Highlight article

249 Cyanobacterial bloom dynamics in Lake Taihu
Katherine Z. Fu, Birget Moe, Xing-Fang Li and X. Chris Le

Regular articles

1 Membrane fouling controlled by coagulation/adsorption during direct sewage membrane filtration (DSMF) for organic matter concentration
Hui Gong, Zhengyu Jin, Xian Wang and Kajun Wang

8 Photodegradation of methylmercury in Jialing River of Chongqing, China
Rongguo Sun, Dingyong Wang, Wen Mao, Shibo Zhao and Cheng Zhang

15 Powdered activated carbon adsorption of two fishy odorants in water: Trans,trans-2,4-heptadienial and trans,trans-2,4-decadienial
Xin Li, Jun Wang, Xiaojian Zhang and Chao Chen

26 Toxic effects of perfluorononanoic acid on the development of Zebrafish (Danio rerio) embryos
Hui Liu, Nan Sheng, Wei Zhang and Jiayin Dai

35 Denitrification and biofilm growth in a pilot-scale biofilter packed with suspended carriers for biological nitrogen removal from secondary effluent
Yunhong Shi, Guangxue Wu, Nan Wei and Hongying Hu

42 Groundwater arsenic removal by coagulation using ferric(III) sulfate and polyferric sulfate: A comparative and mechanistic study
Jinli Cui, Chuanyong Jing, Dongsheng Che, Jianfeng Zhang and Shuxuan Duan

54 Diurnal and spatial variations of soil NOx fluxes in the northern steppe of China
Bing Wang, Xinqing Lee, Benny K.G. Theng, Jianzhong Cheng and Fang Yang

62 Effects of elevated atmospheric CO2 concentration and temperature on the soil profile methane distribution and diffusion in rice-wheat rotation system
Bo Yang, Zhaozhi Chen, Man Zhang, Heng Zhang, Xuhui Zhang, Genxing Pan, Jianwen Zou and Zhengqin Xiong

72 The potential leaching and mobilization of trace elements from FGD-gypsum of a coal-fired power plant under water re-circulation conditions
Patricia Córdoba, Iria Castro, Mercedes Maroto-Valer and Xavier Querol

81 Unraveling the size distributions of surface properties for purple soil and yellow soil
Ying Tang, Hang Li, Xinmin Liu, Hualing Zhu and Rui Tian

90 Prediction of effluent concentration in a wastewater treatment plant using machine learning models
Hong Guo, Kwanho Jeong, Jiyeon Lim, Jeongwon Jo, Young Mo Kim, Jong-pyo Park, Joon Ha Kim and Kyung Hwa Cho

102 Cu-Mn-Ce ternary mixed-oxide catalysts for catalytic combustion of toluene
Hanfeng Lu, Xianxian Kong, Haifeng Huang, Ying Zhou and Yinfei Chen

108 Immobilization of self-assembled pre-dispersed nano-TiO2 onto montmorillonite and its photocatalytic activity
Tingting Zhang, Yuan Luo, Bing Jia, Yan Li, Lingling Yuan and Jiang Yu

118 Effects of fluoride on the removal of cadmium and phosphate by aluminum coagulation
Ruiping Liu, Bao Liu, Lijun Zhu, Zan He, Jiawei Ju, Huachun Lan and Huijuan Liu
CONTENTS

126 Structure and function of rhizosphere and non-rhizosphere soil microbial community respond differently to elevated ozone in field-planted wheat
   Zhan Chen, Xiaoke Wang and He Shang

135 Chemical looping combustion: A new low-dioxin energy conversion technology
   Xiuning Hua and Wei Wang

146 Picoplankton and virioplankton abundance and community structure in Pearl River Estuary and Daya Bay, South China
   Zhixin Ni, Xiaoping Huang and Xia Zhang

155 Chemical characterization of size-resolved aerosols in four seasons and hazy days in the megacity Beijing of China
   Kang Sun, Xingang Liu, Jianwei Gu, Yunpeng Li, Yu Qu, Junling An, Jingli Wang, Yuanhang Zhang, Min Hu and Fang Zhang

168 Numerical study of the effects of Planetary Boundary Layer structure on the pollutant dispersion within built-up areas
   Yucong Miao, Shuhua Liu, Yijia Zheng, Shu Wang, Zhenxin Liu and Bihui Zhang

180 Interaction between Cu²⁺ and different types of surface-modified nanoscale zero-valent iron during their transport in porous media
   Haoran Dong, Guangming Zeng, Chang Zhang, Jie Liang, Kito Ahmad, Piao Xu, Xiaoxiao He and Mingyong Lai

189 Tricrystalline TiO₂ with enhanced photocatalytic activity and durability for removing volatile organic compounds from indoor air
   Kunyang Chen, Lizhong Zhu and Kun Yang

196 Biogenic volatile organic compound analyses by PTR-TOF-MS: Calibration, humidity effect and reduced electric field dependency
   Xiaobing Pang

207 Enhancement of elemental mercury adsorption by silver supported material
   Rattabal Khunphonoi, Pummarin Khamdahsag, Siriluk Chiarakorn, Nurak Grisdanurak, Adjana Paerungruang and Somrudee Predapitakkun

217 Characterization of soil fauna under the influence of mercury atmospheric deposition in Atlantic Forest, Rio de Janeiro, Brazil
   Andressa Cristhny Buch, Maria Elizabeth Fernandes Correia, Daniel Cabral Teixeira and Emmanoel Vieira Silva-Filho

228 Particle size distribution and characteristics of heavy metals in road-deposited sediments from Beijing Olympic Park
   Haiyan Li, Anbang Shi and Xiaoran Zhang

238 Mesoporous carbon adsorbents from melamine-formaldehyde resin using nanocasting technique for CO₂ adsorption
   Chitrakshi Goel, Haripada Bhunia and Pramod K. Bajpai
Effects of fluoride on the removal of cadmium and phosphate by aluminum coagulation

Ruiping Liu1, Bao Liu1,2, Lijun Zhu1, Zan He1,2, Jiawei Ju1, Huachun Lan1,⁎, Huijuan Liu1

1. Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
2. University of Chinese Academy of Sciences, Beijing 100039, China

Article history:
Received 4 August 2014
Revised 21 October 2014
Accepted 24 October 2014
Available online 22 April 2015

ARTICLE INFO

Article history:
Received 4 August 2014
Revised 21 October 2014
Accepted 24 October 2014
Available online 22 April 2015

Keywords:
Fluoride
Aluminum coagulation
Al–F complexes
ζ-Potential
Adsorbent reclamation

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 (Cd²⁺) and phosphate by Al coagulation. Fluoride at R_F:Al ≥ 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., ≤ 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)₃Fₓm. 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 Cd²⁺ 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.

© 2015 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

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.

⁎ Corresponding author. E-mail: hclan@rcees.ac.cn (Huachun Lan).
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 (Driscol 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., Al(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$_{F:Al}$) (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 Al(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. Pommerek 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 (Pommerek 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$_{F:Al}$ 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$_{F:Al}$ 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 (Cd(NO$_3$)$_2$), and potassium phosphate (KH$_2$PO$_4$) 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$_{F:Al}$ was well mixed. This procedure was adopted considering that upon acidification of the spent Al$_2$O$_3$·xH$_2$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 Al$_2$O$_3$·xH$_2$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$_{F:Al}$ 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$_2$PO$_4^-$ 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 Cd, Al, 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$^{13+}$, F$^-$, Al(OH)$^{\text{2+}}$, Al(OH)$_2$(aq), Al(OH)$_3$aq), Al(OH)$_4$aq), Al$^{3+}$, Al$^{5+}$, Al$^{2+}$, AlF$^-$, AlF$_2^-$, AlF$_3^-$, AlF$_4^-$, HF$^-$, HF$_2^-$, AlF$_3^-$, and Al$^{3+}$$_3$(OH)$_4$aq) were included, and the four Al-F complexes of AlF$^-$, AlF$_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 Cd(OH)$_2$(aq), Cd(OH)$_3$aq), Cd(OH)$_4$aq), Cd$^{2+}$, Cd$^{2+}$, Cd$^{2+}$, Cd$^{2+}$, Cd$^{2+}$, Cd$^{2+}$, and Cd(OH)$^{\text{2+}}$ were included, and CdF$^-$ was related to the Cd-F complexes. In the Al-phosphate system, the Al species Al(OH)$_2$(aq), Al(OH)$_3$aq), Al(OH)$_4$aq), Al$^{3+}$, Al$^{5+}$, Al$^{2+}$, Al$^{3+}$, Al$^{5+}$, Al$^{5+}$, Al$^{2+}$, Al$^{2+}$, and AlO$^{\text{2-}}$ 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 Grigoropoulos, 2007), and the dominant interactions between alum and phosphates included the adsorption of phosphate onto Al(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](image-url)
doses increasing from 5 to 50 mg/L. The introduction of fluoride lowered the $\zeta$-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 $\zeta$-potential to below 0 mV occurred at high RF:Al of 3:1 at the relatively low Al dose of 5 mg/L as Al. $\zeta$-Potential reversal was not observed at the elevated Al dose of 40 mg/L. Generally, the absolute values of the $\zeta$-potential approached 0 mV after introducing fluoride. In the phosphate-removing system, much lower $\zeta$-potential was observed even in the absence of fluoride (i.e., RF:Al = 0:1), owing to the attachment and incorporation of negative phosphate ions within Al(OH)$_3$ flocs. Fluoride at high RF:Al of above 3:1 further decreased the $\zeta$-potential (Fig. 2). Comparatively, more significant decrease in $\zeta$-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 $\zeta$-potential reversal, although it did decrease the $\zeta$-potential to some extent (Pomerrenck and Schafran, 2005). In this study, fluoride significantly lowered the $\zeta$-potential and the reversal of the $\zeta$-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.

\[ \text{Al-OH} + F^- \rightarrow \text{Al-F}^- + OH^- \]  

(1)

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 RF: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 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$_{\text{Res/Total}}$, were observed to increase markedly with elevated RF:Al values (Fig. 3). Without fluoride present, residual Al concentrations were consistently below 0.1 mg/L over a wide Al dose range. Elevated RF: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 (RF:Al = 0.53:1) (Gong et al., 2012). The elevation of RF: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 RF:Al of 2.85:1 (Gong et al., 2012). In this study, extremely high RF: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 RF:Al on Cd removal, $\zeta$-potential, and $\Delta$residual Al in pH 6 to 8. $\Delta$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., RF:Al = 0:1, Cd removal increased with elevated pH, and the $\zeta$-potential approached 0 mV accordingly. At pH 6 the removal of Cd was slight, and fluoride showed little effect; nevertheless a decreased $\zeta$-potential was observed. At elevated pH 7 and 8, fluoride showed little effect at RF:Al < 1:1, and further elevated RF:Al adversely inhibited Cd removal. At pH 8 a negative $\zeta$-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 $\zeta$-potential. It is inferred that the ligand exchange between surface hydroxyl groups and fluoride consumes available sites and inhibits Cd removal thereafter. $\Delta$Residual Al increased with elevated RF: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 RF:Al of 6:1.

\[ \text{Al}^{3+} + nF^- \rightarrow \text{Al-F}_n \text{ complexes} \]  

(2)

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, $\zeta$-potential, and $\Delta$residual Al in pH 6 to 8. Fluoride at RF:Al = 1:5 showed little effect on phosphate removal over a wide pH range. At elevated RF: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 RF:Al = 6:1. At pH 7 and 8, fluoride showed little effect on phosphate removal.

\[ \text{Al}^{3+} + nF^- \rightarrow \text{Al-F}_n \text{ complexes} \]  

(2)
Fluoride lowered the $\zeta$-potential of Al precipitates at pH 6–8, and a more significant decrease was observed at elevated $RF:Al$. However, $\zeta$-potential was below 0 mV even in the absence of fluoride, and the fact that fluoride lowers $\zeta$-potential played a limited role to inhibit phosphate removal. Additionally, it was observed that fluoride showed little effect on Al hydrolysis, and $\Delta$ residual Al showed little variation in pH 6–8 even at high $RF:Al$ of 6:1. Comparatively, in the Cd-removing system $\Delta$ residual Al increased remarkably with elevated $RF:Al$ 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 $\Delta$ residual Al at different $RF:Al$ 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-μm membrane filtration. The ratios of complexed-F decreased with elevated $RF:Al$ 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. MINTEQ modeling indicated that the formation of Al–PO$_4$ species (i.e., Al$_2$PO$_4$,$^+$, AlHPO$_4$) 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 $RF:Al$

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

Before being dosed, the species distribution of Al and F in the mixed solution was mainly dependent on $RF:Al$, and free fluoride existed at $RF:Al > 1$ whereas free Al was present at
and Al-P activists did occur; however, these reactions were ignored due to their low ratios (Figs. S5 and S7).

\[
\text{Al}^{3+} + n\text{OH}^− \rightarrow \text{Al(OH)}_{3}^{[3−-n]−}
\]

(3)

\[
n\text{Al}^{3+} + m\text{OH}^− \rightarrow \text{Al}_m^{3+−n}
\]

(4)

\[
\text{Al(OH)}_{3}^{[3−-n]} + m\text{F}^− \rightarrow \text{Al(OH)}_n\text{F}_m
\]

(5)

\[
\text{Al–F}_n\text{complexes} \rightarrow \text{Al–F}_m\text{complexes} + m\text{F}^−
\]

(6)

\[
\text{Al–F}_m\text{complexes} + n\text{OH}^− \rightarrow \text{Al–F}_n\text{OH}_m\text{complexes} + p\text{F}^−
\]

(7)

\[
\text{Al(OH)}_3 + n\text{F}^− \rightarrow \text{Al(OH)}_3\text{F}_n
\]

(8)

\[
\text{Al–F}_n\text{complexes} + n\text{Al(OH)}_3 \rightarrow \text{Al}^{n+1}\text{OH}_3\text{F}_n
\]

(9)

\[
\text{Al(OH)}_3 + \text{OH}^− \rightarrow \text{AlO}_2^− + 2\text{H}_2\text{O}
\]

(10)

\[
\text{AlF}_n\text{OH}_m \rightarrow \text{solubleAl} + m\text{F}^− + \text{H}_2\text{O}
\]

(11)

\[
\text{Al(OH)}_n\text{F}_m \rightarrow \text{solubleAl} + m\text{F}^− + \text{H}_2\text{O}
\]

(12)

The Al-fluoride interactions and their species distribution contributed to the observed varying trends of ζ-potential and
residual Al, and the effect of fluoride on the removal of Cd and phosphate by Al coagulation was highly dependent on pH and $R_{F:Al}$ (Table S2). Briefly, the removal of neither Cd nor phosphate was affected by fluoride at $R_{F:Al}$ of below 1:1 in a wide pH range; however, fluoride at $R_{F:Al}$ > 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 Al(OH)$_3$, AlF$_m$(OH)$_n$, and Al(OH)$_n$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$_2$PO$_4$ 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 Al(OH)$_3$, AlF$_m$(OH)$_n$, and Al(OH)$_n$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 $R_{F:Al}$. Fluoride shows an inhibitive effect on the removal of Cd at $R_{F:Al}$ ≥ 3:1, whereas at low $R_{F:Al}$ a slight beneficial effect is interestingly observed. The removal of phosphate decreases at either high levels of fluoride ($R_{F:Al}$ = 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 $\zeta$-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 Al$_2$O$_3$·xH$_2$O with adsorbed fluoride, after its being dissolved by acid solution, for the removal of Cd and phosphate. As for the spent in-situ Al$_2$O$_3$·xH$_2$O with adsorbed fluoride obtained from real treatment plants, the $R_{F:Al}$ is critically low at below 0.1:1, and the adverse effect of fluoride is slight.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 21177143, 21177144) and the key project of the National “863” High-Tech R&D Program of China (No. 2012AA062604). Moreover, the author Ruiping Liu gratefully acknowledges the support of the Beijing Nova Program (No. 2013054).

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.
REFERENCES


Editorial Board of Journal of Environmental Sciences

### Editor-in-Chief

X. Chris Le  
University of Alberta, Canada

### Associate Editors-in-Chief

<table>
<thead>
<tr>
<th>Name</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jiuhui Qu</td>
<td>Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China</td>
</tr>
<tr>
<td>Shu Tao</td>
<td>Peking University, China</td>
</tr>
<tr>
<td>Nigel Bell</td>
<td>Imperial College London, UK</td>
</tr>
<tr>
<td>Po-Keung Wong</td>
<td>The Chinese University of Hong Kong, Hong Kong, China</td>
</tr>
</tbody>
</table>

### Editorial Board

#### Aquatic environment

<table>
<thead>
<tr>
<th>Name</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baoyu Gao</td>
<td>Shandong University, China</td>
</tr>
<tr>
<td>Maozhong Fan</td>
<td>University of Wyoming, USA</td>
</tr>
<tr>
<td>Chihpin Huang</td>
<td>National Chiao Tung University, Taiwan, China</td>
</tr>
<tr>
<td>Ng Wen Jern</td>
<td>Nanyang Environment &amp; Water Research Institute, Singapore</td>
</tr>
<tr>
<td>Clark C. K. Liu</td>
<td>University of Hawaii at Manoa, USA</td>
</tr>
<tr>
<td>Hokyong Shon</td>
<td>University of Technology, Sydney, Australia</td>
</tr>
<tr>
<td>Zijian Wang</td>
<td>Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China</td>
</tr>
<tr>
<td>Zhiwu Wang</td>
<td>The Ohio State University, USA</td>
</tr>
<tr>
<td>Yuxiang Wang</td>
<td>Queen’s University, Canada</td>
</tr>
<tr>
<td>Min Yang</td>
<td>Beijing Normal University, China</td>
</tr>
<tr>
<td>Daqiang Yin</td>
<td>Tongji University, China</td>
</tr>
<tr>
<td>Environmental toxicology and health</td>
<td></td>
</tr>
<tr>
<td>Jingwen Chen</td>
<td>Dalian University of Technology, China</td>
</tr>
<tr>
<td>Shu Tao</td>
<td>Peking University, China</td>
</tr>
<tr>
<td>Environmental catalysis and materials</td>
<td></td>
</tr>
<tr>
<td>Hong He</td>
<td>Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China</td>
</tr>
<tr>
<td>Environmental biology</td>
<td></td>
</tr>
<tr>
<td>Yong Cai</td>
<td>Florida International University, USA</td>
</tr>
<tr>
<td>Henner Hollett</td>
<td>RWTH Aachen University, Germany</td>
</tr>
<tr>
<td>Jae-Seong Lee</td>
<td>Sungkyunkwan University, South Korea</td>
</tr>
<tr>
<td>Bojan Sedmak</td>
<td>University of Copenhagen, Denmark</td>
</tr>
<tr>
<td>National Institute of Biology, Slovenia</td>
<td></td>
</tr>
<tr>
<td>Institute of Hydrobiology, China</td>
<td></td>
</tr>
<tr>
<td>Environmental analysis and method</td>
<td></td>
</tr>
<tr>
<td>Zongwei Cai</td>
<td>Hong Kong Baptist University, Hong Kong, China</td>
</tr>
<tr>
<td>Municipal solid waste and green chemistry</td>
<td></td>
</tr>
<tr>
<td>Pinjing He</td>
<td>Tongji University, China</td>
</tr>
</tbody>
</table>

#### Atmospheric environment

<table>
<thead>
<tr>
<th>Name</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daqiang Yin</td>
<td>Tongji University, China</td>
</tr>
<tr>
<td>Yuxiang Wang</td>
<td>Peking University, China</td>
</tr>
<tr>
<td>Atmospheric environment</td>
<td></td>
</tr>
<tr>
<td>Environmental biology</td>
<td></td>
</tr>
<tr>
<td>Yong Cai</td>
<td>Florida International University, USA</td>
</tr>
<tr>
<td>Henner Hollett</td>
<td>RWTH Aachen University, Germany</td>
</tr>
<tr>
<td>Environmental catalysis and materials</td>
<td></td>
</tr>
<tr>
<td>Hong He</td>
<td>Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China</td>
</tr>
<tr>
<td>Environmental biology</td>
<td></td>
</tr>
<tr>
<td>Yong Cai</td>
<td>Florida International University, USA</td>
</tr>
</tbody>
</table>

#### Terrestrial environment

<table>
<thead>
<tr>
<th>Name</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Christopher Anderson</td>
<td>Massey University, New Zealand</td>
</tr>
<tr>
<td>Xuejun Wang</td>
<td>Fudan University, China</td>
</tr>
<tr>
<td>Abdelwahid Mellouki</td>
<td>Centre National de la Recherche Scientifique, France</td>
</tr>
<tr>
<td>Yuesi Wang</td>
<td>University of Wisconsin-Madison, USA</td>
</tr>
<tr>
<td>Zhiwu Wang</td>
<td>The Ohio State University, USA</td>
</tr>
<tr>
<td>Yuxiang Wang</td>
<td>Queen’s University, Canada</td>
</tr>
<tr>
<td>Min Yang</td>
<td>Beijing Normal University, China</td>
</tr>
<tr>
<td>Environmental catalysis and materials</td>
<td></td>
</tr>
<tr>
<td>Jingwen Chen</td>
<td>Dalian University of Technology, China</td>
</tr>
<tr>
<td>Sijin Liu</td>
<td>Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China</td>
</tr>
<tr>
<td>Environmental biology</td>
<td></td>
</tr>
<tr>
<td>Yong Cai</td>
<td>Florida International University, USA</td>
</tr>
<tr>
<td>Henner Hollett</td>
<td>RWTH Aachen University, Germany</td>
</tr>
<tr>
<td>Environmental analysis and method</td>
<td></td>
</tr>
<tr>
<td>Zongwei Cai</td>
<td>Hong Kong Baptist University, Hong Kong, China</td>
</tr>
<tr>
<td>Municipal solid waste and green chemistry</td>
<td></td>
</tr>
<tr>
<td>Pinjing He</td>
<td>Tongji University, China</td>
</tr>
</tbody>
</table>

### Editorial office staff

<table>
<thead>
<tr>
<th>Role</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Managing editor</td>
<td>Qingcai Feng</td>
</tr>
<tr>
<td>Editors</td>
<td>Zixuan Wang Suqin Liu</td>
</tr>
<tr>
<td>English editor</td>
<td>Catherine Rice (USA)</td>
</tr>
</tbody>
</table>
Aims and scope

*Journal of Environmental Sciences* is an international academic journal supervised by Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The journal publishes original, peer-reviewed innovative research and valuable findings in environmental sciences. The types of articles published are research article, critical review, rapid communications, and special issues.

The scope of the journal embraces the treatment processes for natural groundwater, municipal, agricultural and industrial water and wastewaters; physical and chemical methods for limitation of pollutants emission into the atmospheric environment; chemical and biological and phytoremediation of contaminated soil; fate and transport of pollutants in environments; toxicological effects of terrorist chemical release on the natural environment and human health; development of environmental catalysts and materials.

For subscription to electronic edition

Elsevier is responsible for subscription of the journal. Please subscribe to the journal via http://www.elsevier.com/locate/jes.

For subscription to print edition

China: Please contact the customer service, Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China. Tel: +86-10-64017032; E-mail: journal@mail.sciencp.com, or the local post office throughout China (domestic postcode: 2-580).

Outside China: Please order the journal from the Elsevier Customer Service Department at the Regional Sales Office nearest you.

Submission declaration

Submission of the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The publication should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Editorial

Authors should submit manuscript online at http://www.jesc.ac.cn. In case of queries, please contact editorial office, Tel: +86-10-62920553, E-mail: jesc@rcees.ac.cn. Instruction to authors is available at http://www.jesc.ac.cn.