Effects of fluoride on coagulation performance of aluminum chloride towards Kaolin suspension

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HIGHLIGHTS

- ▶ Fluoride inhibits coagulation in insufficient Al doses at pH < 8 and $R_{F:Al} > 10:10$.
- ▶ Little effect of is observed over wide $R_{F:Al}$ ranges at pH > 8.
- ▶ Fluoride inhibits particle re-stabilization at overdosed Al to benefit coagulation.
- ▶ Al and F interactions dominate in the effects of fluoride on coagulation.
- ▶ Spent *in-situ* $Al_2O_3 \cdot xH_2O$ with F may reclaim as coagulant after acid dissolving.

GRAPHICAL ABSTRACT

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ABSTRACT

Although many studies have investigated the removal of fluoride by aluminum (Al) coagulation, few studies focus on the effects of fluoride on the coagulation behaviors towards colloids such as kaolin suspensions. In this study the effects of fluoride at different molar ratios of fluoride to Al ($R_{F:Al}$) on turbidity removal, zeta potential, flocs growth, and residual Al levels were investigated by a series of batch experiments, and the Visual MINTEQ software was also used to illustrate the species distribution of Al and fluoride at different $R_{F:Al}$ levels. In insufficient Al dose ranges, fluoride showed adverse effects at $R_{F:Al}$ above 10:10, whereas fluoride exhibited little effect on coagulation at $R_{F:Al}$ below 2:10 at pH < 8. At pH > 8, little effect was observed over wide $R_{F:Al}$ ranges, from 1:10 to 30:30. The adverse effects of fluoride were related to decreased zeta potential, smaller flocs, and elevated levels of residual Al. At pH 6, the fluoride at $R_{F:Al}$ of 10:10 contributed to the decrease of the zeta potential from −1.7 to −6.7 mV, decrease of floc size from 119.7 to 29.0 μm , and increase of residual Al of 0.22 mg/L as Al. For the overdosed dose of 20 mg/L as Al, the presence of fluoride decreased residual turbidity from 22.7 to 20.6 NTU, owing to the lowered zeta potential and the inhibited re-stabilization of particles. Moreover, this study indicates that after adsorbing fluoride, the spent freshly-prepared aluminum hydroxides (*in-situ* $Al_2O_3 \cdot xH_2O$) may be reclaimed as coagulants for colloid removal after being dissolved by acid solution. This strategy is valuable to minimize the reagent cost for the removal of fluoride by *in-situ* $Al_2O_3 \cdot xH_2O$.

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1. Introduction

The long-term exposure to fluoride via drinking water has resulted in the wide occurrence of dental and skeletal fluorosis globally [1,2]. Different defluoridation technologies such as adsorption (electro) coagulation, co-precipitation, membrane separation, and the Nalgonda process, have been proposed and well

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investigated [1–4]. However, to mitigate endemic fluoride diseases for an affected community, the World Health Organization (WHO) and International Water Association (IWA) suggest the alternation of water sources to those with safe and low fluoride levels rather than the implementation of defluoridation facilities [2]. In practice, the long-term stability of these facilities is poor, mainly owing to the high cost, complicated operation, and laborious maintenance [1,2,4]. Additionally, other factors also restrict the successful operation of defluoridation processes. For example, the Nalgonda process is claimed to be promising for defluoridation; unfortunately various disadvantages, e.g., high maintenance cost, boring attendant, unpleasant taste, large space for sludge drying, and the excessive residual aluminum, have also been identified [5].

Adsorption requires little maintenance and monitoring and shows superiority in the removal of fluoride in household point-of-use (POU) systems, decentralized small-scale treatment stations, and even centralized moderate-scale treatment plants [2,3]. Various adsorbents have been proposed and well-studied, and activated alumina is classified as one of the best adsorbents for fluoride removal [3]. However, the use of this established technology is also restricted by its strong dependence of performance on pH and co-existing ions and by the high cost [2]. For a defluoridation technique, it is of crucial importance to decrease the treatment cost as much as possible to enhance its feasibility in engineering.

To minimize the cost and to simplify regeneration procedures, we developed the *in-situ* preparation and regeneration method to maintain the surface adsorption activity as much as possible [6], and freshly-prepared aluminum hydroxides (*in-situ* $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) were included [7]. The equilibrium adsorption capacity in continuous pilot-scale studies was observed to be as high as 23 mg F/g $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ as Al [8]. The high adsorption capacity towards fluoride of this adsorbent prolongs the regeneration cycles and avoids frequent regeneration procedures. Additionally, the *in-situ* preparation and regeneration strategy greatly increases the utilization ratio of adsorbents and decreases the treatment cost to some extent [6]. The reclamation of the spent adsorbents for other purposes is another pathway to decrease the cost from another perspective. As for the *in-situ* $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ with adsorbed fluoride, it is reluctant to dissolve in acidic solution, and the resulting solution mainly contains aluminum and fluoride in different species. Our previous study indicated that the species distribution of aluminum and fluoride are dependent on their concentrations, the molar ratios of fluoride to aluminum ($R_{\text{F:Al}}$), and solution pH [9]. The mixed aluminum and fluoride solution may be reutilized as a coagulant for the removal of colloids. However, to the best of our knowledge, few studies have focused on this before.

On the other hand, the removal of fluoride by aluminum coagulation and electro-coagulation with aluminum electrodes has been widely investigated, and the mechanisms involved such as co-precipitation and adsorption have been reported [10–12]. The defluoridation efficiency was related to $R_{\text{F:Al}}$, aluminum dose, aluminum species, and pH. However, little study has been devoted to the effects of fluoride on the coagulation behaviors towards colloids in defluoridation by coagulation. In F^- -containing drinking water sources and industrial wastewater, the necessity to simultaneously remove fluoride and turbidity does exist.

In this study, we prepared mixed solutions of aluminum chloride (AlCl_3) and sodium fluoride at different $R_{\text{Al:F}}$ values, with the goal of evaluating the effects of fluoride on the coagulation performance of AlCl_3 towards kaolin suspension. The reactions and mechanisms involved in the system are also discussed. This study advances the understanding of the coagulation process for colloid removal with fluoride present. Moreover, the results are valuable in evaluating the feasibility of reutilizing the *in-situ* $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ with adsorbed

fluoride for coagulant preparation and proposing a strategy for the reclamation of spent adsorbents.

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 mixed solution of AlCl_3 and NaF was prepared by adding sodium fluoride (NaF) and aluminum chloride (AlCl_3) into deionized water in polyethylene vessels to obtain the desired concentrations of fluoride, aluminum, and $R_{\text{Al:F}}$ values. pH was not adjusted.

The Kaolin suspension was prepared in the following procedure. First, Kaolin (5 g) (Chemical Grade) was added to a mixed solution (15 L) of tap water and deionized water in the volume ratio of 1:1, and the solution pH was adjusted to 7.5. Second, the suspension was rapidly mixed (150 rpm) for 1 h, and was then settled for 3 h. After that, the supernatant was carefully extracted and the turbidity was determined. The supernatant was then diluted with the mixed solution of tap water and deionized water (1:1) to obtain a turbidity near 100 NTU. Finally, the obtained solution was occasionally mixed before use to avoid particle sedimentation. In cases investigating the effects of pH on coagulation performance, the solution pH was adjusted to the desired values with hydrochloric acid (HCl) and sodium hydroxide (NaOH).

2.2. Experimental methods

Jar tests. Jar tests were performed using a Phipps and Bird six-paddle stirrer. Soon after a 10 s rapid mixing (250 rpm), the mixed solution of AlCl_3 and NaF was added. After that, the coagulation procedures consisted of a 2 min rapid mix (200 rpm), 15 min slow mix (40 rpm), and a 30 min settling period. A small amount of sample was taken immediately to measure the zeta potential (Malvern, Zetasizer 2000, U.K.) after the 1 min rapid mix. After settling for 30 min, supernatants were collected to measure residual turbidity using a HACH2100N turbidimeter and equilibrium pH values with a pH meter (Orion 720 A, U.S.A.). The supernatant was then filtered through 0.45- μm membrane filters to analyze the concentrations of fluoride and Al in the filtrate. The concentrations of fluoride were determined by the ion selective electrode method (PF-1, Shanghai KangYi Technology), and those of Al were measured by ICP-OES (OPTIMA 2000DV, PerkinElmer, USA).

Floc diameter and floc growth. The floc growth during the coagulation processes was studied with a laser particle size analyzer (Malvern Instruments, UK). Jar tests followed similar procedures to that noted above: a 15 s rapid mixing (250 rpm), a 2 min rapid mix (200 rpm), 30 min slow mix (40 rpm), and a 15 min settling period. Jar tests were conducted with 900 mL samples on a programmable jar tester. The Kaolin suspension with aluminum flocs was drawn from the jar through a latex tube to the sample cell of the laser particle size analyzer; and then back to the jar by a peristaltic pump (BT00–300M, Longer, China). To avoid disturbing floc before the measurement, the pump was located downstream of the laser particle size analyzer and run at a rate of 28 rpm, and d_{50} served as the representative floc size. The residual turbidity, residual Al, and equilibrium pH of the supernatant was also measured.

Concentrations of complexed fluoride. The concentrations of complexed fluoride were determined by the difference of total fluoride concentrations and free fluoride concentrations, according to the methods proposed in our previous study [9]. Briefly, the ion selective electrode method was used except that the citrate buffer solution was added prior to the analysis of total fluoride concentrations.

2.3. Modeling methods

The Visual MINTEQ software was also used to illustrate the species distribution of Al and fluoride. The total Al concentration was 2 mg/L, and the concentrations of fluoride were set according to the different $R_{F:Al}$ in molar ratios of 1:25, 1:10, 1:1, 5:1, and 10:1. The different species included were as follows: Al^{3+} , F^- , $Al(OH)^{2+}$, $Al(OH)_4^-$, AlF_2^+ , AlF_2^+ , $AlF_3(aq)$, $AlOH^{2+}$, $HF(aq)$, HF_2^- , AlF_4^- , and $Al_2(OH)_2^{4+}$. The four Al–F complexes of AlF_2^+ , AlF_2^- , AlF_3 , and AlF_4^- were related to both the complexed fluoride and the complexed aluminum.

3. Results and discussion

3.1. Effects of fluoride on turbidity removal by aluminum coagulation

Fig. 1 illustrates the effects of fluoride at different $R_{F:Al}$ values ranging from 0:10 to 30:10 on the coagulation efficiency of $AlCl_3$ towards kaolin suspension over wide pH ranges from 6 to 10. The dose of $AlCl_3$ was 0.5 mg/L as Al. In the absence of fluoride, i.e., $R_{F:Al} = 0:10$, the optimum pH was observed to be 7 to achieve the lowest residual turbidity by aluminum coagulation. The increase of pH to 9 and 10 contributed to a significant increase of residual turbidity to above 40 NTU. The effects of fluoride on the removal of turbidity by aluminum coagulation were dependent on both $R_{F:Al}$ values and solution pH. At the strongly basic pH of 9 and 10, fluoride showed little effect and the residual turbidity was consistently high, close to 40 NTU at different $R_{F:Al}$ values. In the pH range from 6 and 8, residual turbidity showed little variation at $R_{F:Al}$ values below 2:10. Elevated $R_{F:Al}$ values contributed to a significant increase in residual turbidity, which was determined to be 40.7, 26.6, and 32.9 NTU at pH 6, 7, and 8 ($R_{F:Al} = 30:10$), respectively. It was noted that other anionic species such as carbonate, sulfate, and phosphate showed much less effect on the removal of turbidity at the same molar ratios of anions to Al.

Fig. 2 illustrates the effect of fluoride at $R_{F:Al}$ value of 10:10 on the removal of turbidity with $AlCl_3$ dose increasing from 0.1 to 20 mg/L as Al. In the absence of fluoride, residual turbidity was observed to decrease to 16.6 and 1.62 NTU after dosing 0.1 and 0.5 mg/L of $AlCl_3$, respectively. Additionally, the $AlCl_3$ at 5 mg/L as Al contributed to the lowest turbidity of 0.35 NTU, and further increasing $AlCl_3$ doses to 10 and 20 mg/L as Al promptly increased residual

Fig. 2. Effects of fluoride at $R_{F:Al}$ value of 10:10 on residual turbidity after $AlCl_3$ coagulation with the doses of $AlCl_3$ increasing from 0.1 to 20 mg/L as Al [experimental conditions: initial turbidity = 97 NTU, initial pH = 7].

turbidity to 1.44 and 22.7 NTU respectively. The effects of fluoride on the removal of turbidity by $AlCl_3$ coagulation were observed to be dependent on the doses of Al. At the low $AlCl_3$ doses of 0.1 and 0.5 mg/L as Al, the presence of fluoride contributed to a remarkable increase of residual turbidity to 24.9 and 7.03 NTU, respectively. At the high $AlCl_3$ dose of 20 mg/L as Al, residual turbidity decreased from 22.7 to 20.6 NTU in the presence of fluoride. Generally, fluoride showed adverse effects on residual turbidity in low Al dose ranges whereas it benefited the removal of turbidity at high $AlCl_3$ doses.

Fig. S1 compares the residual turbidity in the absence of fluoride (x-axis) to that at $R_{F:Al}$ values of 1:10, 2:10, and 10:10 (y-axis). The Al doses ranged from 0.5 to 2 mg/L and equilibrium pH was in the range from 6.4 to 9.7. The diagonal line with slope of 1 indicates equal residual turbidity between two cases, and this corresponds to a lack of effect of fluoride on turbidity removal. Accordingly, the area above this line corresponds to the inhibitive effects of fluoride whereas that below this line relates to the beneficial effects of fluoride. As shown in Fig. S1, the residual turbidity at $R_{F:Al}$ of 1:10 showed little difference to that at $R_{F:Al}$ of 0:10, and the slope of the fitted curve in correlation analysis was calculated to be 1.00 ($R^2 = 0.98$). The elevated $R_{F:Al}$ value of 2:10 corresponds to a reduced slope of 0.95 and low intercept of 0.87 ($R^2 = 0.98$), and this indicated a slight adverse effect of fluoride on coagulation. At the $R_{F:Al}$ value of 10:10, the data were generally above the diagonal line and a further lowered slope of 0.85 was obtained ($R^2 = 0.93$). This indicated the obvious inhibitive effect of fluoride on the removal of turbidity by coagulation in this case.

3.2. Evaluation on different effects involved in the effect of fluoride on coagulation

3.2.1. Effects of fluoride on zeta potential

The effects of fluoride on zeta potential during coagulation as a function of pH and $R_{F:Al}$ values are illustrated in Fig. S2. With pH ranging from 8 to 10, fluoride at different $R_{F:Al}$ values showed insignificant effects on the zeta potential. In the absence of fluoride, aluminum flocs showed the high zeta potentials of -1.7 and -3.1 mV at pH 6 and 7. At $R_{F:Al}$ value of 30:10, the zeta potential was observed to significantly decrease to as low as -17.0 and -19.6 mV due to the presence of fluoride. A lower extent of zeta potential decrease was observed at lowered $R_{F:Al}$ values. Additionally, over a wide $AlCl_3$ dose range from 0.1 to 20 mg/L as Al without pH adjustment, fluoride at $R_{F:Al}$ value of 10:10 showed a lowering effect

Fig. 1. Effects of fluoride at different $R_{F:Al}$ values from 1:10 to 30:10 on residual turbidity after $AlCl_3$ coagulation in wide pH ranges from 6 to 10 [experimental conditions: $AlCl_3$ dose = 0.5 mg/L as Al, Initial turbidity = 100 NTU].

Fig. 3. Effects of fluoride at $R_{F:Al}$ values ranging from 0 to 10:1 on the zeta potential of flocs after $AlCl_3$ coagulation [experimental conditions: $AlCl_3$ dose = 2 mg/L as Al, initial turbidity = 100 NTU, initial pH = 6.3, 7.0, and 8.0].

on zeta potential (Fig. S3). For example, at the high $AlCl_3$ doses of 10 and 20 mg/L as Al, the zeta potential was determined to be as high as +21.0 and +23.8 mV. The over-reversed zeta potential for the re-stabilized particles contributed to the increase the residual turbidity, as indicated in Fig. 2. The reduced zeta potential after introducing fluoride may be mainly attributed to the interactions between aluminum and fluoride, which will be discussed later. However, the fact that the presence of fluoride lowered the extent of pH decrease also played a role, especially at high $AlCl_3$ doses (Fig. S3). Our previous study indicated that fluoride may substitute for hydroxide ion (OH^-) to interact with Al^{3+} and to inhibit pH decrease thereafter [9].

Fig. 3 illustrates the variation of zeta potential with $R_{F:Al}$ values increasing from 0 to 10:1. The dose of $AlCl_3$ was 2.0 mg/L as Al, and three different initial pH conditions of 6.3, 7.0, and 8.0 were investigated. Similar to the aforementioned trend, the zeta potential was observed to decrease with elevated $R_{F:Al}$ values, and the most significant reduction was achieved at $R_{F:Al}$ values of above 3:1. Additionally, pH affected the behavior of fluoride towards zeta potential during $AlCl_3$ coagulation. At pH 7.0 and 8.0, the fluoride at $R_{F:Al}$ values of below 2:10 showed little influence on zeta potential. At pH 6.3, however, zeta potential decreased from 19.2 mV to 11.2 mV due to the influence of fluoride.

3.2.2. Effects of fluoride on dynamic growth of flocs during coagulation

The dynamic growth of flocs during aluminum coagulation at $R_{F:Al}$ values of 0:10 and 10:10 was compared and illustrated in Fig. 4. In the absence of fluoride, the largest flocs were observed to be formed in the pH range from 6 to 8, and the corresponding maximum d_{50} values were determined to be 119.7, 118.2, and 117.5 μm , respectively. At pH 5 and 9, the significantly lower d_{50} values of 24.5 and 41.6 μm were observed. The presence of fluoride inhibited the formation of flocs and lowered the d_{50} values over a wide pH range from 5 to 9. The most significant decrease of floc size was observed at pH 6, where it decreased from 119.7 to 29.0 μm due to the presence of fluoride ($R_{F:Al}$ = 10:10). Interestingly, at the slightly increased pH of 7, the effect of fluoride on the dynamic growth of flocs decreased to a great extent, and the maximum d_{50} values were determined to be 118.2 and 105.3 μm . Furthermore, after the introduction of fluoride, the inhibited formation of flocs contributed to elevated residual turbidity, and a negative correlation between the maximum d_{50} values and residual turbidity was observed (Fig. S4).

Fig. 4. Comparison of the dynamic growth of flocs during $AlCl_3$ coagulation in the absence of fluoride to that at $R_{F:Al}$ values of 10:10 in wide pH ranges from 5 to 9 [experimental conditions: $AlCl_3$ dose = 0.5 mg/L as Al, initial turbidity = 105 NTU].

3.2.3. Species transformation of fluoride and aluminum at different pH and $R_{F:Al}$

The interactions between fluoride and aluminum dominate in their species transformation and in the effects of fluoride on the coagulation behaviors of aluminum salts thereafter. By using the Visual MINTEQ software, the ratios of complexed fluoride and complexed aluminum may be determined at different $R_{F:Al}$ values. The four Al–F complexes of AlF^{2-} , AlF_2^- , AlF_3 , and AlF_4^- were included; however, other species such as $AlF(OH)^+$ were ignored, although they do exist in the systems with co-existing Al^{3+} , F^- , and OH^- . Fig. 5 illustrates the calculated ratios of complexed fluoride and aluminum over the wide pH range from 0 to 14, and for $R_{F:Al}$ values varying from 1:25 to 10:1. The results indicated that the ratios of complexed aluminum increased whereas those of complexed fluoride decreased with elevated $R_{F:Al}$ values. The highest ratio of complexed aluminum was as low as 5.7% at $R_{F:Al}$ value of 1:25, and increased to 14.1%, 96.7%, 100%, and 100% at $R_{F:Al}$ values of 1:10, 1:1, 5:1, and 10:1, respectively. On the contrary, the highest ratios of complexed fluoride decreased from 99.8% to 99.8%, 98.1%, 41.0%, and 22.5% accordingly, over the wide $R_{F:Al}$ ranges, the Al–F complexes disappeared above pH near 8; and the critical pH values for the disappearance of Al–F complexes were observed to increase with increasing $R_{F:Al}$ values.

The species distribution of fluoride in the mixed solution of $AlCl_3$ and NaF was also analyzed thereafter. Prior to being dosed, the mixed solutions showed the pH values of 3.09, 3.21, 3.56, 4.18, 6.16, and 6.8 at $R_{F:Al}$ values of 0:1, 1:5, 1:1, 3:1, 6:1, and 10:1, respectively. The corresponding ratios of complexed fluoride were determined to be 99.98%, 99.90%, 82.82%, 9.67%, and 2.05% with elevated $R_{F:Al}$ ratios from 1:5 to 10:1.

Fig. 5. The calculated ratios of the complexed fluoride and the complexed aluminum by the Visual MINTEQ software in wide pH ranges from 0 to 14 [experimental conditions $[Al]_{total} = 2 \text{ mg/L}$, $R_{F:Al} = 1:25, 1:10, 1:1, 5:1, \text{ to } 10:1$].

In the absence of fluoride, the species of aluminum is controlled by solution pH, i.e., the OH^- concentrations (Fig. S5). With the steady increase of pH from 1 to 14, Al^{3+} , Al hydrolyzed products, $Al(OH)_3$, and aluminates are the dominant species in sequence. In the presence of fluoride, fluoride may substitute for OH^- to react with Al^{3+} and contribute to the formation of aluminum–fluoride

Fig. 6. Effects of fluoride at $R_{F:Al}$ values ranging from 1:10 to 30:10 on $\Delta\text{Residual Al}$ values after $AlCl_3$ coagulation in wide pH ranges from 6 to 10 [$\Delta\text{Residual Al} = \text{Residual Al } (R_{F:Al} > 0) - \text{Residual Al } (R_{F:Al} = 0)$; experimental conditions: $AlCl_3$ dose = 0.5 mg/L as Al, Initial turbidity = 100 NTU].

complexes (i.e., Al–F complexes, Al–OH–F complexes), and these species are mainly dominant in acidic conditions [9]. With increasing pH, fluoride showed a buffering effect to inhibit the interactions between aluminum and OH^- , and the aluminum–fluoride complexes were less reluctant to transform to Al–OH precipitates than Al^{3+} at pH below 9, as indicated by the slow titration experiments in our previous study [9]. This buffering effect was more significant at elevated $R_{F:Al}$ values, and resulted in the higher critical pH values to achieve the disappearance of Al–F complexes thereafter. In strongly basic conditions, the effect of AlF complexation was subtle owing to the strong competition of OH^- with fluoride [9], and the ratios of complexed fluoride and aluminum were all near to zero at different $R_{F:Al}$ values.

3.2.4. Effects of fluoride on residual aluminum

The species distribution of fluoride and aluminum at different pH and $R_{F:Al}$ values showed influences on the residual Al levels after coagulation. To quantify the effects of fluoride on residual Al, the parameter $\Delta\text{Residual Al}$ was proposed to indicate different residual Al levels between those at different $R_{F:Al}$ values of above 0 and that in the absence of fluoride ($R_{F:Al} = 0$). The values of $\Delta\text{Residual Al}$ may be calculated by Eq. (1).

$$\Delta\text{Residual Al} = \text{Residual Al } (R_{F:Al} > 0) - \text{Residual Al } (R_{F:Al} = 0) \quad (1)$$

Positive $\Delta\text{Residual Al}$ values indicated that fluoride increased the residual Al levels, whereas the negative values corresponded to lowered residual Al levels after introducing fluoride. Fig. 6 illustrates the $\Delta\text{Residual Al}$ values with $R_{F:Al}$ increasing from 0:10 to 30:10 over a wide pH range from 6 to 10. $\Delta\text{Residual Al}$ showed positive values at the weakly acidic and neutral pH of 6 and 7; at higher pH, however, negative $\Delta\text{Residual Al}$ values were observed in most cases. Additionally, $\Delta\text{Residual Al}$ showed higher absolute values at higher $R_{F:Al}$ values, indicating the more significant effects on residual Al at high fluoride levels. On the other hand, for doses of aluminum increasing from 0.5 to 10 mg/L, positive $\Delta\text{Residual Al}$ values were observed (Fig. S6). However, at the elevated aluminum dose of 20 mg/L, $\Delta\text{Residual Al}$ showed the negative value of -0.66 mg/L , and this indicated that fluoride lowered the residual Al levels at high aluminum doses.

The interactions between Al^{3+} , OH^- , and F^- were dependent on the pH, Al doses, and $R_{F:Al}$ values; and in neutral and acidic pH conditions, the main reactions involved may be expressed as Eqs. (2)–(6) [9,13–15]:

Fig. 7. Dominant species distribution and transformation of Al and fluoride at different pH and $R_{F:Al}$ values and the proposed mechanisms of fluoride on the coagulation behaviors of Al towards kaolin suspension.

In the low pH range, the formation of soluble aluminum–fluoride complexes inhibited the hydrolysis of Al^{3+} and the formation of $Al(OH)_3$ precipitates thereafter, and this effect increased residual Al levels. In overdosed Al and the absence of fluoride, the remarkable consumption of OH^- by Al^{3+} hydrolysis significantly decreased pH, and the further hydrolysis of Al^{3+} was inhibited and the residual Al levels increased accordingly. With fluoride present, however, fluoride substitutes for OH^- to react with Al^{3+} and avoids the significant decrease of pH, and this effect contributes to the negative Δ Residual Al values. At strongly basic pH, the buffering effect of fluoride inhibited the transformation of $Al(OH)_3$ precipitates to soluble aluminates due to the formation of Al-F and Al-OH-F complexes, and negative Δ Residual Al values were observed.

3.3. Proposed mechanisms involved in the effect of fluoride on coagulation

In mixed solutions of $AlCl_3$ and NaF where fluoride and aluminum were simultaneously present, the formation of aluminum–fluoride complexes does occur, and the ratios of which were dependent on pH and $R_{F:Al}$ values. According to Fig. 5, complexed aluminum and complexed fluoride were the dominant species in cases where $R_{F:Al}$ was 1. Besides these two complexed species, free fluoride also existed at $R_{F:Al}$ above 1 whereas free aluminum was present at $R_{F:Al}$ below 1.

After being dosed, the species transformation of aluminum and fluoride was dependent on the aluminum dose and the pH of the to-be-treated water. In strongly basic pH above 8, aluminum–fluoride complexes disappear and dissolve to free fluoride and aluminates. In this case, the effect of fluoride on the

coagulation performance of aluminum towards the kaolin suspension was slight (Fig. 1). In neutral and weakly acidic pH, however, the aluminum–fluoride complexes still existed. This effect reduced the aluminum quantity available and decreased the zeta potential to inhibit coagulation, especially at low aluminum doses and high $R_{F:Al}$ values. In overdosed aluminum ranges, however, this formation of aluminum–fluoride complexes benefited the removal of turbidity (Fig. 2), owing to the lower extent of pH decrease and the avoidance of particle re-stabilization. Fig. 7 illustrates the species distribution and transformation of aluminum and fluoride under different conditions and proposes the mechanisms for the effects of fluoride on the coagulation behaviors of aluminum towards kaolin suspension. It is noted that species transformation of aluminum salts at different pH is rather complicated even in the absence of fluoride, and the polymerization of aluminum salts occurs and is highly dependent on pH [16,17]. The presence of fluoride may further complicate the polymerization, hydrolysis, and dissolution of different Al species.

4. Conclusions

The interaction between Al and fluoride complicates their species distribution and transformation, and is highly dependent on pH and ratios of fluoride to Al. In mixed solutions of Al and F^- , the formation of aluminum–fluoride complexes occurs. After being dosed, the aluminum–fluoride complexes dissolve in strongly basic pH conditions, and fluoride shows relatively little effect on the coagulation behaviors of Al salts. At pH below 8, however, the aluminum–fluoride complexes exist and affect the removal of kaolin suspension by Al salts. The effects of fluoride on coagulation are related to $R_{F:Al}$ values, and are slight at low $R_{F:Al}$ values of below 2:10. At elevated $R_{F:Al}$ values of above 10:10, a significant adverse effect on residual turbidity is observed, and this is mainly ascribed to the decreased zeta potential, smaller flocs, and elevated levels of residual Al. Interestingly, fluoride inhibits particle re-stabilization in overdosed Al ranges and exhibits a positive effect to inhibit the increase of residual turbidity accordingly. Moreover, in considering

the equilibrium adsorption capacity of 23 mg F/g $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ as Al (i.e., $R_{\text{F:Al}} = 0.23: 10$), the spent *in-situ* $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ after adsorbing fluoride may be reclaimed as a coagulant for colloids removal after it is dissolved by acid solution.

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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.2012.12.047>.

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