Effect of aluminum fluoride complexation on fluoride removal by coagulation

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ABSTRACT

Effect of aluminum fluoride complexation on fluoride removal by Al salts coagulation was investigated by a series of batch experiments. Transformation of fluoride species in coagulation was studied by simultaneous determination of free fluoride and total fluoride at different pH and fluoride concentrations. Results showed that aluminum fluoride complexes dominated at low pH and high fluoride concentrations but more complexes did not represent higher fluoride removal. Comparison between coagulation with complexation and adsorption by $\text{Al}(\text{OH})_3$ flocs was conducted and coagulation showed higher fluoride removal efficiency than adsorption in the pH range of 6.0–9.0. Titration test showed that Al-F complexes were coprecipitated with less OH^- than Al^{3+} . Characterization of FTIR and XPS also indicated that flocs after complexation was different from $\text{Al}(\text{OH})_3$ flocs with or without fluoride. It was concluded that a new Al-F-OH coprecipitate formed in coagulation and fluoride was effectively removed by the coprecipitation.

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1. Introduction

Fluoride removal receives much attention due to the dental and skeletal fluorosis caused by the excessive intake of fluoride [1]. Among the technologies of fluoride removal coagulation is a simple and effective method in the treatment of drinking water and industrial wastewater [1–3]. In coagulation $\text{Al}(\text{OH})_3$ flocs forms during the hydrolyzation of Al salt and fluoride is removed by attachment to the flocs. In this process aluminum fluoride complexation (Al-F complexation), ion exchange, electronic attraction and physical adsorption are involved [4]. But there is not a clear conclusion about the main mechanism.

Generally, high dose of Al salts are required to achieve promising fluoride removal and the decrease of pH is inevitable. And fluoride removal is strongly dependent on pH, so pH adjustment is often applied in practice [2]. The variation of pH influences the transformation of both Al and fluoride species [5–7]. In previous studies about fluoride removal only total fluoride was determined and variation of free fluoride was ignored. So, fluoride speciation and role of Al-F complexation in fluoride removal was analyzed just by theoretical calculation rather than experiments. Though change of Al and fluoride species can be calculated [8], fluoride removal was also not considered in these chemical calculations. In fact fluoride could

be removed in the range of 5.0–9.0 with the addition of Al salt. For example, when $\text{pH} > 8.0$, almost 100% of fluoride was free fluoride [8] but part of fluoride was removed by $\text{Al}(\text{OH})_3$ flocs. Taking into consideration the fluoride removal, the calculated concentration of fluoride at $\text{pH} > 8.0$ was higher than the actual value. On the other hand, in the researches about Al-F complexation only free fluoride was determined and focused but change of total fluoride was not considered [5,6]. Consequently, it is meaningful and important to simultaneously investigate the complexation and fluoride removal in coagulation by experiments.

In coagulation and electrocoagulation processes Al salts and base are co-added and adsorption is an important role in fluoride removal [4,9]. If Al reacts with fluoride before Al^{3+} hydrolysis, the formation of aluminum fluoride complexes (Al-F complexes) occurs firstly and fluoride is removed in the subsequent coprecipitation [10]. This process is different from conventional coagulation and mechanism of fluoride removal might also be different.

This study aims to understand the variation of fluoride species and mechanism of fluoride removal in coagulation. First, free fluoride and total fluoride are simultaneously determined to investigate the transformation of fluoride species in the removal of fluoride by coagulation. And coagulation with Al-F complexation and adsorption by $\text{Al}(\text{OH})_3$ flocs without complexation are compared. After that the role of complexation in fluoride removal is discussed with the further characterization of precipitates using FTIR and XPS.

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Table 1

The electric potential of standard samples of free fluoride at different pH and ionic strengths.

pH	Ionic strength	Electric potential (mv)				
		Standard 1	Standard 2	Standard 3	Standard 4	Standard 5
3.0	4 mM NaCl	−285	−258	−244	−226	−209
	12 mM NaCl	−285	−258	−244	−227	−209
4.0	4 mM NaCl	−271	−244	−231	−213	−196
	12 mM NaCl	−272	−245	−231	−215	−197
5.0	4 mM NaCl	−271	−244	−230	−213	−196
	12 mM NaCl	−271	−244	−231	−214	−196
6.0	4 mM NaCl	−269	−241	−228	−212	−195
	12 mM NaCl	−270	−243	−230	−214	−195
7.0	4 mM NaCl	−269	−241	−228	−212	−195
	12 mM NaCl	−270	−243	−230	−214	−195
8.0	4 mM NaCl	−268	−242	−229	−212	−195
	12 mM NaCl	−269	−243	−231	−214	−195
9.0	4 mM NaCl	−268	−242	−228	−211	−194
	12 mM NaCl	−268	−242	−228	−213	−195

2. Materials and methods

2.1. Determination of free fluoride and total fluoride

All the reagents in the experiments were analytical grade and deionized (DI) water was used to prepare solutions. The concentration of fluoride was determined by ion selective electrode method (PF-1, Shanghai KangYi Technology). Total fluoride concentration was measured after mixing with total ionic strength adjustment buffer (citrate buffer solution) according to the Methods of Examination of Water and Wastewater [11]. The concentration of free fluoride was also determined by ion selective electrode method [12,13]. Free fluoride was in situ measured but no buffer was added and no dilution was conducted. Standard samples of free fluoride at different pH and ionic strengths were prepared. The range of pH was 4.0–9.0 and pH was adjusted using 0.1/1 M HCl or NaOH (Orion Model 720, Thermo Electron Corp., USA). The ionic strength was evaluated by conductivity (Hach Sension 156, Hach, USA). The ionic strength of 4 mM NaCl was nearly the value after addition of Al salt (dose of Al was 40 mg/L) and the ionic strength of 12 mM NaCl was nearly the value after addition of Al salt at high fluoride concentration (Al was 40 mg/L and fluoride was 80 mg/L). Results of calibration of free fluoride were shown in Table 1. The electric potential of standard samples at pH of 4.0–9.0 showed good linear ships with the logarithmic value of fluoride concentrations (all the relative coefficients were above 0.99). Table 1 also showed that the values of standards at different ionic strengths were almost the same. The effect of ionic strength in the range of this experiment was slight. So, determination of free fluoride in coagulation was available in the pH range of 4.0–9.0 and at low ionic strength. Content of fluoride in complexes was the difference of total fluoride concentration and free fluoride concentration.

2.2. Batch test of coagulation and adsorption

The coagulation test was conducted at room temperature in Plexi glass beakers using a conventional Jar test apparatus (MY 3000-6, QianjiangMeiYu Instruments, China). A 1000 mg/L fluoride stock solution was prepared by dissolving 2.210 g NaF in 1000 mL DI water. Fluoride solution was prepared by diluting the stock solution to certain concentrations with DI water. Al stock solution was prepared using $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. In coagulation the dose of Al was 40 mg/L and the initial fluoride concentration varied in the range of 5–80 mg/L. A total 500 mL of DI water was transferred to a 1 L beaker. Then Al and fluoride stock solution was added and after 2 min of mixing at 100 rpm pH was adjusted to the desired value. In Jar test of coagulation 2 min rapid mixing at 250 rpm was applied,

followed by 20 min of slow stirring at 50 rpm. After settlement for 30 min the supernatants were filtered through a 0.45 μm membrane and analyzed. The Al concentration was measured by ICP-OES (OPTIMA 2000DV, PerkinElmer, USA). Blank test was prepared to avoid the effect of dilution after addition of Al or fluoride stock solution.

The adsorption by $\text{Al}(\text{OH})_3$ flocs was performed in the same procedure in the coagulation but the order of addition of Al and fluoride was different. The same dose of Al stock solution was added to 500 mL DI water and pH was adjusted to 7.0. The suspension of $\text{Al}(\text{OH})_3$ flocs was stirred for 10 min at 100 rpm. Then fluoride stock solution was added and stirring started as in the coagulation. During the adsorption, pH of solution was maintained at the designed value (4.0–9.0).

Kinetics of fluoride removal of coagulation and adsorption was also studied. In coagulation Al and fluoride were added into 1 L Plexi glass beakers while Al was 40 mg/L and fluoride were 5 and 15 mg/L, respectively. With stirring at 100 rpm pH was adjusted to 7.0 within 1 min and sample was collected at the desired time and analyzed. For adsorption Al was firstly added and pH was adjusted to 7.0. After fluoride was added samples were collected and analyzed. In adsorption pH was maintained at 7.0 in the whole process.

2.3. Titration of Al at different fluoride concentrations

Mixed liquor of Al and fluoride solution was prepared in 1 L Plexi glass beakers. Dose of Al was 40 mg/L with fluoride of 0, 5, and 20 mg/L, respectively. With stirring at 200 rpm 1 M NaOH was added to the mixed liquor using a 100 μL microsyringe. The titration was conducted at room temperature and N_2 was provided in the whole test. Volume of base and pH were recorded and plotted.

2.4. Characterization of FTIR and XPS

Characterization of precipitates in coagulation and adsorption were carried out using FTIR (Nicolet 5700, Thermo Electron Corp., USA) and XPS (Axis Ultra, Kratos Analytical Ltd., UK), respectively. Three samples were prepared: $\text{Al}(\text{OH})_3$ flocs without fluoride at pH 7.0, and flocs in adsorption and flocs in coagulation (dose of Al and fluoride was 40 and 15 mg/L, respectively). Suspension in coagulation and adsorption was filtered using 0.45 μm membrane and the powders were collected and dried at 60 °C. After characterization results were further analyzed using PeakFit Version 4.12.

Fig. 1. Fluoride species distribution at different pH with fluoride of (a) 5 mg/L and (b) 15 mg/L. Dose of Al = 40 mg/L.

3. Results and discussion

3.1. Fluoride species distribution and fluoride removal at different pH

The fluoride species distribution and fluoride removal were studied in the pH range of 4.0–9.0. As shown in Fig. 1, the concentration of fluoride with different species varied with different trends. The concentration of free fluoride increased with the increase of pH and was equal to the concentration of total fluoride at pH >7.0 but the content of fluoride in complex decreased in the whole pH range. The ratio of free fluoride to total fluoride increased from 0.2% to 98.7% as pH increased from 5.0 to 7.0 (Fig. 1b). At pH <5.0, fluoride was mostly in the form of Al–F complexes, there was little free fluoride. Due to competition of OH[−], complexes were dissociated and free fluoride increased at higher pH. The change of total fluoride in Fig. 1 reflected the removal of fluoride at different pH. The minimum concentration of fluoride was 0.5 and 3.6 mg/L at pH 7.0 with initial fluoride concentration of 5 and 15 mg/L, respectively. For total fluoride removal the optimal pH was 7.0, and fluoride removal decreased at lower or higher pH. Fig. 1 also indicated that the transformation of fluoride species and fluoride removal were

strongly dependent on pH. Weak acidic conditions were beneficial to the complexation between Al and fluoride. As pH increased to 7.0 complexes were completely dissociated to free fluoride and the best removal of total fluoride was obtained.

3.2. Formation of Al–F complexes and fluoride removal at different fluoride concentrations

Effect of fluoride concentration on Al–F complexation and fluoride removal in coagulation was studied at pH 6.0, 7.0 and 8.0. As shown in Fig. 2a, the ratio of fluoride in complexes to total fluoride increased from 19.6% to 83.4% as fluoride concentration increased from 20 mg/L to 80 mg/L at pH 6.0. At pH 7.0 the percent of fluoride in complexes was below 0.5% while the initial fluoride concentration was lower than 40 mg/L and finally increased to 39.2% at fluoride concentration was 80 mg/L. At pH 8.0, free fluoride was the dominant species and the percent of fluoride in complexes was below 0.1% with fluoride concentration of 5–80 mg/L. At weak acidic and neutral conditions higher fluoride concentration induced more Al–F complexes. Fig. 2b illustrated the effect of initial fluoride concentration on fluoride removal. The removal of fluoride firstly increased as fluoride concentration increased and decreased after initial fluoride concentrations were above 40, 60 and 60 mg/L at pH 6.0, 7.0 and 8.0, respectively. Low pH and high fluoride concentration were advantageous for Al–F complexation but disadvantageous for fluoride removal.

Results in Fig. 2c indicated that the dissolving of Al occurred at low pH and high fluoride concentration. The complexation increased the content of soluble Al and the Al–F complexes were the main species for soluble Al [5]. The dissolving Al and fluoride were in the form of soluble Al–F complexes but still remained in the aqueous solution. From this perspective, the complexation was disadvantageous to fluoride removal at low pH and high fluoride concentration.

3.3. Comparison of fluoride removal between coagulation and adsorption

Coagulation by Al salt and adsorption by Al(OH)₃ flocs are two processes with different mechanisms. In this study the removal of fluoride by coagulation and adsorption at different fluoride concentrations was compared and results were shown in Figs. 3 and 4.

As shown in Fig. 3 fluoride concentration in coagulation was lower than that in adsorption at pH of 6.0–9.0. The optimal pH for fluoride removal in coagulation and adsorption was about 7.0 and 6.0, respectively. Fig. 4 showed the kinetic removal of fluoride in coagulation and adsorption. The removal of fluoride by coagulation was completed within 2 min. Comparatively, fluoride removal by adsorption achieved equilibrium after 15 min with fluoride concentration of 5 mg/L. While fluoride was 15 mg/L, more than 60 min was needed to reach the equilibrium. The process of coagulation involved Al–F complexation, Al hydrolysis and precipitation. All the reactions were strongly dependent on pH and were quick processes with time scale of 10² s [12,14]. During the adsorption process, fluoride was removed by ion exchange with OH[−] [8,11]. The acidic condition favored the release of OH[−] and fluoride removal. This slow reaction of ion exchange also required more time to achieve equilibrium. As seen in Figs. 3 and 4, the coagulation showed higher removal efficiency and faster removal than adsorption. It was implied that Al–F complexation promoted fluoride removal in coagulation.

Fig. 2. Effect of initial fluoride concentration on (a) Al–F complexation, (b) fluoride removal and (c) dissolving of aluminum. Dose of Al = 40 mg/L, and initial fluoride concentration = 5–80 mg/L.

Fig. 3. Comparison of fluoride removal between coagulation and adsorption at different pH. Dose of Al = 40 mg/L.

Fig. 4. Kinetic removal of fluoride by coagulation and adsorption at (a) fluoride = 5 mg/L and (b) fluoride = 15 mg/L. Dose of Al = 40 mg/L and pH 7.0.

3.4. Al hydrolysis with Al–F complexation

Role of complexation in coagulation was further studied by titration method. Fig. 5 illustrated the variation of pH during the addition of NaOH into AlCl_3 solution at fluoride concentrations of 0, 5, and 20 mg/L, respectively. The pH increased with the addition of NaOH and the 'S' shape curves were observed. At pH of about 7.0 the volume of NaOH were 1880, 1800, 1580 μL at fluoride concentrations of 0, 5, and 20 mg/L, respectively. The volume of NaOH decreased at higher fluoride concentration and the correspondence between dosage of base and fluoride concentration was ascribed to the effect of formed Al–F complexes. When pH increased to 9.0, the total volumes of NaOH at different fluoride concentration increased to the same value. Due to the strong competition of OH^- with fluoride the effect of complexation was subtle at higher pH.

Titration of Al with different concentration of fluoride was the reaction of OH^- and Al ions or Al–F complexes. Considering the transformation of fluoride species and fluoride removal at different pH (Fig. 1), titration could reflect the changes of complexes, Al ions and OH^- in fluoride removal. The Al–F complexes were dominant at acidic conditions before titration. As OH^- was added, Al–F complexes were partly dissociated to Al^{3+} , free fluoride and other species, such as $\text{Al}(\text{OH})_2^+$ and $\text{AlF}(\text{OH})^+$ [5,15]. In aqueous solution the soluble species mainly included Al–F complexes, Al–OH complexes, Al^{3+} and free fluoride. Fig. 2c showed that little Al^{3+} was dissolved with fluoride concentration below 20 mg/L at pH 7.0. With addition of base most of Al species were precipitated at neutral pH. Decrease of volume of NaOH after complexation implied that complexes could be directly precipitated. So, it was predicted that Al–F complexes reacted with less OH^- and a new precipitate of Al–F–OH was formed. The main reactions were expressed as Eqs. (1)–(4):

Compared with Al^{3+} , the Al–F complexes could react with less OH^- and then act as the precursor or nucleus of coprecipitate. While the complexes and free fluoride were coprecipitated or incorporated in coprecipitate the removal of fluoride was achieved. As base was further added, competition between OH^- and fluoride occurred at pH above 7.0 and the process of coprecipitation was

Fig. 5. Titration curve of Al by NaOH with different fluoride concentrations. Dose of Al = 40 mg/L and NaOH = 1 M.

Table 2

XPS binding energies of different samples in coagulation and adsorption.

	Binding energy (eV)		
	Al 2p	O 1s	F 1s
$\text{Al}(\text{OH})_3$ flocs	74.27	532.02	
Flocs of adsorption	74.57	532.12	685.12
Flocs of coagulation	74.81	532.36	685.22
$\text{AlF}_3 \cdot 3\text{H}_2\text{O}$	76.28		686.33
Na_3AlF_6	75.31		685.19

negatively affected. This corresponded to the decrease of fluoride removal at high pH as shown in Figs. 1 and 3.

3.5. Characterization of FTIR and XPS of flocs

FTIR spectroscopy was useful for investigating characteristics of amorphous oxides and flocs. The FTIR spectra of precipitates in coagulation and adsorption were given in Fig. 6. The peaks in the 400–1500 cm^{-1} region corresponded to the stretching and bending modes of Al–O [16]. Peaks of flocs in coagulation at 590 and 995 cm^{-1} shrunk and shifted compared with that of $\text{Al}(\text{OH})_3$ flocs in adsorption. Results of peak fitting showed that some peaks of Al–O bond (727 and 1207 cm^{-1}) disappeared in flocs of

Fig. 6. FTIR of flocs in coagulation and adsorption. Dashed lines are the results after peak fitting.

coagulation. The differences between coprecipitates in coagulation and $\text{Al}(\text{OH})_3$ flocs indicated that bands of Al–O were affected by fluoride [17]. This indicated the involvement of Al–F complexation in coagulation. The FTIR spectra of flocs before and after adsorption were almost the same. In adsorption fluoride was removed by ion exchange of fluoride with OH^- on the surface of $\text{Al}(\text{OH})_3$, so main chemical structure of $\text{Al}(\text{OH})_3$ remained as before.

The precipitates were further characterized by XPS and results were shown in Table 2. The O 1s binding energy (532.36 eV) and Al 2p binding energy (74.81 eV) of flocs in coagulation were much higher than that of $\text{Al}(\text{OH})_3$ flocs with or without fluoride. The higher binding energy was attributed to the transfer or share of electron between Al or O and fluoride and indicated the strong bonding of Al–F in coagulation. The difference of binding energy showed that the flocs in coagulation with Al–F complexation was not $\text{Al}(\text{OH})_3$ flocs. The differences of the Al 2p binding energy between flocs and solids of AlF_3 and Na_3AlF_6 showed that the flocs were not in the form of AlF_3 or Na_3AlF_6 . The binding energy of F 1s of flocs in coagulation (685.22 eV) was close to that of Na_3AlF_6 (685.19 eV). It was indicated that fluoride was incorporated in the flocs with the bonding of Al–F [5]. From characterization of FTIR and XPS it could be concluded that a new coprecipitate of Al–F–OH formed in coagulation with Al–F complexation. Complexation in coagulation also induced strong bonding between Al and fluoride in the formed coprecipitate. As a result effective fluoride removal was achieved in coagulation after Al–F complexation.

4. Conclusions

The Al–F complexation and fluoride removal in coagulation was quantified at different pH and fluoride concentrations. The concentration of free fluoride decreased with pH and the optimal pH for removal of total fluoride was about 7.0. Low pH and high fluoride concentration favored for Al–F complexation but showed negative effect on fluoride removal. Comparatively, coagulation with complexation showed higher removal efficiency toward fluoride than $\text{Al}(\text{OH})_3$ adsorption, and this indicated the promotion of Al–F complexation on fluoride removal. The effect of Al–F complexation on Al hydrolysis was proved by the titration test. Al–F complexes reacted with less OH^- with comparison to Al^{3+} and were directly precipitated at neutral pH. Characterization of FTIR and XPS also showed that precipitate after complexation was different from $\text{Al}(\text{OH})_3$ flocs with or without fluoride. It was concluded that

Al–F–OH coprecipitate formed with Al–F complexes as precursor in coagulation and the coprecipitation with complexation benefited the removal of fluoride by coagulation.

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