



Simultaneous removal of arsenic and fluoride by freshly-prepared aluminum hydroxide



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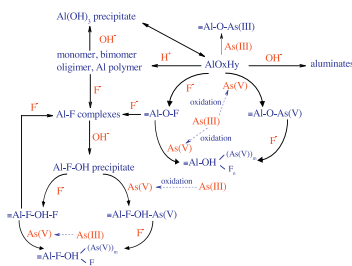
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HIGHLIGHTS

- Fluoride show more significant inhibition on As(V) removal than on As(III) removal.
- Negative As(V) show more significant adverse effect on F removal than neutral As(III) does.
- Fluoride dissolve AlOxHy and the formation of Al–F complexes occur at acidic pH.
- As(III) oxidation and pH adjustment to achieve simultaneous removal of As and F.

GRAPHICAL ABSTRACT



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ABSTRACT

The coexistence of arsenic (As) and fluoride (F) in some underground waters creates challenges in the simultaneous removal of these two toxic elements. This study investigates the effect of fluoride at different molar ratios of fluoride to arsenic (As) ($R_{F:As}$) on the removal of arsenic [i.e., arsenite (As(III), arsenate (As(V))] by freshly-prepared aluminum hydroxide (AlOxHy), and that of arsenic at different molar ratios of arsenic to fluoride ($R_{As:F}$) on fluoride removal. In single pollutant solutions, the removal of neutral As(III) is independent on pH at $R_{As(III):Al} \leq 0.70:1$ and is much lower than that of As(V). The optimum As(V) removal is at weak acidic pH of 5 and 6 whereas that of fluoride is at pH 7 and 8. Fluoride at $R_{F:As(V)} > 35:1$ significantly impairs the removal of As(V) with more significant inhibition at elevated pH. The negatively-charged As(V) inhibits fluoride removal to a larger extent than the neutral As(III) does. The adverse effect of fluoride on As(V) removal is mainly attributed to the lowered ζ -potential, which is controlled by the combined effects of pH and $R_{F:As(V)}$. In relative terms, the removal of fluoride is highly pH dependent, although $R_{As(V):F}$ does show some effects. The oxidation of As(III) to As(V) and the adjustment of pH to weak acidic range is well preferred to achieve the simultaneous removal of As and F by AlOxHy adsorption.

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1. Introduction

The widespread distribution of arsenic (As) and fluoride (F) in underground water has generated great concern [1,2], and more

than 400 million individuals are exposed to either of these two toxic elements via drinking water globally. In some cases with special geochemical conditions, the simultaneous occurrence of As and F is observed [2]. The combined toxic effects between As and F have been proposed [3,4], and this further complicates the situation and creates challenges in the simultaneous removal of As and F. Additionally, some industries such as semiconductors production and rare earths refinery also produce complicated wastewaters with

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high levels of fluoride and arsenic, and the molar ratios of F to As ($R_{F:As}$) may differ to a large extent.

The Al-based coagulants and adsorbents are practically valuable for the removal of fluoride [5–7], and the exchange between fluoride and the hydroxyl groups occurs on the surfaces of aluminum (hydro)-oxides. The formation of aluminum fluoride complexes (Al–F complexes) occurs at acidic condition [7–9], and this effect facilitates fluoride removal as compared to its direct adsorption onto Al(OH)₃ precipitates [7]. Additionally, Al–F complexes formation also affects the species distribution of aluminum ions and their hydrolysis products [9], and assumedly impacts the coagulation behaviors of Al salt towards arsenic thereafter. As for the removal of arsenic, the Fe-based coagulants and adsorbents showed priority due to their strong affinity towards arsenic [10,11], and the formation of bi-nuclear bidentate and monodentate complexes on the iron hydro (oxide) surfaces has been proposed [10,13,14]. To achieve the simultaneous removal of As and F, the coagulation by the combined use of iron (Fe) and aluminum (Al) salts works well [6,15], and the electro-coagulation with Fe and Al plates also exhibits promising efficiency [15]. Comparatively, Al hydro (oxide) is more effective than that of Fe in terms of the simultaneous removal of As and F, owing to the weak affinity of iron hydro (oxide) towards fluoride [6]. Al coagulation shows promising As removal efficiency and has been successfully implemented in some drinking water treatment plants [16]. Aluminum hydroxide (AlOxHy) achieves the simultaneous removal of arsenic and fluoride, and their removal efficiency is highly dependent on pH [7].

In the treatment of water with coexisting As and F, the mutual effects between them, i.e., the effect of one species on the removal of the other species, may be complicate and rare studies have focused on this before. Fluoride was reported to show inhibitive effect on the removal of particles and organic matter by Al coagulation [17]. Our previous study also indicated the adverse effect of fluoride on the coagulation behavior of aluminum chloride (AlCl₃) towards kaolin suspensions, and the formation of Al–F complexes at high fluoride levels plays an important role [18]. Besides the formation of Al–F complexes, the attachment of fluoride onto Al hydroxide decreased the surface charge and particles stability [19], and this effect was assumedly to inhibit the removal of negatively-charged arsenate [As(V)]. Additionally, the competitive effect between As(V) and F occurs to affect their adsorption onto AlOxHy, and this adverse effect may be remarkably alleviated by introducing iron oxides to AlOxHy [6]. Furthermore, the strong interactions between Al and F may contribute to the dissolution of Al hydro (oxide) and affect its removal behaviors towards As and F; however, rare study has focused on it to the best of our knowledge.

The freshly-prepared metal hydroxides show active surfaces and high BET surface areas, and more importantly, they can be in situ coated onto porous carriers to achieve adsorbents granulation [20]. This study uses the freshly-prepared AlOxHy as an adsorbent, and investigates the mutual effects between F and As on their removal over a wide pH range. Two arsenic species of As(III) and As(V) were included, and the molar ratios of F to As ($R_{F:As}$) and that of As to F ($R_{As:F}$) varied over a wide range. The dominant factors on the removal of As and F were evaluated and the main reactions involved in were proposed accordingly. This study is practically valuable for the simultaneous removal of As and F in drinking water and some industrial wastewater.

2. Materials and methods

2.1. Reagents and materials

Unless otherwise noted, all chemicals were of analytical-reagent grade and were used without further purification. The stock solutions of sodium arsenite (NaAsO₂, 3.47 g/L), sodium arsenate

Table 1
Characteristics of the tap water used in this study.

Items	Values
pH (20 °C)	8.10 ± 0.05
Turbidity (NTU)	0.35 ± 0.02
DOC (mg/L)	0.62
Alkalinity (mg CaCO ₃ /L)	150
Hardness (mg CaCO ₃ /L)	155
Aluminum (mg/L)	0.08
Iron (mg/L)	0.05
Total phosphorus (mg/L)	0.016
SO ₄ ²⁻ (mg/L)	31.7
Cl ⁻ (mg/L)	8.90
Mn ²⁺ (mg/L)	0.09
As (mg/L)	N.D.*
F (mg/L)	N.D.*

* Not detected.

(Na₃AsO₄·12H₂O, 11.31 g/L), and sodium fluoride (NaF, 4.66 g/L) were, respectively, prepared in de-ionized water every 10 days. The sodium salts rather than calcium salts were used to avoid the side effect of divalent calcium ion on the adsorption of As and F. The AlCl₃ stock solution (26.8 g/L) was freshly prepared prior to use.

To prepare raw water with desired concentrations of As(III)/As(V) and fluoride, the stock solutions of As(III)/As(V) and fluoride at different volumes were diluted into tap water, and the characteristics of which was illustrated in Table 1. The tap water was kept in the dark for several days prior to use, and the levels of residual chlorine were below detection limit, as determined by the *N,N*-diethyl-*p*-phenylenediamine (DPD) ferrous titration method. The raw water with coexisting As(III) and fluoride is expressed as As(III)–F system whereas that with coexisting As(V) and fluoride is indicated as As(V)–F system. Their initial concentrations were expressed by the molar ratios of initial As/F concentrations to AlOxHy doses, i.e., $R_{As(III):Al}$, $R_{As(V):Al}$, and $R_{F:Al}$ (mol/mol), and varied from 0.13:1 to 1.77:1. The solution pH was adjusted to the desired values with hydrochloric acid (HCl) and sodium hydroxide (NaOH).

AlOxHy was freshly prepared by the method illustrated in our previous study [21]. Briefly, the stock solutions of AlCl₃ and NaOH, at stoichiometric ratio of 1:3, were mixed for 2-min reaction prior to being dosed into raw water samples. The completed reaction between AlCl₃ and NaOH was achieved as indicated by the low concentrations of residual Al (i.e., <0.1 mg/L). The doses of AlOxHy are expressed by Al in mg/L, and are controlled by extracting desired volumes of AlCl₃ stock solution.

2.2. Experimental methods

Jar tests were performed using a Phipps and Bird six-paddle stirrer in 500-mL beakers. Soon after a 10-s rapid mixing (250 rpm) of the raw water samples (300 mL), the freshly-prepared AlOxHy at desired doses was dosed. After that, the adsorption procedure consisted of a 2-min rapid mix (200 rpm), 15-min slow mix (40 rpm), and a 30-min settling period. The experimental procedures simulates the widely-used unit processes of mixing, flocculation, and sedimentation, and enables the feasibility evaluation on the enhanced removal of As and F by AlOxHy on the basis of conventional treatment processes. A small amount of sample was taken immediately for the analysis of zeta potential after the 2-min rapid mix. It was noted that the oxidation of As(III) to As(V) by oxygen might occur; however, preliminary experiments indicated that the extent was rather slight. The half-lives of As(III) has been determined to be as long as 4–9 days while being exposed to saturated air [22]. pH was adjusted during the 15-min slow mixing period. After settling for 30 min, supernatants were collected at 2-cm below the water level and then filtered through 0.45-μm membrane filters.

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