Effects of fulvic acid and humic acid on aluminum speciation in drinking water

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Abstract

This article focused on the influences of fulvic acid and humic acid on aluminum speciation in drinking water. Factors including the concentration of residual chlorine and pH value had been concerned. Aluminum species investigated in the experiments included inorganic mononuclear, organic mononuclear, mononuclear, polymer, soluble, and suspended forms. It was found that the effects of fulvic acid and humic acid on aluminum speciation depended mainly on their molecular weight. Fulvic acid with molecular weight less than 5000 Dalton had little influence on aluminum speciation; while fulvic acid with molecular weight larger than 5000 Dalton and humic acid would increase the concentration of soluble aluminum significantly even at concentration below 0.5 mg/L (calculated as TOC). Aluminum species, in the present of fulvic acid with molecular weight larger than 5000 Dalton and humic acid, were more stable than that in the present of fluvic acid with molecular mass less than 5000 Dalton, and varied little with reaction time. Within pH range 6.5–7.5, soluble aluminum increased notably in water with organic matter. As the concentration of residual chlorine increased, the effects of fulvic acid and humic acid became weak. The reactions between humic acid, fulvic acid with large molecular weight, and aluminum were considered to be a multi-dentate coordination process. With the consideration of aluminum bioavailability, reducing the concentration of fulvic acid and humic acid and keeping the pH value among 6.5–7.5 were recommended during drinking water treatment.

Key words: aluminum species; drinking water; fluorometric method; fulvic acid; humic acid

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Introduction

The high frequency occurrence of acid rain and the over-loaded agriculture in recent years have resulted in worldwide acidized soil and more and more aluminum immersing into natural water that increase the level of aluminum in drinking water. Meanwhile, aluminum salts are widely used as coagulants in drinking water treatment process. Although they are effective in removing turbidity, Al-based coagulants, especially alum, may result in high concentration of aluminum in treated water. Letterman and Driscoll (1988) reported that approximately 11.0% of the aluminum input remained in the treated water as residual aluminum. Surveys of residual aluminum in China (Cui et al., 2002), the United States (Miller et al., 1984; Letterman and Driscoll, 1988), and Europe (Sollars et al., 1989) also showed similar result. It was reported that aluminum salts, used in coagulation process, could increase residual aluminum concentration notably (Kriewall et al., 1996; Van Alstyne et al., 2007).

Aluminum in drinking water mainly existed in soluble form, which might be highly cytotoxic to plant (Szatanik-

Kloc and Jozefaciuk, 2007) and animal, as it could be assimilated directly. Meanwhile, different forms of soluble aluminum also presented different toxicities. Al^{3+} was known to be severely neurotoxic (Glynn et al., 1995; Berthon, 2002), leading to dementia, osteomalacia, and ultimately death when the natural protection of the intestinal and blood-brain barriers was bypassed (Dave and Syal, 2002; Colomina and Roig, 2005; Gillette-Guyonnet et al., 2007). Thus, it was also considered to be associated with the formation of neurofibrillary tangles (Walton, 2007) and senile plaques in brain. While, when Al^{3+} combined with other ligands, especially organic matters its bio-availability decreased significantly. The existence of organic matters, such as fulvic acid (FA) and humic acid (HA), could both decrease the coagulation effect and increase the concentration of residual aluminum (Jelel, 1986; Browne and Discoll, 1993; Weng et al., 2002). Therefore, evaluation on the influence of aluminum in water distribution or human health should concern to certain aluminum species.

Organic matters, such as hydroxamate siderophores, sugar acids, phenols, FA and HA, were mainly produced by living organisms or formed by secondary synthesis reactions (Desroches and Dayde, 2000; Liu et al.,

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2007). However, FA and HA were complex organic substances that had defied complete characterization despite of extensive study. Their reactive characters could be explained by a series of oxygen-containing functional groups, including carboxyl, phenolic-OH, enolic, alcoholic-OH, and carbonyl. Therefore, FA and HA could react with aluminum by the formation of stable complexes. Moreover, the existence of FA and HA in natural water or drinking water would affect aluminum speciation. The disinfection process would also destroy the structure of organic matter and thus change their binding capacities with aluminum species, which attracted little attention (Hoff, 1978; Sadiq and Rodriguez, 2004; Singer, 2006; Sadiq et al., 2007).

The treatment style of the most universal drinking water is base on the coagulation-sediment-filtration-disinfection model which is effective in colloidal and suspended matter removal; while, it is difficult to remove most of the dissolved matters, such as soluble FA and HA. The present of FA and HA both in water treatment and water distribution processes would change aluminum speciation and its solubility in drinking water. Basing on the common species and quantity of dissolvable organic matters in natural water, this study utilized the liquid chlorine as disinfectant to investigate the effects of FA and HA on the speciation of aluminum before and after disinfection.

1 Materials and methods

Laboratory jar tests were carried out to study the effects of FA and HA on aluminum speciation applying polyaluminium chloride (PAC) synthetic water over a period of 4 to 7 days. The reaction time selected was consistent with the general drinking water retention time in water distribution system. The concentration of total aluminum (Tol-Al) was controlled at 0.20 mg/L according to the Standards for Drinking Water Quality of China (GB 5749-2006). The values of each factor were selected basing on the water quality standards and their typical concentration in drinking water, as shown in Table 1.

In the experiment, ultrafiltration membrane with 5000 Dalton molecular weight cutoff was applied to separate FA into two parts: one part with molecular weight less than 5000 Dalton (FA < 5000) and the other with molecular weight larger than 5000 Dalton (FA ⩾ 5000). Humic

acid was dissolved in basic condition, and filtrated with a 0.45-μm microfiltration membrane to remove the insoluble matter. After preparation, FA and HA storage solution were stored in polyethylene bottles at 4°C. Synthetic waters were prepared according to the values shown in Table 1. The reaction bottles were airproofed and stirred by magnetic stirrers. Reagent grade chemicals were used except noted. A 0.10 mol/L of NaOH and 0.10 mg/L of HNO$_3$ were used to adjust solution pH.

Aluminum species including mononuclear aluminum (Mon-Al), soluble aluminum (Sol-Al), and Tol-Al were measured using the 8-Hydroxyquinoline (8-HQ) fluorometric method; and inorganic mononuclear aluminum (IM-Al) was measured using Eriochrome blue black R (EBBR) fluorometric method (Lian et al., 2004). The concentrations of organic mononuclear aluminum (OM-Al), polymer aluminum (Pol-Al), and suspended aluminum (Sus-Al) could be obtained by following Eqs. (1)–(3):

$$C_{\text{Sus-Al}} = C_{\text{Tol-Al}} - C_{\text{Sol-Al}} \qquad (1)$$
$$C_{\text{Pol-Al}} = C_{\text{Sol-Al}} - C_{\text{Mon-Al}} \qquad (2)$$
$$C_{\text{OM-Al}} = C_{\text{Mon-Al}} - C_{\text{IM-Al}} \qquad (3)$$

The minimum detection limits for 8-HQ fluorometric method and EBBR fluorometric method were 0.010 mg/L and 0.001 mg/L, respectively, where accuracies (% recovery) were 92.3%–105.6% and 91.7%–106.1%, the precisions (relative standard deviation, $n = 6$) were 0.68% and 1.8%, and their linearity ranges were 0.027–0.270 mg/L and 0.003–0.270 mg/L, respectively. Aluminum species were identified by a spectrofluorometer (Model F-2500, Hitachi High-Technologies Corporation, Japan). The total organic carbon (TOC) was measured by a TOC determinator (TOC-Vwp, Shimazu Company, Japan), and residual chlorine was determined by a residual chlorine determinator (Model AQ2070, Thermo Electron Corporation, USA).

2 Results and discussion

2.1 Effects of FA and HA concentration on aluminum speciation

In solution with FA < 5000, aluminum speciation varied little with the content of organic acid increasing (Fig. 1a). When the concentration of organic acid increased from 0 to

Table 1 Water quality factors used in the experiments

Experimental condition				Levels of each variation factor					
Organic matter	pH	Water temperature (°C)	TOC (mg/L)	1	2	3	4	5	6
				TOC (mg/L)					
FA < 5000 Da	7.5	20.0	Variable	0.0	0.5	1.0	3.0	5.0	10.0
FA ⩾ 5000 Da	7.5	20.0	Variable	0.0	0.5	1.0	3.0	5.0	10.0
HA	7.5	20.0	Variable	0.0	0.5	1.0	3.0	5.0	10.0
				pH					
FA < 5000 Da	Variable	20.0	3.0	6.5	7.0	7.5	8.0	8.5	9.0
FA ⩾ 5000 Da	Variable	20.0	3.0	6.5	7.0	7.5	8.0	8.5	9.0
HA	Variable	20.0	3.0	6.5	7.0	7.5	8.0	8.5	9.0
				Residual chlorine (mg/L)					
FA ⩾ 5000 Da	7.5	20.0	3.0	0.0	0.05	0.3	0.8	1.6	4.0
HA	7.5	20.0	3.0	0.0	0.05	0.3	0.8	1.6	4.0

10 mg/L, the concentration of Sol-Al increased from 0.120 to 0.143 mg/L. Meanwhile, the concentration of OM-Al increased to 0.032 mg/L, occupying 16.5% of the Tol-Al, indicating that the increment of Sol-Al mainly contributed by the OM-Al formed in reaction between FA < 5000 and aluminum. It was also shown that the binding ability between FA < 5000 and aluminum was weaker than that between analytical reagent (8-HQ) and aluminum.

In the presence of FA $\geqslant$ 5000, the Sol-Al in solution increased quickly (Fig. 1b). When the concentration of FA exceed 1.0 mg/L, Sol-Al concentration increased rapidly from 0.11 to 0.20 mg/L, accounting for more than 90% of Tol-Al. Meanwhile, the concentration of Pol-Al also increased obviously. It was due to the strong binding ability between FA $\geqslant$ 5000 and aluminum. The increment of Pol-Al represented the aluminum that was combined by FA $\geqslant$ 5000, which would be further explained in Section 2.4. As the concentration of FA $\geqslant$ 5000, the concentration of IM-Al varied little, at about 0.08 mg/L. The reason was that

part of them formed organic coordinated aluminum with free aluminum ion after the introduction of FA, leading to the increase of OM-Al and Sol-Al. Simultaneously, to equalize the concentration of IM-Al, the transformation reaction from Sus-Al to IM-Al was promoted. Consequently, the final concentration of IM-Al was stable under the experimental condition.

The effect of HA on the aluminum speciation was similar to that of FA $\geqslant$ 5000. HA had little effect on IM-Al; while the concentration of Pol-Al increased significantly as HA increased, which indicated that the organic matters, with large molecular mass, would promote its reaction with aluminum. Comparing Fig. 1b with Fig. 1c, it was found that when the concentration of organic acids was 1.0 mg/L, the effect of HA on the concentration of Sol-Al was less than that of FA $\geqslant$ 5000 under the same conditions. It might be due to that the main organic matters that reacted with free aluminum ion were middle molecular organic matters. While organic acids with significant small or significant large molecular mass had weak effect on speciation of aluminum. The standard of drinking water in China sets the limit of dissolved organic matters $\leqslant$ 5.0 mg/L (calculated by TOC). However, even at concentration below 0.5 mg/L, FA $\geqslant$ 5000 would still increase the concentration of Sol-Al significantly (Fig. 1b). Organic matters in drinking water were mainly small molecular acids after coagulation; large molecular acids such as FA $\geqslant$ 5000 and HA were little presented. Consequently, the effect of organic matter on aluminum speciation in drinking water would be much less than FA $\geqslant$ 5000 did under the experimental condition.

The effect of reaction time on aluminum speciation was also studied (Fig. 2). Aluminum speciation varied little with reaction time in solution with FA $\geqslant$ 5000 and HA acids, indicating that the reaction products between aluminum and organic matters were stable, and thus aluminum was difficult to be removed from drinking water in water treatment and distribution process.

As shown in Fig. 1, FA $\geqslant$ 5000 had significant effect on aluminum speciation in PAC synthetic water. When the concentration of FA $\geqslant$ 5000 was above 1.0 mg/L, Sol-Al concentration increased to above 0.2 mg/L. Contrast to OM-Al and Sol-Al, the concentration of IM-Al varied little with organic matter increasing. FA < 5000 and HA had little effect on aluminum speciation. Meanwhile, in solution with FA $\geqslant$ 5000 and HA, aluminum speciation was stable with little change during reaction time (Fig. 2). Organics would also transform part of aluminum into OM-Al. When source water contained large molecular weight organic matters, coagulation process would increase the solubility of aluminum in drinking water treatment plant, and lead to excess aluminum in drinking water. While, according to toxicology studies, organic compounded aluminum has the least toxicity and was harmless to human (Walton, 2007).

2.2 Effect of pH on aluminum speciation

Effect of pH on aluminum speciation was studied in solution with certain concentration of HA and FA (Fig. 3). The organic matter concentration was controlled at
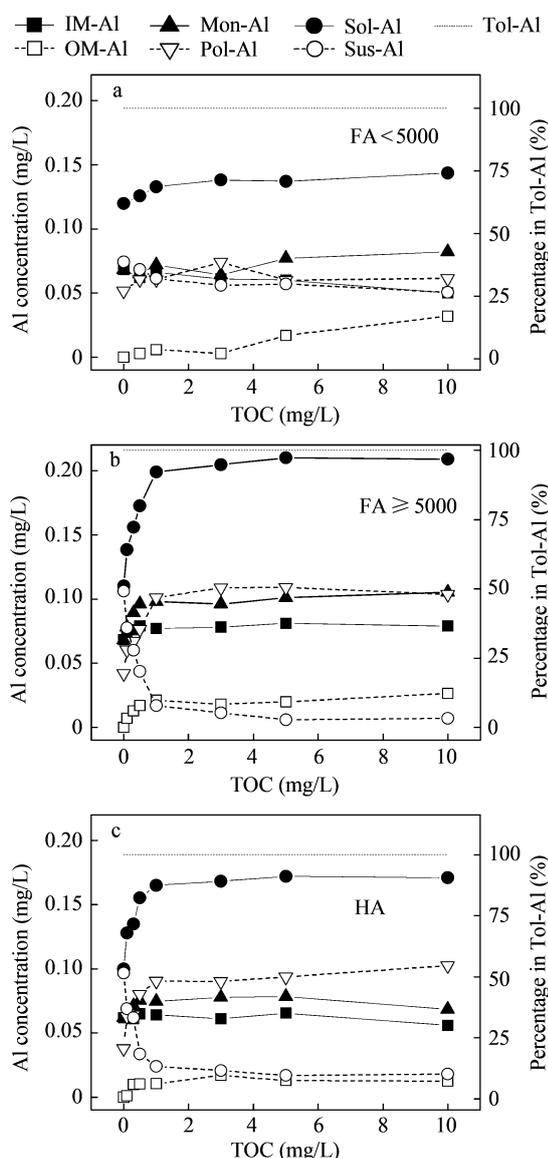

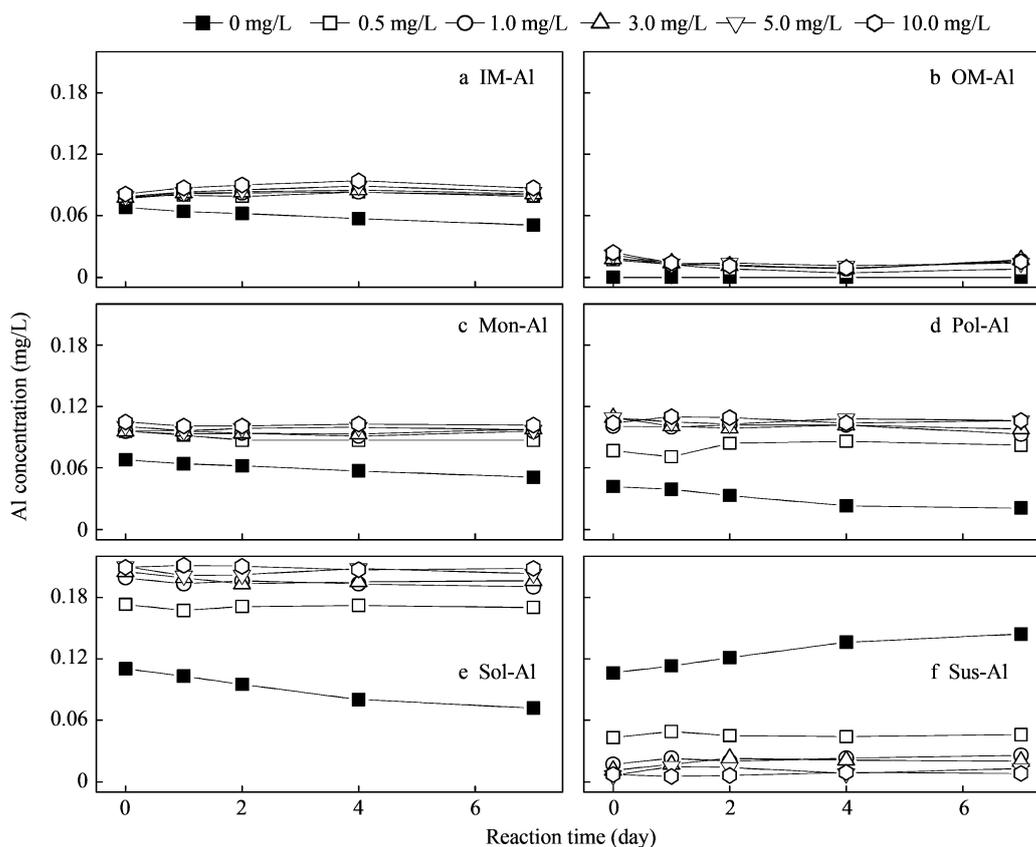**Fig. 1** Effects of FA and HA concentration on aluminum speciation at initial time (pH 7.5).

Fig. 2   Aluminum species variation with reaction time in solution with FA ⩾ 5000.

3.0 mg/L (calculated by TOC). The concentrations of IM-Al, Mol-Al, and Sol-Al were higher in solution with FA < 5000 than that in solution without organic matter, especially at pH below 8.0 (Fig. 3a, b). It was shown that FA < 5000 promoted aluminum dissolution in acidic conditions. While, in solution with FA ⩾ 5000, the concentrations of IM-Al and Mol-Al had little variation compared with the values in solution without organic matter, further indicating that FA ⩾ 5000 had little effect on IM-Al (Fig. 3c). The concentration of Sol-Al increased from 0.178 to 0.206 mg/L as solution pH increased from 6.5 to 9.0. Meanwhile, the concentration of Pol-Al at each pH value was obviously higher than that in the solution without organic matter, and was decreased as solution pH increase (Fig. 3c).

The effect of pH on aluminum speciation in solution with HA was similar to that in solution with FA ⩾ 5000. While in the presence of HA, the concentrations of IM-Al, Mon-Al, and Sol-Al were lower than that in solution with FA ⩾ 5000 under the same conditions. This might be due to the precipitation process, when aluminum complexed with HA. Consequently, the existence of HA and FA in PAC synthetic water would increase the concentration of Sol-Al notably, especially in neutral and acidic environment. The concentration of Sol-Al was high and varied little with solution pH. The effect of FA ⩾ 5000 and HA on aluminum speciation was much more prominent than FA < 5000, and their effects decreased with the increase of pH value.

In weak acidic and neutral environment, Al^{3+} could bind strongly with the negatively charged organic functional

groups. While in basic environment, Al^{3+} would combine with high concentration of OH^- by forming $Al(OH)_4^-$ which was stable thermodynamically. HA and FA were acidic electrolyte, which had competitive coordination functions at low pH. In the neutral environment, Al^{3+} could self-hydrolyze to form $Al(OH)_3(s)$ sedimentation. Therefore, basic environment was not favor to the reaction between organic matter and aluminum. Comparing with the aluminum speciation in solution without organic matter, it could be found that the existence of HA and FA would promote Sol-Al from minor to major species. High pH value would enhance the transformation from Pol-Al and OM-Al to IM-Al. This may explain why Pol-Al concentration decreased with increasing pH. Basing on the analysis before, for the factories adopting PAC as coagulating agent, the pH of raw water is need to be adjusted to 6.5–7.5 for good coagulation effect and low Sol-Al residual. However, in source water with large molecule mass organic acids, it was still possible for the existence of excess aluminum in treated water.

2.3 Effect of residual chlorine concentration on aluminum speciation

As shown in Fig. 4, residual chlorine had the most significant effect on Pol-Al. When the concentration of residual chlorine was 4.0 mg/L, both the concentrations of Pol-Al in synthetic water with FA ⩾ 5000 and HA decreased by 37%, indicating that residual chlorine could destroy organic structure and lead the transformation of OM-Al to IM-Al. Consequently, the addition of
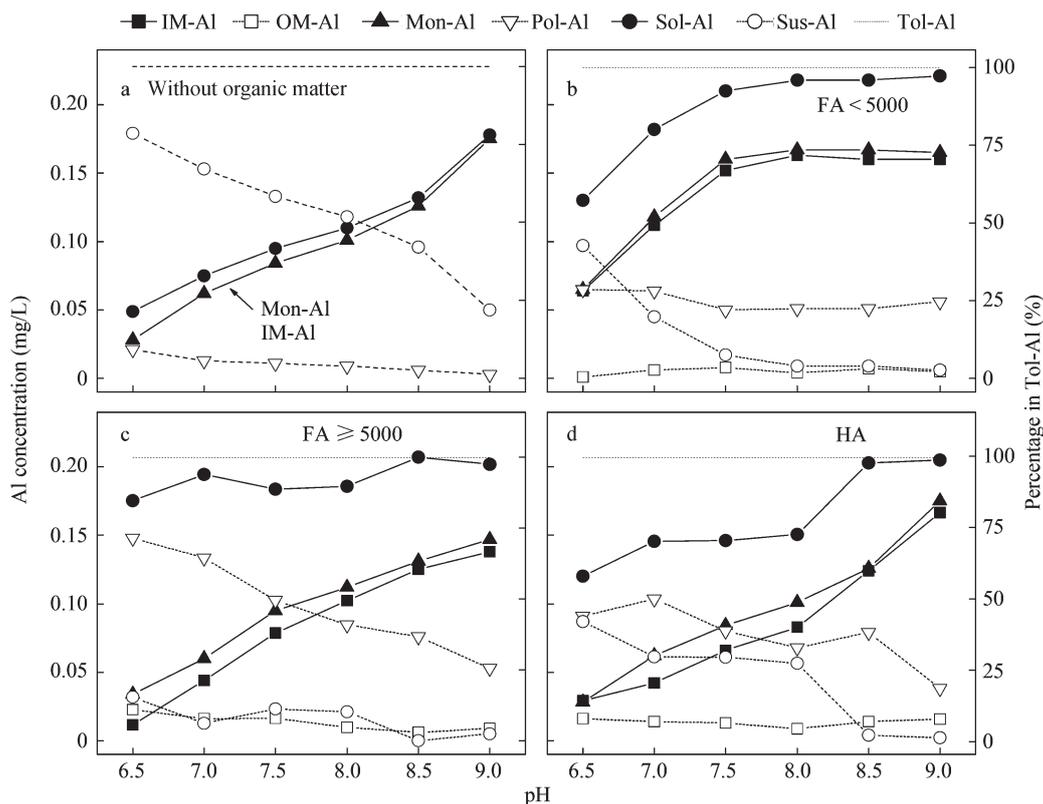
Fig. 3 Aluminum species variation with solution pH at initial time.

disinfectant would increase the concentration of Mon-Al and decrease the concentrations of Pol-Al and Sol-Al. When the concentration of residual chlorine increased from 0 to 4.0 mg/L, the concentration of Sol-Al decreased from 0.2 to 0.179 mg/L; and Pol-Al decreased from 0.12 to 0.075 mg/L in solution with FA $\geqslant$ 5000. In solution with HA, Sol-Al decreased from 0.193 to 0.179 mg/L; Pol-Al decreased from 0.115 to 0.054 mg/L. However, with the increase of residual chlorine, the concentration of IM-Al varied little. The concentration of OM-Al, formed between organic matter and aluminum by weak combination, increased slowly. Comparing the concentration of OM-Al in solution with FA $\geqslant$ 5000 and HA, it could be concluded that residual chlorine would affect aluminum speciation

indirectly by destroying the strong compounding structure formed between large molecular organic matters and aluminum.

Liquid chlorine would produce hypochlorous acid which is highly oxidative and can react with organic matters in disinfection process. The addition of disinfectant would increase the concentrations of OM-Al with weak compounding structure and IM-Al, and decrease the concentration of Sol-Al. Therefore, residual chlorine had strong damage to OM-Al with strong compounding structure, which altered the structure of OM-Al or broke it down to IM-Al. The increase of IM-Al would promote the formation of $Al(OH)_3$(s), leading to Sol-Al transforming to Sus-Al gradually. Accordingly, when there were organic
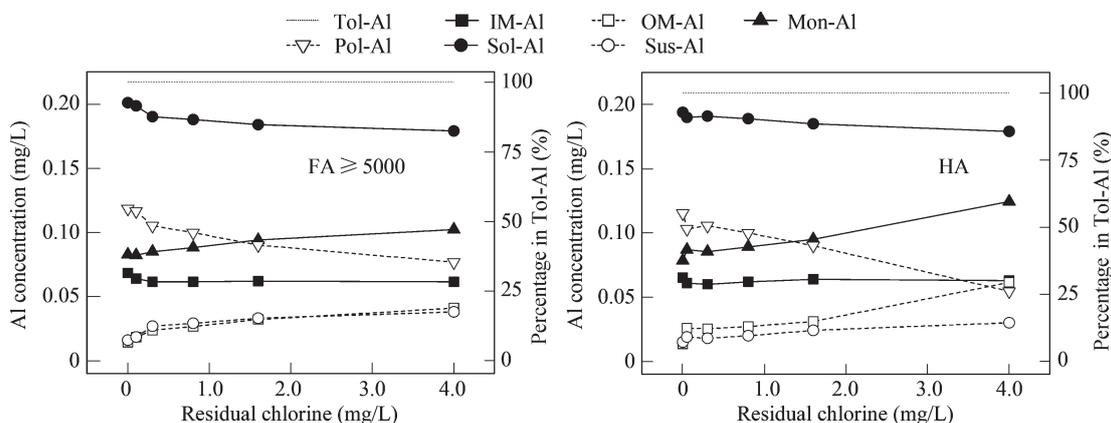

Fig. 4 Effect of residual chlorine on aluminum speciation in solution with FA $\geqslant$ 5000 and HA at initial time. pH: 7.5; concentrations of FA $\geqslant$ 5000 and HA: 3.0 mg/L.

matters in source water, liquid chlorine disinfection would be propitious to control the concentration of Sol-Al by destructing the structure of organic matter. However, the reaction byproducts would greatly increase the biotoxicity of drinking water. In order to ensure the safety of drinking water quality, raw water is needed to be pre-processed when large molecular organic matters existed at concentration above 0.5 mg/L.
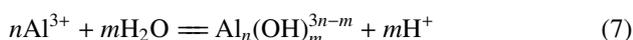
2.4 Reaction mechanism

As discussed above, when FA ⩾ 5000 and HA existed in solution, the concentration of Pol-Al increased significantly, while OM-Al concentration varied little. Browne and Discoll (1993) found the similar phenomenon in studying the reaction between FA and aluminum. In order to explain the process that Pol-Al increasing in the presence of HA, two possible hypothesis reaction processes had been suggested. According to Browne's theoretic, when IM-Al combined with FA ⩾ 5000 or HA in solution, its activation energy to form hydroxyl bonded bridge was reduced. Therefore, it was easy to polymerize with other aluminum ions leading to Pol-Al concentration increase. The process could be expressed by Reactions (4) and (5).

$$Al^{3+} + HA = Al\text{-}HA^{3+} \tag{4}$$

$$Al\text{-}HA^{3+} + Al(OH)_2^+ = Al_2(OH)_2\text{-}HA^{4+} \tag{5}$$
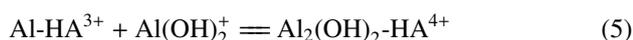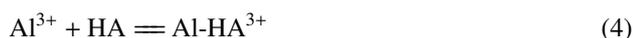
Basing on above hypothesis, it was considered that after polymerization, the ability of polymerized aluminum to combine with organic matter decreased and degraded gradually. Organic acids such as FA ⩾ 5000 and HA acted as catalyst in the reaction. Ultimately, part of aluminum existed in the form of inorganic Pol-Al, as shown in Reactions (6) and (7).

$$Al_2(OH)_2\text{-}HA^{4+} = Al_2(OH)_2^{4+} + HA \tag{6}$$
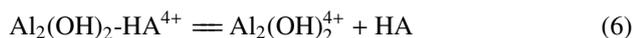
The ultimate reaction was

$$nAl^{3+} + mH_2O = Al_n(OH)_m^{3n-m} + mH^+ \tag{7}$$

The above two hypothesizes could successfully explain the phenomenon that Pol-Al concentration increased notably in the presence of FA and HA. However, they were difficult to be certified and could not explain the experiment results reasonably. For FA < 5000, they could combined with IM-Al as effectively as FA ⩾ 5000 and HA did, while Pol-Al concentration varied little as FA < 5000 increasing. Meanwhile, the formation of Pol-Al would lead to a notable decrease of IM-Al concentration; while IM-Al concentration also varied little with HA or FA increasing.

It was believed that the reaction between FA ⩾ 5000/HA and aluminum were multi-dentate coordination reaction. The aluminum combined by FA ⩾ 5000 and HA could not be captured by analytical reagent (8-HQ) at normal condition, leading to the analyzed concentration of Mon-Al lower than its actual value; while the effect on Sol-Al determination was little, and leading to the concentration of Pol-Al increased proportional to FA ⩾ 5000 and HA concentration ostensibly. For FA < 5000, its reaction

products with aluminum were mainly weak coordination compounds which had little effect on aluminum species analysis.

In order to further validate the reaction mechanism between organic acids and aluminum, 27Al-NMR was applied to study the spectrum variation between solution with and without FA ⩾ 5000. It was difficult to found new Pol-Al peaks in solution with large molecular weight FA (the spectrum was not shown); basing on this result it was difficult to eliminate the produce of Pol-Al as the introduction of FA ⩾ 5000. However, the addition of disinfectants could decrease the concentration of Pol-Al, and increase the concentration of OM-Al, which further proved that the reaction between FA ⩾ 5000/HA and aluminum was multi-dentate coordination reaction. The variation of Pol-Al in determination indicated the concentration variation of OM-Al in drinking water indirectly.

3 Conclusions

The effects of FA and HA on aluminum speciation were studied applying PAC synthetic water. The results showed that FA < 5000 had little effect on aluminum speciation. The existence of FA ⩾ 5000 and HA would significantly increase OM-Al and Sol-Al concentration. When the concentration of FA ⩾ 5000 was above 0.5 mg/L, Sol-Al occupied more than 90% of the Tol-Al. The concentration of IM-Al varied little, and maintained stable in the time period studied. Alkaline condition was against the existence of OM-Al.

With the increase concentration of residual chlorine, the concentration of Sol-Al decreased notably, and IM-Al and OM-Al exhibited increase trend. When there were organic matters in source water, liquid chlorine disinfection process would destruct the structure of organic matter and lead the increase of Sol-Al concentration. However, by the disinfection process using chlorine, the biotoxicity produced by disinfection byproducts and IM-Al was difficult to control.

The reaction between FA ⩾ 5000/HA and aluminum was supposed to be multi-dentate coordination reaction; and the organic matter could not accelerate or catalyze the formation of polymer aluminum. For factories adopting PAC as coagulation agent, in order to ensure the safety of drinking water quality, raw water needed to be pre-processed when large molecular organic matters concentration was above 0.5 mg/L and pH value is needed to be maintained between 6.5–7.5 in the coagulation process.

References

Berthon G, 2002. Aluminium speciation in relation to aluminium bioavailability, metabolism and toxicity. *Coordination*

Chemistry Reviews, 228: 319–341.

Browne B A, Discoll C T, 1993. pH-dependent binding of aluminum by a fulvic acid. *Environmental Science and Technology*, 27(5): 915–922.

Colomina M T, Roig J L, 2005. Concurrent exposure to aluminum and stress during pregnancy in rats: effects on postnatal development and behavior of the offspring. *Neurotoxicology and Teratology*, 27(4): 565–574.

Cui F Y, Hu M C, Zhang Y, Cui C W, 2002. Investigation on aluminum concentration in drinking water in part of China's cities. *China Water and Wastewater*, 18(1): 4–7.

Dave K R, Syal A R, 2002. Effect of long-term aluminum feeding on kinetics attributes of tissue cholinesterases. *Brain Research Bulletin*, 58: 225–233.

Desroches S, Dayde S, 2000. Aluminum speciation studies in biological fluids: Part 6. Quantitative investigation of aluminum(III)-tartrate complex equilibria and their potential implications for aluminum metabolism and toxicity. *Journal of Inorganic Biochemistry*, 81(4): 301–312.

Gillette-Guyonnet S, Andrieu S, Vellas B, 2007. The potential influence of silica present in drinking water on Alzheimer's disease and associated disorders. *Journal of Nutrition Health & Aging*, 11(2): 119–124.

Glynn A W, Sparen A, Danielsson L G, Haegglund G, Jorhem L, 1995. Bioavailability of labile aluminum in acidic drinking-water – A study in the rat. *Food and Chemical Toxicology*, 33(5): 403–408.

Hoff J C, 1978. The relationship of turbidity to disinfection of potable water. Evaluation of the Microbiology Standards for Drinking Water. US Environmental Protection Agency, Washington, DC.

Jelel M, 1986. Interactions of humic acids and aluminum salts in the flocculation process. *Water Research*, 20(12): 1535–1542.

Kriewall D, Harding R, Maisch E, Schantz L, 1996. The impact of aluminum residual on transmission main capacity. *Public Works*, 127(12): 28–30, 67.

Letterman R D, Driscoll C T, 1988. Survey of residual aluminum in finished water. *Journal of American Water Works Association*, 80(4): 154–158.

Lian H Z, Kang Y F, Yasen A, Bi S P, Li D N, 2004. Speciation of aluminum in natural waters by fluorimetry. *Spectroscopy and Spectral Analysis*, 24(11): 1391–1394.

Liu G J, Zhang X R, Talley J W, 2007. Effect of copper(II) on natural organic matter removal during drinking water coagulation using aluminum-based coagulants. *Water Environment Research*, 79(6): 593–599.

Miller R D, Kopfler F C, Kelty K C, Stober J A, Ulmer N S, 1984. The occurrence of aluminum in drinking water. *Journal of American Water Works Association*, 76(1): 84–91.

Sadiq R, Kleiner Y, Rajani B, 2007. Water quality failures in distribution networks – Risk analysis using fuzzy logic and evidential reasoning. *Risk Analysis*, 27(5): 1381–1394.

Sadiq R, Rodriguez M J, 2004. Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: A review. *Science of the Total Environment*, 321(1–3): 21–46.

Singer P C, 2006. DBPs in drinking water: Additional scientific and policy considerations for public health protection. *Journal American Water Works Association*, 98(10): 73–80.

Sollars C J, Bragg A M, Simpson A M, Perry R, 1989. Aluminum in European drinking waters. *Environmental Technology Letters*, 10(2): 130–150.

Szatanik-Kloc A, Jozefaciuk G, 2007. Changes in micropore system of roots of wheat and triticale seedlings under aluminum stress as determined using water vapor adsorption – desorption. *Acta Physiologiae Plantarum*, 29(5): 425–430.

Van Alstyne R, McDowell L R, Davisa P A, Wilkinsona N S, O'Connorb G A, 2007. Effects of an aluminum-water treatment residual on performance and mineral status of feeder lambs. *Small Ruminant Research*, 73(1-3): 77–86.

Walton J R, 2007. A longitudinal study of rats chronically exposed to aluminum at human dietary levels. *Neuroscience Letters*, 412(1): 29–33.

Weng L P, Temminghoff E J M, Van Riemsdijk W H, 2002. Aluminum speciation in natural waters: measurement using Donnan membrane technique and modeling using NICA-Donnan. *Water Research*, 36: 4215–4226.