Removal of bromide by aluminium chloride coagulant in the presence of humic acid

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Abstract

Bromide can form disinfection by-products (DBPs) in drinking water disinfection process, which have adverse effects on human health. Using aluminium chloride as a model coagulant, removal of bromide by coagulation was investigated in the absence or presence of humic acid (HA) in synthetic water and then was conducted in raw water. Results demonstrated that in synthetic water, 93.3–99.2% removal efficiency of bromide was achieved in the absence of HA with 3–15 mg/L coagulant, while 78.4–98.4% removal efficiency of bromide was obtained in the presence of HA with the same coagulant dosage and 86.8–98.8% HA was removed simultaneously. Bromide in raw water was removed 87.0% with 15 mg/L coagulant. HA apparently reduced the removal of bromide with low coagulant dosage or at high pH, while minor influence on removal of bromide was observed with high coagulant dosage or at low pH. Thus, bromide could be reduced effectively by enhanced coagulation in drinking water treatment.
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Keywords: Bromide; Removal; Coagulation; Humic acid; Drinking water

1. Introduction

Bromide is naturally present in raw water, especially in groundwater and surface water in coastal region. With rapid growth of industrial activities, brine runoff from oil field and use of methyl bromide for pest control, more bromide is discharged to environment [1,2]. 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 [3,4].

It is well known that disinfectors have been used to kill pathogen in drinking water treatment. However, an obvious drawback of disinfection is the formation of disinfection by-products (DBPs) [5,6]. Although bromide is generally considered non-toxic at concentrations found in most drinking water sources, it reacts with a variety of commonly used disinfectants, most notably ozone, chlorine and chloramine, to produce bromo-DBPs. For examples, bromide can be oxidized by ozone and generate bromate, which are highly toxic for human health. According to the standard of WHO, 25 µg/L

is the maximum concentration of bromide permitted in drinking water [7]. Chlorine or chloramine can rapidly oxidize bromide to hypobromous acid and thus yield mixed bromo- or bromochloro-trihalomethanes (THMs) and haloacetic acids (HAAs) by reacting with natural organic matter (NOM) [8–10]. US EPA limited the maximal concentration lever of THMs and HAAs in disinfectant/disinfection by-products rule (D/DBP) I with the value of 80 and 60 µg/L, respectively [11]. Bromo- or bromochloro-THMs and HAAs are generally considered more carcinogenic than their chlorinated analogues [4,8,9]. Accordingly, bromide, as a crucial precursor forming bromo-DBPs, should be removed before disinfection during drinking water treatment.

Large quantities of investigations focused on using biologically active carbon filtration and granular activated carbon adsorption to control bromate after ozone disinfection [12,13]. Meanwhile, nanofiltration, hyperfiltration and reverse osmosis were tested on removing bromide or bromate [14,15]. Recently, some new methods were studied to reduce bromide directly. Ag-doped activated carbon aerogels was examined for bromide and iodide removal in drinking water and was tested how the activation of Ag-doped aerogels affected their behaviors [16]. Electrochemical removal was presented as a promising new

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water treatment process that lowered the concentration of bromide, for bromide could be oxidized by electrolysis to bromine and then the bromine apparently volatilized with carbon dioxide [7,17]. These methods are demonstrated to be effective in reducing bromide.

Except methods mentioned above, in practical drinking water treatment, coagulation is an important unit process. 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 NOM [18]. Researchers have extensively investigated removal efficiency and mechanism of NOM in coagulation [19–21]. Furthermore, some inorganic compounds, such as phosphate, fluoride, soluble silica, were found that could associate 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 sulfate and estimated that by charge neutralization in low pH or by adsorption on the surface of $Al(OH)_3$ in high pH, more than 90% of phosphate was removed in the presence of HA. Based on these results, it is presumed that bromide would also be reduced through similar mechanism in conventional coagulation. In raw water, humic acid (HA), a typical NOM, is present to various degrees with the concentration range of 1–12 mg/L, constituting the major component of TOC concentration in most waters [25,26]. Hence, the effects of HA on coagulation of bromide should not be ignored. Though some methods were studied to control bromide, the removal of bromide by coagulation and the effects of HA on this process were limited and not investigated in detail.

This paper selected aluminium chloride as a model coagulant and studied the behaviour of bromide in coagulation. The objectives of this paper were to (1) test bromide removal efficiency in synthetic water and in raw water, (2) to investigate the effects of HA on the removal of bromide, and (3) to present a coagulation mechanism of bromide in the presence of HA consistent with the experimental data.

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 deioned water. 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 $AlCl_3·6H_2O$) was prepared with aluminium chloride hexahydrate (Shanghai Chemical Co., China, reagent grade) and then diluted to the target concentration with deioned 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 $4.60 ± 0.02$. Deioned water was obtained from Milli-Q pure water (Mill-Q SP VOC, Millipore Co., Bedford, MA).

2.2. Coagulation procedures

To synthetic water, the coagulation experiments were conducted by adding 0–2.0 mg/L bromide and 6 mg/L HA in deioned water. The pH of solution was adjusted to 4–9 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 Co.). To raw water (Taken from Xiangjiang River, main water source of Hunan Province, China), 0.2 mg/L bromide was added and pH was adjusted to 6–8 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 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 HA and bromide were 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 wavelength 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 analyzed 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.

TOC was analyzed by TOC-V_{CPH} (Shimdzu, Japan) and raw water was filtrated with 0.45 μm PTFE film before TOC analysis. The carbonate (mg/L, calculated as $CaCO_3$) of raw water was analyzed by acid and alkali titration.

3. Results and discussion

3.1. Removal of bromide in the absence of HA

To test behaviour of bromide in coagulation process, first, experiments were performed with synthetic water in the absence of HA with three different coagulant dosages at pH 4–9.

From Fig. 1a–c, it was observed that bromide removal was affected by coagulant dosage. Bromide removal efficiency improved with enhancing dosage, while this increase became minor when dosage was enhanced to a high value. For example, at pH 6.0, when the initial concentration of bromide was 2.0 mg/L, the removal efficiency changed from 22.3% to 30.4%,
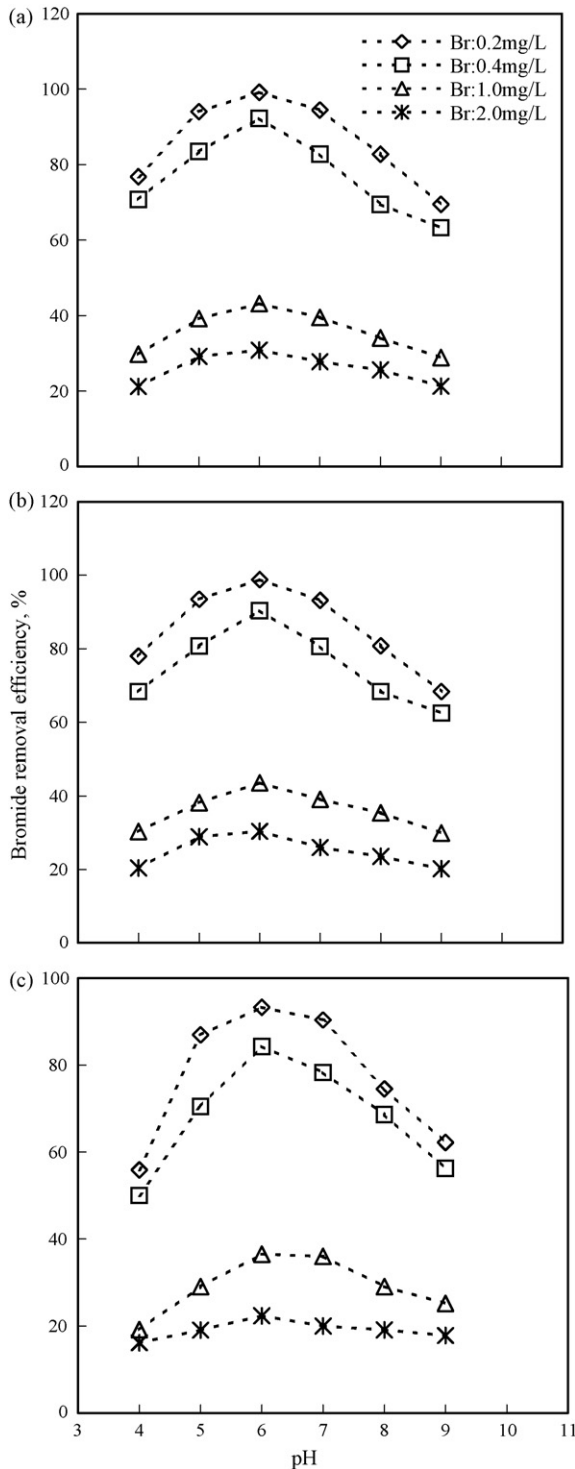
Fig. 1. Removal efficiency of bromide in the absence of HA (0.2–2.0 mg/L Br, (a) 15 mg/L Al; (b) 7 mg/L Al; (c) 3 mg/L Al).

ciency increased from 30.9% to 99.2% at dosage 15 mg/L, from 30.4% to 98.8% at dosage 7 mg/L, from 22.3% to 93.3% at dosage 3 mg/L, respectively. This implied that in coagulation process, low concentration bromide was easier to be removed.

Fig. 1 also showed that bromide removal efficiency was affected by pH. The removal efficiency reduced when pH is too high or too low. The peak value occurred at pH 6 with three different dosages. Whereas, the effects of pH on removal efficiency were minor when initial concentration of bromide improved to 1.0–2.0 mg/L.

3.2. Removal of bromide in the presence of HA

Then, 6 mg/L HA was added in synthetic water and other experimental conditions were in accord with those in 3.1. It was found that HA significantly reduced bromide removal efficiency when coagulant dosage was low or pH was high, while minor effects on bromide removal efficiency was observed with high coagulant dosage or at low pH.

As shown in Fig. 2a, when dosage was 15 mg/L, with bromide initial concentration 0.2 mg/L and pH 6, the removal efficiency of bromide was 98.4% with HA, in contrast to 99.2% without HA in Fig. 1a, declined just 0.8% in the presence of HA. However, when decreasing coagulant dosage to 3 mg/L, the removal efficiency of bromide was 73.2% with HA in Fig. 2c, but was as high as 93.3% in the absence of HA in Fig. 1c, reducing 20.1% due to the presence of HA.

Meanwhile, with enhancing pH, bromide removal efficiency declined in the presence of HA in contrast to that in the absence of HA, and the effects of improving pH on removal efficiency were more significant with low coagulant dosage than with high coagulant dosage. When bromide initial concentration was 0.2 mg/L, the removal efficiency had minor change at pH 4–8 in Fig. 2b contrasting to the corresponding data in Fig. 1b, however, the removal efficiency decreased to 44.2% in Fig. 2b and the corresponding value was 68.3% in Fig. 1b at pH 9; While in Fig. 2c, when dosage decreasing to 3 mg/L, improving pH to 6–9, the removal efficiency declined sharply to 73.2–29.5% in contrast to the corresponding results 93.3–62.2% in Fig. 1c.

3.3. Effect of bromide on removal of HA

The removal efficiency of HA was investigated simultaneously under the same conditions with Section 3.2 and the results were depicted in Fig. 3.

From Fig. 3a–c, it was illustrated that bromide slightly reduced the removal of HA at high pH or with low dosage. For example, in Fig. 3a, the removal efficiency of HA varied little at pH 4–7 when adding bromide to the solution. Whereas, the removal efficiency of HA declined from 88.6% to 75.1% at pH 8 and declined from 43.1% to 30.8% at pH 9 with dosage 15 mg/L. In Fig. 3c, when the dosage decreased to 3 mg/L, the removal efficiency changed from 90.1% to 80.6% at pH 4 and from 87.6% to 78.7% at pH 5 due to the presence of bromide.

However, coagulant dosage and pH significantly affected the removal efficiency of HA. When there is 0.2 mg/L bromide in the solution, the removal efficiency kept at 76.7–86.8% at pH 4–6
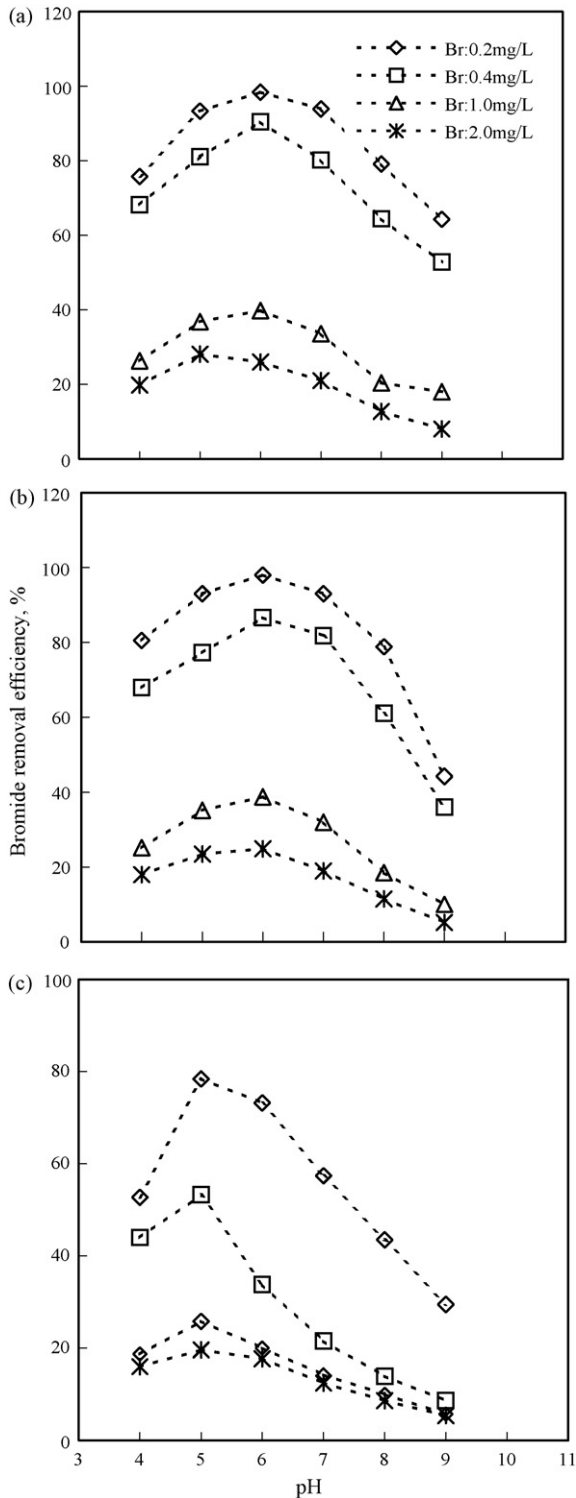
increasing 8.1% due to enhancing dosage from 3 to 7 mg/L, while just increasing to 30.9% with dosage 15 mg/L.

Meanwhile, bromide removal efficiency was high related with its initial concentration. Under a given dosage, the removal efficiency of bromide increased gradually with decreasing bromide initial concentration. In Fig. 1, as decreasing the initial concentration of bromide from 2.0 to 0.2 mg/L at pH 6, the effi-

Fig. 2. Removal efficiency of bromide in the presence of HA (0.2–2.0 mg/L Br, 6 mg/L HA, (a) 15 mg/L Al; (b) 7 mg/L Al; (c) 3 mg/L Al).

Fig. 3. Effect of bromide on HA removal efficiency (6 mg/L HA, 0–2.0 mg/L Br, (a) 15 mg/L Al; (b) 7 mg/L Al; (c) 3 mg/L Al).

and notably decreased to 8.7% at pH 7 when dosage was 3 mg/L. Improving coagulant dosage to 7 mg/L, the removal efficiency kept 80.3–98.2% in the pH range 4–8 and decreased to 18.6% at pH 9. Therefore, the effective pH range of HA removal could be enlarged with enhancing aluminium chloride dosage, which was in according with results by Cheng et al. [27] in studying
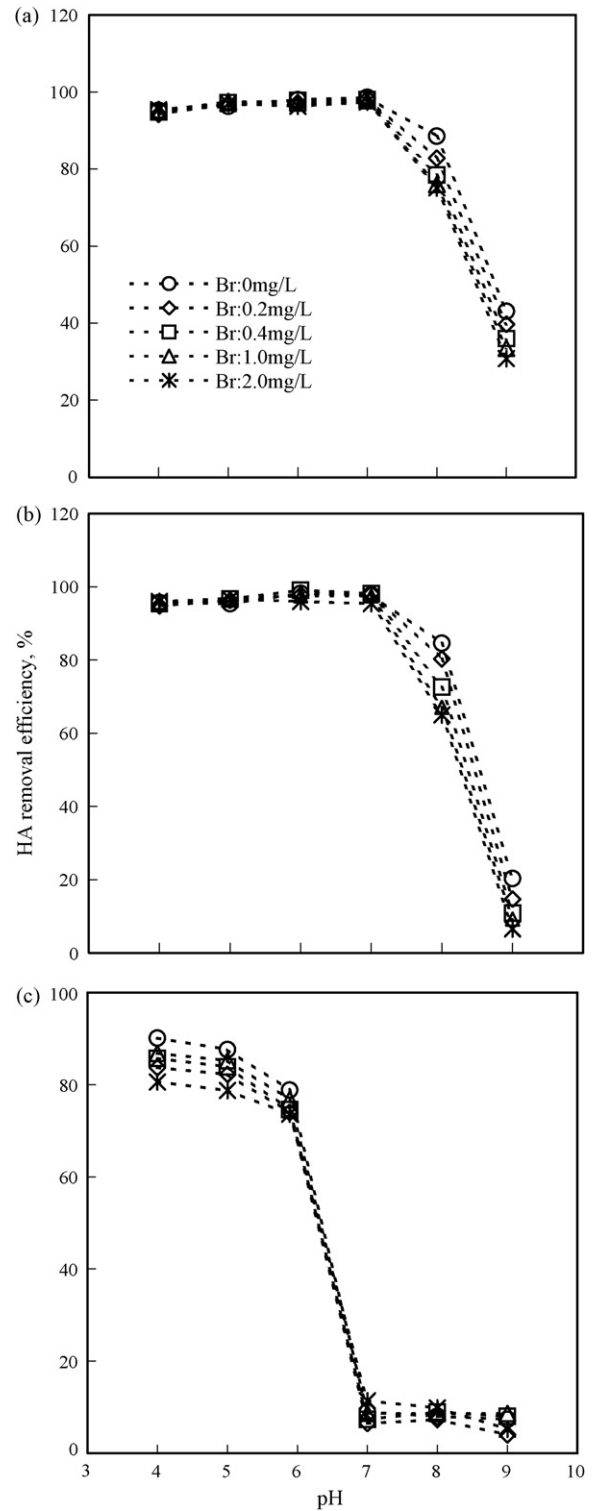
the coagulation mechanism of polyferric sulfate reacting with humic acid.

3.4. Removal of bromide in raw water

Further experiments were conducted with raw water to examine bromide removal in practical water treatment. The chemical
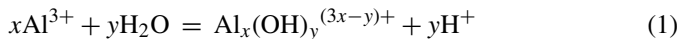
Table 1
Chemical properties of raw water

	Raw water
pH	6.64
Br^- (mg/L)	0.02
Carbonate (mg/L)	201.12
Humic acid (mg/L)	5.93
TOC (mg/L)	3.46

Table 3
Hydrolysis reaction of Al(III) in coagulation

Reaction equation	$\log K$
$Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+$	−4.97
$Al^{3+} + 2H_2O \rightleftharpoons Al(OH)_2{}^+ + 2H^+$	−9.30
$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3 (aq)^a + 3H^+$	−15.0
$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3 (am)^b + 3H^+$	−33.0
$Al^{3+} + 4H_2O \rightleftharpoons Al(OH)_4{}^- + 4H^+$	−23.0

[a] aq, aqueous.
[b] am, amorphous.

properties of raw water tested in the experiment were illustrated in Table 1. Since bromide concentration was very low, 0.2 mg/L bromide were added and the coagulation results were shown in Table 2. It was observed that the removal efficiency of bromide was higher related to coagulant dosage and pH in raw water than in synthetic water. Enhancing dosage or reducing pH improved removal efficiency significantly. 87.0% bromide was rejected with 15 mg/L coagulant at pH 6. This value was lower than the corresponding results in Fig. 1a (99.2%) and Fig. 2a (98.4%) when treating synthetic water under the same conditions. It suggested that bromide in raw water could be reduced effectively by enhanced coagulation. Meanwhile, in nature water, except the influence of HA, other factors, e.g., coexisted anions, would also affect the coagulation efficiency of bromide.

3.5. Removal mechanism of bromide with Al(III) coagulant in the presence of HA

When aluminium chloride was added in aqueous solution, hydrolysis reactions occurred and formed various hydrolysis products. The hydrolysis reaction of Al(III) can be depicted as Eq. (1):

$$xAl^{3+} + yH_2O = Al_x(OH)_y^{(3x-y)+} + yH^+ \qquad (1)$$

To clearly illustrate 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 3. Though the hydrolysis process was complex, it was generally considered that Al^{3+} existed when pH < 4, $Al(OH)^{2+}$ and $Al(OH)_2{}^+$ existed when pH < 6. The main hydrolysis products were $Al(OH)_{3(am)}$ gel-precipitation in pH 6–8 and $Al(OH)_4{}^-$ when pH > 8 [28].

The removal mechanism of bromide was considered to be charge neutralization at low pH in coagulation. Plankey et al. [22] reported that halogen ion associated with Al(III) mainly by electrostatic affinity. Thus, this process would occur in three

Table 2
Removal efficiency of bromide in raw water

Coagulant dosage (mg/L)	pH	Type of water	Removal efficiency (%)
15	6	0.2 mg/L Br + raw water	87.0
	7	0.2 mg/L Br + raw water	74.5
	8	0.2 mg/L Br + raw water	62.1
7	6	0.2 mg/L Br + raw water	62.3
	7	0.2 mg/L Br + raw water	55.9
	8	0.2 mg/L Br + raw water	43.5

pathways described as Eqs. (2)–(4):

$$(H_2O)_6Al^{3+} + Br^- = (H_2O)_5Al(H_2O), Br^{2+}$$
$$(H_2O)_5Al(H_2O), Br^{2+} \rightleftharpoons (H_2O)_5AlBr^{2+} \qquad (2)$$

$$(H_2O)_5AlOH^{2+} + Br^- = (H_2O)_5AlOH, Br^+$$
$$(H_2O)_5AlOH, Br^+ \rightleftharpoons (H_2O)_4AlOHBr^+ \qquad (3)$$

$$(H_2O)_4Al(OH)_2{}^+ + Br^- = (H_2O)_4Al(OH)_2, Br$$
$$(H_2O)_4Al(OH)_2, Br \rightleftharpoons (H_2O)_3Al(OH)_2Br \qquad (4)$$

And then, when enhancing pH gradually, bromide would be adsorbed on the fresh surface of $Al(OH)_{3(am)}$ precipitates, which was similar with previous investigation that phosphate associated with aluminium species [23]. Since HBr is strong acid, the possible configuration of HBr in solution is Br^- in the pH range 4–9, consequently, the effect of pH on the removal efficiency of bromide in coagulation was minor in contrast to the removal efficiency of phosphate, which was significantly affected by pH in the similar process.

On the other hand, HA is an organic matter with high molecular weight and complex configuration. For there are a number of aromatic nuclei with functional groups in HA, e.g., –OH and –COOH, HA was easy to bind with Al(III) by complexation, and the complexes could be illustrated by Eq. (5) [21]:

$$(5)$$
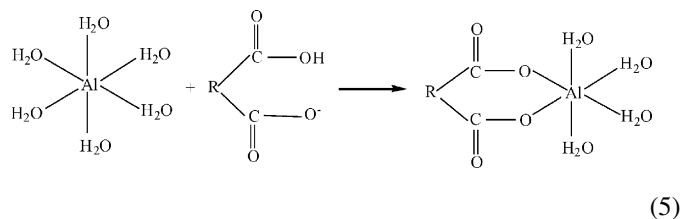
In the complexation process, pH is a crucial factor affecting the reaction. In acid condition, more HA was removed by Al(III) for the complexation process was accelerated. With increasing pH, the functional groups of HA, carboxylic and phenolic acids, were deprotonated, meanwhile, more $Al(OH)_{3(am)}$ and $Al(OH)_4{}^-$ was formed. HA^- was hard to be combined with negative-charged $Al(OH)_4{}^-$, thus, the removal efficiency declined sharply in alkaline condition [23].

Adding HA to solution, the removal efficiency of bromide reduced significantly when coagulant dosage was low or pH was high in coagulation process. These phenomena suggested that bromide and HA would compete for combination with aluminium species. In the pH range of 4–6, Br^- and HA combined

Al(III) by charge neutralization and complexation. For the negatively nature of Br^- and the difficulty of proton dissociating from HA in acidic media, the effect of HA was not obviously in combination with positively charged aluminium species. With improving pH to 6–8, more $Al(OH)_{3(am)}$ formed. HA is an large organic matter, which is easy to be adsorbed on the surface of $Al(OH)_{3(am)}$. Since the adsorption of HA was stronger than that of Br^-, HA might reduce the opportunity for bromide to contact with $Al(OH)_{3(am)}$. These results was analogical with previous study, which reported that HA and phosphate ions are competitively adsorbed onto the flocs of $Al(OH)_{3(am)}$ at high pH [23]. When pH enhanced to 9, $Al(OH)_4^-$ and negatively charge HA^- repelled each other, Br^- was hard to be removed by precipitation and filtration.

4. Conclusions

Bromide in source water forms adverse bromo-DBPs in water disinfection. Using aluminium chloride as model coagulant, it was found that bromide could be reduced by coagulation and HA had influence on this process. 93.3–99.2% removal efficiency of bromide was achieved in the absence of HA with 3–15 mg/L coagulant, and 78.4–98.4% removal efficiency of bromide was obtained in the presence of HA. Meanwhile, bromide in raw water was removed 87.0% with 15 mg/L coagulant. HA apparently reduced the removal of bromide with low coagulant dosage or at high pH, while minor effects on removal of bromide was observed with high coagulant dosage or at low pH. Thus, through enhanced coagulation, bromide in drinking water could be reduced effectively.

Acknowledgements

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