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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 (R²) of 0.87. The correlation of metallic species with removal efficiencies of the DOC and the UV₂₅₄ produced higher R² 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 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: $\text{Al}(\text{OH})_3 + \text{HCl} \rightarrow \text{AlCl}_3 + 3\text{H}_2\text{O}$, and $2\text{mAlCl}_3 \rightarrow (\text{Al}_2\text{Cl}_n(\text{OH})_{6-n})_m$ under alkaline conditions (Zheng *et al.* 2011). In brief, the formation of PACl is a reaction converting Al³⁺ to

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Al(OH)_{3(s)} (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 (UV₂₅₄), 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 PACl species include timed spectrophotometric ferron-complexation, termed the 'ferron method' (Zhou *et al.* 2006), and nuclear magnetic resonance (²⁷Al NMR) spectroscopy (Bertsch *et al.* 2010). In the ferron method, the Al species are divided into Al_a, Al_b and Al_c, corresponding to monomeric species, medium size polymeric species and colloidal species (Hu *et al.* 2001), respectively. Often, the proportion of Al_b species is found to dominate in the PACl, playing a significant role in the ability to control water pollution. In the ²⁷Al NMR method, the species can be further divided into mononuclear aluminum (Al_m), dimeric aluminum (Al₂) and aluminum tridecamer [Al₁₃(OH)₃₂⁷⁺ Al₁₃O₄(OH)₂₄⁷⁺] (Al₁₃) as well as undetectable aluminum (Al_{un}) (Tang *et al.* 2015). The Al₁₃ species is an active Al species playing an important role in coagulation, which can be tested using ²⁷Al NMR (Liu *et al.* 2009). The results of the species classification using the ferron and the ²⁷Al NMR methods produce similar results, showing the medium size polymeric species (Al_b and the Al₁₃) are both key in determining the performance of coagulation using PACl. 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 PACl 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 UV₂₅₄ (%) and the DOC (%). The degree of correlation was determined by the adjusted square of the correlation coefficient (R^2).

METHODS

Materials

The PACl was synthesised in the laboratory. Other reagents used in this study were of analytical grade and included aluminum 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 Al₂O₃ 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_2O_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 $Al_t - Al_a - Al_b$. The Al_t 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

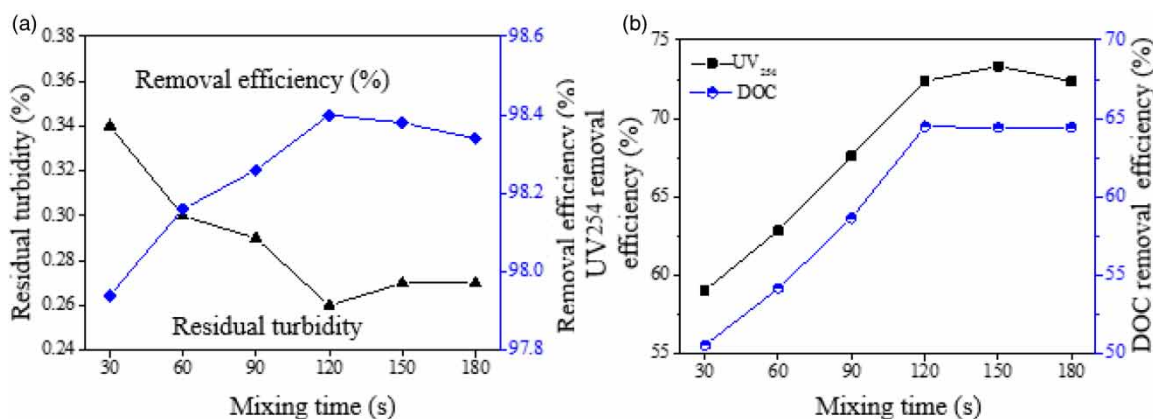


Figure 1 | Effect of mixing time on water treatment efficiencies of (a) turbidity (b) DOC and UV_{254} .

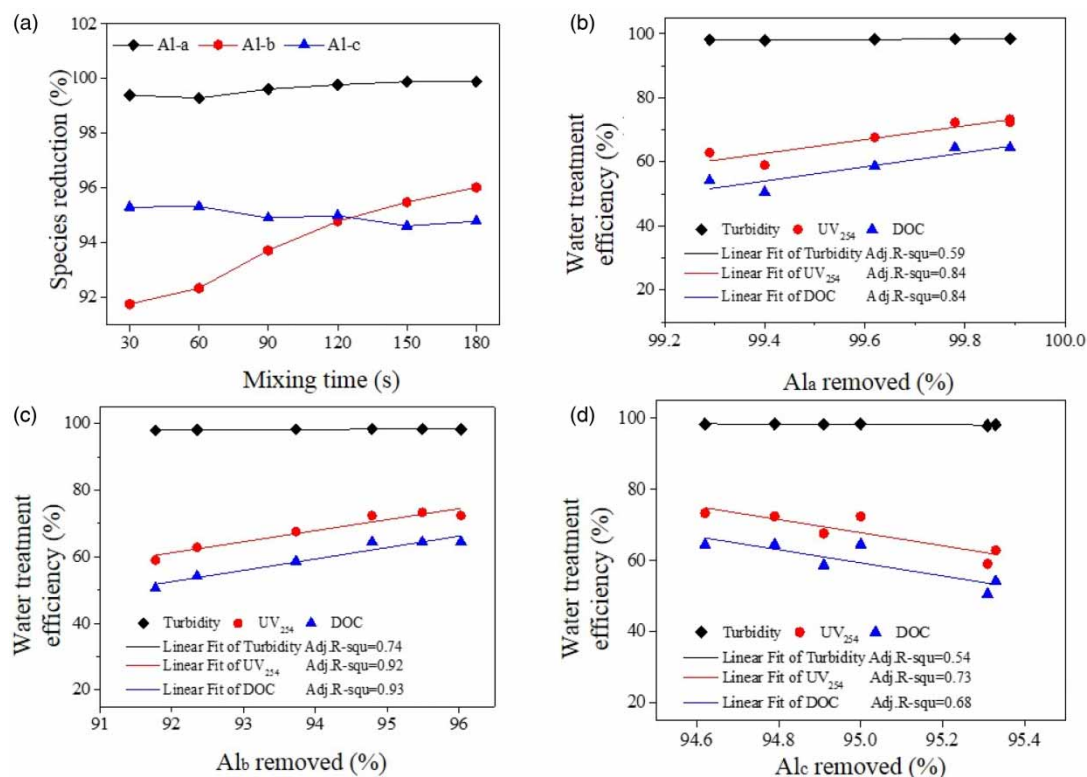


Figure 2 | (a) The removal rates of Al species; (b)–(d) correlation of the species removal rate and water treatment efficiencies.

for both turbidity and UV₂₅₄ 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, UV₂₅₄ 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_a and Al_c species removal rates had slightly variable responses with an increase in the mixing time, while the Al_b 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 R² was higher for Al_b and the R² 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 UV₂₅₄ than for turbidity, which followed a descending correlation: Al_b > Al_a > Al_c. The R² between Al_b removal and turbidity removal was 0.74, while for DOC it was up to 0.93. The R² for removal of Al_a with efficiency of turbidity removal was 0.59, for removal of DOC was up to 0.84, and for UV₂₅₄ up to 0.84. The R² for removal of Al_c with removal of turbidity was 0.54, for DOC up to 0.68, and for UV₂₅₄ up to 0.73. Overall, the removal of Al_b species had a better correlation with removal efficiencies of the DOC and the UV₂₅₄ 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, UV₂₅₄ 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, UV₂₅₄ 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, UV₂₅₄ and DOC increased. However, with a further increase in the time, increased removal efficiency

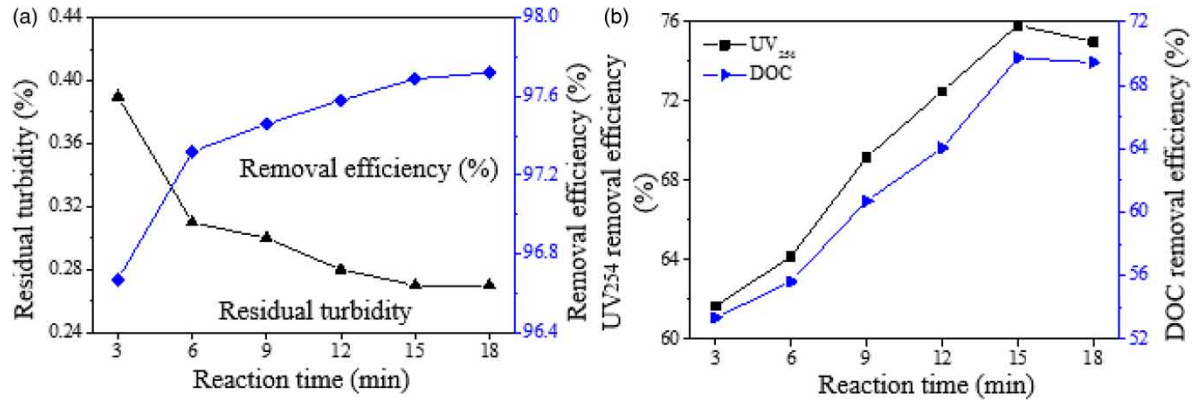


Figure 3 | Effect of flocculation time on water treatment efficiencies of: (a) turbidity and (b) DOC and UV₂₅₄.

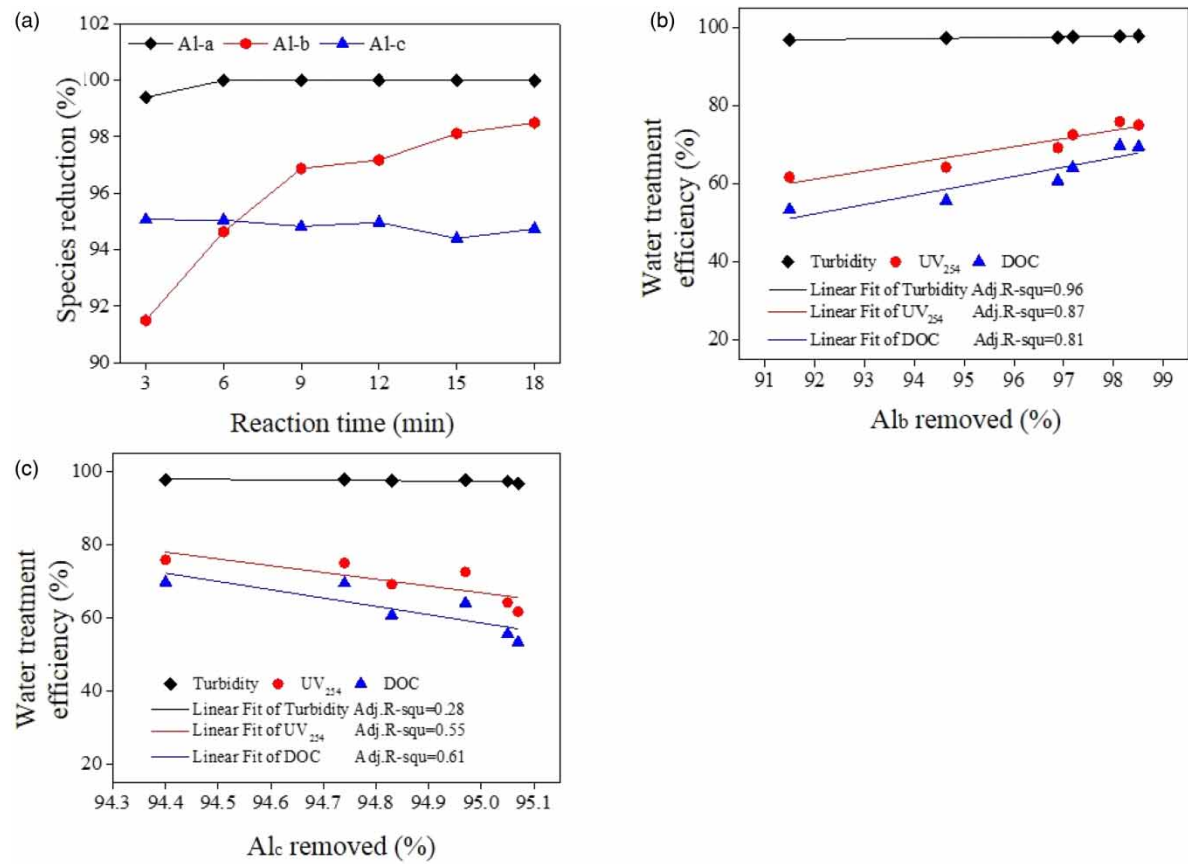


Figure 4 | (a) The removal rates of Al species; (b) and (c) correlation of the species removal rate with water treatment efficiencies.

for turbidity was shown, while it decreased for DOC and UV₂₅₄. For 15 min of flocculation, the maximum turbidity, UV₂₅₄ 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_a species remained constant throughout the flocculation time, except at 3 min. The Al_b increased all the time and the Al_c species removal rate had slight unregulated variations. In the investigation of flocculation time, the removal of Al_a species was nearly 100%, while the Al_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 R² was higher in the relationship between the Al_b and the water treatment efficiencies than for Al_c. A negative correlation was observed between the removal of Al_c and the water

treatment efficiency. The removal of Al_b species correlated with the removal of turbidity better than with the DOC or UV_{254} . Because the removal of Al_a and the Al_c species were less affected, a good correlation of the Al species removal with water treatment efficiencies was found. In comparison, the removal of Al_c species showed a strong correlation with the removal of the DOC and UV_{254} , and was better than for the removal of turbidity. The R^2 for removal of Al_c with removal of turbidity was 0.28, with DOC up to 0.61. The R^2 for removal of Al_b with turbidity was up to 0.96, with DOC up to 0.81, and UV_{254} up to 0.87. Unfortunately, the removal of the Al_c species had a negative correlation with organic matter removal, suggesting that with higher Al_c species concentration it may not result in better DOC or UV_{254} removal, with higher Al_c 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 Al_c species. The results imply that the Al_b had a much more important role in turbidity removal by flocculation, while the Al_c would be the most effective for removal of dissolved organic matter. The correlation characteristics also demonstrated the fact that the Al_a and Al_b 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, UV_{254} 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, UV_{254} 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, UV_{254} and DOC increased to a plateau. With a rapid stirring speed 250 rpm, better treatment efficiencies (97.6% of turbidity, 81.2% of UV_{254} , 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 Al_a 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 Al_a and water treatment efficiencies was also difficult to obtain. With the increase of the rapid stirring speed, the Al_b and the Al_c species removal increased. Among them, the degree of the increase for the Al_c species removal rate was not very high. However, both of them had a higher R^2 with water treatment efficiencies (see Figure 6(b) and 6(c)). The R^2 for removal of Al_b with turbidity efficiency was up to 0.90, and for DOC up to 0.80. The R^2 for removal of Al_c 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 Al_c species and water treatment efficiencies. The results showed that under these conditions, the Al_b and Al_c 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, UV_{254} 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

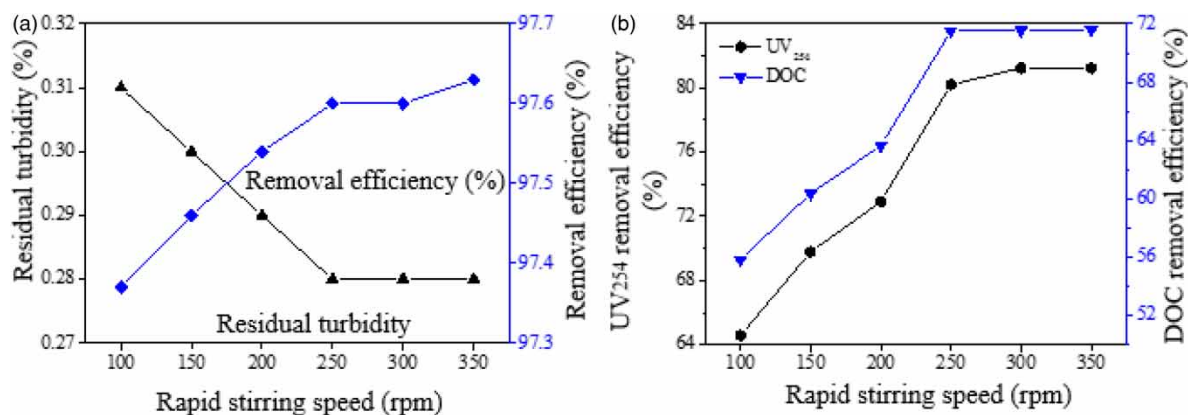


Figure 5 | Effect of rapid stirring speed on water treatment efficiencies of (a) turbidity (b) DOC and UV_{254} .

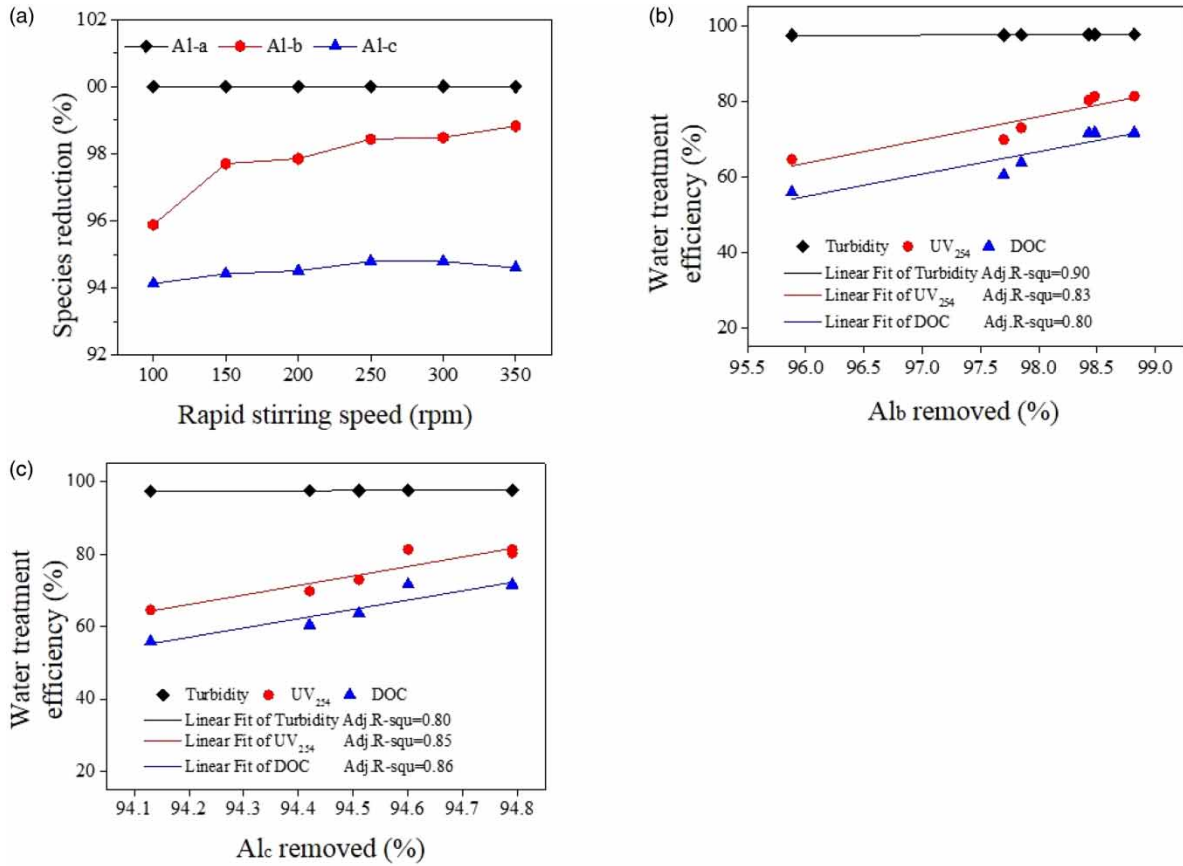


Figure 6 | (a) The removal rates of Al species; (b) and (c) correlation of the species removal rate with water treatment efficiencies.

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, UV₂₅₄ 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, UV₂₅₄ 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.

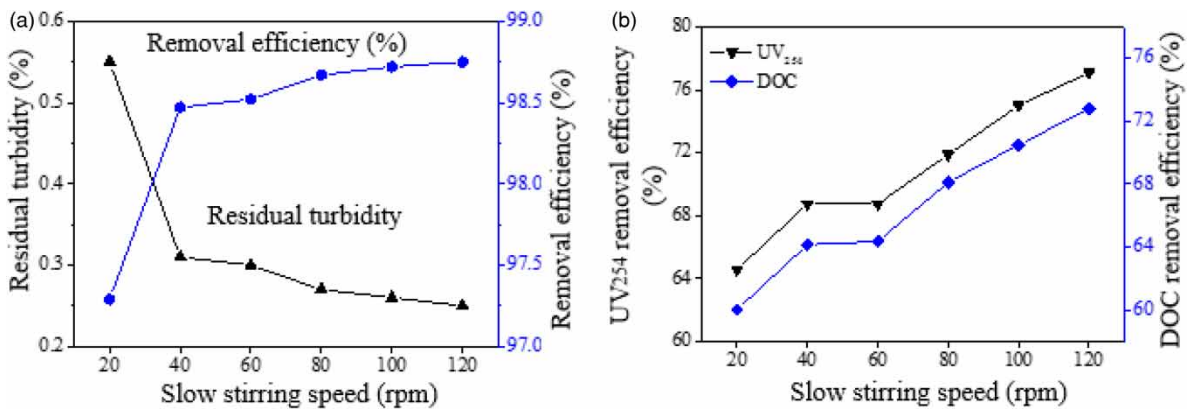


Figure 7 | Effect of slow stirring speed on water treatment efficiencies of: (a) turbidity; (b) DOC and UV₂₅₄.

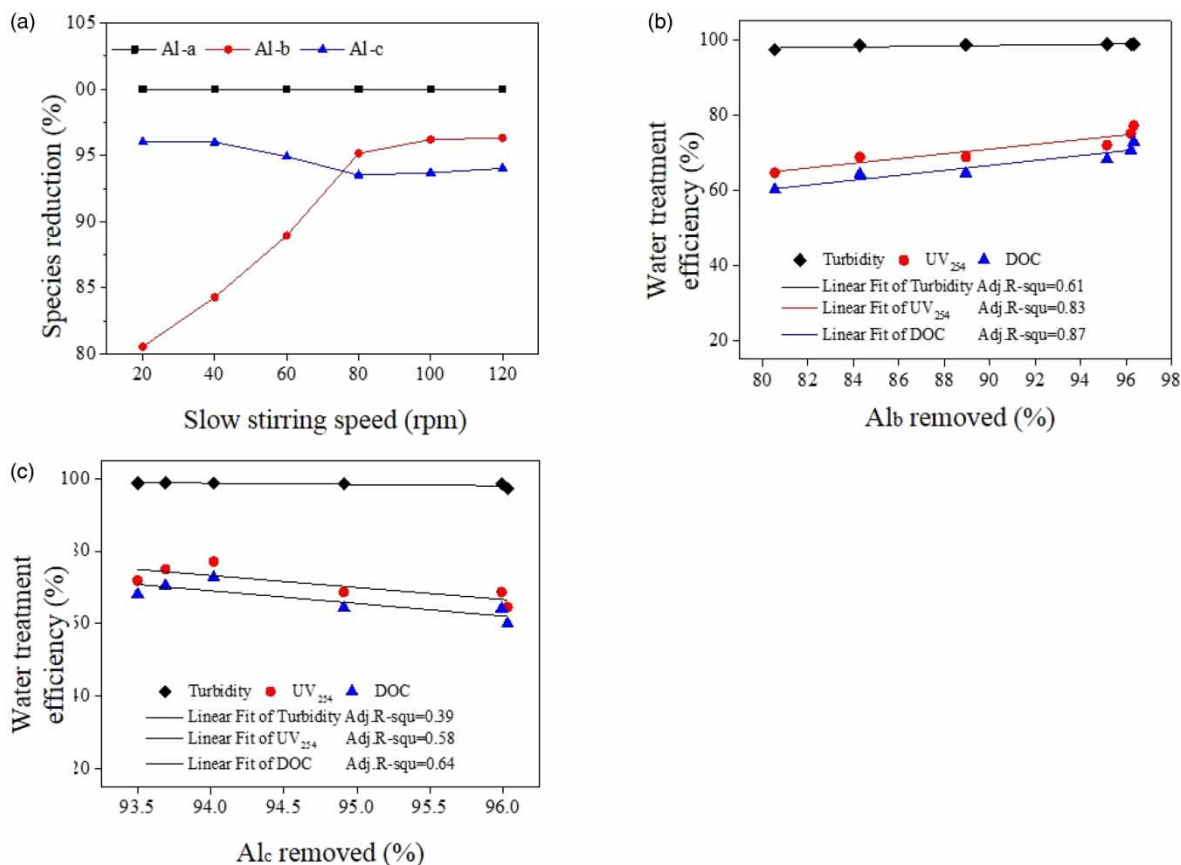


Figure 8 | (a) The removal rates of Al species; (b) and (c) correlation of the species removal rate with water treatment efficiencies.

In contrast, the removal of Al_c 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 Al_b and the water treatment efficiencies compared to the relationship between Al_c, 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 Al_c and water treatment efficiency. Therefore, it may not be conducive to the removal of organic matter or turbidity with an increased amount of Al_c. Because the removal of Al_a did not change significantly, a correlation was absent with the efficiency of water treatment. The R² of for removal of Al_b with turbidity was up to 0.61, and for DOC removal up to 0.87. The R² of removal of Al_c with turbidity was 0.39, and DOC efficiency up to 0.64. The removal of Al_b species showed a larger variation and better correlation with treatment efficiencies than for the Al_c species. The correlation highlights showed the fact that the Al_a and the Al_b 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 (Al_a, Al_b and Al_c) in coagulation were directly correlated with water treatment efficiencies: the removal of Al_b and the Al_c correlated well with water treatment efficiency; however, the correlation of the Al_b 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 Al_b species was positively correlated with water treatment efficiency. Both positive and negative correlations were found between the removal of Al_c species and water treatment efficiency. Under some conditions, negative correlations identified limitations for the use of Al_c 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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