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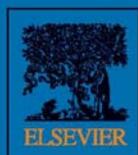
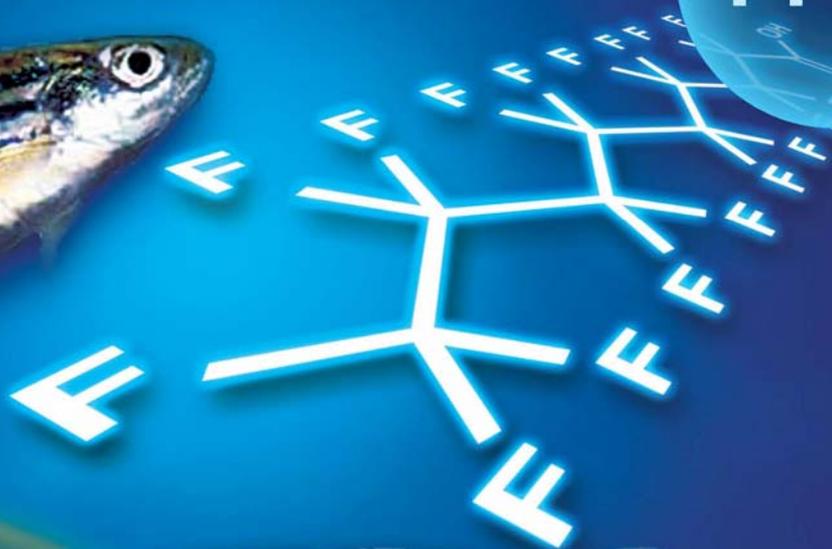
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Effects of fluoride on the removal of cadmium and phosphate by aluminum coagulation

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ABSTRACT

This study focuses on the effects of pH and fluoride at different molar ratios of fluoride to Al ($R_{F:Al}$) on the removal of cadmium (Cd^{2+}) and phosphate by Al coagulation. Fluoride at $R_{F:Al} \geq 3:1$ inhibits the removal of Cd over wide Al dose ranges from 5 to 10 mg/L as Al. The removal of phosphate decreases significantly at high $R_{F:Al}$ of 10:1 whereas at lowered $R_{F:Al}$ (i.e., $\leq 6:1$), an adverse effect is observed only at insufficient Al doses below 2 mg/L. Fluoride shows inhibitive effects towards the removal of Cd at pH 7 and 8 and that of phosphate at pH 6. Fluoride decreases the ζ -potential in both systems, and the decreasing extent is positively correlated to the elevated $R_{F:Al}$. The Al fluoride interactions include the formation of Al-F complexes and the adsorption of fluoride onto $Al(OH)_3$ precipitates, i.e., the formation of $Al(OH)_nF_m$. Al-F complex formation inhibits Al hydrolysis and increases residual Al levels, and a more significant increase was observed at lower pH. Al-F complexes at high $R_{F:Al}$ complicate the coagulation behavior of Al towards both negative and positive ionic species. Moreover, fluoride at low $R_{F:Al}$ shows little effect on Al coagulation behavior towards Cd^{2+} and phosphate, and the spent defluoridation adsorbent, i.e., aluminum (Al) hydro(oxide) with adsorbed fluoride at $R_{F:Al}$ of below 0.1:1, may be reclaimed as a coagulant after being dissolved.

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Introduction

Some industries, e.g., semiconductor production, tantalum and niobium refinery, and rare earth refinery, produce complicated wastewaters with fluoride concentrations from several to several tens of thousand mg/L, and soluble species such as heavy metals, phosphate, and arsenic are sometimes simultaneously present (Wen and Du, 2001; Zhu et al., 2005; Zhang et al., 2006). The simultaneous removal of these pollutants has practical value from an engineering point-of-view. Coagulation and/or electro-coagulation are feasible ways to remove the positively-charged heavy metals and

negative anions such as phosphate, arsenic, and fluoride (Aguilar et al., 2002; Meng et al., 2000; Merzouk et al., 2009; Akbal and Camci, 2010; Gong et al., 2012). Coagulation by aluminum (Al) salts shows promise to achieve their simultaneous removal due to the good affinity of Al hydro (oxide) towards them. By comparison, iron salts exhibit little efficacy for the removal of fluoride, although they show strong affinity towards arsenic and phosphate.

Although the removal of fluoride by Al-based (electro)-coagulation has been studied (Gong et al., 2012; Zhao et al., 2009; Bhatnagar et al., 2011), studies investigating the effects of fluoride on the removal of abovementioned ions are rare.

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Aluminum-fluoride interactions dominate in the species distribution, transport and toxicity of aluminum. In acidic deposition areas, the formation of aluminum fluoride complexes (Al-F complexes) was reported to be extremely important in the transport of elemental aluminum and its toxicity towards fish in surface waters (Driscoll et al., 1980; Radic and Bralic, 1995). The rate of aluminum fluoride complexation is observed to be highly dependent on pH (Neal, 1995), and the formation of hydrolyzed Al(III) species (i.e., $\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$) at pH above 4.5 significantly increases the complexation rate (Plankey et al., 1988). As indicated by potentiometric study and thermodynamic modeling, the Al-F complexes' speciation is rather complicated and their species distribution is highly dependent on pH, fluoride concentrations, and ionic strength (Corbillon et al., 2008). The ratios of complexed fluoride to total fluoride were observed to be strongly dependent on solution pH and the molar ratios of F to Al ($R_{\text{F:Al}}$) (Gong et al., 2012). The effects of aluminum-fluoride interactions on the coagulation behaviors of Al salts should be carefully evaluated. Al-F complex formation affects the hydrolysis of Al^{3+} and the formation of $\text{Al}(\text{OH})_3$ precipitates, and presumably inhibits the removal of negatively-charged anions such as arsenate and phosphate. Our previous study indicated the adverse effect of fluoride on aluminum coagulation in kaolin suspensions, and the formation of Al-F complexes at high fluoride levels dominated in its inhibitive effect (Liu et al., 2013). Besides Al-F complex formation, the adsorption of fluoride onto Al hydro (oxide) also plays a role. Pommerenk and Schafran (2005) indicated that the attachment of fluoride on hydrous aluminum oxide decreased its surface charge and adversely affected the removal of natural organic matter (NOM) accordingly (Pommerenk and Schafran, 2005). Furthermore, aluminum oxide tends to dissolve in the acidic pH range. The dissolution may be enhanced after it is dosed into fluoride-containing water, and the removal of other species might be inhibited thereafter. However, the effect of fluoride on the removal of coexisting ions by Al coagulation is far from being well characterized to the best of our knowledge.

On the other hand, the wide occurrence of fluorosis has received great concern globally (Fawell et al., 2006). Although various techniques have been proposed for defluoridation (Bhatnagar et al., 2011; Fawell et al., 2006; Mohapatra et al., 2009), their implementation has been restricted by high cost, labor-intensive maintenance, and/or low ratios of water production (Mohapatra et al., 2009). The control of cost is of crucial importance (Fawell et al., 2006; Mohapatra et al., 2009), and the reclamation of spent adsorbents is economically valuable. This may be feasible considering the low equilibrium adsorption capacity (Q_{eq}) towards fluoride for most adsorbents (Bhatnagar et al., 2011; Liu et al., 2011). The spent aluminum hydroxide, with adsorbed fluoride, may be reused as a coagulant to remove particulate colloids after being dissolved by acid solution (Liu et al., 2013). However, the feasibility of its reclamation for the removal of soluble ions such as cadmium (Cd^{2+}) and phosphate should be properly evaluated.

On the basis of these considerations, this study aims to: (1) investigate the effects of fluoride at different $R_{\text{F:Al}}$ ratios on the removal of positive Cd^{2+} and negative phosphate by Al coagulation over a wide pH range; (2) determine the effects of

fluoride on the variation of residual Al levels and ζ -potential involved in Al coagulation; and (3) propose the dominant species interactions between aluminum and fluoride over wide pH and $R_{\text{F:Al}}$ ranges. Besides bench-scale experiments, the MINTEQ software was used to illustrate the interactions between Al^{3+} , Cd^{2+} , F^- , and phosphate over a wide pH range.

1. Materials and methods

1.1. Reagents and materials

Unless otherwise noted, all chemicals were of analytical-reagent grade and were used without further purification. Stock solutions of Al^{3+} , F^- , Cd^{2+} , and phosphate were prepared by dissolving aluminum chloride (AlCl_3), sodium fluoride (NaF), cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$), and potassium phosphate (KH_2PO_4) into deionized water, respectively. The NaF solution was kept in a polyethylene vessel.

Prior to being dosed, the stock solution of Al^{3+} and F^- at different $R_{\text{F:Al}}$ was well mixed. This procedure was adopted considering that upon acidification of the spent $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ with adsorbed fluoride for its reclamation, a mixed solution of Al^{3+} and F^- was obtained. Additionally, other contaminants may coexist in underground waters and can be adsorbed onto the spent $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$; however, their interfering effects can be assumed to be slight and were ignored in this study. The equilibrium pH values and the ratios of complexed fluoride (the analysis methods are described in Section 1.3) in the mixed solutions at different $R_{\text{F:Al}}$ ratios are illustrated in Fig. S1.

Raw water was respectively prepared by dosing stock solutions of Cd^{2+} or phosphate in tap water to desired concentrations of 3 mg/L as Cd and 2 mg/L as P. The characteristics of the tap water are illustrated in Table S1. In pH-effect experiments, solution pH was adjusted to the desired values with hydrochloric acid (HCl) and sodium hydroxide (NaOH). The species distribution of Cd and phosphate over wide pH ranges from 4 to 10, as calculated by the Visual MINTEQ software (see Section 1.4), is illustrated in Fig. S2. Cd^{2+} is the dominant species in the pH range from 4 to 9, and the ratios of Cd^{2+} to total Cd decrease from 100% at pH 4 to 92.4% at pH 9. H_2PO_4^- and HPO_4^{2-} are the main species at pH from 4 to 9, and at pH above 7.2 the ratio of HPO_4^{2-} is over 50.6%.

1.2. Experimental methods

Jar tests were performed using a Phipps and Bird six-paddle stirrer. Soon after a 10-s rapid mixing period (250 r/min), the mixed solution of AlCl_3 and NaF was added. After that, the coagulation procedures consisted of a 2-min rapid mix (200 r/min), 15-min slow mix (40 rpm), and a 30-min settling period. Samples for zeta potential (ζ -potential) analysis were sampled soon after the 10-s rapid mixing period, whereas pH adjustment was carried out in the 2-min rapid mixing period when necessary. After 30-min settling, supernatants were collected and then filtered through 0.45- μm membrane filters for further analysis.

1.3. Analysis methods

ζ -Potential was determined with a Zetasizer 2000 zeta potential analyzer (Malvern Co., Malvern Town, U.K.) and solution pH was analyzed with a Orion 720A pH meter (ThermoFisher Co., Waltham, Massachusetts, USA). The concentrations of Al, Cd, and phosphate as P were determined using an OPTIMA 2000DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (PerkinElmer Co., Waltham, Massachusetts, USA). The quantity of insoluble Al precipitates as Al was determined by subtracting the residual Al concentrations from the initial Al doses.

The concentrations of fluoride (free fluoride and total fluoride) were determined by the ion selective electrode method (PF-1, Shanghai KangYi Technology). The concentrations of complexed fluoride were determined by subtracting the concentration of free fluoride from that of total fluoride, according to the methods proposed in our previous study (Gong et al., 2012). Briefly, the abovementioned method was used except that a citrate buffer solution was added prior to the analysis of total fluoride concentrations.

1.4. Modeling methods

The visual MINTEQ software (Version 3.0, beta) was used to illustrate the species distribution of Cd and phosphate over wide pH ranges as well as the interactions between Cd, Al, fluoride, and phosphate. The concentrations of these elements were set according to the actual concentrations used in this study, and pH ranged from 4 to 10. In the Al–F system, the species Al^{3+} , F^- , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_3(\text{aq})$, $\text{Al}(\text{OH})_4^-$, AlF^{2+} , AlF_2^+ , $\text{AlF}_3(\text{aq})$, AlOH^{2+} , $\text{HF}(\text{aq})$, HF_2^- , AlF_4^- , and $\text{Al}_2(\text{OH})_4^{2+}$ were included, and 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 Al. In the Cd–F system, the Cd species $\text{Cd}(\text{OH})_2(\text{aq})$, $\text{Cd}(\text{OH})_3^-$, $\text{Cd}(\text{OH})_4^{2-}$, Cd^{2+} , $\text{Cd}_2\text{OH}^{3+}$, CdF^+ , and CdOH^+ were included, and CdF^+ was related to the Cd–F complexes. In the Al–phosphate system, the Al species $\text{Al}(\text{OH})_3^+$, $\text{Al}(\text{OH})_3(\text{aq})$, $\text{Al}(\text{OH})_4^-$, Al^{3+} , $\text{Al}_2(\text{OH})_4^{2+}$, $\text{Al}_2\text{PO}_4^{3+}$, $\text{Al}_3(\text{OH})_5^+$, AlHPO_4^+ , and AlOH^{2+} were included. The concentrations of Cd, phosphate, Al, and F in modeling were equal to those used in bench-scale experiments.

2. Results and discussion

2.1. Effects of fluoride on the removal of Cd and phosphate at different Al doses

Fig. 1 illustrates the effects of fluoride at $R_{\text{F:Al}}$ values from 0:1 to 10:1 on the removal of Cd and phosphate by Al coagulation with elevated Al doses. In the absence of fluoride ($R_{\text{F:Al}} = 0:1$), Al coagulation showed only slight efficiency in removing Cd, and residual Cd was as high as 1.54 mg/L even at the high Al dose of 50 mg/L as Al. Al coagulation showed low removal efficiency towards positive Cd^{2+} , and limited removal of other cationic ions as nickel and chrome by flocculation has also been reported before (Santinelli et al., 2012). Comparatively, Al coagulation showed significantly higher removal efficiency of phosphate, and residual phosphate was as low as 0.31 and 0.05 mg/L as P at AlCl_3 doses of 3 and 5 mg/L as Al, respectively. The remarkable removal of phosphate by Al coagulation has been reported before (Aguilar et al., 2002; Santinelli et al., 2012; Georgantas and Grigoropoulou, 2007), and the dominant interactions between alum and phosphates included the adsorption of phosphate onto $\text{Al}(\text{OH})_3$, the incorporation of phosphate onto stabilized colloids via sweep flocculation, and the formation of insoluble Al–P precipitates (Aguilar et al., 2002).

The introduction of fluoride showed critically different effects on Al coagulation regarding the removal of Cd and phosphate. Fluoride at low $R_{\text{F:Al}}$ of 1:5 and 1:1 showed a beneficial effect on the removal of Cd, whereas at elevated $R_{\text{F:Al}}$, higher levels of residual Cd were observed. As for the removal of phosphate, fluoride at the $R_{\text{F:Al}}$ value of 10:1 contributed to a significant increase in residual phosphate over a wide Al dose range, from 0.5 to 10 mg/L. At $R_{\text{F:Al}}$ values below 10:1, little effect of fluoride on residual phosphate was observed at sufficient Al doses, above 3 mg/L. However, in insufficient Al dose ranges of 0.5 and 1 mg/L as Al, fluoride at $R_{\text{F:Al}}$ of above 1:1 inhibited the removal of phosphate and the levels of residual phosphate increased to a large extent.

In the absence of fluoride, the ζ -potential of Al flocs in the Cd-removing system was consistently above 0 mV with Al

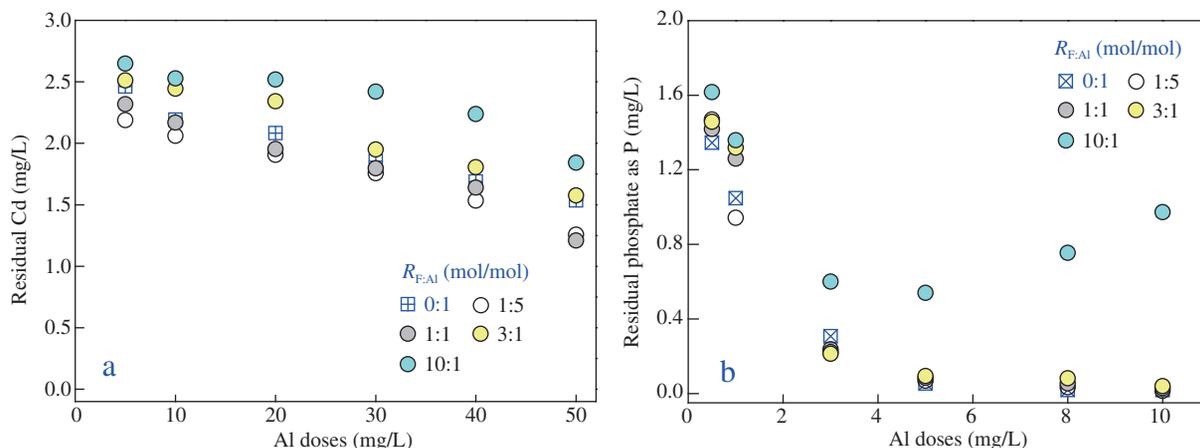


Fig. 1 – Effects of fluoride at $R_{\text{F:Al}}$ values on the removal of (a) Cd and (b) phosphate by Al coagulation with elevated Al doses. Conditions: pH = 7.06, $[\text{Cd}]_0 = 3 \text{ mg/L}$, $[\text{phosphate}]_0 = 2 \text{ mg/L}$ as P.

doses increasing from 5 to 50 mg/L. The introduction of fluoride lowered the ζ -potential of Al flocs, and a more significant decrease was observed either at higher fluoride levels or at lower Al doses (Fig. 2). The reversal of ζ -potential to below 0 mV occurred at high $R_{F:Al}$ of 3:1 at the relatively low Al dose of 5 mg/L as Al. ζ -Potential reversal was not observed at the elevated Al dose of 40 mg/L. Generally, the absolute values of the ζ -potential approached 0 mV after introducing fluoride. In the phosphate-removing system, much lower ζ -potential was observed even in the absence of fluoride (i.e., $R_{F:Al} = 0:1$), owing to the attachment and incorporation of negative phosphate ions within $Al(OH)_3$ flocs. Fluoride at high $R_{F:Al}$ of above 3:1 further decreased the ζ -potential (Fig. 2). Comparatively, more significant decrease in ζ -potential was observed in the Cd-removing system than in the phosphate-removing system (Fig. S3).

The adsorption of fluoride onto hydrous aluminum oxides via ligand exchange, as indicated by Eq. (1), cannot contribute to ζ -potential reversal, although it did decrease the ζ -potential to some extent (Pommerenk and Schafran, 2005). In this study, fluoride significantly lowered the ζ -potential and the reversal of the ζ -potential to negative values was observed. It was assumed that besides adsorbing onto the surfaces of $Al(OH)_3$ precipitates, fluoride also participated in the hydrolysis of Al salts and in the formation of Al precipitates. Al-F complex formation was involved in the removal of fluoride by Al coagulation, and the formed flocs differed greatly from the $Al(OH)_3$ flocs with adsorbed fluoride (Gong et al., 2012). The formed Al precipitates in these two systems were assumed to be significantly different from the $Al(OH)_3$ precipitates.



The removal of fluoride in these two systems was compared in terms of the adsorption density of fluoride (Q_F , i.e., mg of removed fluoride per mg insoluble Al precipitates as Al). Q_F values increased with elevated $R_{F:Al}$ in both systems (Fig. S4), and the maximum Q_F values were 4.7 and 3.0 mgF/mgAl in Cd- and P-removing system, respectively. Phosphate inhibited the

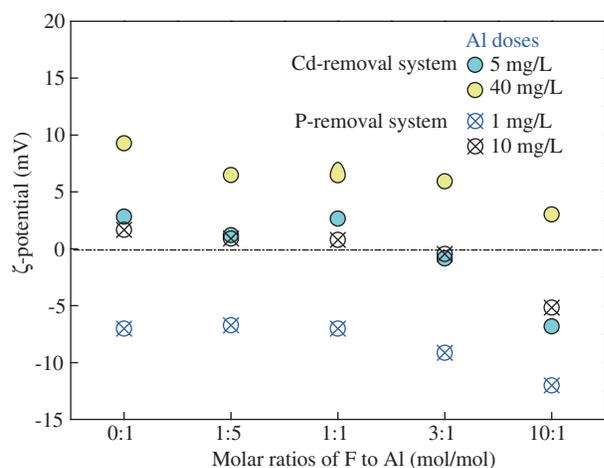


Fig. 2 – Effects of fluoride at different $R_{F:Al}$ values on ζ -potential in the removal of (a) Cd and (b) phosphate by Al coagulation. Conditions: pH = 7.06, $[Cd]_0 = 3$ mg/L, $[phosphate]_0 = 2$ mg/L as P.

attachment of fluoride onto Al precipitates and the removal of total fluoride thereafter.

Fluoride also contributed to elevated levels of residual Al in both systems; the ratios of residual Al to total Al, as indicated by Al_{Res}/Al_{Tot} , were observed to increase markedly with elevated $R_{F:Al}$ values (Fig. 3). Without fluoride present, residual Al concentrations were consistently below 0.1 mg/L over a wide Al dose range. Elevated $R_{F:Al}$ favored the formation of soluble Al-F complexes and inhibited the hydrolysis and precipitation of Al salts thereafter. Al-F complex formation was dependent on pH, and the ratios of complexed fluoride were above 99% at acidic pH < 5, whereas at pH 7.0, Al-F complexes tended to dissociate into free fluoride, and complexed fluoride was below the detection limit ($R_{F:Al} = 0.53:1$) (Gong et al., 2012). The elevation of $R_{F:Al}$ to above 2.13:1 enabled the formation of Al-F complexes at pH 7.0, whereas at pH 8.0 their formation rarely occurred even at high $R_{F:Al}$ of 2.85:1 (Gong et al., 2012). In this study, extremely high $R_{F:Al}$ benefited Al-F complex formation and reduced the particulate Al available for the removal of Cd and phosphate. Comparatively, the negative phosphate ion inhibited Al fluoride interactions, and the effect of fluoride on residual Al was less significant than that in the Cd-removing system.

2.2. Effects of fluoride on the removal of Cd and phosphate at different pH

2.2.1. Effects of fluoride on the removal of Cd at different pH

Fig. 4 indicates the effects of fluoride at different $R_{F:Al}$ on Cd removal, ζ -potential, and Δ residual Al in pH 6 to 8. Δ Residual Al was calculated by the subtraction of the residual Al concentration from that obtained in the absence of fluoride. In the absence of fluoride, i.e., $R_{F:Al} = 0:1$, Cd removal increased with elevated pH, and the ζ -potential approached 0 mV accordingly. At pH 6 the removal of Cd was slight, and fluoride showed little effect; nevertheless a decreased ζ -potential was observed. At elevated pH 7 and 8, fluoride showed little effect at $R_{F:Al} < 1:1$, and further elevated $R_{F:Al}$ adversely inhibited Cd removal. At pH 8 a negative ζ -potential was observed due to the introduction of fluoride. However, this effect did not favor the removal of positively-charged Cd. The removal of Cd by Al coagulation was independent of ζ -potential. It is inferred that the ligand exchange between surface hydroxyl groups and fluoride consumes available sites and inhibits Cd removal thereafter. Δ Residual Al increased with elevated $R_{F:Al}$ at pH 6, owing to the more significant formation of Al-F complexes (Eq. (2)). At elevated pH, the complexed fluoride (complexed-F) was insignificant, and residual Al was only slightly affected by fluoride even at high $R_{F:Al}$ of 6:1.



2.2.2. Effects of fluoride on the removal of phosphate at different pH

Fig. 5 illustrates the effects of fluoride on the removal of phosphate, ζ -potential, and Δ residual Al in pH 6 to 8. Fluoride at $R_{F:Al} = 1:5$ showed little effect on phosphate removal over a wide pH range. At elevated $R_{F:Al}$ of above 1:1, phosphate removal was greatly inhibited at pH 6, and residual phosphate significantly increased from 0.14 to 1.78 mg/L at $R_{F:Al} = 6:1$. At pH 7 and 8, fluoride showed little effect on phosphate removal.

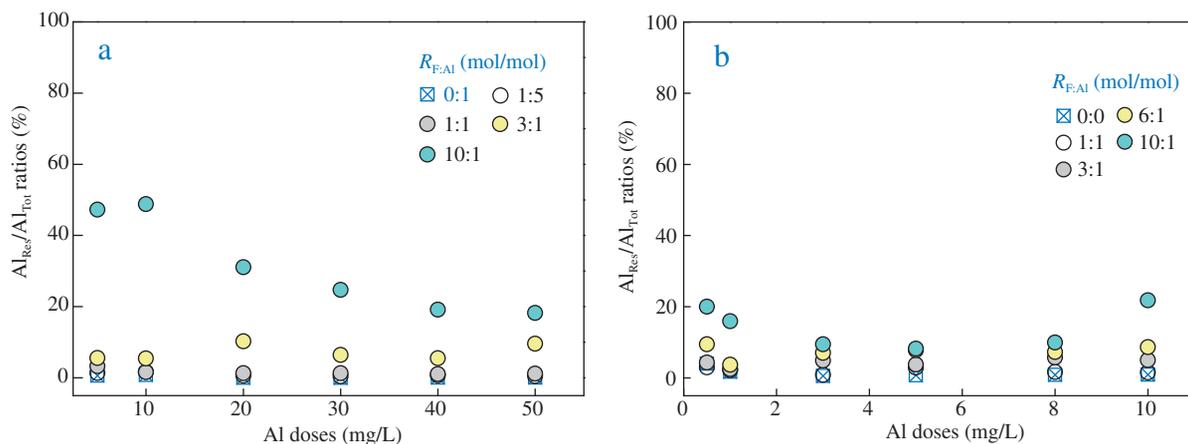


Fig. 3 – Effects of fluoride at different $R_{F:Al}$ values on residual Al in the removal of (a) Cd and (b) phosphate by Al coagulation. Conditions: pH = 7.06, $[Cd]_0 = 3$ mg/L, $[phosphate]_0 = 2$ mg/L as P.

Fluoride lowered the ζ -potential of Al precipitates at pH 6–8, and a more significant decrease was observed at elevated $R_{F:Al}$. However, ζ -potential was below 0 mV even in the absence of fluoride, and the fact that fluoride lowers ζ -potential played a limited role to inhibit phosphate removal. Additionally, it was observed that fluoride showed little effect on Al hydrolysis, and Δ residual Al showed little variation in pH 6–8 even at high $R_{F:Al}$ of 6:1. Comparatively, in the Cd-removing system Δ residual Al increased remarkably with elevated $R_{F:Al}$ at pH 6 (Fig. 4c). This was first attributed to the much higher Al dose, i.e., 30 mg/L as Al, than that in the Cd-removing system (3 mg/L as Al). Additionally, in the phosphate-removing system, phosphate at 2 mg/L as P inhibited Al hydrolysis, and the adverse effect of fluoride towards Al hydrolysis was lowered accordingly. The stable Δ residual Al at different $R_{F:Al}$ inferred the determining role of Al-F complex formation in the inhibition of phosphate removal at pH 6. At elevated pH 7 and 8, the formation of Al-F complexes was slight and little effect was observed thereafter.

2.3. Al-F complex formation at different pH

Fig. 6 illustrates the ratios of complexed-F to total fluoride in the treated water after removing particulate fluoride by 0.45- μ m membrane filtration. The ratios of complexed-F decreased with elevated $R_{F:Al}$ values, owing to less Al being available for Al-F complex formation. Additionally, the ratios of

complexed-F decreased with increasing pH, and free fluoride was the dominant species at pH above 6 in both systems for the removal of Cd and phosphate. The dissociation of complexed-F to free fluoride was ascribed to the strong competition of OH⁻ towards Al as high pH levels (Gong et al., 2012). Furthermore, phosphate inhibited Al-F complex formation, and the observed ratios of complexed-F were lower than those in the Cd-removing system. MINTEQA2 modeling indicated that the formation of Al-PO₄ species (i.e., Al₂PO₄³⁺, AlHPO₄²⁺) did occur; however, the ratio was as low as below 4.5% (Fig. S5). The consumption of Al salts by phosphate was negligible. The lower complexed-F ratios in the P-removing system were attributed to the inhibition of the Al fluoride interaction by phosphate.

2.4. Proposed dominant Al fluoride interactions at different pH and $R_{F:Al}$

The effects of fluoride on the removal of Cd and phosphate by Al coagulation were dependent on the species distribution of Al and fluoride, $R_{F:Al}$, and the interactions among these species. The species distribution of Al and F and the main reactions over wide equilibrium pH and $R_{F:Al}$ ranges are illustrated in Fig. 7.

Before being dosed, the species distribution of Al and F in the mixed solution was mainly dependent on $R_{F:Al}$, and free fluoride existed at $R_{F:Al} > 1$ whereas free Al was present at

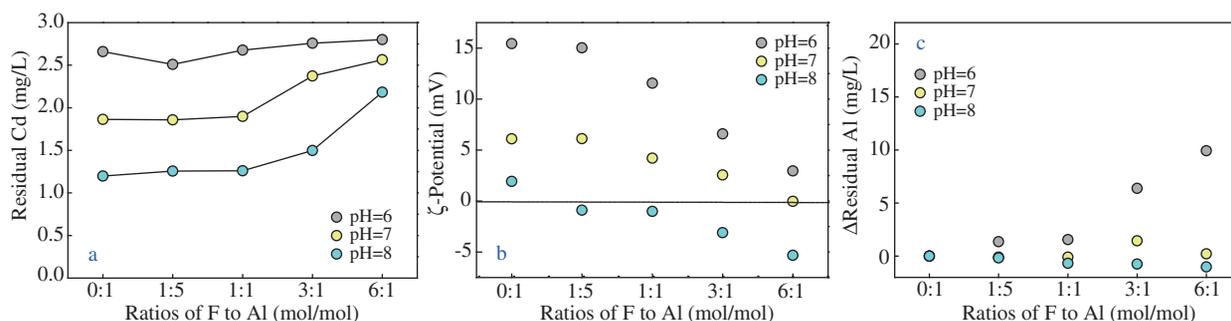


Fig. 4 – Effects of fluoride at different $R_{F:Al}$ on Cd removal, ζ -potential, and Δ residual Al over a wide pH range from 4 to 8 in Cd-removing system at Al dose of 30 mg/L as Al.

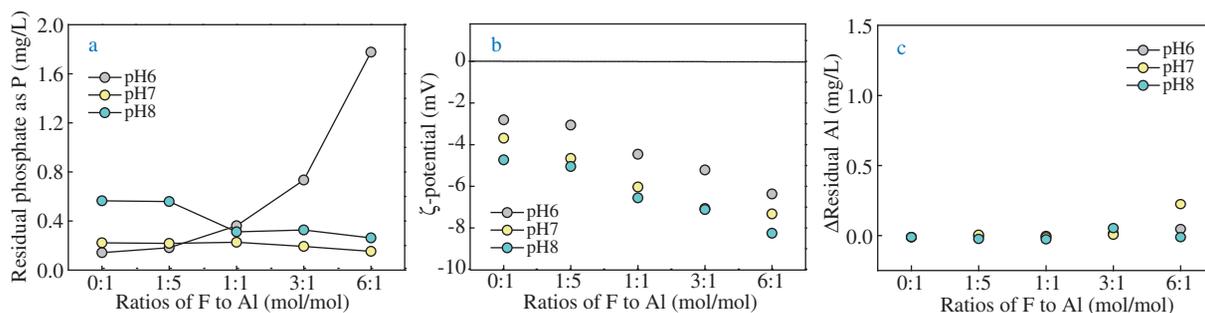
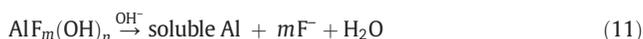
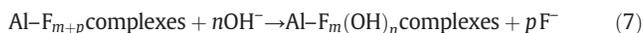


Fig. 5 – Effects of fluoride at different $R_{F:Al}$ on phosphate removal, ζ -potential, and Δ residual Al over a wide pH range from 4 to 8 in phosphate-removing system at Al dose of 3 mg/L as Al.

$R_{F:Al} < 1$ (Fig. 7a). pH also played a role, and the dissolution of Al-F complexes to free F^- occurred at high $R_{F:Al}$ owing to the elevated pH (Fig. S1).

After being dosed, the equilibrium pH impacted the main reactions involved and the species distribution of Al and F thereafter (Fig. 7b). In the case with free Al present ($R_{F:Al} < 1$), the hydrolysis and polymerization of Al^{3+} occurred at pH above 4 (Georgantas and Grigoropoulou, 2007) (Eqs. (3)–(4)), and the ratios of each Al polymer with different extent of polymerization (Al_3 – Al_{21}) were highly dependent on pH (Zhao et al., 2009). Al^{3+} and the hydrolyzed Al(III) species tend to form Al-F complexes at acidic pH (Eqs. (2) and (5)), which can be rapidly achieved within several seconds (Plankey et al., 1988). At $pH > 5$, Al-F complexes dissociated into free fluoride (Eq. (6)), owing to the competition of OH^- towards Al (Gong et al., 2012). Additionally, Al-F complexes may directly react with OH^- and form insoluble $AlF_m(OH)_n$ precipitates (Eq. (7)), and free F^- and Al-F complexes can also adsorb onto $Al(OH)_3$ precipitates (Eqs. (8)–(9)). These two effects contributed to the transformation of free fluoride to insoluble fluoride, and the removal of total fluoride thereafter (Fig. S6). At elevated pH, the dissolution of insoluble $Al(OH)_3$, $AlF_m(OH)_n$, and $Al(OH)_nF_m$ into soluble Al species occurred (Eqs. (10)–(12)), and the levels of free fluoride and soluble Al increased accordingly. The species distribution of fluoride and Al in different pH and $R_{F:Al}$ ranges is illustrated in Fig. 7c. It was noted that the formation of CdF^+ complexes

and $Al-PO_4$ species did occur; however, these reactions were ignored due to their low ratios (Figs. S5 and S7).



The Al-fluoride interactions and their species distribution contributed to the observed varying trends of ζ -potential and

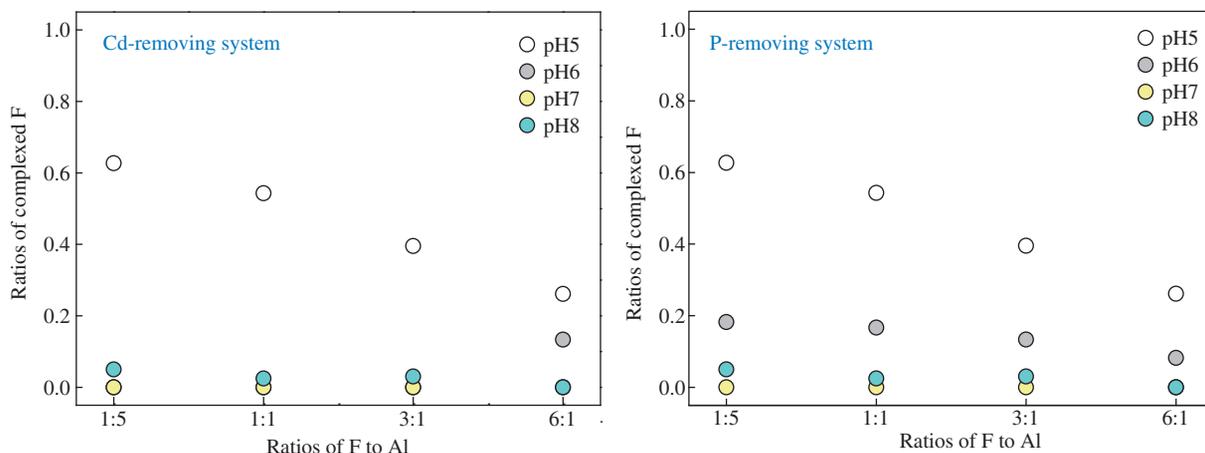


Fig. 6 – Ratios of complexed-F to total fluoride over a wide pH range from 4 to 8 in (a) Cd-removing system and (b) phosphate-removing system at Al dose = 3 mg/L as Al.

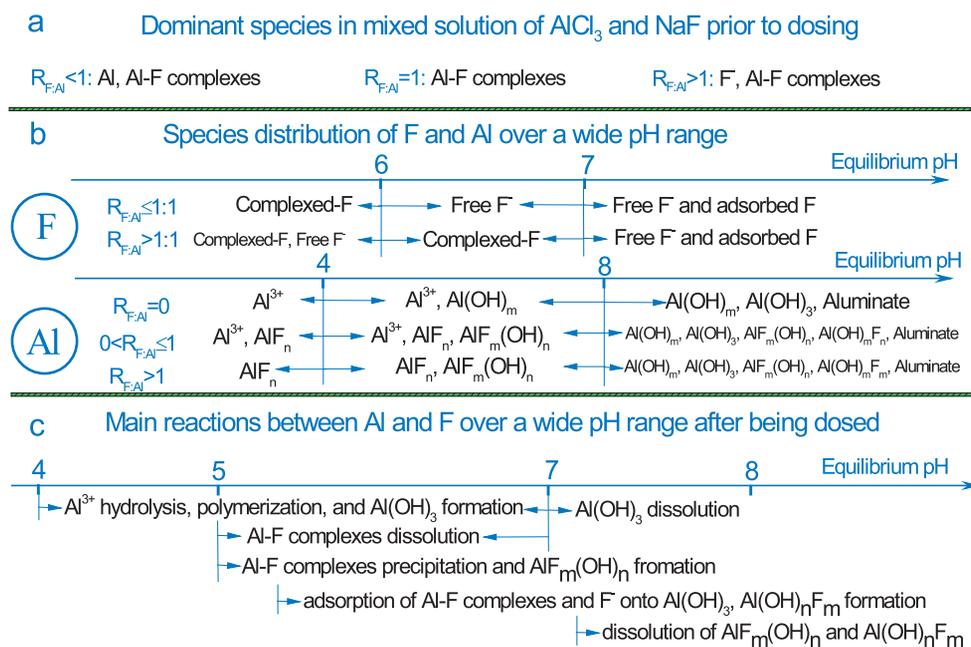


Fig. 7 – Proposed main species distribution and transformation of Al and F over wide equilibrium pH and $R_{\text{F:Al}}$ ranges. a: Dominant species of Al and F in the mixed solution of AlCl_3 and NaF prior to dosing; b: species distribution of F and Al; c: main reactions between Al and F over a wide pH range after being dosed.

residual Al, and the effect of fluoride on the removal of Cd and phosphate by Al coagulation was highly dependent on pH and $R_{\text{F:Al}}$ (Table S2). Briefly, the removal of neither Cd nor phosphate was affected by fluoride at $R_{\text{F:Al}}$ of below 1:1 in a wide pH range; however, fluoride at $R_{\text{F:Al}} > 3:1$ showed significant adverse effects on their removal. Additionally, the inhibitive effect of fluoride was pH dependent, and its remarkable inhibition of Cd removal was observed in neutral and basic pH of 7 and 8, whereas that on phosphate removal was prominent in weakly acidic pH of 5 and 6.

The Cd ion rarely participates in Al hydrolysis, and its removal may be mainly achieved by the formation of outer-sphere complexes between Cd and the hydroxyl groups on the surfaces of $\text{Al}(\text{OH})_3$, $\text{AlF}_m(\text{OH})_n$, and $\text{Al}(\text{OH})_n\text{F}_m$. The oxygen on adsorbent surfaces was reported to be a strong Lewis base and tended to form complexes with Cd(II) ions as electron acceptors (Cooper et al., 2002). As for phosphate, the formation of insoluble Al- PO_4 precipitates such as Al_2PO_4^+ and AlHPO_4^- may play a role; however, this effect is relatively low. The removal of phosphate may be mainly attributed to its incorporation into stabilized colloids via sweep flocculation and to its attachment onto the surfaces of $\text{Al}(\text{OH})_3$, $\text{AlF}_m(\text{OH})_n$, and $\text{Al}(\text{OH})_n\text{F}_m$. Besides this, other mechanisms such as electrostatic attraction, ionic exchange, and surface micro-precipitation may also be involved in their removal, and further studies are required to elucidate the mechanisms.

3. Conclusions

Fluoride adversely affects the removal of both Cd and phosphate by Al coagulation, and the extent of this effect is highly dependent on pH and $R_{\text{F:Al}}$. Fluoride shows an inhibitive effect on the removal of Cd at $R_{\text{F:Al}} \geq 3:1$, whereas at low $R_{\text{F:Al}}$ a slight

beneficial effect is interestingly observed. The removal of phosphate decreases at either high levels of fluoride ($R_{\text{F:Al}} = 10:1$) or insufficient Al doses of below 2 mg/L as Al. Fluoride inhibits rather than improves Cd removal over a wide pH range, although it does lower ζ -potential. Fluoride inhibits the removal of phosphate at the acidic pH 6, and the formation of Al-F complexes plays an important role. At pH 7 to 8, fluoride shows little effect on phosphate removal due to the dissociation of Al-F complexes into free F⁻. Moreover, phosphate inhibits Al-F complex formation and the removal of total fluoride. This study promotes the understanding of the removal of heavy metals and phosphate by Al coagulation in the simultaneous presence of fluoride. Besides this, this study also indicates the feasibility of using the spent *in-situ* $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ with adsorbed fluoride, after its being dissolved by acid solution, for the removal of Cd and phosphate. As for the spent *in-situ* $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ with adsorbed fluoride obtained from real treatment plants, the $R_{\text{F:Al}}$ is critically low at below 0.1:1, and the adverse effect of fluoride is slight.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2014.10.024>.

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