

Effects of coexisting anions on removal of bromide in drinking water by coagulation

Fei Ge^{a,b}, Lizhong Zhu^{a,*}

^a Department of Environmental Science, Zhejiang University, Hangzhou, Zhejiang 310028, China

^b Department of Environmental Engineering, Xiangtan University, Xiangtan, Hunan 411105, China

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Abstract

Bromo-DBPs (disinfection by-products) are generated by bromide and disinfectant in drinking water disinfection, which have adverse effects on human health. In this study, effects of coexisting anions on removal of bromide by aluminium coagulation were investigated. It was observed that bromide was removed of 62.1–87.0% in raw water, while the removal efficiency of bromide was achieved 82.8–99.2% in deionized water through the combination of Br⁻ with Al(III) in various pathways. The coexisting anions in raw water significantly affected the removal of bromide. Removal efficiency decreased by 11.5, 21.2, 14.6, 8.0 and 40.8% with the addition of HCO₃⁻, SO₄²⁻, Cl⁻, NO₃⁻ and H₂PO₄⁻, respectively, for their affinities with Al(III) or accelerating the formation of Al(OH)_{3(am)}. These results demonstrated that bromo-DBPs in drinking water could be controlled though removing bromide by enhanced coagulation.

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1. Introduction

Disinfectors have been used extensively to kill pathogen in drinking water treatment. However, an obvious drawback of disinfection is the formation of disinfection by-products (DBPs). Since the pioneer work of Rook [1] in 1974, more than 600 DBPs have been reported and new DBPs are identified with sensitive analyse [2,3].

Bromo-DBPs, which are generated by bromide and disinfectors, have been focus on due to their carcinogenic to public health [4]. Bromate, a typical bromo-DBPs produced in ozone disinfection, is permitted with the maximum concentration of 25 µg/L in drinking water according to the standard of WHO [5,6]; Bromo-, or bromochloro-trihalomethanes (THMs) and haloacetic acids (HAAs), which are produced in chlorine and chloramine disinfection, are limited with the maximal concentration of 80 µg/L (THMs) and 60 µg/L (HAAs) by US EPA in disinfectant/disinfection by-products rule (D/DBP)I, respectively [7–9]. Bromo-, or bromochloro-THMs and HAAs are

generally considered more carcinogenic than their chlorinated analogues [8–10].

As the precursor for the formation of bromo-DBPs, bromide is naturally present in raw water, especially in groundwater and surface water in coastal region. For rapid growth of industrial activities, brine runoff from oil field and use of methyl bromide for pest control, more bromide is discharged to environment [11,12]. The mean occurrence level of bromide was reported to be 62 µg/L with an overall observed range of <5–429 µg/L in USA and the highest concentration of bromide was estimated to be 2 mg/L in drinking water source [13,14]. Accordingly, in order to control bromo-DBPs, bromide should be removed before disinfection in drinking water.

In water treatment, nanofiltration, hyperfiltration and reverse osmosis were used to reduce bromide and/or bromate by adsorption, size exclusion and high pressure [15], meanwhile, biological activated carbon were reported to have the capacity to reduce bromate to bromide after ozonation [16]. Some new methods, e.g., Ag-doped activated carbon aerogels were investigated to remove bromide and how the activation of Ag-doped aerogels affects their behavior [17], electrochemical method was presented to lower bromide by oxidation of bromine to bromine and the volatilization of bromine with carbon dioxide [5]. These

* Corresponding author. Tel.: +86 571 88273733; fax: +86 571 88273733.

E-mail addresses: gefei@xtu.edu.cn (F. Ge), zlz@zju.edu.cn (L. Zhu).

methods were proved to be effective though the cost would be high in actual usage.

Coagulation is a key and basic unit process in water purification. Enhanced coagulation is recommended by US EPA as an optimal way to control DBPs at the first stage in performing D/DBP rule for its high efficiency in removing nature organic matter (NOM) [18]. The removal efficiency and mechanism of NOM in coagulation had been extensively investigated [19–21]. Furthermore, some inorganic compounds, such as phosphate, fluoride, soluble silica, were found that could bind with Al(III) or Fe(III) salt in coagulation process [22–24]. Planky et al. [22] investigated the kinetic of aluminium fluoride complexation in acid water and reported different formation pathways of AlF^{2+} . Cheng et al. [23] studied the effects of phosphate on removal of humic substances by aluminium sulphate and found that most of phosphate was removed in the presence of humic acid. These results implied that bromide would also be reduced through similar mechanism in conventional coagulation. However, in actual environment, except humic acid, large amount of anions, e.g., HCO_3^- , SO_4^{2-} , Cl^- , NO_3^- , H_2PO_4^- and F^- coexist with bromide in raw water. Some of these anions were reported that had influence or could be removed in coagulation process [25,26]. Hence, the effects of coexisting ions on coagulation removal of bromide should be considered. Though some methods were studied to reduce bromide in drinking water, few investigations were conducted in the removal of bromide by coagulation and the corresponding factors influencing removal efficiency.

The objectives of this study were to: (1) test and compare the removal efficiency of bromide by aluminium coagulation in different water samples, (2) investigate the effects of coexisting anions on the removal efficiency of bromide. Results from this investigation can provide valuable information in removal of bromide effectively and thus to control bromo-DBPs in drinking water.

2. Material and methods

2.1. Material

Bromide stock solution (1 g/L, Calculated as Br^-) was prepared with KBr (Shanghai Chemical Co., China, 99%) and then diluted to the target concentration with deionized water. Humic acid (HA) stock solution was composed of 1.0 g HA (Shanghai Chemical Co., China, biochemical reagent grade) and 1 L 0.025 mol/L NaOH, which was stirred for 4 h and filtered with 0.45 μm PTFE film to removed residual nondissolved HA powder. Aluminium stock solution (1 g/L, calculated as $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) was prepared with aluminium chloride hexahydrate (Shanghai Chemical Co., China, analytical reagent grade) and then diluted to the target concentration with deionized water. Meanwhile, 0.24 mg/L of Phenol red, 2 g/L of Chloramine-T and 2.5 g/L of sodium hyposulfite were prepared for measuring the bromide in solution. The buffer solution was prepared by 68 g sodium acetate trihydrate and 30 mL of acetic acid, then pH was adjusted to 4.60 ± 0.02 . Sodium bicarbonate, sodium fluoride, potassium nitrate, sodium sulphate, sodium chloride and potassium dihydrogen phosphate were all analytical reagent

grade (Shanghai Chemical Co., China). Deionized water was obtained from Milli-Q pure water (Milli-Q SP VOC, Millipore Co., Bedford, MA).

2.2. Coagulation procedures

To deionized water sample, the coagulation experiments were conducted by adding 0–2.0 mg/L bromide and/or 6 mg/L HA in deionized water. The pH of solution was adjusted to 4, 5, 6, 7, 8 and 9 by 0.1 mol/L NaOH or 0.1 mol/L H_2SO_4 before coagulation, which was measured by Thermo 520 pH meter (Thermo Electron Corporation). To raw water sample (taken from the water source of an drinking water plant), 0.2 mg/L bromide was added and pH was adjusted to 6, 7, 8 before coagulation, respectively. Then 3, 7, 15 mg/L Al coagulant was added in solution. The coagulation procedure involved rapid mixing at 120 rpm for 2 min, followed by slow stirring at 30 rpm for 30 min, and a quiescent settling period 2 h followed the slow stirring. The final pH of the solution in the each experiment was also recorded. Samples were taken from the surface of water and filtered with 0.45 μm PTFE film before analysis. The concentration of bromide was detected after filtration.

2.3. Analysis methods

Bromide was determined by standard phenol red spectrophotometric method with Chloramine-T reaction with a 722-Spectrophotometer analyzer (Shanghai, China) at a wavelength of 590 nm. Buffer solution was added to solution to fix up pH at 4.60 ± 0.02 before determination.

HA was analyzed by a UV analyzer (Hitachi model U-2010, Japan) at wave-length of 254 nm. A preliminary experiment showed that no significant difference was detected at pH above 7.5, accordingly, the solution was adjusted to pH 7.5–8.0 before each measurement. The standard sample of HA (1–10 mg/L) was analysed and then a standard curve was illustrated. Raw water was filtrated 0.45 μm PTFE film before analyzed, and then the concentration of HA in raw water could be calculated from the standard curve. The anions in raw water, carbonate (mg/L, Calculated as CO_3^{2-}) was analysed by acid and alkali titration, sulfate (mg/L, calculated as SO_4^{2-}), chlorite (mg/L, calculated as Cl^-) and nitrate (mg/L, calculated as NO_3^-) was analyzed by ion chromatogram, phosphate (mg/L, calculated as P) was analyzed by molybdenum–antimony anti-spectrophotometric method.

3. Results and discussion

3.1. Removal of bromide in deionized water

First, experiments were conducted in deionized water for examining the behaviour of bromide in coagulation process.

In Fig. 1a, it was observed that the removal efficiency of bromide was closely related with its initial concentration. When the initial concentration of bromide decreased from 2.0 to 0.2 mg/L, the efficiency increased from 30.9 to 99.2% at pH 6, from 27.8 to 94.5% at pH 7, from 25.6 to 82.8% at pH 8 with coagulant dosage 15 mg/L, respectively. These results suggested that bromide in

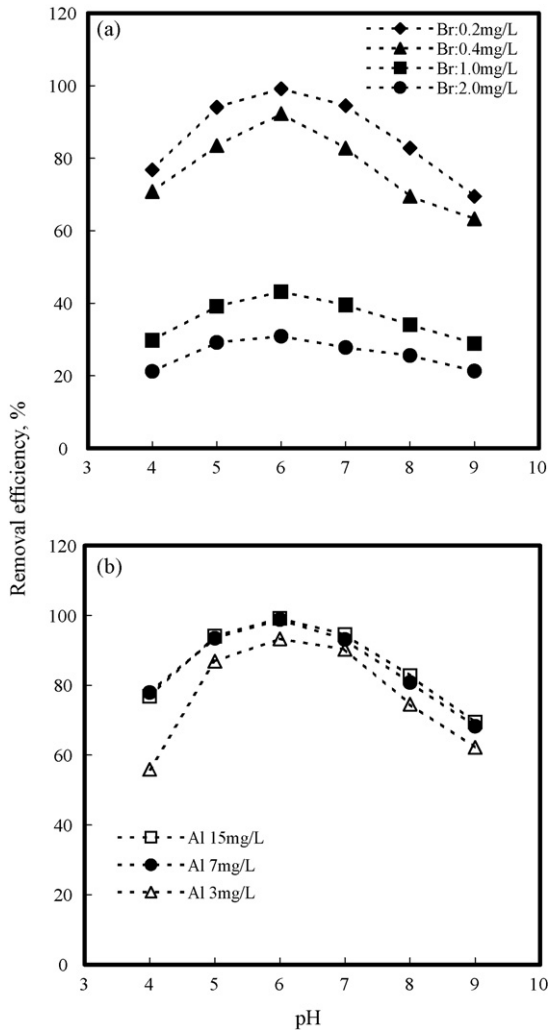


Fig. 1. Removal efficiency of bromide in deionized water (Br^- : 0.2–2.0 mg/L, Al: 3–15 mg/L, pH: 4–9).

low concentration was easier to be removed in coagulation process. Meanwhile, the removal efficiency was also affected by pH. In Fig. 1a, it was found that the peak value occurred at pH 6 and the removal efficiency declined when pH is too high or too low.

Then, the effect of coagulant dosage on removal efficiency of bromide was performed with the initial concentration of 0.2 mg/L bromide. It was observed little change occurred when coagulant dosage diminished from 15 to 7 mg/L. However, the removal efficiency declined about 6.0–28.5% at pH 4–9 with coagulant dosage 3 mg/L in contrasting to the corresponding value with coagulant dosage 15 mg/L.

When aluminium chloride was added in aqueous solution, hydrolysis reactions occurred and formed various hydrolysis products. Clark et al. [27] have summarized Al(III) equilibria leading to the alternatives of aqueous polymer and solid phases as follows.

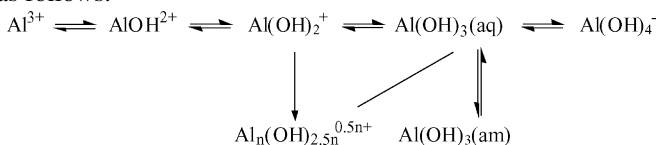


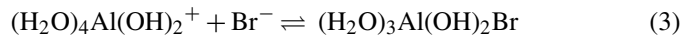
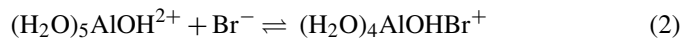
Table 1
Hydrolysis reaction of Al(III) in coagulation

Reaction equation	log K
$\text{Al}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_2^+ + \text{H}^+$	−4.97
$\text{Al}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_2^+ + 2\text{H}^+$	−9.30
$\text{Al}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_3(\text{aq})^a + 3\text{H}^+$	−15.0
$\text{Al}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_3(\text{am})^b + 3\text{H}^+$	−33.0
$\text{Al}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_4^- + 4\text{H}^+$	−23.0

^aaq: aqueous; ^bam: amorphous.

To clearly illustrated the mechanism suitable with experimental data, the possible hydrolysis reaction of Al(III) in drinking water coagulation and the corresponding reaction constants were listed in Table 1. It was generally considered that Al^{3+} existed when $\text{pH} < 4$, Al(OH)_2^+ and Al(OH)_2^+ existed when $\text{pH} < 6$. The main hydrolysis products were $\text{Al(OH)}_3(\text{am})$ gel-precipitation in pH 6–8 and Al(OH)_4^- when $\text{pH} > 8$ [28].

Plankey et al. [22] reported that halogen ion associated with Al(III) mainly by electrostatic affinity. Hence, the removal mechanism of bromide was considered to be charge neutralization at low pH in coagulation. This process would occur in three pathways described as equation (1)–(3).



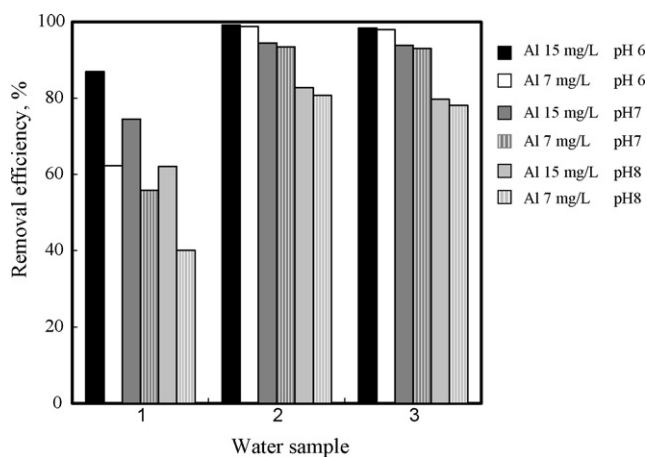
Bromide could be adsorbed on the fresh surface of $\text{Al(OH)}_3(\text{am})$ precipitates with enhancing pH gradually, which was similar with previous investigation that phosphate associated with aluminium species [23]. Due to the possible configuration of bromide in solution is Br^- at pH 4–9, the effects of pH on the removal efficiency of bromide in coagulation were minor in contrast to the removal efficiency of phosphate, which was significantly affected by pH in the similar process.

3.2. Removal of bromide in different water samples

Further experiments were performed to compare bromide removal efficiency in different water samples. The physico-chemical properties of raw water tested in the experiment were illustrated in Table 2. From Table 2, it was known that the concentration of humic acid was 5.93 mg/L and large amount of

Table 2
Physico-chemical properties of raw water

No.	Item	Value
1	pH	6.64
2	Bromide (mg/L)	0.02
3	Humic acid (mg/L)	5.93
4	Carbonate (mg/L)	120.06
5	Sulfate (mg/L)	38.03
6	Chloride (mg/L)	18.12
7	Nitrate (mg/L)	9.52
8	Phosphate (mg/L)	0.01
9	Fluoride (mg/L)	0.73

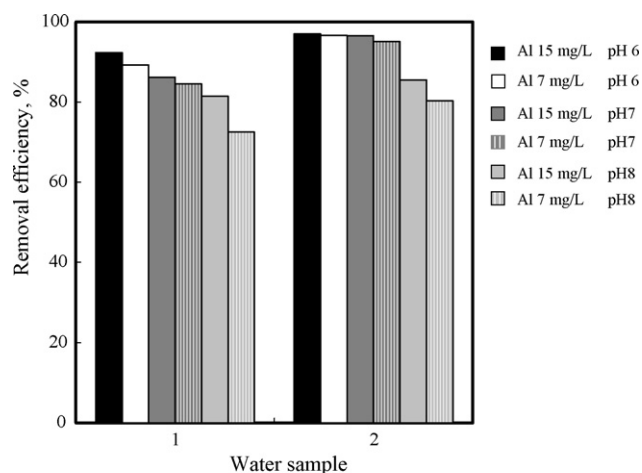


1. Raw water + 0.2 mg/L Br⁻ 2. Deionized water + 0.2 mg/L Br⁻
3. Deionized water + 6 mg/L Humic acid + 0.2 mg/L Br⁻

Fig. 2. Removal efficiency of bromide in different water samples (raw water + 0.2 mg/L Br⁻, deionized water + 0.2 mg/L Br⁻, deionized water + 6 mg/L humic acid + 0.2 mg/L Br⁻, Al: 7–15 mg/L, pH: 6–8).

anions coexisted with bromide. 0.2 mg/L bromide was added in the raw water due to the low concentration of bromide, meanwhile, 0.2 mg/L bromide and/or 6 mg/L humic acid were added to deionized water under the same the coagulation conditions to compare the removal efficiency of bromide in different water samples and the results were shown in Fig. 2. In Fig. 2, 62.1–87.0% bromide was removed with 7–15 mg/L coagulant at pH 6 in raw water. This demonstrated that bromide in raw water could be reduced effectively by enhanced coagulation. Meanwhile, it was observed that coagulant dosage and pH have more significant effects on bromide efficiency in raw water than in deionized water. 43.5–87.0% bromide was removed in raw water with 7–15 mg/L coagulant at pH 6–8, in contrast to the corresponding value of 80.8–99.2% in deionized water. The lower removal efficiency in raw water implied that some factors, e.g., humic acid, coexisting anions, would have effects on bromide removal. First, the effects of humic acid on bromide was investigated with adding 6 mg/L humic acid in deionized water. The removal efficiency was 78.1–98.4% in the presence of 6 mg/L humic acid in contrast to the corresponding value of 80.8–99.2% in the absence of humic acid in deionized water with 7–15 mg/L coagulant at pH 6–8. It suggested that humic acid had minor influence on bromide removal with high coagulant dosage. Furthermore, the removal of humic acid in deionized water and in raw water under the same condition as removal of bromide was also studied and the results were illustrated in Fig. 3. It was noted that the removal efficiency of humic acid was 92.3% in raw water and was 97.0% in deionized water with 15 mg/L coagulant at pH 6 in the presence of 0.2 mg/L bromide. This result demonstrated that humic acid was reduced in great part simultaneously in removing bromide.

Since the removal efficiency of bromide was obviously lower in raw water than that in deionized water and humic acid was proved to have minor influence with high coagulant dosage, thus, coexisting anions in raw water would have major influence on the removal of bromide.



1. Raw water + 0.2 mg/L Br⁻
2. Deionized water + 6 mg/L Humic acid + 0.2 mg/L Br⁻

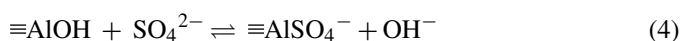
Fig. 3. Removal efficiency of humic acid in different water samples (raw water + 0.2 mg/L Br⁻, deionized water + 6 mg/L humic acid + 0.2 mg/L Br⁻, Al: 7–15 mg/L, pH: 6–8).

3.3. Effects of anions on removal efficiency of bromide

It was reported that anions had influence on the coagulant process [25,26]. For there are large amount of anions coexisting with Br⁻, hence, the effects of anions on removal of bromide were studied. The conventional anions in raw water, HCO₃⁻, SO₄²⁻, Cl⁻, NO₃⁻, H₂PO₄⁻ and F⁻ were selected in experiments. According to the possible concentration range of anions in surface water, HCO₃⁻, SO₄²⁻, Cl⁻ with the concentration of 0–250 mg/L, NO₃⁻ with the concentration of 0–10 mg/L, H₂PO₄⁻ with the concentration of 0–0.4 mg/L and F⁻ with the concentration of 0–1.5 mg/L were added in deionized water, respectively.

First, the effects of anions with different concentration were tested at pH 7.0 and the results were depicted on Fig. 4. It was noted that the removal efficiency of bromide decreased with the addition of HCO₃⁻, SO₄²⁻, Cl⁻ and NO₃⁻ and the decreasing trend became gently when concentration of these ions gradually increased. The removal efficiency of bromide declined from 94.5 to 83.8, 74.5, 80.7, 87.0% with the addition of 250 mg/L HCO₃⁻, SO₄²⁻, Cl⁻ and 10 mg/L NO₃⁻, being reduced by 11.5, 21.2, 14.6, 8.0%, respectively. However, for H₂PO₄⁻, the influence was more significant. The removal efficiency was reduced sharply to 55.9%, decreasing 40.8% in contrast to the value of 94.5% when 0.4 mg/L H₂PO₄⁻ was added in deionized water. Being compared to the above anions, F⁻ had minor influence and the efficiency kept at 94.5–96.5% with 0–1.5 mg/L F⁻.

It was reported that the tendency of an anion to alter the behavior of hydrolyzed metal coagulants was related to its electronegativity and its tendency to react with the metal ion or positively charged sites on the metal hydroxide precipitate. Hohl et al. [29] had considered that there existed neutral $\equiv\text{Al}_2\text{SO}_4$ and electronegative $\equiv\text{AlSO}_4^-$ when SO₄²⁻ existed in solution according to the following Eqs.:



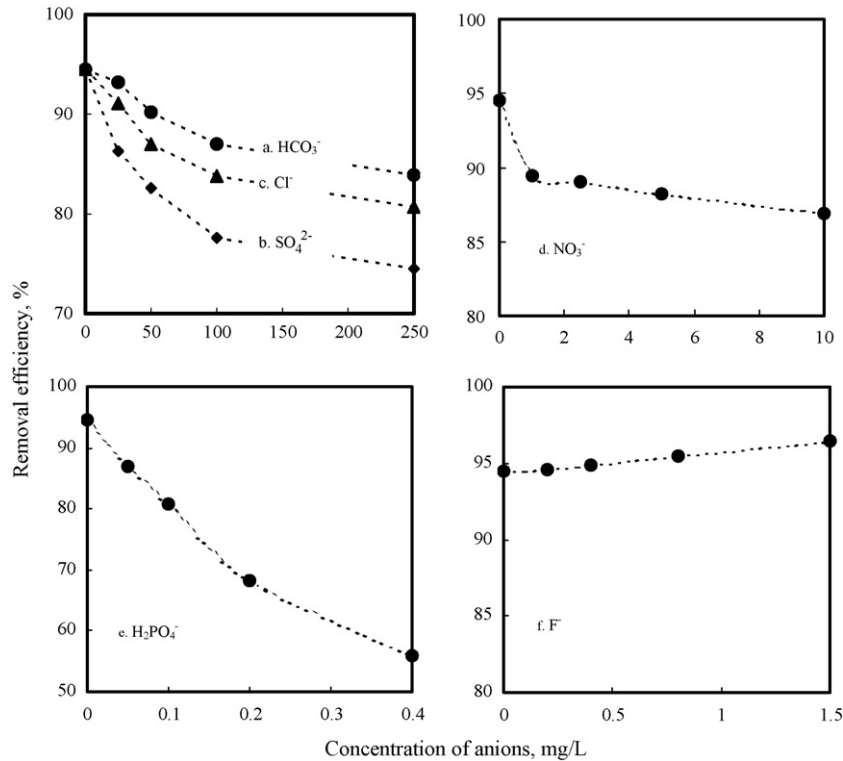


Fig. 4. Effects of anions with different concentration on removal efficiency of bromide (Br⁻: 0.2 mg/L, Al: 15 mg/L, pH: 7, a: HCO₃⁻, b: SO₄²⁻, c: Cl⁻, d: NO₃⁻, e: H₂PO₄⁻, f: F⁻).



Thus, the concentration of Al(OH)₂²⁺ and Al(OH)₂⁺ were reduced. Apparently, more aluminum was required for removal of Br⁻ when the adsorption of sulfate reduced the positive charge of the aluminum hydrolysis products. Other anions, e.g., Cl⁻, NO₃⁻, had affinities with Al(III) and the affinities of these anions with Al(III) was reported to be SO₄²⁻ > Cl⁻ > NO₃⁻ [26]. HCO₃⁻ in solution would accelerate the formation of gel-precipitation Al(OH)₃(am) and thus the opportunity for Br⁻ in combination with Al(OH)₂⁺ and Al(OH)₂²⁺ was minimized [30]. As for H₂PO₄⁻, in the neutral condition, it could bind with Al(III) and thus generated electronegative Al(OH)₂HPO₄⁻, Al(OH)₂⁺HPO₄²⁻ and neutral Al(OH)₂H₂PO₄ and Al(OH)HPO₄ according to Eqs. (6)–(9) [31]:



Due to the strong complexation with Al(III), H₂PO₄⁻ significantly reduced the bromide removal. F⁻ would bind with Al(III) with the similar pathway as Br⁻ did, according to the results in the experiment, it would be known that the combination of Al–F was weaker than that of Al–Br.

Further more, the effects of anions at different pH on the removal efficiency were tested and results were illustrated on

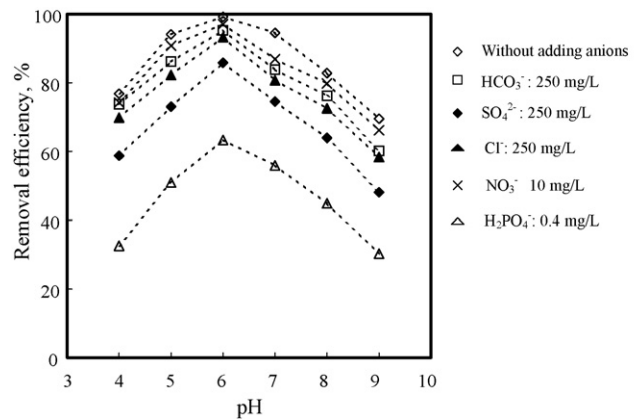


Fig. 5. Effects of anions at different pH on the removal efficiency of bromide (Br⁻: 0.2 mg/L, Al: 15 mg/L, HCO₃⁻, SO₄²⁻, Cl⁻: 250 mg/L, NO₃⁻: 10 mg/L, H₂PO₄⁻: 0.4 mg/L, pH: 4–9).

Fig. 5. It was observed that the peak value occurred at pH 6 with adding anions, which was similar to the results without adding anions. The peak value of removal efficiency was 95.3, 85.8, 93.2, 97.1 and 63.3% with addition of HCO₃⁻, SO₄²⁻, Cl⁻, NO₃⁻ and H₂PO₄⁻, respectively, in contrast to the corresponding value of 99.2% in deionized water without these anions.

4. Conclusions

The results in this study showed that bromide was removed of 62.1–87.0% in raw water through the combination of Br⁻

with Al(III) in various pathways. Coexisting anions had significant effects on the removal of bromide. The removal efficiency of bromide decreased by 11.5, 21.2, 14.6, 8.0 and 40.8% with the addition of HCO_3^- , SO_4^{2-} , Cl^- , NO_3^- and H_2PO_4^- , respectively. These results demonstrated that bromo-DBPs in drinking water could be controlled though removing bromide by enhanced coagulation.

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