Variation of Al species during water treatment: correlation with treatment efficiency under varied hydraulic conditions

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ABSTRACT

The concentration of hydrolyzed coagulant ion species is a key factor in determining drinking water treatment efficiency. Direct correlation of water treatment efficiency with changes in species during coagulation has not been addressed. We investigated the correlation under different hydraulic conditions and water treatment efficiencies including changes in removal of turbidity, ultraviolet adsorption at 254 nm (UV254) and dissolved organic carbon (DOC). Results highlighted that Al species (monomeric species as Al a, medium polymeric species as Al b and colloidal species as Al c) behaved differently during coagulation and treatment efficiencies were affected. When varying the mixing speed, the removal of Al c species had a strong negative correlation with water treatment efficiency but under other hydraulic conditions positive correlations were found. The removal of Al a species was positively correlated with water treatment efficiency, but under other hydraulic conditions the low abundance of Al a species meant the correlation was difficult to observe. The Al b species were significantly and positively correlated with water treatment efficiency with the highest correlation coefficient (R 2) of 0.87. The correlation of metallic species with removal efficiencies of the DOC and the UV254 produced higher R 2 values. Correlation of the rate of removal of Al b species with the removal efficiencies of the DOC or the UV254 was better than for Al c.

Key words: Al species, hydraulic conditions, polyaluminum chloride, water treatment efficiency

HIGHLIGHTS

- Hydrolyzed coagulant ion species is considered as one of key factors in determining drinking water treatment efficiency.
- Drinking water treatment efficiency is often correlated with the distribution species in coagulant rather than water.
- The variation of the species removal was investigated in the coagulation system.
- Under varied hydraulic conditions a positive response in correlation was presented.

INTRODUCTION

With continuous population growth and industrialization, an inevitable increased demand for clean water creates challenges for its continual supply. Coagulation is a core operational unit in drinking water treatment processes, and its performance is affected by many parameters such as the nature of the coagulant species, the dose and pH (Matilainen et al. 2010; Zhu et al. 2012; Sillanpaa et al. 2018). The use of traditional inorganic metallic salts such as (aluminum sulfate), is considered to have relatively low efficiency (Chang et al. 1993) compared to pre-polymeric metallic salts. Currently, widely used pre-polymeric metallic salts such as poly aluminium chloride (PACl) have been widely studied to improve the performance of water treatment prioritized due to their high molecular weight and charge and as a substitute for aluminum sulfate to avoid forming large quantities of Al(OH) 3.

A typical PACl is prepared using the following reactions: Al(OH) 3 + HCl → AlCl 3 + 3H 2 O, and 2mAlCl 3 → (Al 2 Cl n (OH) 6–n ) m under alkaline conditions (Zheng et al. 2011). In brief, the formation of PACl is a reaction converting Al 3+ to
Al (OH)\textsubscript{35+} (Chang et al. 1993), during which various polymerization products are generated, including monomeric species, medium range polymeric species and colloidal species. These species have a significant role in determining coagulation behavior (Tang 2006; Masion et al. 2015), such as providing neutral charge and sorption characteristics. However, attaining a good coagulation result also depends on water type, coagulant species composition and distribution. For example, in some studies, the medium polymeric species have a better effect on the removal of dissolved organic carbon (DOC) and ultraviolet adsorption at 254 nm (UV\textsubscript{254}), than the colloidal and monomeric species (Yang et al. 2013; Sadrnourmohamadi & Gorczyca 2015). Therefore, the nature of the correlation between coagulation efficiency with these species becomes an important means to adjust the coagulation performance and provide a better explanation of the mechanism of coagulation. Generally, the correlation between metallic species in the coagulant and water treatment efficiency is more frequently studied. Less research is focused on the variation of the coagulant species in water (Gao et al. 2005a, 2005b; Zhang et al. 2008; Huang et al. 2012; Zhu et al. 2016). It is important to see if the variation in the aquatic species correlates with water treatment efficiency and its relevance to the production of high quality water.

Commonly used methods for the determination of PACI species include timed spectrophotometric ferron-complexation, termed the ‘ferron method’ (Zhou et al. 2006), and nuclear magnetic resonance (\textsuperscript{27}Al NMR) spectroscopy (Bertsch et al. 2010). In the ferron method, the Al species are divided into Al\textsubscript{m}, Al\textsubscript{b} and Al\textsubscript{c}, corresponding to monomeric species, medium size polymeric species and colloidal species (Hu et al. 2001), respectively. Often, the proportion of Al\textsubscript{b} species is found to dominate in the PACI, playing a significant role in the ability to control water pollution. In the \textsuperscript{27}Al NMR method, the species can be further divided into mononuclear aluminum (Al\textsubscript{m}), dimeric aluminum (Al\textsubscript{2}) and aluminum tridecamer [Al\textsubscript{13}(OH)\textsubscript{24}]\textsuperscript{7+} (Al\textsubscript{13}) as well as undetectable aluminum (Al\textsubscript{un}) (Tang et al. 2015). The Al\textsubscript{13} species is an active Al species playing an important role in coagulation, which can be tested using \textsuperscript{27}Al NMR (Liu et al. 2009). The results of the species classification using the ferron and the \textsuperscript{27}Al NMR methods produce similar results, showing the medium size polymeric species (Al\textsubscript{b} and the Al\textsubscript{13}) are both key in determining the performance of coagulation using PACI. However, compared with NMR, the ferron method does not require a complex experimental platform. With its low operational cost it is much easier to include the species analysis in an industrial process using the ferron method.

In this study, we evaluated the variation of the PACI species under different hydraulic conditions using the ferron method, and investigated the correlation between the changes in species abundance (%) in aquatic solution with water treatment efficiency, including the removal of turbidity (%), the UV\textsubscript{254} (%) and the DOC (%). The degree of correlation was determined by the adjusted square of the correlation coefficient ($R^2$).

**METHODS**

**Materials**

The PACI was synthesised in the laboratory. Other reagents used in this study were of analytical grade and included aluminium chloride (Tianjing Stellar Reagent Co., Ltd, China), sodium acetate (Sinopharm Chemical Reagent Beijing Co., Ltd, China), hydrochloric acid (Zhuzhou XingKong Huabo Co., Ltd, China), sodium carbonate (Tianjin Institute of Chemical Reagents, China), and ferron (8-hydroxy-7-iodoquinoline-5-sulfonic acid) (Sinopharm Chemical Reagent Beijing Co., Ltd, China). All aqueous solutions were prepared with ultrapure water using an ultrapure LBY-20 water purifier (Chongqing OWEN Science and Technology Co., Ltd). The glassware and other labware were acid-washed, rinsed thoroughly with ultrapure water, and dried prior to use. Water samples for coagulation experiments were collected from an artificial lake, located on the campus of Hunan University of Science and Technology, Hunan, South China.

**Coagulation test**

Jar tests were conducted with a program-controlled jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co., Ltd, Shenzhen, China) at room temperature. One litre of raw water sample was transferred into a beaker. Sample was rapidly mixed at the defined stirring speed of 100–350 rpm and mixing time of 30–180 s, followed by a slow mixing phase, stirring speed 20–120 rpm for stirring time of 3–180 min, followed by a 30 min settling time. The supernatant sample was extracted from the beaker 2 cm below the water surface for measurement of water quality parameters. The concentration of coagulant added to the water sample was calculated using the quantity of Al\textsubscript{2}O\textsubscript{3} component and the optimum dose of 20 mg/L for treatment of raw water was used.
Analytical methods
Water quality parameters including turbidity, DOC and UV$_{254}$, were measured using a 2100Q Portable Turbidimeter (HACH, USA), the vario MICRO Cube (Elementar Analysensysteme GmbH, Germany), and a TU-1910 UV-Vis spectrophotometer (Beijing Puxi General Instrument Co., Ltd, Beijing, China), respectively. The Al$_2$O$_3$ content in the PACl was measured with an acid-base titration method according to the Chinese standard of poly aluminium chloride for treatment of drinking water (GB 15892–2009). The Al species test was conducted using the ferron method. The reaction between the Al hydrolysate species and ferron reagent form a colour complex, which occurs an adsorption peak at $\lambda = 362$ nm. In the Al range of $10^{-5}$–$10^{-4}$ mol/L, the absorbance of the complexation product in sodium acetate solution (35%, m/m) at pH 5 is linear to Al concentration. Absorbance of three kinds of hydrolytic species of Al was measured including Al$_a$, Al$_b$ and Al$_c$, respectively. Among them, the absorbance occurring within 1 min corresponded to Al$_a$, while the absorbance occurring beyond 1 min corresponded to Al$_b$. The Al$_c$ does not react with ferron reagent, thus its amount may be calculated as Al$_1$–Al$_a$–Al$_b$. The Al$_1$ was the total Al species content. The absorbance was measured as a function of time at $\lambda = 362$ nm to quantify the amount of hydrolytic species. The amount of the species added (denoted as D$_b$) in water at a fixed pH and those (denoted as D$_a$) of settled water after the coagulation within the same pH were measured. The species removal rate (%) was a percentage ratio of the D$_b$–D$_a$ to the D$_a$.

RESULTS AND DISCUSSION
Research on the correlation between the Al species removal and pollutants removal will help to understand the interaction between these species and pollutants including turbidity, DOC and UV$_{254}$. In the process of coagulation, the Al$_a$, the Al$_b$ and the Al$_c$ play an important role in the removal of water pollutants (Zhu et al. 2016). Among them, the Al$_a$ often plays the most important role in charge neutralization, the Al$_b$ has charge neutralization and adsorption bridging functions, whereas the Al$_c$ only has the adsorption bridging effect. The role of these species may change under different conditions (Wang et al. 2019). Turbidity removal and organic matter are both affected by the neutralization and the adsorption bridging effect, and competition for adsorption sites would occur between the Al$_c$ and the Al$_b$. Previous studies mainly focused on the correlation within coagulant dosage and pH effect (Wang et al. 2019). As the hydraulic conditions may affect the final effluent quality, this study mainly focused on the correlation within the range of influence of the hydraulic conditions.

Effect of mixing time
The experiment to investigate the effect of mixing time (rapid stirring) on treatment efficiencies for turbidity, UV$_{254}$ and DOC was conducted with a flocculation time of 10 min, rapid stirring speed of 200 rpm, and slow stirring speed of 75 rpm with a slow stirring time fixed between 30 and 180 s. The initial pH of raw water was 7.9 and the coagulant dose was 20 mg/L for treatment of turbidity at 16.5 NTU, UV$_{254}$ at 0.035 cm$^{-1}$, and DOC at 20.36 mg/L. The experimental results are shown in Figures 1 and 2.

As illustrated in Figure 1(a) and 1(b), with the increase of the mixing time from 30 to 120 s, water treatment efficiencies for turbidity, UV$_{254}$ and DOC increased. A further increase in the mixing time led to a slight decrease in the removal efficiency.
for both turbidity and UV$_{254}$ after 150 s. The main reason for the decrease could be attributed to the flocs being destroyed due to strong mechanical stirring (Zhu et al. 2020). With 120 s of mixing time the turbidity, UV$_{254}$ and DOC removal efficiencies reached 98.4, 72.4, and 64.5%, respectively. Under these conditions we investigated the variations in the removal of Al species during coagulation. As illustrated in Figure 2(a), the Al$_b$ and Al$_c$ species removal rates had slightly variable responses with an increase in the mixing time, while the Al$_a$ species removal rate increased all the time. As illustrated in Figure 2(b) and 2(c), the results of a linear fit of the Al species removal rate and water treatment efficiency showed that the $R^2$ was higher for Al$_b$ and the $R^2$ value between Al$_b$ and water treatment efficiency was higher than the value between Al$_a$ or Al$_c$ and water treatment efficiency. A negative correlation was observed between the removal of Al$_c$ and water treatment efficiency. The explanation being that, under these conditions, the Al$_b$ species more competitive in adsorbing pollutants than the Al$_c$ species (Wang et al. 2019) and therefore increasing the Al$_c$ species would not result in a strong effect. The removal of the Al species correlated better with the removal efficiencies for DOC and the UV$_{254}$ than for turbidity, which followed a descending correlation: Al$_b$ > Al$_a$ > Al$_c$. The $R^2$ between Al$_b$ removal and turbidity removal was 0.74, while for DOC it was up to 0.95. The $R^2$ for removal of Al$_b$ with efficiency of turbidity removal was 0.59, for removal of DOC was up to 0.84, and for UV$_{254}$ up to 0.84. The $R^2$ for removal of Al$_b$ with removal of turbidity was 0.54, for DOC up to 0.68, and for UV$_{254}$ up to 0.73. Overall, the removal of Al$_b$ species had a better correlation with removal efficiencies of the DOC and the UV$_{254}$ than that for turbidity. These results also showed that the charge neutralization effect and adsorption bridging effect of the Al$_b$ are possibly greater than those of other species at different mixing times.

**Effect of flocculation time**

The experiment to investigate the effect of flocculation time on treatment efficiencies for turbidity, UV$_{254}$ and DOC in the range of 3–18 min was conducted with a mixing time 2 min, rapid stirring speed of 200 rpm, and slow stirring speed of 75 rpm. The initial pH of raw water was 7.9 and coagulant dosage was 20 mg/L for treatment of turbidity at 11.7 NTU, UV$_{254}$ at 0.040 cm$^{-1}$, and DOC at 20.91 mg/L. The experimental results are shown in Figures 3 and 4.

As illustrated in Figure 3(a) and 3(b), with the increase of the flocculation time from 3 to 15 min, the water treatment efficiencies for turbidity, UV$_{254}$ and DOC increased. However, with a further increase in the time, increased removal efficiency
for turbidity was shown, while it decreased for DOC and UV\textsubscript{254}. For 15 min of flocculation, the maximum turbidity, UV\textsubscript{254} and DOC removal efficiencies reached 97.8, 75.8, and 70.0\%, respectively. Under these conditions, we investigated the variation in removal of Al species during water treatment. As illustrated in Figure 4(a), the removal of Al\textsubscript{a} species remained constant throughout the flocculation time, except at 3 min. The Al\textsubscript{b} increased all the time and the Al\textsubscript{c} species removal rate had slight unregulated variations. In the investigation of flocculation time, the removal of Al\textsubscript{a} species was nearly 100\%, while the Al\textsubscript{c} removal was around 95\%. As illustrated in Figure 4(b) and 4(c), the results of a linear fit of the removal of Al species and water treatment efficiency showed that the R\textsuperscript{2} was higher in the relationship between the Al\textsubscript{b} and the water treatment efficiencies than for Al\textsubscript{c}. A negative correlation was observed between the removal of Al\textsubscript{c} and the water
treatment efficiency. The removal of Al₈ species correlated with the removal of turbidity better than with the DOC or UV₂₅₄. Because the removal of Al₈ and the Alc species were less affected, a good correlation of the Al species removal with water treatment efficiencies was found. In comparison, the removal of Alc species showed a strong correlation with the removal of the DOC and UV₂₅₄, and was better than for the removal of turbidity. The R² for removal of Alc with removal of turbidity was 0.28, with DOC up to 0.61. The R² for removal of Al₈ with turbidity was up to 0.96, with DOC up to 0.81, and UV₂₅₄ up to 0.87. Unfortunately, the removal of the Al₈ species had a negative correlation with organic matter removal, suggesting that with higher Alc species concentration it may not result in better DOC or UV₂₅₄ removal, with higher Alc species concentration it may not result in better turbidity removal because of a lower correlation between removal efficiency of the turbidity and removal efficiency of the Alc species. The results imply that the Al₈ had a much more important role in turbidity removal by flocculation, while the Alc would be the most effective for removal of dissolved organic matter. The correlation characteristics also demonstrated the fact that the Al₈ and Alc species are the active components leading to charge neutralization and adsorption.

**Effect of rapid stirring speed**

The experiment to investigate the effect of rapid stirring speed on treatment efficiencies for turbidity, UV₂₅₄ and DOC in the range of 100–350 rpm was conducted with a mixing time of 120 s, flocculation time of 15 min, and slow stirring speed of 75 rpm. The initial pH of raw water was 7.9 and the coagulant dosage was 20 mg/L for treatment of turbidity at 11.8 NTU, UV₂₅₄ at 0.032 cm⁻¹, and DOC at 18.62 mg/L. The experimental results are shown in Figures 5 and 6.

As illustrated in Figure 5(a) and 5(b), with the increase of the rapid stirring speed from 100 to 350 rpm, the water treatment efficiencies for turbidity, UV₂₅₄ and DOC increased to a plateau. With a rapid stirring speed 250 rpm, better treatment efficiencies (97.6% of turbidity, 81.2% of UV₂₅₄, and 71.5% of DOC) were obtained. Under such conditions, we investigated the variation in the removal of Al species during water treatment. As illustrated in Figure 6(a), the Al₈ species removal rate increased with the increase of rapid stirring speed from 100 to 150 rpm, but when further increasing the rapid stirring speed it had no further effect, remaining with an approximately 100% removal. As a result, the linear relationship between removal of Al₈ and water treatment efficiencies was also difficult to obtain. With the increase of the rapid stirring speed, the Al₈ and the Alc species removal increased. Among them, the degree of the increase for the Alc species removal rate was not very high. However, both of them had a higher R² with water treatment efficiencies (see Figure 6(b) and 6(c)). The R² for removal of Al₈ with turbidity efficiency was up to 0.90, and for DOC up to 0.80. The R² for removal of Alc with turbidity was 0.80, and for DOC up to 0.86. In contrast to the results of the effects of the mixing time and flocculation reaction time and the slow stirring speeds, the effect of the rapid stirring speed resulted in a positive correlation between the removal of Alc species and water treatment efficiencies. The results showed that under these conditions, the Al₈ and Alc were both the active components leading to charge neutralization and adsorption.

**Effect of slow stirring speed**

The experiment to investigate the effect of slow stirring speed on treatment efficiencies of turbidity, UV₂₅₄ and DOC in the range of 20–120 rpm, was conducted with a mixing time of 120 s, flocculation time of 15 min, and mixing stirring speed of
250 rpm. The initial pH of raw water was 7.9 and the coagulant dose was 20 mg/L for the treatment of turbidity at 20.3 NTU, UV$_{254}$ at 0.032 cm$^{-1}$, and DOC at 22.11 mg/L. The experimental results are shown in Figures 7 and 8.

As illustrated in Figure 7(a) and 7(b), with the increase of slow stirring speed from 20 to 120 rpm, the turbidity, UV$_{254}$ and DOC removal efficiencies increased. With the slow stirring speed of 120 rpm, the corresponding removal efficiencies were 98.8, 77.1 and 72.7%, respectively. Under such conditions, we investigated the variations in the removal of Al species during water treatment. As illustrated in Figure 8(a), the Al$_a$ species removal rate was constant throughout the slow stirring speed period. The removal in Al$_b$ species increased and reached a constant value with an increase of the slow stirring speed.

Figure 6 | (a) The removal rates of Al species; (b) and (c) correlation of the species removal rate with water treatment efficiencies.

Figure 7 | Effect of slow stirring speed on water treatment efficiencies of: (a) turbidity; (b) DOC and UV$_{254}$. 
In contrast, the removal of Alc species decreased with the increase of the slow stirring speed and finally reached a constant value. As illustrated in Figure 8(b) and 8(c), the results of a linear fit of the removal of Al species and water treatment efficiency showed that the R² was higher for the relationship between Alb and the water treatment efficiencies compared to the relationship between Alc, although the removal of Al species correlated with the removal efficiencies for DOC and UV254 much better than for turbidity. However, a negative correlation was observed between the removal of Alc and water treatment efficiency. Therefore, it may not be conducive to the removal of organic matter or turbidity with an increased amount of Alc. Because the removal of Alc did not change significantly, a correlation was absent with the efficiency of water treatment. The R² of for removal of Alb with turbidity was up to 0.61, and for DOC removal up to 0.87. The R² of removal of Alc with turbidity was 0.39, and DOC efficiency up to 0.64. The removal of Alb species showed a larger variation and better correlation with treatment efficiencies than for the Alc species. The correlation highlights showed the fact that the Alb and the Alc species are the active components leading to charge neutralization and adsorption under a slow stirring speed.

**CONCLUSIONS**

The composition of the Al species in the PACl is a determining factor of coagulation performance. In this study, the variations of the Al species during coagulation was observed, which gave an insight into a direct correlation of the Al species with water treatment efficiencies under varied hydraulic conditions. It was concluded that the removal of PACl species (Ala, Alb and Alc) in coagulation were directly correlated with water treatment efficiencies: the removal of Alb and the Alc correlated well with water treatment efficiency; however, the correlation of the Alb species with water treatment efficiency was better, especially for the removal of the DOC and the UV254, which resulted in higher R² values. The removal of the Alb species was positively correlated with water treatment efficiency. Both positive and negative correlations were found between the removal of Alc species and water treatment efficiency. Under some conditions, negative correlations identified limitations for the use of Alc species to treat water quality pollutants.
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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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