Simultaneous removal of arsenic and fluoride by freshly-prepared aluminum hydroxide

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HIGHLIGHTS

- Fluoride show more significant inhibition on As(V) removal than on As(III) removal.
- Negative As(V) show more significant adverse effect on F removal than neutral As(III) does.
- Fluoride dissolve AlOxHy and the formation of Al–F complexes occur at acidic pH.
- As(III) oxidation and pH adjustment to achieve simultaneous removal of As and F.

GRAPHICAL ABSTRACT

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ABSTRACT

The coexistence of arsenic (As) and fluoride (F) in some underground waters creates challenges in the simultaneous removal of these two toxic elements. This study investigates the effect of fluoride at different molar ratios of fluoride to arsenic (As) ($R_{F:As}$) on the removal of arsenic [i.e., arsenite (As(III)), arsenate (As(V))] by freshly-prepared aluminum hydroxide (AlOxHy), and that of arsenic at different molar ratios of arsenic to fluoride ($R_{As:F}$) on fluoride removal. In single pollutant solutions, the removal of neutral As(III) is independent on pH at $R_{As(III):Al} \leq 0.70:1$ and is much lower than that of As(V). The optimum As(V) removal is at weak acidic pH of 5 and 6 whereas that of fluoride is at pH 7 and 8. Fluoride at $R_{F:As(V)} > 35:1$ significantly impairs the removal of As(V) with more significant inhibition at elevated pH. The negatively-charged As(V) inhibits fluoride removal to a larger extent than the neutral As(III) does. The adverse effect of fluoride on As(V) removal is mainly attributed to the lowered ζ -potential, which is controlled by the combined effects of pH and $R_{F:As(V)}$. In relative terms, the removal of fluoride is highly pH dependent, although $R_{As(V):F}$ does show some effects. The oxidation of As(III) to As(V) and the adjustment of pH to weak acidic range is well preferred to achieve the simultaneous removal of As and F by AlOxHy adsorption.

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1. Introduction

The widespread distribution of arsenic (As) and fluoride (F) in underground water has generated great concern [1,2], and more

than 400 million individuals are exposed to either of these two toxic elements via drinking water globally. In some cases with special geochemical conditions, the simultaneous occurrence of As and F is observed [2]. The combined toxic effects between As and F have been proposed [3,4], and this further complicates the situation and creates challenges in the simultaneous removal of As and F. Additionally, some industries such as semiconductors production and rare earths refinery also produce complicated wastewaters with

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high levels of fluoride and arsenic, and the molar ratios of F to As ($R_{F:As}$) may differ to a large extent.

The Al-based coagulants and adsorbents are practically valuable for the removal of fluoride [5–7], and the exchange between fluoride and the hydroxyl groups occurs on the surfaces of aluminum (hydro)-oxides. The formation of aluminum fluoride complexes (Al–F complexes) occurs at acidic condition [7–9], and this effect facilitates fluoride removal as compared to its direct adsorption onto $Al(OH)_3$ precipitates [7]. Additionally, Al–F complexes formation also affects the species distribution of aluminum ions and their hydrolysis products [9], and assumedly impacts the coagulation behaviors of Al salt towards arsenic thereafter. As for the removal of arsenic, the Fe-based coagulants and adsorbents showed priority due to their strong affinity towards arsenic [10,11], and the formation of bi-nuclear bidentate and monodentate complexes on the iron hydro (oxide) surfaces has been proposed [10,13,14]. To achieve the simultaneous removal of As and F, the coagulation by the combined use of iron (Fe) and aluminum (Al) salts works well [6,15], and the electro-coagulation with Fe and Al plates also exhibits promising efficiency [15]. Comparatively, Al hydro (oxide) is more effective than that of Fe in terms of the simultaneous removal of As and F, owing to the weak affinity of iron hydro (oxide) towards fluoride [6]. Al coagulation shows promising As removal efficiency and has been successfully implemented in some drinking water treatment plants [16]. Aluminum hydroxide ($AlOxHy$) achieves the simultaneous removal of arsenic and fluoride, and their removal efficiency is highly dependent on pH [7].

In the treatment of water with coexisting As and F, the mutual effects between them, i.e., the effect of one species on the removal of the other species, may be complicate and rare studies have focused on this before. Fluoride was reported to show inhibitive effect on the removal of particles and organic matter by Al coagulation [17]. Our previous study also indicated the adverse effect of fluoride on the coagulation behavior of aluminum chloride ($AlCl_3$) towards kaolin suspensions, and the formation of Al–F complexes at high fluoride levels plays an important role [18]. Besides the formation of Al–F complexes, the attachment of fluoride onto Al hydroxide decreased the surface charge and particles stability [19], and this effect was assumedly to inhibit the removal of negatively-charged arsenate [$As(V)$]. Additionally, the competitive effect between $As(V)$ and F occurs to affect their adsorption onto $AlOxHy$, and this adverse effect may be remarkably alleviated by introducing iron oxides to $AlOxHy$ [6]. Furthermore, the strong interactions between Al and F may contribute to the dissolution of Al hydro (oxide) and affect its removal behaviors towards As and F; however, rare study has focused on it to the best of our knowledge.

The freshly-prepared metal hydroxides show active surfaces and high BET surface areas, and more importantly, they can be in situ coated onto porous carriers to achieve adsorbents granulation [20]. This study uses the freshly-prepared $AlOxHy$ as an adsorbent, and investigates the mutual effects between F and As on their removal over a wide pH range. Two arsenic species of $As(III)$ and $As(V)$ were included, and the molar ratios of F to As ($R_{F:As}$) and that of As to F ($R_{As:F}$) varied over a wide range. The dominant factors on the removal of As and F were evaluated and the main reactions involved in were proposed accordingly. This study is practically valuable for the simultaneous removal of As and F in drinking water and some industrial wastewater.

2. Materials and methods

2.1. Reagents and materials

Unless otherwise noted, all chemicals were of analytical-reagent grade and were used without further purification. The stock solutions of sodium arsenite ($NaAsO_2$, 3.47 g/L), sodium arsenate

Table 1

Characteristics of the tap water used in this study.

Items	Values
pH (20 °C)	8.10 ± 0.05
Turbidity (NTU)	0.35 ± 0.02
DOC (mg/L)	0.62
Alkalinity (mg $CaCO_3$ /L)	150
Hardness (mg $CaCO_3$ /L)	155
Aluminum (mg/L)	0.08
Iron (mg/L)	0.05
Total phosphorus (mg/L)	0.016
SO_4^{2-} (mg/L)	31.7
Cl^- (mg/L)	8.90
Mn^{2+} (mg/L)	0.09
As (mg/L)	N.D.*
F (mg/L)	N.D.*

* Not detected.

($Na_3AsO_4 \cdot 12H_2O$, 11.31 g/L), and sodium fluoride (NaF , 4.66 g/L) were, respectively, prepared in de-ionized water every 10 days. The sodium salts rather than calcium salts were used to avoid the side effect of divalent calcium ion on the adsorption of As and F. The $AlCl_3$ stock solution (26.8 g/L) was freshly prepared prior to use.

To prepare raw water with desired concentrations of $As(III)/As(V)$ and fluoride, the stock solutions of $As(III)/As(V)$ and fluoride at different volumes were diluted into tap water, and the characteristics of which was illustrated in Table 1. The tap water was kept in the dark for several days prior to use, and the levels of residual chlorine were below detection limit, as determined by the *N,N*-diethyl-*p*-phenylenediamine (DPD) ferrous titration method. The raw water with coexisting $As(III)$ and fluoride is expressed as $As(III)$ –F system whereas that with coexisting $As(V)$ and fluoride is indicated as $As(V)$ –F system. Their initial concentrations were expressed by the molar ratios of initial As/F concentrations to $AlOxHy$ doses, i.e., $R_{As(III):Al}$, $R_{As(V):Al}$, and $R_{F:Al}$ (mol/mol), and varied from 0.13:1 to 1.77:1. The solution pH was adjusted to the desired values with hydrochloric acid (HCl) and sodium hydroxide (NaOH).

$AlOxHy$ was freshly prepared by the method illustrated in our previous study [21]. Briefly, the stock solutions of $AlCl_3$ and NaOH, at stoichiometric ratio of 1:3, were mixed for 2-min reaction prior to being dosed into raw water samples. The completed reaction between $AlCl_3$ and NaOH was achieved as indicated by the low concentrations of residual Al (i.e., <0.1 mg/L). The doses of $AlOxHy$ are expressed by Al in mg/L, and are controlled by extracting desired volumes of $AlCl_3$ stock solution.

2.2. Experimental methods

Jar tests were performed using a Phipps and Bird six-paddle stirrer in 500-mL beakers. Soon after a 10-s rapid mixing (250 rpm) of the raw water samples (300 mL), the freshly-prepared $AlOxHy$ at desired doses was dosed. After that, the adsorption procedure consisted of a 2-min rapid mix (200 rpm), 15-min slow mix (40 rpm), and a 30-min settling period. The experimental procedures simulates the widely-used unit processes of mixing, flocculation, and sedimentation, and enables the feasibility evaluation on the enhanced removal of As and F by $AlOxHy$ on the basis of conventional treatment processes. A small amount of sample was taken immediately for the analysis of zeta potential after the 2-min rapid mix. It was noted that the oxidation of $As(III)$ to $As(V)$ by oxygen might occur; however, preliminary experiments indicated that the extent was rather slight. The half-lives of $As(III)$ has been determined to be as long as 4–9 days while being exposed to saturated air [22]. pH was adjusted during the 15-min slow mixing period. After settling for 30 min, supernatants were collected at 2-cm below the water level and then filtered through 0.45- μ m membrane filters.

The filtrates were air-tightly kept at 4 °C for further analysis of the concentrations of As, fluoride, and Al.

2.3. Analyzing instruments and methods

The equilibrium pH of the supernatants was determined with a pH meter (Orion 720A, USA). Zeta potential was measured by a zeta potential analyzer (Zetasizer 2000, Malvern, UK), and results indicated the average values of triplicate analysis.

The concentrations of total fluoride were directly measure by the ion selective electrode method (PF-1, Shanghai KangYi Technology, China). The concentrations of free fluoride were determined by the method indicated in our previous study [7], and the concentrations of complexed fluoride (complexed-F) were calculated by subtracting total fluoride with free fluoride.

The concentrations of Al and As were determined using an inductively coupled plasma optical emission spectroscopy (ICP-OES) (OPTIMA 2000DV, PerkinElmer, USA), and the detection limits were 0.8 µg/L for Al and 4 µg/L for As.

3. Results and discussion

3.1. Adsorption of As(III), As(V), and F by AlOxHy in single pollutant solutions

Fig. 1 illustrates the removal of As(III), As(V), and F by AlOxHy over a wide pH range from 4 to 9, and the initial concentrations

Fig. 1. The removal of As(III), As(V), and F by AlOxHy in single pollutant solutions over a wide pH range from 4 to 9 (experimental conditions: Al dose = 10 mg/L, $R_{As:Al}$ and $R_{F:Al}$ is in the range from 0.13:1 to 1.77:1).

of these pollutants as expressed by $R_{As(III):Al}$, $R_{As(V):Al}$, and $R_{F:Al}$ increased from 0.13:1 to 1.77:1. In this pH range As(III) mainly exists as neutral H_3AsO_3 whereas As(V) as $HAsO_4^{2-}$ and $H_2AsO_3^-$ [23]. The removal of neutral As(III) was independent on pH at $R_{As(III):Al} \leq 0.70:1$, and at elevated $R_{As(III):Al}$ of 1.40:1 and 1.77:1, the increase of pH from 4 to 7 benefited As(III) removal. Comparatively, the removal of negatively-charged As(V) was more significant than that of non-ionic As(III) by AlOxHy in pH 4 to 7. At $R_{As:Al}$ of 0.70:1, the maximum adsorption capability of AlOxHy was determined to be 45.1 mmol As(III)/g Al at pH 4 and 53.6 mmol As(V)/g Al at pH 5, respectively.

The removal of fluoride by AlOxHy increased with elevated pH from 5 to 8 and then decreased to some extent at pH 9, and the optimum removal was observed at pH 7 and 8 (Fig. 1c). The maximum adsorption capability of AlOxHy towards fluoride, at $R_{F:Al}$ of 0.70:1, was 67.3 mmol F/g Al at pH 7. The removal of fluoride by AlOxHy at relatively low $R_{F:Al}$, i.e., 0.18:1 and 0.21:1, has been investigated before, and maximum fluoride removal was observed at weak acidic pH of 6 and 7 [21]. The different trend may be attributed to the much higher $R_{F:Al}$ values used in this study. To further illustrate this, the dissolution of AlOxHy, as indicated by the aqueous Al levels, was investigated over wide pH and $R_{F:Al}$ ranges (Fig. 2). In the absence of these pollutants, the extent of AlOxHy dissolution was slight to be below 0.07 mg/L at pH 6 and 7. In acidic and basic pH of 4 and 9, aqueous Al levels increased significantly to as high as 12.56 and 5.04 mg/L, owing to the dissolving

Fig. 2. The concentrations of residual As and F after the adsorption of As(III), As(V), and F by AlOxHy in single pollutant solutions over a wide pH range from 4 to 9 (experimental conditions: Al dose = 10 mg/L, $R_{As:Al}$ and $R_{F:Al}$ is in the range from 0.13:1 to 1.77:1).

Fig. 3. Effect of fluoride at different $R_{F:As}$ from 0:1 to 116:1 on the removal quantity of fluoride (Q_F) and summative quantity of fluoride and arsenic (Q_{F+As}) at per gram $Al(OH)_3$ precipitates as Al by Al coagulation ((a) Q_F in As(III)–F system, (b) Q_F in As(V)–F system, (c) $Q_{F+As(III)}$ in As(III)–F system, (d) $Q_{F+As(V)}$ in As(V)–F system) (experimental conditions: Al dose = 10 mg/L, $[As(III)]_0/[As(V)]_0 = 2$ mg/L; $R_{As:Al} = 0.08:1$).

of $AlOxHy$ into Al^{3+} and aluminates, respectively. It was interestingly observed that fluoride greatly enhanced the dissolution of $AlOxHy$, and the fluoride-dissolving effect was more significant at elevated $R_{F:Al}$ and lower pH. At pH 6, aqueous Al levels increased from 0.06 mg/L to 1.18 and 13.19 mg/L after introducing fluoride at $R_{F:Al}$ of 0.35:1 and 1.77:1. At the same $R_{F:Al}$ of 0.35:1, aqueous Al levels increased from 1.18 mg/L at pH 6 to 6.38 mg/L at pH 5 and 32.64 mg/L at pH 4. The dissolution effect decreased the amount of $AlOxHy$ available and inhibited fluoride removal accordingly. At elevated pH of 7 and 8, the fluoride-dissolving effect decreased to a large extent, and the increase of aqueous Al concentrations was as low as below 0.5 mg/L at pH 8. At low $R_{F:Al}$, the adsorption of fluoride by $AlOxHy$ is mainly achieved by fluoride replacing surface hydroxyl and the formation of outer sphere Al–O–F complexes [21]. At high $R_{F:Al}$, the dissolved Al^{3+} tends to form Al–F complexes with fluoride, and the complexed-F concentrations increased with elevated $R_{F:Al}$ and lowered pH (Fig. S1), and this trend was demonstrated by MINTEQA2 modeling analysis (Fig. S2). The formation of Al–F complexes contributed to continuous dissolution of $AlOxHy$ and adversely affected its removal behavior towards fluoride thereafter.

Interestingly, the presence of As(III) and As(V) inhibited rather than facilitated the $AlOxHy$ dissolution at pH 4 and 9, and the higher $R_{As:Al}$ was generally relative to more significant decrease of aqueous Al levels (Fig. 2). MINTEQA2 modeling analysis indicates that the formation of soluble complexes between Al^{3+} and arsenic rarely occurred, and the effect of arsenic on $AlOxHy$ dissolution was assumedly slight. Additionally, the arsenic-rich surfaces might inhibit the H^+ -dissolving effect towards $AlOxHy$, although further study is required to illustrate it.

3.2. Adsorption of As(III)/As(V) and F by $AlOxHy$ in coexisting systems

3.2.1. Removal quantity of fluoride and arsenic over a wide $R_{F:As}$ range

Fig. 3 illustrates the removed quantity of arsenic and fluoride per gram $Al(OH)_3$ precipitate as Al, which was determined by subtracting Al doses with residual Al concentrations, with elevated $R_{F:As}$ values from 0:1 to 116:1. In the As(III)–F coexisting system, Al coagulation contributed most to the removal of fluoride, and the removed quantity of fluoride (Q_F) increased with elevated $R_{F:As}$ values, i.e., the higher initial fluoride concentrations. At $R_{F:As}$ value of 116:1 ($[F]_0 = 70.3$ mg/L), Q_F showed the maximum values of 157.4, 174.7, 208.5 mmol/g at equilibrium pH 5.9, 6.8, and 7.5, respectively. The removed quantity of As(III) ($Q_{As(III)}$) was much lower than that of fluoride, and was consistently below 0.5 mmol/g in wide ranges of pH and $R_{F:As(III)}$. This may be first attributed to the low $R_{As(III):Al}$ of as low as 0.08:1. At elevated $R_{As(III):Al}$ of 0.13:1, $Q_{As(III)}$ was determined to be below 2 mmol/g in pH range from 4 to 9 in the absence of fluoride (Fig. 1a). Additionally, fluoride showed adverse effects to inhibit As(III) removal, and $Q_{As(III)}$ was observed to decrease from 0.50 mmol/g to 0.27 and 0.21 mmol/g with $R_{F:As(III)}$ increasing from 12:1 to 35:1 and 70:1 at pH 6. The contributive ratios of $Q_{As(III)}$ to the summarized values of $Q_{As(III)}$ and Q_F , as being expressed by $Q_{As(III)+F}$, were very low, and As(III) showed no inhibitive effect on the removal of fluoride by $AlOxHy$.

In the As(V)–F coexisting system, the removal of As(V) by Al coagulation in terms of $Q_{As(V)}$ were much higher than $Q_{As(III)}$ in As(III)–F coexisting system. For example, at the same $R_{F:As}$ of 12:1, $Q_{As(V)}$ were determined to be 6.98, 5.33, and 3.76 mmol/g whereas

Fig. 4. Effect of arsenic at different $R_{As:F}$ from 0:1 to 0.95:1 on the removal quantity of fluoride (Q_F), arsenic (Q_{As}) and summative quantity of arsenic and fluoride (Q_{As+F}) at per gram $Al(OH)_3$ precipitates as Al by Al coagulation ((a) Q_F in As(III)–F system, (b) Q_F in As(V)–F system, (c) $Q_{As(III)}$ in As(III)–F system, (d) $Q_{As(V)}$ in As(V)–F system, (e) $Q_{As(III)+F}$ in As(III)–F system, (f) $Q_{As(V)+F}$ in As(V)–F system) (experimental conditions: Al dose = 10 mg/L; $[F]_0 = 3.2$ mg/L; $R_{F:Al} = 0.45:1$).

$Q_{As(III)}$ were as low as 0.27, 0.40, and 0.15 mmol/g at pH 5.7, 6.6, and 7.5 accordingly. The significant As(V) removal contributed to much higher ratios of $Q_{As(V)}$ to $Q_{As(V)+F}$ than those of $Q_{As(III)}$ to $Q_{As(III)+F}$ (Fig. S3). The more significant adsorption of As(V) adversely inhibited the removal of fluoride, as indicated by the lower Q_F values in As(V)–F coexisting system than those in As(III)–F coexisting system. On the other hand, fluoride showed remarkable inhibitive effects on As(V) adsorption at $R_{F:As(V)}$ of above 70:1, and more significant inhibition was observed at elevated pH.

3.2.2. Removal quantity of fluoride and arsenic at different $R_{As:F}$

Fig. 4 illustrates the variation of Q_{As} and Q_{As+F} with elevated $R_{As:F}$ from 0.05:1 to 0.95:1. $Q_{As(III)}$ removal was consistently below 1 mmol/g at $R_{As(III):F}$ of below 0.2:1. The maximum $Q_{As(III)}$ was observed at $R_{As(III):F}$ of 0.95:1 and was, respectively, determined to be 7.90, 10.32, and 8.83 mmol/g at pH 6, 7, and 8. The corresponding $Q_{As(V)}$ was significantly higher than $Q_{As(III)}$, and the summarized values of $Q_{As(V)}$ and Q_F , i.e., $Q_{As(V)+F}$, was higher than $Q_{As(III)+F}$ accordingly. $Q_{As(V)}$ contributed most to the $Q_{As(V)+F}$ especially at high

$R_{As(V):F}$ ranges of above 0.10:1, and the corresponding ratios of Q_F to $Q_{As(V)+F}$ were below 23.5%. In contrast, Q_F dominated in $Q_{As(III)+F}$ and the ratio of $Q_{As(III)}$ to $Q_{As(III)+F}$ was consistently below 30.5% in $R_{As(III):F}$ range of below 0.48:1. The removal quantity of fluoride in As(V)–F coexisting system was lower than that in As(III)–F coexisting system, owing to the more significant As(V) adsorption and its inhibitive effect towards fluoride thereafter. These results indicated the more significant adverse effect of As(V) on fluoride removal than that of As(III), which was in accordance with results in Fig. 3.

3.2.3. Simultaneous removal of arsenic and fluoride at different $R_{As:F}$

In engineering point-of-view it is valuable to achieve the simultaneous removal of arsenic and fluoride by Al coagulation. Fig. 5 illustrates the average removal efficiency of arsenic and fluoride over a wide initial pH range from 4 to 9 in As–F coexisting system. The initial As concentrations varied from 0 to 10 mg/L, and that of fluoride was stable to be 3.30 mg/L. The removal efficiency

Fig. 5. Statistic analysis on the effect of pH (from 4 to 9) and arsenic ($[As]_0 = 0.5$ to 10 mg/L) on the removal of arsenic and fluoride in (a) As(III)-F coexisting system and (b) As(V)-F coexisting system (experimental conditions: Al dose = 10 mg/L, $[F]_0 = 3.5$ mg/L, $R_{F:Al} = 0.50:1$).

Fig. 6. Proposed dominant reactions involved in the removal of arsenic and fluoride by AlOxHy in single and coexisting systems and possible pathways to achieve simultaneous removal of arsenic and fluoride.

of As(III) was independent on pH and was poor to be below 11%. Comparatively, As(V) removal was much higher to be above 95% in pH ranges from 5 to 8. The average removal efficiency of As(V) slightly decreased to 85.5% at pH 9. It was observed that the removal of fluoride was highly dependent on solution pH rather than the concentrations of either As(III) or As(V). In both systems the optimum fluoride removal was observed at pH 6 with the average removal efficiency of 72.3%. At elevated pH of 7 and 8, the average fluoride removal decreased to 56.1% and 39.8% accordingly. While treating water with coexisting arsenic and fluoride, the simultaneous removal of these two toxic elements by AlOxHy may be achieved by oxidizing As(III) to As(V) and by adjusting pH to weak acidic pH ranges from 6 to 7.

3.3. Proposed dominant effects on the removal of As and F by AlOxHy adsorption

Basically the inhibitive effects of arsenic and fluoride on their removal by AlOxHy included the following pathways. First, the fluoride-dissolving effect and the formation of Al-F complexes increases the residual Al levels, and reduces the quantity of Al in the solid phase (Al_{solid}) available for adsorption. Arsenic might also show effect on residual Al levels; however, the extent was slight in wide pH range from 4 to 9 (Fig. 2). Additionally, the attachment of fluoride and arsenic onto AlOxHy may decrease their surface charge and show inhibition on their removal thereafter (Fig. S4). The removal of As(III) was consistently below 20% (Fig. 5a) and was relative to neither ζ -potential nor Al_{solid} ; however, the removal of As(V) with elevated $R_{F:Al}$ was negatively correlated with ζ -potential. AlOxHy showed positive ζ -potential at $R_{F:Al}$ of below 3:1 and the corresponsive removal efficiency of As(V) was above 80%. At elevated $R_{F:Al}$, the ζ -potential of AlOxHy decreased and inhibited the removal of As(V) accordingly. Comparatively, the Al_{solid} played a more important role on the removal of fluoride than ζ -potential did. Al_{solid} decreased at pH < 5 and at pH > 8 due to the H^+ -dissolving effect and the formation of soluble aluminates, and the presence of fluoride further enhanced AlOxHy

dissolution. The removal of fluoride was more significantly affected by pH than by the presence of either As(III) or As(V) accordingly (Fig. 5). At a specified pH condition, As(V) showed more inhibitive effect on fluoride removal than As(III) did (Fig. 4).

In the treatment of arsenic and/or fluoride by AlOxHy adsorption, the different interactions involved in this system, as briefly described in Fig. 6, complicated the situation to a large extent. In the single pollutant solution, AlOxHy achieves the removal of As(III), As(V), and fluoride, and the removal quantity is dependent on pH and their initial concentrations. In As–F coexisting systems, AlOxHy with adsorbed As(V) [i.e., $\equiv\text{Al}-\text{O}-\text{As}(\text{V})$] and that with adsorbed fluoride [i.e., $\equiv\text{Al}-\text{O}-\text{F}$] can further remove the other species, and the abovementioned adverse effects between As(V) and fluoride have been proposed. In excessive fluoride system, fluoride-dissolving effect occurs to increase the soluble Al levels. AlOxHy dissolution also occurs at low pH, i.e., excessive H^+ . Soluble Al includes bimonomer, oligimer, and Al polymer besides monomer Al as Al^{3+} , owing to the hydrolysis and polymerization reactions at pH above 4 [24]. Soluble Al may directly act with either of arsenic and fluoride. MINTEQA modeling indicated that the formation of Al–F complexes does occur especially at acidic pH ranges (Fig. S2), and the levels of complexed-F are dependent on pH and $R_{\text{F:Al}}$ (Fig. S1). However, the formation of Al–As precipitates or complexes rarely occur even at their highest concentrations employed in this study, as indicated from MINTEQA modeling. These soluble Al may further transform to insoluble Al such as $\text{Al}(\text{OH})_3$ precipitate in case of sufficient alkalinity and to soluble aluminates at excessive alkalinity. Additionally, soluble Al–F complexes tend to directly precipitate with fluoride to achieve the formation of Al–F–OH precipitate [7]. The attachment of arsenic and free fluoride onto the surfaces of either $\text{Al}(\text{OH})_3$ or Al–F–OH precipitates enables their removal, and the dominant mechanisms such as coulombic attraction and specific chemical adsorption have been reported [25]. The adsorption of As(III) onto AlOxHy, $\equiv\text{Al}-\text{O}-\text{As}(\text{V})$, $\equiv\text{Al}-\text{O}-\text{F}$, or Al–F–OH does occur; however, the extent is relatively low. The oxidation of As(III) to As(V) is well preferred to improve arsenic removal.

4. Conclusions

The coexisting arsenic and fluoride complicates their removal by Al coagulation as compared to the single-component systems. Fluoride forms soluble Al–F complexes and shows dissolving effect towards AlOxHy to increase residual Al levels thereafter. Moreover, the attachment of fluoride onto AlOxHy also decreases the ζ -potential to a large extent. These effects impair the removal of As(V) by AlOxHy at high $R_{\text{F:As}}$, and the lowered ζ -potential plays a dominant role. As(V) also impairs the removal of fluoride; however, the extent of inhibition is highly dependent on pH rather than $R_{\text{As(V):F}}$. The removal of As(III) is slightly affected by fluoride because its removal is low even without fluoride present. Al coagulation can achieve the simultaneous removal of As(V) and fluoride, and the weak acidic pH is well preferred. In cases that As(III) is the dominant species, the oxidation of As(III) to As(V) is recommended to improve arsenic removal.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2014.10.007>.

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