Defluoridation by Al-based coagulation and adsorption: Species transformation of aluminum and fluoride

Zan He^{a,b}, Ruiping Liu^{a,*}, Jin Xu^a, Huijuan Liu^a, Jiuhui Qu^a

^a Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Science, Chinese Academy of Sciences, Beijing 100085, China

^b University of Chinese Academy of Sciences, Beijing 100039, China

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ABSTRACT

The species transformation of Al and fluoride in fluoride removal by Al-based coagulation and adsorption is far from being well-characterized. This study used batch- and pilot-scale experiments to compare the fluoride removal efficiency and species transformation of Al and fluoride in Al coagulation with that in Al precipitate (AlOxHy) adsorption. Al coagulation showed superior removal of fluoride compared to AlOxHy adsorption. In the coagulation process, the formation of complexed fluoride (Com-F) occurred, and Com-F concentrations increased with elevated Al dose, i.e., lowered pH. At initial pH of 8.6, free fluoride (Free-F) dominated in the adsorption system even at the high AlOxHy dose of 200 mg Al/L whereas at pH < 7.0, Com-F was the dominant species in both systems. Fluoride had an influence on Al³⁺ hydrolysis and favored the transformation of Al³⁺ and Al–F complexes to Al–F precipitates, and the removal of fluoride by coagulation was improved thereafter. Fluoride also promoted the dissolution of AlOxHy, the extent of which was more significant at lowered pH from 7.0 to 4.0 and at elevated ratios of fluoride to Al from 0.15 to 2.45. The formation of Al–F complexes impaired fluoride removal by adsorption. A pilot-scale field study also indicated that coagulation showed higher efficiency than adsorption in the removal of fluoride. The average ratios of Com-F to total fluoride were 0.14:1 and 0.04:1, respectively, in coagulation and adsorption processes.

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1. Introduction

Excessive exposure to fluoride via drinking water has aroused wide concern due to the widespread occurrence of dental and skeletal fluorosis. Many technologies to remove fluoride from groundwater and industrial wastewater such as (electro)coagulation, adsorption, ion exchange, precipitation, and membrane separation have been well studied [1–6]. Coagulation and adsorption are highly efficient and cost-effective, and require less maintenance and show higher water production ratios than other processes. From an engineering point-of-view, they are therefore more feasible and available in underdeveloped rural areas.

Aluminum (Al) salts are most widely used for coagulation, and the removal of fluoride is mainly achieved by adsorption, charge neutralization and enmeshment, complex precipitation, and electronic attraction, etc. [7]. However, the dominant mechanism may be highly dependent on the operation procedures. In cases where Al ion (Al³⁺) and base solutions are simultaneously dosed, the adsorption of fluoride onto Al(OH)₃ precipitates dominates in

fluoride removal [7,8]. When Al³⁺ solution is dosed prior to adding base solution, the formation of aluminum fluoride complexes (Al–F complexes) occurs prior to Al³⁺ hydrolysis. Al–F complexes may directly transform to Al–F–OH precipitates and achieve the removal of fluoride [1]. The participation of fluoride in precipitate formation may differ greatly from its direct adsorption onto Al(OH)₃ precipitate. However, few studies have carefully illustrated the different removal behaviors toward fluoride or the mechanisms involved in these two procedures. Our previous study indicated that the formation of Al–F complexes is more significant at lower pH and higher ratios of fluoride to Al ($R_{F:Al}$) [9]. The removal of fluoride by (electro) coagulation has been observed to be strongly dependent on Al dose, pH, Al species, and $R_{F:Al}$ [1,10–12]. Generally, the addition of Al³⁺ contributes to the decrease of pH owing to Al³⁺ hydrolysis, and this effect could affect the species distribution of Al and fluoride, and subsequently fluoride removal is sensitive to the above factors. The Al–F complexes play important roles in promoting fluoride removal to a large extent [9]. Additionally, these complexes may also have an influence on Al hydrolysis and the species distribution and transformation of Al and fluoride.

* Corresponding author. Tel.: +86 10 62849128; fax: +86 10 62849160.

E-mail address: liuruiping@rcees.ac.cn (R. Liu).

Activated alumina is one of the best adsorbents for fluoride removal and has been widely used in practice [13]. However, its application is restricted by its relatively low adsorption capacity, *i.e.*, equilibrium adsorption capability of 2–4 mg/g, as well as the complicated regeneration procedures required. The granulation of conventional adsorbents is achieved at the expense of significantly lowered adsorption capacity. To overcome these drawbacks, we successfully developed a novel adsorbent by coating ferric and manganese binary oxide (FMBO) onto diatomite *in-situ* [14]. The freshly-prepared aluminum hydroxide, *i.e.*, *in-situ* $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, as briefly expressed by AlOxHy , shows maximum adsorption capacity higher than 110 mg F/g Al, and exhibits superior performance compared to other conventional adsorbents such as activated alumina, nano-scale aluminum oxide hydroxide, and Zr–Mn composite material [15–17]. The *in-situ* coating method may be also applicable in the preparation of a defluoridation adsorbent. Additionally, alumina with different acidity–alkalinity can be prepared through controlling the surface density of hydroxyl groups [18], and it indicates that alumina is an amphoteric oxide. Therefore, AlOxHy tends to dissolve into soluble Al in acidic and basic pH ranges, although the extent is relatively slight [19]. The presence of fluoride complicates the situation for AlOxHy dissolution considering that free fluoride tends to form Al–F complexes with the dissolved Al^{3+} at low pH. However, few studies have evaluated the effect of fluoride on AlOxHy dissolution and the removal of fluoride thereafter.

This study used groundwater collected from the suburb of Langfang City, Hebei Province in China, with fluoride concentrations of 3.3–4.4 mg/L, and aimed to: (1) compare the two processes of Al^{3+} coagulation and AlOxHy adsorption with respect to fluoride removal and fluoride species transformation as a function of Al dose and pH; (2) determine the effect of fluoride at different $R_{\text{F:Al}}$ on Al^{3+} hydrolysis and the dissolution and fluoride removal of AlOxHy over a wide pH range; (3) propose the dominant pathways involved in the species transformation of fluoride and Al at different pH and $R_{\text{F:Al}}$; and (4) evaluate the fluoride removal behavior and species transformation for these two processes in a continuous pilot-scale system.

2. Materials and methods

2.1. Chemicals and materials

Unless specifically noted, all chemicals used in the experiments were analytical grade and were used without further purification. The stock solutions of Al^{3+} (4 g/L) and fluoride (13 g/L) were respectively prepared by dissolving aluminum sulfate [$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$] and sodium fluoride (NaF) in deionized water. pH adjustment was accomplished using 1 M hydrochloric acid (HCl) and sodium hydroxide (NaOH).

The groundwater, collected from the suburb of Langfang City, Hebei Province, was employed in both the laboratory and pilot-scale studies, and the fluoride concentration was determined to range from 3.3 to 4.4 mg/L. The main characteristics of the groundwater are illustrated in Table S1. Water containing higher fluoride concentrations used in study than raw water was prepared by adding appropriate amounts of the fluoride stock solution to raw water.

2.2. Experimental methods

2.2.1. Batch tests

2.2.1.1. Coagulation test. Coagulation tests were conducted using a Phipps and Bird six-paddle stirrer (MY 3000-6, QianjiangMeiYu Instruments, China) at room temperature. Raw water at 300 mL

was transferred to a 500-mL beaker, and Al stock solution was added to obtain an Al dose of 40 mg/L. The procedures used were as follows: 2-min mixing at 100 rpm for pH adjustment to desired pH values, 2-min rapid mixing at 200 rpm, 15-min slow mix at 40 rpm, and 30-min settling period. After that, the final coagulation pH was measured and the supernatant at 2-cm below the water level was collected and filtered through a 0.45- μm membrane filter. The filtrates were carefully kept air-tight at 4 °C for further analysis of the concentrations of fluoride and Al.

2.2.1.2. Adsorption tests. Adsorption tests followed the abovementioned procedures except that the AlOxHy was used. AlOxHy was prepared by the method described in our previous study [19], *i.e.*, reaction between $\text{Al}_2(\text{SO}_4)_3$ and NaOH at equivalent molar ratio of 1:3. AlOxHy was dosed into the 300-mL raw water immediately after being prepared. While investigating the removal behavior of AlOxHy toward fluoride at elevated fluoride concentrations, the fluoride stock solution was added to obtain the desired fluoride concentrations of 16.3, 31.6, 52.7, and 69.0 mg/L.

2.2.1.3. Titration experiments on Al^{3+} hydrolysis. A mixed liquor of Al and fluoride solution was prepared in a 1 L Plexiglass beaker. With stirring at 300 rpm, 1 M NaOH was continually added to the mixed liquor by a 100- μL microsyringe. The volume of base and pH were recorded and plotted. The process of titration was ended at pH 9.0. To avoid dissolution of carbon dioxide in the mixture, nitrogen was continuously purged. The dose of Al was 40 mg/L with fluoride concentrations of 4.4, 16.3, and 31.6 mg/L.

2.2.2. Pilot-scale field test

The pilot-scale field study was carried out in a village located in the suburb of Langfang City, and the groundwater was directly used as raw water without any pretreatment. The pilot-scale system with a designed treatment scale of 0.5 m³/h included one raw water tank, one adsorption reactor with internal diameter of 700 mm and height of 1600 mm (R_{Ads}), one reactor with two combined subunits for coagulation and sedimentation ($R_{\text{Coag+Sed}}$), and one sand filter with quartz sand as the filter medium (Fig. 1). The designed upflow velocity in R_{Ads} was 1.3 m/h with an empty bed contact time (EBCT) of 60 min. As for $R_{\text{Coag+Sed}}$, the designed hydraulic retention times were 15 and 120 min for the 3-stage coagulation and sedimentation subunits, respectively. The height of the filter bed was 1000 mm and the diameter of the quartz sand was in the range 0.5–1 mm. The R_{Ads} and $R_{\text{Coag+Sed}}$ units were able to be separately operated, and the effluents of both units flowed into the sand filter, at the filtration velocity of 6.5 m/h, for the removal of suspended particles.

While investigating the fluoride removal efficiency of coagulation, an $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (Industrial Grade) stock solution at

Fig. 1. The schematic set-up of pilot-scale coagulation and adsorption processes.

9.6 g/L as Al was continuously dosed by a metering pump to obtain the designed dose of 35 mg/L as Al. The dosing-point of the $\text{Al}_2(\text{SO}_4)_3$ solution was prior to the elevation pump and was well agitated with the raw water therein. After flowing through the $\text{R}_{\text{Coag+Sed}}$ and sand filter, the effluent was sampled to analyze equilibrium pH and the residual concentrations of total Al, total fluoride ($[\text{F}]_{\text{total}}$), and complexed fluoride (Com-F).

While investigating the fluoride removal efficiency of adsorption, raw water was pumped and flowed through the adsorption and filtration units in sequence. To adjust pH, a stock solution of nitric acid (0.27 g/L) was continuously dosed by a metering pump at designed flow rates of 73, 104, 135, and 166 mL/min to obtain desired pHs near 6.90, 6.70, 6.50, and 6.30. The nitric acid solution was also agitated in the elevation pump. The AlOxHy was loaded into the adsorption reaction by the method developed in our previous study [14]. The filter effluents were also sampled at intervals for further analysis.

2.3. Analytical methods

pH was measured with a high precision pH meter (Orion 720A, U.S.A.). $[\text{F}]_{\text{total}}$ was determined using a fluoride ion selective electrode (PF-1, Kangyi instrument Ltd., China). The concentrations of free fluoride (Free-F) were determined by the method indicated in our previous study [9], and the Com-F concentrations were calculated by subtracting Free-F from $[\text{F}]_{\text{total}}$.

Residual Al concentrations were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) (SCIEX Perkin-Elmer Elan mode 5000).

Zeta potential was measured by a zeta potential analyzer (Zetasizer 2000, Malvern, UK). At least 3 runs were used for each of the measurements, and the average data are presented. Solid-state ^{27}Al nuclear magnetic resonance (NMR) spectroscopy was performed by a Varian UNITYINOVA (500 MHz) spectrometer to determine the Al species within the obtained precipitates after batch experiments employing these two processes. Details of the operating approach and parameters of the apparatus can be found in the literature [20].

2.4. Modeling methods

Visual MINTEQ Version 3.0 software was used to calculate the content of different fluoride species and complexed Al (Com-Al). The different species included were as follows: Al^{3+} , F^- , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_4^-$, AlF^{2+} , AlF_2^+ , $\text{AlF}_3(\text{aq})$, AlOH^{2+} , $\text{HF}(\text{aq})$, HF_2^- , AlF_4^- , and $\text{Al}_2(\text{OH})_4^{4+}$, and the four Al-F complexes of AlF^{2-} , AlF_2^- , AlF_3^- , and AlF_4^- were related to the Com-F and Com-Al.

3. Results and discussion

3.1. Removal of fluoride by coagulation and adsorption

3.1.1. Effects of Al dose on species transformation and removal of fluoride

The variation of residual fluoride in terms of total fluoride (Total-F), Free-F, and Com-F with elevated Al dose is illustrated in Fig. 2. Al coagulation contributed to steady decrease of $[\text{F}]_{\text{total}}$ from 3.71 to 0.56 mg/L with the increase of Al dose from 0 to 50 mg/L. Further increase of Al dose adversely affected the removal of fluoride, and $[\text{F}]_{\text{total}}$ increased to as high as 2.46 mg/L at the elevated Al dose of 70 mg/L. Additionally, it was observed that elevated Al doses from 20 to 50 mg/L increased the zeta potential of Al flocs from +5.1 to +18.1 mV, and with further elevation of Al dose to 70 mg/L, the zeta potential slightly decreased to +13.2 mV. The variation trends of zeta potential corresponded well

Fig. 2. The concentration of residual fluoride and solution pH after coagulation (a) and adsorption (b) at different doses of Al (Experimental conditions: $[\text{F}]_0 = 3.71$ mg/L).

to the removal of fluoride by Al coagulation, and this indicated that the surface charge of Al flocs had a significant effect on the removal of negatively-charged fluoride. The equilibrium pH continuously decreased from 8.6 to 4.7 with steady increase of Al dose from 0 to 70 mg/L. This was attributed to the hydrolysis of Al^{3+} and the consumption of OH^- , which was more significant at elevated Al doses. At Al doses of above 40 mg/L the equilibrium pH decreased to below 6.5, and the formation of Al-F complexes occurred. Generally, the formation of Com-F occurs under weakly acidic and acidic conditions [9]. With Al dose increasing from 20 to 70 mg/L the concentration of Com-F increased remarkably from 0.07 to 2.45 mg/L, whereas that of Free-F decreased accordingly. The elevated $[\text{F}]_{\text{total}}$ at excessive Al dose was attributed to the formation of soluble Al-F complexes, and at Al doses of above 60 mg/L little difference could be observed between the concentrations of Com-F and Total-F. Additionally, the dissolution of Al-based precipitates occurred at lowered pH (Fig. S1a), and this effect decreased the amount of Al precipitates available and inhibited fluoride removal. The maximum removal of fluoride by Al coagulation was achieved at the optimum Al dose of 30 mg/L.

By using the visual MINTEQ software, the ratios of different Com-F species to total Com-F were further quantified for the residual fluoride after Al coagulation over a wide Al dose range from 20 to 70 mg/L (Fig. S2), and four Al-F complexes, i.e., AlF^{2+} , AlF_2^+ , AlF_3^- and AlF_4^- , were included. These four Com-F species showed different variation trends with elevated Al dose. The ratio of AlF_3^- decreased from 53.6% at Al dose of 20 mg/L to 39.9%, 22.1%, and 4.4% at Al doses of 30, 40, and 50 mg/L, respectively. AlF_2^+ was the dominant Com-F species in the Al doses range from 20 to 60 mg/L, and the ratios of AlF_2^+ were in the range from 41.6% to 72.6% accordingly. At elevated Al doses of 60 and 70 mg/L, AlF^{2+} was the dominant species and accounted for 57.7% and 86.5% of total Com-F. The ratio of AlF_4^- was below 2.6% over a wide Al dose range from 20 to 70 mg/L. Additionally, it was indicated that the formation of AlF_3^- was benefited at low Al doses, whereas that of AlF^{2+} was favored at high Al doses. The ratios of different Com-F species were dependent on pH and $\text{R}_{\text{F:Al}}$.

As shown in Fig. 2b, the removal of fluoride by its adsorption onto AlOxHy showed critically different trends from that by Al coagulation. $[F]_{\text{total}}$ gradually decreased from 3.71 to 0.81 mg/L at 200 mg/L of AlOxHy dose as Al, and equilibrium pH decreased slightly from 8.6 to 7.8 accordingly. The removal of fluoride by adsorption was attributed to the removal of Free-F, which decreased from 3.01 to 0.68 mg/L and showed a trend similar to that of $[F]_{\text{total}}$. Comparatively, the levels of Com-F were consistently below 0.16 mg/L, and it was inferred that the formation of Al-F complexes was slight in this system. Moreover, the dissolution of Al-based precipitates showed little variation over a wide Al dose range and occurred to a remarkably lower extent than in the coagulation system (Fig. S1b). To achieve the maximum contaminant level (MCL) of fluoride (<1 mg/L) in the drinking water standard, the optimum Al doses were determined to be 30 and 160 mg/L for coagulation and adsorption, respectively.

3.1.2. Effects of pH on species transformation and removal of fluoride

Fig. 3 compares the species distribution of fluoride between the coagulation and adsorption systems over a wide pH range from 4 to 9, at the Al dose of 40 mg/L. In both processes the removal of Total-F was most significant in weakly acidic and neutral pH of 6 and 7. In the coagulation system, complexation between Al and fluoride occurs at pH below 7 [9], and Al-F complexes consume less OH^- to transform into Al-F-OH coprecipitates compared to precipitate formation for Al^{3+} at weakly acidic and neutral pH of 6 and 7. Additionally, the removal efficiency of fluoride was observed to be positively correlated with zeta potential, and the maximum zeta potential of the Al-based coagulant and adsorbent were determined to be +22.0 and +17.5 mV at pH 6.0 for adsorption and coagulation systems. Zeta potential analysis indicated that the Al flocs and AlOxHy exhibited positive surface charge over pH 4–9, and the adsorption of negatively charged fluoride was favored accordingly. Additionally, Al (hydro)oxide exhibits amphoteric character, and its transformation in different pH ranges may be described by Eqs. (1) and (2). At low pH the removal of fluoride was inhibited by the insufficient hydrolysis of Al ions (Eq. (1)) whereas at high pH, the formation of aluminates (Eq. (2)) adversely affected fluoride removal.

Fig. 3. Fluoride species distribution at different pH after coagulation and adsorption, and coagulation and adsorption were shown as dotted line and solid line of bar graph, respectively. (Experimental conditions: $[F]_0 = 4.44$ mg/L, Al doses = 40 mg/L, $[F]_{\text{total}} = [F]_{\text{Free-F}} + [F]_{\text{Com-F}}$).

Additionally, it was observed that Com-F was dominant at $\text{pH} < 7$ in both systems, and Free-F could hardly be detected at pH 4 and 5. The concentrations of Com-F, Free-F, and Total-F were determined to be 2.92, 0.01, 2.93 mg/L at pH 5.0 and to be 0.53, 0.24, 0.77 mg/L at pH 6.0, respectively. At elevated pH above 7, Free-F was the dominant fluoride species and contributed most to Total-F, and these two fluoride species showed similar variation trends accordingly. Quantitatively, the concentrations of Free-F increased from 0.24 to 3.02 mg/L whereas those of Total-F increased from 0.76 to 3.07 mg/L as pH increased from 6.0 to 9.0. At elevated pH, OH^- at higher concentrations showed more significant competitive effects toward Al ions than fluoride did [9], and contributed to the dissociation of Com-F to Free-F thereafter.

In both systems the extent of Com-F dissociation increased with elevated pH, and the Com-F not only dissociated into Free-F but also directly transformed to insoluble Al-F-OH precipitates. The dominant products were observed to be highly dependent the pH range. With pH increasing from 4 to 5, the Com-F mainly transformed into insoluble fluoride and the formation of Free-F was slight. At elevated pH from 5 to 6 the transformation of these two fluoride species occurred, and significant removal of Total-F was achieved by the formation of Al-F-OH precipitates. In contrast, the increase of pH from 6 to 7 mainly contributed to the transformation of Com-F to Free-F. The further increase of pH to above 7 was conducive to the dissolution of insoluble fluoride to Free-F. Coagulation showed better efficiency than adsorption with respect to the removal of Total-F over wide pH ranges from 5 to 9, and the formation of Com-F was inferred to benefit fluoride removal over wide pH ranges. Interestingly, it was observed that Com-F did exist in the adsorption system, especially under acidic pH conditions. At acidic pH the dissolution of AlOxHy into Al ions such as Al^{3+} and AlOH^{2+} occurred [21], and this contributed to the formation of Al-F complexes thereafter. The dominant reactions between Al and fluoride taking place in these two systems were different, and this contributed to their different removal efficiencies toward fluoride. Interestingly, the formed precipitates in coagulation and adsorption systems showed little difference in terms of aluminum species, as indicated by solid-state ^{27}Al NMR analysis (Fig. S3). Specifically, after the removal of fluoride by coagulation and adsorption at pH of 5, 6, 7, and 9, all of these precipitates showed a single peak at 0 ppm, which was assigned to octahedrally coordinated Al [22].

The exact species of Al-F complexes cannot be directly quantified by chemical analysis, and the visual MINTEQ software was

Fig. 4. Titration curve of Al^{3+} (dose of Al = 40 mg/L) by 1 mol/L NaOH at different fluoride concentrations.

Fig. 5. The concentration of Com-F, Free-F (a) and Com-Al (b) over wide pH ranges from 4.0 to 9.0. (Experimental conditions: dose of Al = 40 mg/L, $[F]_0 = 4.4, 16.3$ and 31.6 mg/L).

used to provide more information on the complex interactions between Al and fluoride. Fig. S4 illustrates the ratios of four Al-F complexes (i.e., AlF_2^{2+} , AlF_2^+ , AlF_3 and AlF_4^-) to total Com-F in the pH range from 4 to 6. In the coagulation system, the ratio of Total-F to total soluble Al ($R_{Tot-F:Tot-Al}$) increased from 0.15:1 at pH 4 to 3.66:1 at pH 6 and the ratio of Com-Al (i.e., AlF_2^{2+} , AlF_2^+ , AlF_3 and AlF_4^-) to total soluble Al ($R_{Com-Al:Tot-Al}$) increased from 0.14:1 to 0.72:1 accordingly. Additionally, the ratio of AlF_2^{2+} to total Com-F decreased from 0.98:1 at pH 4 to 0.81:1 at pH 5 and 0.15:1

at pH 6, whereas the ratio of AlF_2^{2+} to total Com-F increased from 0.02:1 to 0.19:1 and 0.77:1 accordingly. The transformation of AlF_2^{2+} to the Al-F complexes with higher $R_{F:Al}$, i.e., AlF_2^+ and AlF_3 , was benefited at elevated pH and $R_{Tot-F:Tot-Al}$ (Fig. 4Sa). This may be attributed to the fact that AlF_2^{2+} consumes less OH^- than AlF_2^+ to form insoluble Al-F-OH precipitates. On the other hand, elevated $R_{Com-Al:Tot-Al}$ also benefits the transformation of soluble Al and fluoride to insoluble Al-F-OH precipitates (Fig. 4Sb). The increased removal of fluoride with elevated pH from 4 to 6, as observed in Fig. 3, was in good accordance with the increased $R_{Com-Al:Tot-Al}$ and the ratio of AlF_2^{2+} to total Com-F.

Similar trends in terms of the species transformation of fluoride with elevated pH were also observed in the adsorption system (Fig. S5). However, the pathway to form Al-F complexes is critically different between the coagulation and adsorption processes. In the coagulation system, Al-F complexes formed immediately after dosing with the Al^{3+} solution and acted as intermediates for the formation of insoluble Al-F precipitates to remove fluoride thereafter. In the adsorption system, fluoride first adsorbed onto the $AlOxHy$ surfaces through the hydroxyl replacement mechanism and electrostatic interaction as discussed in our previous study [19]. Additionally, the adsorption of fluoride also contributed to the dissolution of $AlOxHy$ and the formation of Al-F complexes; this effect will be discussed in detail later. Al-F complexes may also remove fluoride by transforming to F-Al-OH precipitates. However, this effect was less significant than direct adsorption in removing fluoride.

3.2. Effects of fluoride on species transformation of Al

3.2.1. Effect of fluoride on Al^{3+} hydrolysis and the formation of Al-based precipitates

To illustrate the effect of fluoride on the hydrolysis of Al^{3+} , the equilibrium pH was continuously measured during slow titration of NaOH solution (1 mol/L) into Al^{3+} solutions (40 mg/L) with different fluoride concentrations, i.e., 4.4, 16.3, and 31.6 mg/L; the results are indicated in Fig. 4. The groundwater used in this experiment contained the co-existing ions silicate, phosphate, and carbonate at the concentrations of 0.18, 0.001, and 0.017 mmol/L, respectively. MINTEQ modeling indicated that these anions showed little effect on the consumption of OH^- by Al ions (Fig. S6).

It can be observed in Fig. 4 that equilibrium pH gradually increased with continuous addition of NaOH solution, and the most

Fig. 6. Species distribution of Com-F over wide pH ranges from 4.0 to 9.0. (Experimental conditions: doses of Al = 40 mg/L, $[F]_0 = 4.4, 16.3$ and 31.6 mg/L).

significant pH increase appeared in the pH range from 5.5 to 7.0. At higher $[F^-]_0$, a lower amount of NaOH solution was required to achieve the same equilibrium pH. For example, the volume of NaOH consumed was determined to be 3400, 2800 and 2100 μL at $[F^-]_0$ of 4.4, 16.3 and 31.6 mg/L to achieve an equilibrium pH of 5.5. Fluoride can also participate in the hydrolysis of Al^{3+} , and the formation of insoluble precipitates of $\text{AlF}_2(\text{OH})$, $\text{AlF}(\text{OH})_2$, and AlF_3 as well as $\text{Al}(\text{OH})_3$ has been reported before, as indicated in Eqs. (3)–(5) [9]. Fluoride reduced the amount of NaOH required to achieve the formation of insoluble Al-based precipitates (e.g., $\text{Al}(\text{OH})_3$, Al-OH-F , and Al-F-OH precipitates) in the abovementioned pH ranges from 5.5 to 7.0. Further increase in pH contributed to the dissolution of Al-based precipitates into aluminates. The interaction between fluoride and aluminates was slight, and the NaOH volumes required to achieve the high pH of 9 were observed to be independent of the $[F^-]_0$ levels.

Fig. 7. Effect of initial fluoride concentrations on (a) Al dissolution, (b) Comp-F, and (c) fluoride removal after AlOxHy adsorption. (Experimental conditions: dose of AlOxHy = 40 mg/L as Al, $[F^-]_0$ = 4.3–69 mg/L).

The corresponding concentrations of Com-F, Free-F, and Com-Al were further quantified by the visual MINTEQ software (Fig. 5). Interestingly, it was observed that Com-F showed little variation, whereas Com-Al decreased with increasing pH from 4 to 7, and this indicated the dissociation of Com-Al. At the expense of the lowered content of Com-Al, the ratios of $R_{F:Al}$ within Al-F complexes increased accordingly (Fig. 6). These species transformations of fluoride and Al achieved constant concentrations of Com-F in the pH range 4–7, and favored the formation of insoluble Al-F-OH precipitates. This effect contributed to the consumption of less OH^- for the precipitation of Al ions and to the observed lower amount of OH^- required to achieve the same pH at elevated $[F^-]_0$. At pH above 7.0, the dissociation of Com-F to Free-F and the dissolution of Al-based precipitates occurred, and the removal of fluoride was inhibited thereafter. The formation of Al-F complexes was inferred to play an important role in the removal of fluoride by Al coagulation.

3.2.2. Effect of fluoride on the dissolution of AlOxHy

AlOxHy removes Total-F by transforming Free-F to insoluble fluoride. The adsorption of fluoride also shows an effect on the transformation of Al species and the removal of fluoride thereafter. Fig. 7a illustrates the effect of fluoride at initial concentrations ($[F^-]_0$) increasing from 4.3 to 69 mg/L on the dissolution of the AlOxHy , as indicated by the soluble Al concentration, over a wide equilibrium pH range from 4 to 9. The dose of AlOxHy was 40 mg/L as Al. At a given $[F^-]_0$, the level of soluble Al was observed to decrease with increasing pH from 4 to 8, and then slightly increased at pH 9. Additionally, fluoride favored the dissolution of AlOxHy into soluble Al over a wide pH range from 4 to 9, and more significant dissolution was observed at elevated $[F^-]_0$. This effect was slight at low $R_{F:Al}$ ($\leq 1.2:1$) for pH 8–9. At pH below 7.0, the released Al^{3+} tended to form Al-F complexes with Free-F as expressed in Eq. (6). The consumption of Al^{3+} leads to the continuous dissolution of AlOxHy into soluble Al (Eq. (6)) and the formation of Al-F complexes thereafter. Additionally, fluoride can also directly form Al-F complexes with AlOxHy (Eq. (7)). The Com-F were observed to be the dominant fluoride species (Fig. 7b), and this was in accordance with a previous study [9]. At elevated $[F^-]_0$, i.e., higher molar ratios of fluoride to Al ($R_{F:Al}$), more significant dissolution of AlOxHy was observed. In basic conditions at pH 8 and 9, the levels of Com-F were much lower, at 6.4 and 7.5 mg/L,

Fig. 8. Proposed dominant reactions involved in the removal of fluoride by Al coagulation and adsorption.

Fig. 9. The variation of pH, F, Al, and $R_{\text{Com-F:Tot-F}}$ in the AlOxHy adsorption system (a and b) and the Al coagulation system (c and d) in pilot-scale continuous method.

even at extremely high $R_{\text{F:Al}}$ of 2.45:1, and the corresponding Free-F concentrations were determined to be 41.6 and 46.8 mg/L. At $\text{pH} \geq 8$, soluble Al mainly exists as aluminates rather than Al^{3+} ions. Interactions between soluble aluminates and Free-F rarely occurred, and fluoride showed much less effect on Al dissolution, except at extremely high $R_{\text{F:Al}}$ (Fig. 7b).

These effects also had an influence on the removal of fluoride by AlOxHy (Fig. 7c). Generally, the removed fluoride increased with elevated $[\text{F}^-]_0$ over a wide pH range from 4 to 9, owing to the higher concentration gradient between fluoride and AlOxHy, and the maximum removal of fluoride was observed at weakly acidic and neutral pH of 6 and 7; this was consistent with results in Fig. 3. However, at extremely high $[\text{F}^-]_0$ of 69 mg/L (i.e., $R_{\text{F:Al}} = 2.45:1$), the removed fluoride decreased slightly in the range pH 4–6 rather than increasing with elevated $[\text{F}^-]_0$, as observed in pH 7–9. This may be attributed to the more significant effect of fluoride on AlOxHy dissolution at low pH than that in high pH ranges. Generally, the formation of Al–F complexes was favored under acidic conditions and elevated $[\text{F}^-]_0$. This effect facilitated the AlOxHy dissolution and decreased the amount of Al available for fluoride removal thereafter. However, at pH 7–9, Al fluoride complex formation was slight, and the extent of Al–F complexation (Fig. 7b) and AlOxHy dissolution (Fig. 7a) also were slight relative to that at pH 4–6. In the pH range 7–9, fluoride removal was mainly attributed to its adsorption onto the surface of AlOxHy. The extent of AlOxHy dissolution was slight even at high $R_{\text{F:Al}}$ of 2.45:1, and the adverse effect of fluoride concentration on fluoride removal was insignificant thereafter.

The enhanced dissolution of AlOxHy favored the formation of Al–F complexes, as indicated by the increased Com-F concentrations at elevated $[\text{F}]_0$ over a wide pH range from 4 to 9 (Fig. 7b). It was noted that Com-F was detected at high pH of 8 and 9, although the ratios of Com-F to total-F were as low as 0.15:1 or

less. This was unexpected, that Com-F could exist under alkaline conditions. This result inferred that fluoride at higher $R_{\text{F:Al}}$ also would lead to the dissolution of AlOxHy even under alkaline conditions and inhibit fluoride removal afterward, and the exact species involved should be characterized in future study.

3.3. Dominant reactions involved in the removal of fluoride by coagulation and adsorption

On the basis of the abovementioned results, the dominant reactions involved in the removal of fluoride by Al^{3+} coagulation and AlOxHy adsorption are illustrated in Fig. 8. In the Al^{3+} coagulation system, Al^{3+} hydrolysis and the formation of Al–F complexes occur immediately after dosing Al^{3+} into fluoride-containing water. Al–F complex formation is favored at low pH, whereas the extent of Al^{3+} hydrolysis increases with elevated pH. Insufficient Al^{3+} hydrolysis at pH 4–6 contributes to Al^{3+} polymerization and to the formation of Al polymers, i.e., $\text{Al}_2\text{--Al}_4$, $\text{Al}_5\text{--Al}_{12}$, and $\text{Al}_{13}\text{--Al}_{16}$ [23,24]. These Al polymers can also react with fluoride to form Al–F complexes, as indicated by ESI–MS analysis (Fig. S7, Fig. S8, and Table S2). At elevated pH, these Al polymers can either transform to amorphous $\text{Al}(\text{OH})_3$ or precipitate as insoluble Al–F–OH, both of which can further adsorb fluoride. Moreover, the amorphous $\text{Al}(\text{OH})_3$ formed *in-situ* can achieve fluoride removal via an adsorption mechanism to form Al–OH–F. Additionally, the Al–F complexes at different $R_{\text{F:Al}}$ can transform to insoluble Al–F–OH with increased pH. At further elevated pH, the dissolution of $\text{Al}(\text{OH})_3$, Al–F–OH, and Al–OH–F into aluminates occurs.

In the AlOxHy adsorption system, the replacement of surface hydroxyl groups by fluoride, i.e., the formation of Al–OH–F, contributes to the removal of fluoride [12]. The dissolution of AlOxHy occurs even in the absence of fluoride, and more significant dissolution occurs at $\text{pH} < 6$ and $\text{pH} > 8$ [12]. The presence of fluoride facilitates the dissolution of AlOxHy, especially in the low pH range (Fig. 7a). The released Al^{3+} from AlOxHy dissolution follows the above-noted pathways of species transformation. The dominant reactions between Al and fluoride species are highly

dependent on equilibrium pH and $R_{F:Al}$, and impact the removal of fluoride by these two processes.

3.4. Fluoride removal by coagulation and adsorption in pilot-scale continuous experiments

Fig. 9 illustrates the fluoride removal of the coagulation and adsorption processes in the pilot-scale system. $[F]_0$ was in the range from 3.3 to 4.4 mg/L, whereas pH ranged from 6.2 to 8.4. In the adsorption process, residual fluoride increased rapidly and exceeded the MCL of fluoride as issued by the National Drinking Water Standard, i.e., 1 mg/L, after a run length of 150 h. This corresponded to 150 bed volumes (BVs). By decreasing influent pH from 8.4 to 7.0 and 6.2, the levels of residual fluoride were kept below 1 mg/L for run lengths from 150 h to 353 h. The equilibrium adsorption capacity of the $AlOxHy$ was calculated to be 25.1 mg/g as Al with respect to the equilibrium fluoride concentration of 1 mg/L (Table S3). By comparison, residual fluoride was found to be consistently below 1 mg/L in the coagulation process at an Al dose of 35 mg/L throughout the 350-h run length. Although nitric acid solution was not added, the hydrolysis of Al decreased effluent pH to the optimum pH range of near 6.5. Additionally, the precipitation of Al–F complexes was also favored and the removal of fluoride was increased greatly (Fig. 3). It is noted that a small amount of colloid particles inevitably existed in the groundwater, although the turbidity was as low as 0.3 NTU. In this case, the sweep coagulation mechanism was also involved in removal of fluoride, considering the extremely high Al dose of 35 mg/L at pH 6.5, as indicated by the design and operation diagram of aluminum coagulation [25]. The equilibrium adsorption capacity for equilibrium F below 1 mg/L, as expressed by the total removed fluoride divided by the total dosed Al coagulant, was determined to be 85.2 mg/g as Al.

Besides the pH-decreasing effect, the remarkable superiority of Al coagulation over $AlOxHy$ adsorption may be attributed to the involvement of Al–F complex formation and Al–F–OH precipitation. In the adsorption system, the ratios of Com-F to Total-F ($R_{Com-F:Tot-F}$) were below 0.04:1 and in the range from 0.04:1 to 0.11:1 in the effluent pH ranges of 8.2–8.4 and 6.2–7.0, respectively (Fig. 9b). The effluents in the coagulation system showed higher $R_{Com-F:Tot-F}$, with the average value of 0.14:1 (Fig. 9d). Interestingly, elevated $R_{Com-F:Tot-F}$ decreased rather than increased residual Al levels, which were continuously below the Al MCL (0.2 mg/L). In the adsorption system, residual Al concentrations were above 0.2 mg/L throughout the 150-h run length, owing to the dissolution of $AlOxHy$. After adjusting influent pH to below 7.0, residual Al decreased to below 0.2 mg/L.

4. Conclusions

- (1) Al coagulation shows higher removal efficiency toward fluoride than $AlOxHy$ adsorption, not only at the same pH but also the same Al dose, and Al–F complexation plays a determining role in removing fluoride for both Al coagulation and $AlOxHy$ adsorption.
- (2) Fluoride favors the transformation of Al^{3+} and Al–F complexes to insoluble Al–F–OH, and fluoride removal by coagulation is improved thereafter. However, Al–F complexation adversely inhibits the adsorption of fluoride onto $AlOxHy$, especially at excessive fluoride concentrations.
- (3) The pilot-scale field experiment demonstrates that Al coagulation shows superior fluoride removal compared to $AlOxHy$ adsorption, and a higher $R_{Com-F:Tot-F}$ is observed in the coagulation system than in the $AlOxHy$ adsorption system.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.seppur.2015.05.005>.

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