissociation [37]. There was no

suppression of As(III) oxidation and removal in the presence of Fe(II) in present study. Arsenic remaining in solution was all oxidized As(V). Moreover, the oxidation of As(III) in solution might be promoted in the presence of Fe(II) in air-saturated water [38,39].

3.6. Effect of Mn(II)

The effect of Mn(II) on As(III) removal by UVA/Ti(SO₄)₂ coagulation was examined at Mn(II) concentration of 100 and 500 µg/L in the pH range of 4–10. The results are shown in Fig. 7.

As shown in Fig. 7a, As(III) removal was not affected in the presence of 100 and 500 µg/L Mn(II) in the acid pH range (i.e., pH 4–6), which was in line with the effect of Fe(II). However, the effect of Mn(II) was complex at neutral and alkaline pH range (i.e., pH 7–10). At pH 7, As(III) removal efficiency increased by 10% when Mn(II) was present, while this effect did not increase with the increase of Mn(II) concentration from 100 to 500 µg/L. The enhanced removal of As(III) was likely attributable to the precipitation of Mn(II), which resulted in the increase of active sites for arsenic adsorption. Concurrently, the formation of precipitate between arsenic and Mn(II), which could be written as follow: $Mn^{2+} + H_2AsO_4^- + H_2O = MnHAsO_4 \cdot H_2O + H^+$, would also contribute to the increase of arsenic removal [40]. The filtrated manganese concentration decreased to

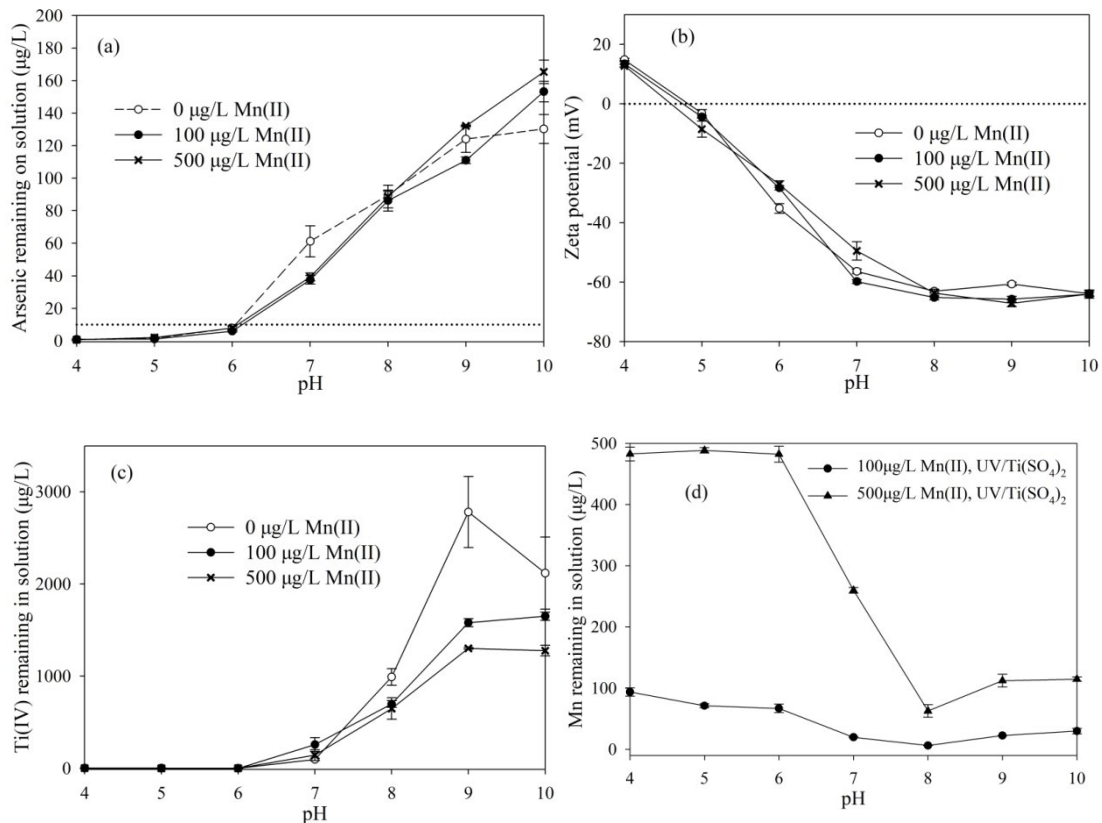


Fig. 7. Effect of Mn(II) on As(III) removal by UVA/Ti(SO₄)₂ coagulation. Conditions: $C_{0,As(III)} = 200 \mu\text{g/L}$, $\text{Ti}(\text{SO}_4)_2$ dose = 5 mg Ti/L, $I_s = 0.59 \text{ mW/cm}^2$, $C(\text{Mn(II)}) = 100$ or $500 \mu\text{g/L}$. (a) As remaining in solution vs. pH, (b) zeta potentials of coagulated precipitates vs. pH, (c) Ti(IV) remaining in solution vs. pH, and (d) Mn remaining in solution vs. pH.

20 and 260 μg/L for initial Mn(II) concentration of 100 and 500 μg/L, respectively (Fig. 7d). At pH 8, As(III) removal was not affected by the addition of Mn(II). However, the presence of 100 μg/L Mn(II) made As(III) removal efficiency increase by 7% at pH 9 but decrease by 12% at pH 10. And the presence of 500 μg/L Mn(II) was found to suppress As(III) removal at pH 9 and 10, As(III) removal efficiency decreased by 4% and 18%, respectively. It was reported that the presence of Mn(II) inhibited As(III) oxidation, as Mn(II) adsorption and oxidation were preferred over As(III) on the MnO₂ surface [23]. The presence of 100 and 500 μg/L Mn(II) did not show significantly influence on the surface charge of Ti(SO₄)₂ precipitates (Fig. 7b). While filtrated Ti(IV) concentration decreased by 6%, 24%, and 9% in the presence of 100 μg/L Mn(II) at pH 8, 9, and 10, respectively (Fig. 7c). There was a corresponding decrease of filtrated Ti(IV) concentration (7%, 30%, and 17% at pH 8, 9, and 10, respectively) with the increase of Mn(II) concentration from 100 to 500 μg/L. However, As(III) removal efficiency did not increase with the increase of Ti(IV) precipitates.

4. Conclusions

This study examined the As(III) removal efficiency by simultaneous ultraviolet photocatalytic oxidation-coagulation of titanium sulfate using UVA ($\lambda = 365 \text{ nm}$) as ultraviolet light source (UVA/Ti(SO₄)₂ coagulation). The effect of size of

Ti(SO₄)₂ precipitate particles and solution chemistry factors such as pH, co-existing SO₄²⁻, F⁻, Fe(II), and Mn(II) on As(III) removal by UVA/Ti(SO₄)₂ coagulation were investigated. The major findings are listed below:

- As(III) removal efficiency by UVA/Ti(SO₄)₂ coagulation was greater than 96% at acid pH (4–6) but decreased at neutral to alkaline pH (7–10) at the Ti dose of 5 mg/L and initial As(III) concentration of 200 μg/L, behaved huge discrepancy compared with As(III) removal by Ti(SO₄)₂ coagulation. Arsenic remaining in filtrate was all in the oxidized form of As(V). The results implied the oxidation of As(III) during UVA/Ti(SO₄)₂ coagulation. As(III) removal by UVA/TiCl₄ coagulation was comparable with UVA/Ti(SO₄)₂ coagulation at pH 4–7, but relatively lower than that for UVA/Ti(SO₄)₂ at pH 8–10, probably resulted from the reduce of Ti(IV) precipitates at alkaline pH for UVA/TiCl₄ coagulation. Improvement of NaCl concentration from 1 to 100 mmol/L led to an obvious increase of As(III) removal by both UVA/Ti(SO₄)₂ and UVA/TiCl₄ coagulation at pH 8. The As(III) removal rate by UVA/Ti(SO₄)₂ coagulation decreased as the size of Ti(IV) precipitate particle increased.
- The effect of sulfate on As(III) removal was greatly dependent on solution pH. Sulfate had little influence on As(III) removal at pH 4–7 but reduced As(III) removal at pH 8–10, the further decrease did not occur

with the increment of sulfate concentration from 100 to 250 mg/L. The IEP of precipitate particles shifted to acid pH slightly in the presence of sulfate. Sulfate ions slightly affect the hydrolysis of Ti(IV) and the formation of titanium hydroxide precipitates, the drop in arsenic removal caused by sulfate might be mainly associated with the competition between arsenic and sulfate for the active adsorption sites on the surface of Ti(IV) precipitates.

- The presence of 5 and 10 mg/L fluoride reduced As(III) removal efficiency by 9%–33% across the pH range of 4–10. Zeta potentials of $\text{Ti}(\text{SO}_4)_2$ precipitates became more negative in the presence of fluoride, with the great shift of IEP to the more acid side (less than pH 4). Fluoride might form soluble Ti(IV)–F complex with Ti(IV) and exerted negative impact on the formation of Ti(IV) precipitates. In addition, there would be competitive adsorption between fluoride and arsenic. Fluoride exerted a much more significant decrease in arsenic removal than sulfate.
- The presence of 300 and 1,000 $\mu\text{g/L}$ Fe(II) had little effect on As(III) removal by UVA/Ti(SO₄)₂ coagulation at pH 4–6, but improved As(III) removal at pH 7–10. The amount of Ti(IV) attained in precipitates increased at pH 7–10. The improvement of As(III) removal by Fe(II) might be attributable to the increase of precipitate solids. The presence of 100 and 500 $\mu\text{g/L}$ Mn(II) exerted little effect on As(III) removal at pH 4–6, while the effect varied with solution pH and Mn(II) concentration at pH 7–10. The addition of Mn(II) increased the amount of Ti(IV) attained in precipitates.

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