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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  $\text{Al}^{3+}$  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 hydroxide (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 ( $Q_{\text{eq}}$ ) 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 ( $\text{Cd}^{2+}$ ) 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  $\text{Cd}^{2+}$  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  $\zeta$ -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 MINTEQA2 software was used to illustrate the interactions between  $\text{Al}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{F}^-$ , and phosphate over a wide pH range.

## 1. Materials and methods

### 1.1. Reagents and materials

Unless otherwise noted, all chemicals were of analytical-grade and were used without further purification. Stock solutions of  $\text{Al}^{3+}$ ,  $\text{F}^-$ ,  $\text{Cd}^{2+}$ , and phosphate were prepared by dissolving aluminum chloride ( $\text{AlCl}_3$ ), sodium fluoride (NaF), cadmium nitrate ( $\text{Cd}(\text{NO}_3)_2$ ), and potassium phosphate ( $\text{KH}_2\text{PO}_4$ ) into deionized water, respectively. The NaF solution was kept in a polyethylene vessel.

Prior to being dosed, the stock solution of  $\text{Al}^{3+}$  and  $\text{F}^-$  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  $\text{Al}^{3+}$  and  $\text{F}^-$  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  $\text{Cd}^{2+}$  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 MINTEQA2 software (see Section 1.4), is illustrated in Fig. S2.  $\text{Cd}^{2+}$  is the dominant species in the pH range from 4 to 9, and the ratios of  $\text{Cd}^{2+}$  to total Cd decrease from 100% at pH 4 to 92.4% at pH 9.  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  are the main species at pH from 4 to 9, and at pH above 7.2 the ratio of  $\text{HPO}_4^{2-}$  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  $\text{AlCl}_3$  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 ( $\zeta$ -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- $\mu\text{m}$  membrane filters for further analysis.

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