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Fluoride removal by Al, Ti, and Fe hydroxides and coexisting ion effect

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ARTICLE INFO

Article history:

Received 2 November 2016

Revised 13 March 2017

Accepted 13 March 2017

Available online 28 March 2017

Keywords:

Fluoride removal

Co-precipitation

Aluminum sulfate

Anion effect

ABSTRACT

Batch experiments were conducted to evaluate fluoride removal by Al, Fe, and Ti-based coagulants and adsorbents, as well as the effects of coexisting ions and formation of aluminum–fluoride complexes on fluoride removal by co-precipitation with alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$). Aluminum sulfate was more efficient than the other coagulants for fluoride removal in the pH range between 6 and 8. Nano-crystalline TiO_2 was more effective for fluoride removal than Al and Fe hydroxides in a pH range of 3–5. Coexisting anions in water decreased the removal of fluoride in the order: phosphate (2.5 mg/L) > arsenate (0.1 mg/L) > bicarbonate (200 mg/L) > sulfate (100 mg/L) = nitrate (100 mg/L) > silicate (10 mg/L) at a pH of 6.0. The effect of silicate became more significant at pH > 7.0. Calcium and magnesium improved the removal of fluoride. Zeta-potential measurements determined that the adsorption of fluoride shifted the PZC of $\text{Al}(\text{OH})_3$ precipitates from 8.9 to 8.4, indicating the chemical adsorption of fluoride at the surface. The presence of fluoride in solution significantly increased the soluble aluminum concentration at pH < 6.5. A Visual MINTEQ modeling study indicated that the increased aluminum solubility was caused by the formation of AlF^{2+} , AlF_2^+ , and AlF_3 complexes. The AlF_x complexes decreased the removal of fluoride during co-precipitation with aluminum sulfate.

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Introduction

Naturally occurring fluoride in groundwater is typically below 0.5 mg/L. However, in many parts of the world, the fluoride concentration is elevated to 8.0 mg/L and even exceeds 20.0 mg/L. Weathering and erosion of geologic formations cause fluoride to be released from minerals and create unsafe drinking water conditions. Groundwater with elevated fluoride is, to a large degree, found in locations where volcanic igneous rocks are; such areas include India, China and the desert southwest of the United States, among others (Brindha and Elango, 2011).

Fluoride in drinking water has a narrow optimum concentration range in relation to human health. It can prevent dental caries in the range of 0.7–1.2 mg/L, but is responsible for dental and skeletal fluorosis if it is higher than 1.5 mg/L. The World Health Organization (WHO) Guidelines for Drinking Water Quality put forth a recommendation that fluoride be present in the range of 0.5–1.0 mg/L (WHO (World Health Organization), 2011). In the United States, the US Environmental Protection Agency (US EPA) has mandated a maximum contaminant level (MCL) of 4.0 mg/L, while states like California have adopted a strict 2.0 mg/L limit for fluoride in drinking water.

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Many methods can be used to remove fluoride from water, including adsorption by activated alumina (AA) (Ghorai and Pant, 2005; Sovinelli and Black, 1958), reverse osmosis (Cohen and Conrad, 1998), electrodialysis and electro-sorption (Amor et al., 2001; Lounici et al., 1997), adsorption by limestone (Reardon and Wang, 2000), goethite (Hiemstra and Van Riemsdijk, 2000) and kaolinite (Weerasooriya et al., 1998), acid-treated spent bleaching earth (Mahramanlioglu et al., 2002), red mud (Çengelöglu et al., 2002), polyaluminum chloride (Malhbtra et al., 1997), and various other low-cost materials, including bentonite, char fines, lignite and nirmali seeds (Srimurali et al., 1998) and some novel hybrid adsorbents (Bhatnagar et al., 2011). Although WHO and US EPA classify activated alumina adsorption as one of the best demonstrated available technologies (BDAT) for fluoride removal, it is relatively expensive and its adsorption capacity is affected by pH and the presence of coexisting ions in water such as silicate, sulfate, bicarbonate and phosphate (Tang et al., 2009; Tressaud, 2006).

Aluminum sulfate hydrolyzes and forms $\text{Al}(\text{OH})_3$ precipitates, which are highly effective at removing fluoride from groundwater. Common concerns when using alum as a treatment option are aluminum residuals in the effluent stream and a reduction in water pH, since alum is an acidic salt. The aims of this study were to compare the effectiveness of Al, Fe, and Ti-based coagulants for fluoride removal, to evaluate the effect of anions and cations on fluoride removal, and to determine the influence of aluminum fluoride complexation on the removal of fluoride and on the solubility of aluminum.

1. Materials and methods

Alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) was purchased from Eaglebrook Inc. located in Quebec, Canada. All other chemicals used in the experiments were analytical grade and purchased from Aldrich or Fisher Scientific and used as received.

Fluoride stock solution ($\text{F}^- = 1000 \text{ mg/L}$) was prepared by dissolving 2.21 g of sodium fluoride (NaF) (Fisher Scientific, Pittsburgh, PA, USA) in 1 L of deionized water and was prepared monthly. A 0.4 mol/L sodium chloride (NaCl) (Fisher) stock solution was made by dissolving 23.2 g of NaCl in 1 L of DI water for background ionic strength adjustment. Phosphate (as P), silicate (as Si), bicarbonate (as HCO_3^-), calcium, magnesium, sulfate (as SO_4^{2-}) and nitrate (as NO_3^-) stock solutions (1000 mg/L) were prepared by dissolving 4.39 g of KH_2PO_4 , 7.6 g of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, 1.4 g of NaHCO_3 , 2.8 g of CaCl_2 , 3.91 g of MgCl_2 , 1.48 g of Na_2SO_4 and 1.37 g of NaNO_3 (Fisher) in 1 L of DI water respectively. The bicarbonate stock solution was made weekly, while anionic stock solutions were made monthly. Fluoride concentration was measured using ion selective electrodes (Corning and Thermo Orion ISE) and a pH meter (Thermo Orion 925/525). A buffer solution was used for accurate analysis of soluble F according to Method 4500-F-C in Standard Methods for Examination of Water and Wastewater. The buffer solution contained CDTA (1,1,2, N'N'N'diamino-tetraacetic acid), which preferentially complexes aluminum and iron, allowing accurate determination of soluble fluoride (Farrah et al., 1987).

Fluoride solutions were prepared by diluting the fluoride stock solution to 8.0 mg/L of F^- with DI water; the ionic

strength of solution was controlled at 0.04 mmol/L using NaCl as a background electrolyte. After desired amounts of alum or other coagulants were added into the solutions, the suspensions formed were separated into 10,125-mL polypropylene bottles for each coagulant. The pH of the suspensions was adjusted to pH values ranging between about 2 and 12 using NaOH and HCl solutions. After 60 min of mixing, the final pH was measured and a portion of the suspensions were centrifuged at 10,000 r/min for 10 min to separate the liquid from the solids for the analysis of residual soluble fluoride and other target compounds.

Simulated groundwater was prepared by diluting MgCl_2 , CaCl_2 , NaHCO_3 , Na_2SiO_3 , NaH_2PO_4 , and Na_2SO_4 stock solutions in DI water to determine anion or cation effects on fluoride removal. The highest concentrations of the solutes found in groundwater were used in most of the tests to determine the maximum competitive effect. In some cases lower concentrations were used to determine factors that might be encountered in real world settings. All adsorption experiments were repeated to confirm the adsorption results. However, only a set of representative data were presented for each experiment in the figures and no experimental errors were calculated because the final or equilibrium pH values in the duplicate experiments were not the same.

Aluminum, silicon, and other metals were analyzed using an atomic absorption spectrometer (FAAS, Varian Zeeman 400 Spectra-AA) and an inductively coupled plasma optical emission spectrometer (ICP-OES, Varian Vista MPX). Phosphorus was determined using a HACH 2000 spectrophotometer following the ascorbic acid Method 4500-P-E in Standard Methods for Examination of Water and Wastewater. Zeta-potential measurements were completed using a Nano ZetaSizer ZEN3600 (Malvern Instrument, UK). Turbidity readings were completed using a HACH 2100P turbidity NTU meter.

2. Results and discussion

2.1. Fluoride removal

The batch experimental results in Fig. 1 show the fluoride removal efficiency by FeCl_3 , $\text{Al}_2(\text{SO}_4)_3$, TiSO_4 and nano-crystalline TiO_2 as a function of final solution pH. The pH had significant effects on the removal of fluoride. The optimum pH for fluoride removal was about 6.5 for aluminum sulfate and about 3.5 for Ti and Fe coagulants and adsorbents. Among the materials, aluminum sulfate performed most effectively under circumneutral pH conditions, which was consistent with the reported optimum pH values between 5.5–7.5 for various aluminum-based coagulants (Bhatnagar et al., 2011; Sovinelli and Black, 1958; Sujana et al., 1998). It should be noted that the nano-crystalline TiO_2 had much higher fluoride removal than the other precipitates in a pH range 3–5. Other batch experimental results indicate that the removal of fluoride reached equilibrium rapidly in about 5 min (data not reported).

2.2. Anion and cation effects on fluoride removal

Batch experimental results in Table 1 show that an Al dose of 10 mg/L was not sufficient to treat all samples collected from

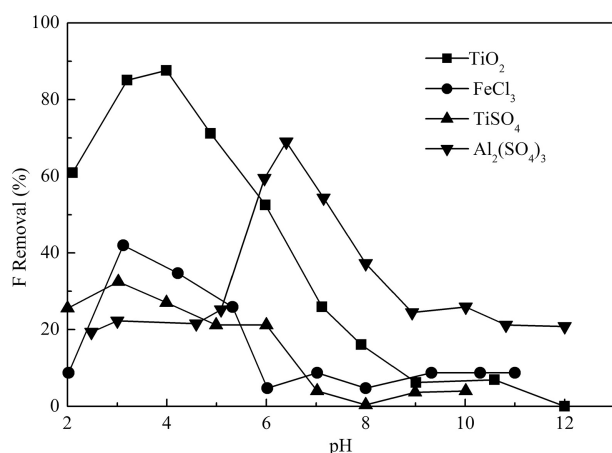


Fig. 1 – Optimum pH for removal of fluoride with aluminum sulfate, ferric chloride, titanium sulfate, and nano-crystalline titanium dioxide at 20 mg/L treatment dose, F = 8.0 mg/L in 0.04 mol/L NaCl solution.

different locations of the continental United States. It was difficult to remove F from some water although the F concentration was relatively low, which might be attributed to the effects of coexisting ions. Table 2 shows that the groundwater samples collected at the Fort Irwin sites had high sulfate, bicarbonate, and silicate concentrations.

The removal of fluoride from solutions in the presence of different concentrations of anions and cations was investigated. Fig. 2 shows the effects of phosphate (as P), silicate (as Si), bicarbonate (as HCO₃), and arsenate (As(V)). Sulfate (SO₄) and nitrate (NO₃) had relatively weak effects (8% and 6% at pH 6.5, respectively, data not shown in the figure). At pH 6.0, the effects of the anions varied in the order: PO₄ > As(V) > HCO₃ > SO₄ = NO₃ > silicate (Si). When the pH was 7.0, the negative effect of silicate increased significantly and the order changed to: PO₄ > silicate (Si) > As(V) > HCO₃ > SO₄ = NO₃.

The significance of phosphate and arsenate on the removal of fluoride was attributed to strong adsorption of the compounds by Al(OH)₃ through inner sphere surface complexation. The anions competed with fluoride for the hydroxyl groups on Al(OH)₃ and reduced available sites for fluoride adsorption. On the other hand, the adsorption affinity of Al(OH)₃ for bicarbonate, sulfate and nitrate was low. Therefore, those anions did not have strong effect on the fluoride adsorption. Silicate adsorption by metal hydroxide was low at pH < 6 and increased when pH increased from 6 to

Table 1 – Removal of fluoride from different groundwater samples.

Sample index and site	F (mg/L)	Al dose (mg/L)	F Removal (%)
L-1 (Fort Irwin, CA)	7.9	10.0	34
L-3 (Fort Irwin, CA)	3.8	10.0	31
L-5 (Fort Irwin, CA)	8	10.0	40
KFR (Yuma, AZ)	5.8	10.0	54
5# (Hawthorne, NV)	6.5	10.0	44

Table 2 – Chemical characteristics of Fort Irwin water.

Chemicals/index	Constituents and parameters	
	L-1 well site	L-3 well site
As (μg/L)	13.5	11.6
Al (μg/L)	18.0	10.3
Silicate (Si) (mg/L)	10.8	11.9
F (mg/L)	7.9	3.8
Ca (mg/L)	11	11
Mg (mg/L)	4.1	4
Fe (μg/L)	383	533
W (μg/L)	114	25
Bicarbonate (mg/L)	244	200
P (mg/L)	0.018	<0.010
Sulfate (mg/L)	83.3	99.2
pH	8.1	8.3
Conductivity (μS)	358	448
Turbidity (NTU)	0.49	0.43

9. Thus the effect of silicate on fluoride adsorption increased significantly with increasing pH.

Fig. 3 shows the combined effect of anions and cations on the removal of F⁻. When the solution contained 2.5 mg/L of P

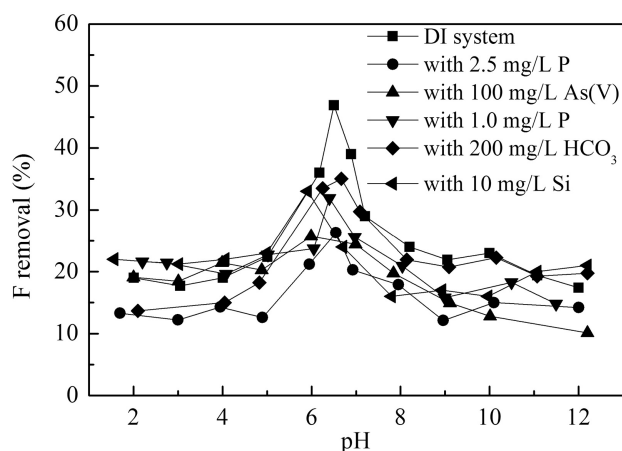


Fig. 2 – Anion effects on fluoride removal with alum, Al = 10 mg/L, F = 8 mg/L, 0.04 mol/L NaCl.

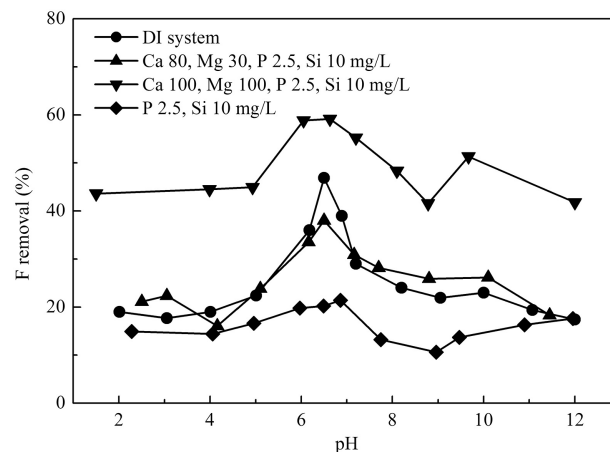


Fig. 3 – Combined effect of cations and anions on fluoride removal by alum, Al = 10 mg/L, F = 8 mg/L, 0.04 mol/L NaCl.

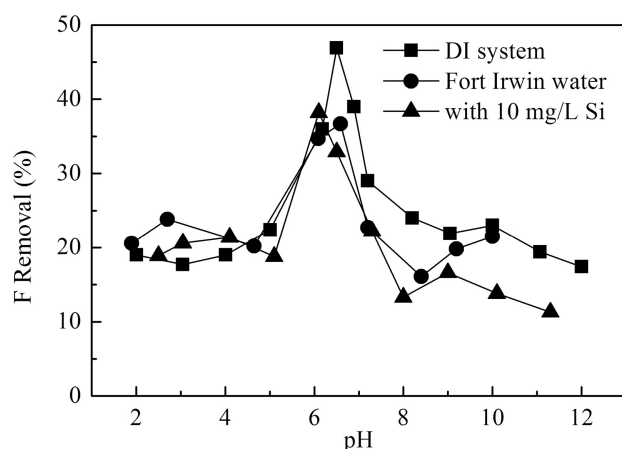


Fig. 4 – Comparison of F^- removal from F^- solution, F^- solution with 10 mg/L Si, and Fort Irwin water containing 10.8 mg/L Si. Al = 10 mg/L, F = 7.9 mg/L, and NaCl = 0.04 mol/L in all solutions.

and 10 mg/L of Si, a 25% reduction in fluoride removal was seen at pH 6.5 compared to the removal in the 2.5 mg/L P solution in Fig. 2. The addition of 200 mg/L of bicarbonate into the P and Si binary anion solution did not cause further decrease in F^- removal (data not presented). The addition of 80 mg/L Ca and 30 mg/L of Mg into the P-Si- HCO_3^- solution increased the F^- removal to a similar level as in the 0.04 mol/L NaCl solution. When the concentration of both Ca and Mg was 100 mg/L, the efficiency of F^- removal was obviously better than in the NaCl solution. High Ca and Mg concentrations improved the removal of fluoride.

The removal of F^- from solutions with and without the presence of silicate and from a Fort Irwin (L-1 well) groundwater sample by alum treatment is compared in Fig. 4. The presence of silicate in the solution decreased F^- removal at pH greater than 6.5, compared to the DI solution. Similar amounts of F^- were removed in the Fort Irwin groundwater and in the solution containing silicate. The results indicated that F^- removal from the groundwater was mainly affected by

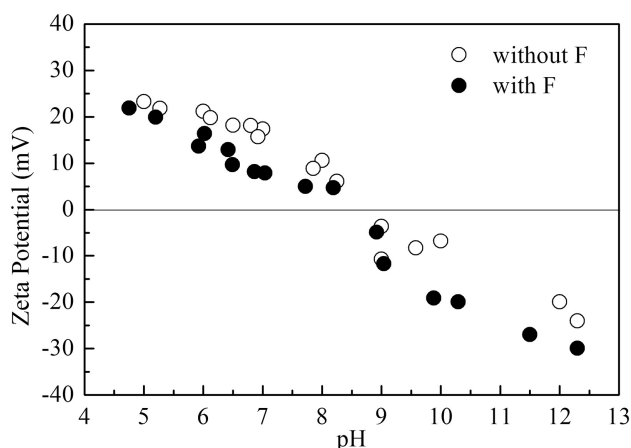


Fig. 5 – Zeta-potential of $Al(OH)_3$ in the absence of fluoride and in the presence of fluoride as a function of pH, Al = 10 mg/L, F = 8 mg/L.

Table 3 – Reactions and parameters used for calculations for development of model.

Reactions	Parameter	References
I. Surface and solution parameters		
Surface site ($=SOH$) density	1.11 sites/ nm^2	(Dzombak and Morel, 1990)
Surface area	597 m^2/g	(Dzombak and Morel, 1990)
Ionic strength	0.04 mol/L	NA
Adsorbent concentration	0.01 g/L	NA
Site concentration	0.011 mmol/L	(Dzombak and Morel, 1990)
II. Surface complexation reactions		
	LogK	
1. $=SOH + H^+ + F^- \rightleftharpoons SF + H_2O$	9.05	This work
2. $=SOH + H^+ \rightleftharpoons =SOH_2^+$	6.37	(Rakotonarivo et al., 1988)
3. $=SOH \rightleftharpoons =SO^- + H^+$	-10.03	(Rakotonarivo et al., 1988)
4. $=SOH_2Cl \rightleftharpoons =SO^- + Cl^-$	3.40	(Rakotonarivo et al., 1988)
5. $=SONa^+ \rightleftharpoons =SO^- + H^+$	-6.45	(Rakotonarivo et al., 1988)
6. $=SOHNa^+ \rightleftharpoons =SOH + Na^+$	0.094	(Rakotonarivo et al., 1988)
7. $=SOHCl^- \rightleftharpoons =SOH + Cl^-$	-0.088	(Rakotonarivo et al., 1988)
III. Aqueous reactions		
$Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+$	-4.997	(David and Allison, 1999)
$Al^{3+} + 2H_2O \rightleftharpoons AlOH_2^+ + 2H^+$	-10.294	(David and Allison, 1999)
$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3(aq) + 3H^+$	-16.9	(David and Allison, 1999)
$Al^{3+} + 4H_2O \rightleftharpoons Al(OH)_4^- + 4H^+$	-22.1	(Wesolowski, 1992)
$2Al^{3+} + 2H_2O \rightleftharpoons Al_2OH_2^{4+} + 2H^+$	-7.694	(David and Allison, 1999)
$3Al^{3+} + 4H_2O \rightleftharpoons Al_3(OH)_4^{5+} + 4H^+$	-13.888	(David and Allison, 1999)
$Al^{3+} + Cl^- \rightleftharpoons AlCl^{2+}$	-0.39	(David and Allison, 1999)
$Al^{3+} + F^- \rightleftharpoons AlF^{2+}$	7.01	(David and Allison, 1999)
$Al^{3+} + 2F^- \rightleftharpoons AlF_2^+$	12.63	(David and Allison, 1999)
$Al^{3+} + 3F^- \rightleftharpoons AlF_3(aq)$	16.7	(David and Allison, 1999)
$Al^{3+} + SO_4^{2-} \rightleftharpoons AlSO_4^+$	3.84	(David and Allison, 1999)
$Al^{3+} + 2SO_4^{2-} \rightleftharpoons Al(SO_4)_2^-$	5.58	(David and Allison, 1999)
$H^+ + F^- \rightleftharpoons HF(aq)$	3.18	(David and Allison, 1999)
$H^+ + 2F^- \rightleftharpoons HF_2^-$	3.78	(David and Allison, 1999)
$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$	1.99	(David and Allison, 1999)
$Na^+ + Cl^- \rightleftharpoons NaCl(aq)$	-0.3	(David and Allison, 1999)
$Na^+ + F^- \rightleftharpoons NaF(aq)$	0.02	(David and Allison, 1999)
$Na^+ + H_2O \rightleftharpoons NaOH(aq) + H^+$	-13.897	(David and Allison, 1999)

(continued on next page)

Table 3 (continued)

Reactions	Parameter	References
$\text{Na}^+ + \text{SO}_4^{2-} = \text{NaSO}_4$	0.74	(David and Allison, 1999)
$\text{H}_2\text{O} = \text{OH}^- + \text{H}^+$	-13.997	(David and Allison, 1999)
IV. Precipitation reactions		
$\text{Al}^{3+} + 3\text{H}_2\text{O} = \text{Al(OH)}_3(\text{am}) + 3\text{H}^+$	9.7	(Bi et al., 2001)
$\text{Al}^{3+} + 2\text{F}^- + \text{H}_2\text{O} = \text{AlOHF}_2^0 + \text{H}^+$	0.407	(David and Allison, 1999)

silicate. The groundwater contained very low P (<0.02 mg/L), low Ca (11 mg/L), and Mg (4 mg/L), and these should not have much effect on F^- removal. The bicarbonate concentration (200–240 mg/L) in the groundwater did not reduce the F^- removal efficiency, which was consistent with experimental results in P–Si– HCO_3 solutions.

2.3. Effect of fluoride adsorption on zeta-potential of Al(OH)_3

Zeta-potential results in Fig. 5 show that the point of zero charge of Al(OH)_3 precipitates was 8.9. When fluoride was adsorbed on the precipitates, the PZC value shifted to 8.4. The results suggest that fluoride is adsorbed on the Al(OH)_3 through the formation of inner sphere surface complex $=\text{SOH} + \text{H}^+ + \text{F}^- \leftrightarrow =\text{SF} + \text{H}_2\text{O}$ (Stumm and Morgan, 1981). It is possible that formation of $=\text{S-F}$ surface complex reduced the positively charged surface sites $=\text{S-OH}_2^+$ and decreased the surface potential. If F^- was adsorbed on Al(OH)_3 precipitate surface through the formation of outer sphere species $=\text{S-OH}_2^+\text{F}^-$, the adsorbed F^- would be located in the diffuse layer. The formation of the outer sphere species does not affect the surface charge and the PZC.

2.4. Modeling study of interactions between Al and F

The effect of soluble AlF_x complexes on the removal of F^- and on the solubility of Al was investigated using the Visual MINTEQ3.0 chemical equilibrium model. The Diffuse Layer Model (DLM) was used to simulate the adsorption of fluoride on Al(OH)_3 (David and Allison, 1999). The model parameters, surface and solution reactions, and constants are listed in Table 3 (Bi et al., 2001; David and Allison, 1999; Dzombak and Morel, 1990; Rakotonarivo et al., 1988; Wesolowski, 1992). The adsorption of fluoride on Al(OH)_3 is described by Eq. (1) in Table 3. The best-fit adsorption constant was determined by fitting the model-calculated adsorption curve to the experimental data in Fig. 6a. The model curve fit the fluoride removal peak relatively well. The calculated distribution of fluoride forms is presented in Fig. 6b. When pH was in the range of 2–6, more than 90% of F formed soluble complexes AlF_x with Al. As pH increased from 6 to 9, the free F^- ions increased from less than 10% to greater than 90%. The adsorbed F^- species were formed in the pH range between 6 and 9.5, with a maximum peak at pH 7.

The F^- removal curve in Fig. 7c was calculated without considering the AlF_x complexes in the model to evaluate the effect of the AlF_x on F^- adsorption. The model predicted that

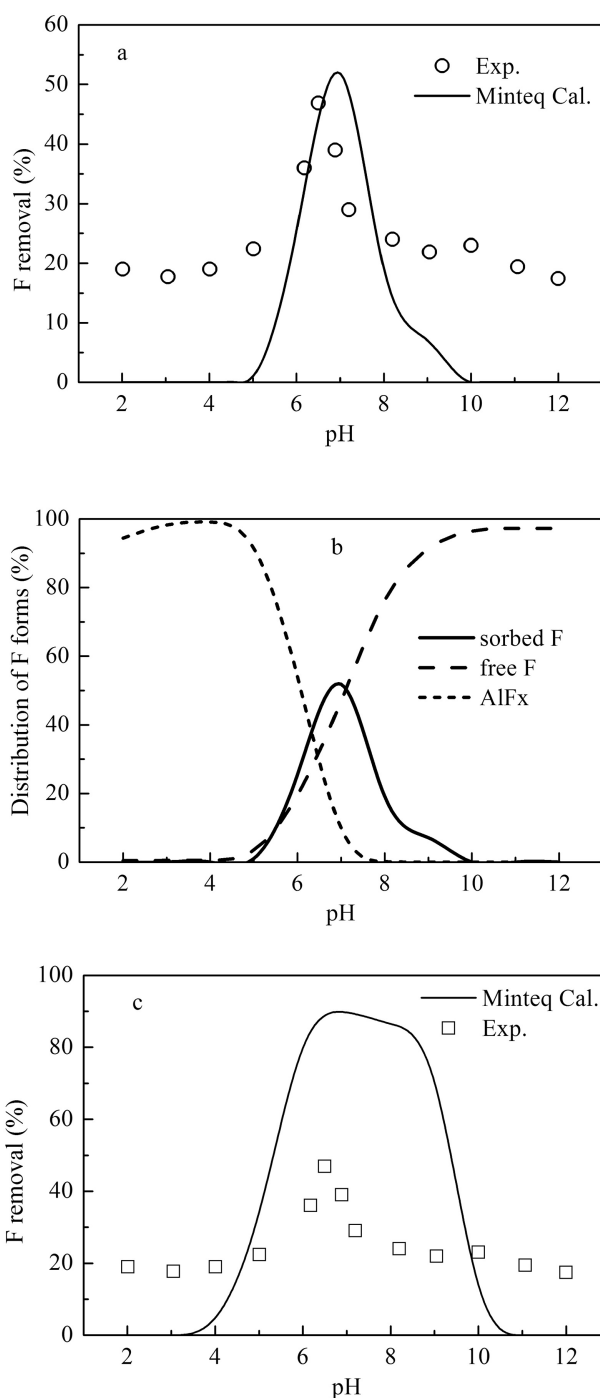


Fig. 6 – (a) MINTEQ model simulation of fluoride removal, (b) model calculations for fluoride species distribution, (c) model simulation of fluoride removal without considering the formation of AlF_x complexes in the calculations, $\text{Al} = 10 \text{ mg/L}$, $\text{F} = 8 \text{ mg/L}$, 0.04 mol/L NaCl .

approximately 90% of F^- would be removed if there was no formation of AlF_x complexes. The modeling results indicate that the AlF_x complexes cannot be adsorbed by AA and that they significantly decrease the removal of F^- .

The model-calculated total soluble aluminum concentration using the parameters in Table 3 is compared with the analyzed data in Fig. 7. The total soluble aluminum includes

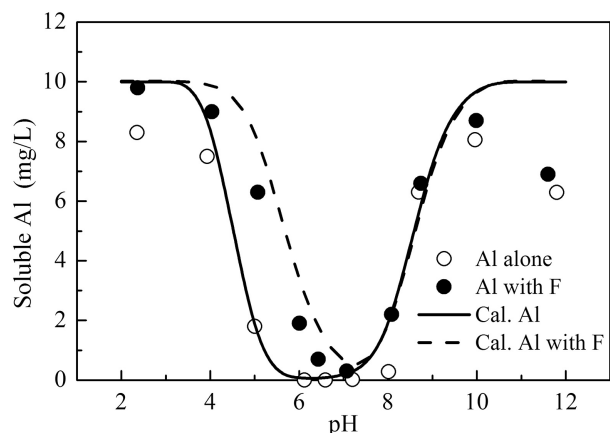


Fig. 7 – Comparison of model-calculated soluble Al concentration with the experimental data in solution with and without F, Al = 10 mg/L, F = 8 mg/L, 0.04 mol/L NaCl solution.

Al^{3+} cations and its complexes listed in the aqueous reactions in Table 3. The experimental data show that aluminum has a minimum solubility in the pH range of 6–8 in the solution without the presence of F^- . The addition of F^- significantly increased aluminum solubility at $\text{pH} < 6.5$, and did not have an obvious effect on Al solubility at $\text{pH} > 8.3$. The model-calculated curves fit well with the analytical data, which suggests that the increased Al solubility was caused by the formation of AlF^{2+} , AlF_2^+ , and AlF_3 complexes.

3. Conclusions

Aluminum-based coagulant is more effective for removal of fluoride than ferric and titanium coagulants and adsorbents at circumneutral pH, while iron and titanium-based coagulants are more effective at $\text{pH} < 5$. Silicate significantly decreases fluoride removal by aluminum coagulants at $\text{pH} > 7$. The formation of AlF^{2+} , AlF_2^+ , and AlF_3 complexes significantly increases the soluble aluminum concentration and decreases the removal of fluoride during co-precipitation with aluminum sulfate at $\text{pH} < 6.5$.

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