

Preparation and characterization of polymeric phosphate-aluminum sulphate for source water treatment

Guocheng Zhu, Chuang Wang, Xianbin Liu, Xingwei Dong, Peng Zhang, Jun Yin, Bozhi Ren and Zhenghua Wang

ABSTRACT

Aluminum sulphate (AS) as a common coagulant has been widely used in water treatment. Pre-hydrolysed AS (PAS) has higher molecular weight, presenting stronger water treatment performance; however, its poor stability has greatly limited its application. Therefore, there is still a need to obtain a stable PAS. In this study, a method for stabilizing PAS product was proposed and a new coagulant, phosphate-aluminum sulphate (PPAS), was prepared. The parameters affecting PPAS performance, such as $n(P)/n(Al)$ and $n(OH)/n(Al)$ molar ratios, and organic stabilizer dose containing a mixture of tartaric acid and sodium potassium tartrate, were examined. The coagulation–flocculation performance of PPAS was assessed by measuring source water treatment efficiency. The results showed that the PPAS at $n(P)/n(Al)$ molar ratio of 0.15, $n(OH)/n(Al)$ molar ratio of 0.2 and the stabilizer dose of 7.5% presented good performance and stability. PPAS was significantly distinct from AS in the morphology and species distribution, which indicated that the distribution of the Al_b and Al_c in PPAS largely affected the coagulation–flocculation performance, especially the Al_b . The coagulation–flocculation examined at an appropriate pH was effective for source water turbidity, ultraviolet adsorption at 254 nm and total dissolved organic nitrogen removal in the investigated range.

Key words | aluminum sulphate, coagulant, coagulation-flocculation, phosphate-aluminum sulphate, source water

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INTRODUCTION

The coagulation–flocculation process is a key environmental protection technology that finds a wide range of applications in water and wastewater treatment facilities (Zhu *et al.* 2011, 2012; Zheng *et al.* 2011b; Tolkou & Zouboulis 2015). It is regarded as a viable option for the production of drinking water through removing suspended solids, colloidal particles and natural organic matter from surface waters, as well as the treatment of heavy loaded, toxic or hazardous wastewater (Meriç *et al.* 2005; Assaad *et al.* 2007; Matilainen *et al.* 2010; Zhu *et al.* 2014, 2016). The most common coagulants used for the coagulation–flocculation process are

hydrolysing metals of aluminum or iron salts such as $AlCl_3$, $Al_2(SO_4)_3$, $FeCl_3$, $Fe_2(SO_4)_3$, etc. (Duan & Gregory 2003; Moussas *et al.* 2011). Their major drawback is that during dilution, their rapid formation of coagulant species could result in uncontrollable formation of hydrolysis species (Tshukudu *et al.* 2013), which would decrease their stability. To overcome this problem, a relatively new type of coagulant commonly known as inorganic polymer coagulant, such as polymeric forms of ferric chloride and ferric sulphate, polymeric aluminum sulphate (PAS) and aluminum chloride (PAC), have been developed worldwide (Lei

et al. 2009; Zhu *et al.* 2011; Luo *et al.* 2015). These coagulants include hydrolysis and polymeric species, which are able to slow the speed of hydroxide precipitation upon dilution allowing polymeric species to be maintained for a longer period.

Although the PAS as a pre-hydrolysed coagulant has a similar property to PAC, its stability during dilution is relatively weak compared with other hydrolysed coagulants (Lin Wang *et al.* 2009). During preparation of pre-hydrolysed coagulants, controlling their species distribution is significantly important because their species distribution and transformation laws, characterization, and the influence of the species on the stability and performance of one coagulant closely relates to the coagulant's physico-chemical properties (Fu *et al.* 2007). There are two viable ways of changing the physico-chemical properties of the inorganic coagulant. One is to increase the proportion of polymeric species in the original composition and the other is to add extra components to produce new composite coagulants. Zouboulis *et al.* (Moussas & Zouboulis 2008; Zouboulis & Moussas 2008) suggested three types of compounds as modifiers: inorganic anions, such as poly-silicates and phosphates; organic anions, such as various organic acids; and organic polyelectrolytes, which are cationic, non-anionic or anionic. For example, a modified PAS with the sodium silicate as modifier indicates that its stability is stronger than without modification (Liu *et al.* 1999; Wei & Gu 2005). Introducing an appropriate amount of phosphate in PAS can produce a modified PAS, polymeric phosphate aluminum sulphate (PPAS), which is a new class of high charge with multi-core phosphate intermediate complex similar to those coagulants modified by phosphate (Voegelin *et al.* 2010; Zheng *et al.* 2011b; Razack *et al.* 2015).

In this study, PPAS was prepared. Fourier transform infrared spectroscopy (FT-IR) and a scanning electron microscope (SEM) were utilized to characterize the structure and morphology of PPAS. The Al-Ferron method was adopted to measure Al(III) species distribution in PPAS. The parameters affecting PPAS performance, such as $n(\text{P})/n(\text{Al})$ molar ratio, $n(\text{OH})/n(\text{Al})$ molar ratio, and organic stabilizer dose were examined. The coagulation performance of PPAS was examined by measuring its treatment effect on source water turbidity, ultraviolet adsorption at 254 nm (UV254) and total dissolved organic nitrogen (TDN).

MATERIAL AND METHODS

Materials

The reagents used for preparation of PPAS mainly consisted of aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3$), sodium carbonate (Na_2CO_3), aurointricarboxylic acid triammonium salt, potassium dihydrogen phosphate (KH_2PO_4), tartaric acid and sodium potassium tartrate, which were analytical grade. For analysis of PPAS species, the analytical grade Ferron reagent (8-hydroxy-7-iodoquinoline-5-sulfonic acid) was used. Aluminum potassium sulphate ($\text{KAl}(\text{SO}_4)_2$) (guaranteed reagent) and aluminum powder were applied in measuring the content of Al(III). All other reagents were analytical grade. All aqueous solutions were prepared with deionized water.

Water sample

Water samples were collected from the Xiangjiang River with sampling located in Xiangtan, China. This source water has suffered from serious pollution by agricultural, industrial and domestic pollutants, which has led to water quality deterioration. The quality analysis of the raw water was investigated in this study. The results are shown in Table 1. The results showed that UV254, pH, turbidity, ammonia, nitrate, nitrite and TDN were between 0.05 and 0.1, 7.0 and 8.0, 8 and 30 NTU, 0.5 and 1 mg/L, 1 and 2 mg/L, 0.1 and 0.3 mg/L, and 5.0 and 7.0 mg/L, respectively. The water temperature tested in this study ranged from 18 to 22 °C.

Table 1 | Results of quality analysis of the raw water

Items	Values
UV254 (cm^{-1})	0.05–0.1
pH	7.0–8.0
Turbidity (NTU)	8–30
Ammonia (mg/L)	0.5–1
Nitrate (mg/L)	1–2
Nitrite (mg/L)	0.1–0.3
TDN (mg/L)	5.0–7.0

Preparation of PPAS

The PPAS investigated in this study was a composite coagulant and the steps for its preparation were as follows.

Firstly, a given mass of $\text{Al}_2(\text{SO}_4)_3$ and 150 mL deionized water were mixed slowly in a water bath at 100°C for 1 hour. The reaction temperature was controlled using a thermostatic water bath. Then, the temperature was dropped to 60°C , accompanied by rigorous stirring using a magnetic stirrer. A certain amount of Na_2CO_3 was added to the liquid system gently according to the predetermined $n(\text{OH})/n(\text{Fe})$ molar ratio. The $n(\text{OH})/n(\text{Fe})$ molar ratio was determined following the procedure reported by Tang (Tang 2006). The reaction time was kept constant for 10 min. After the addition of Na_2CO_3 , KH_2PO_4 was added to the reaction system with a slow agitation speed for 30 min to increase the degree of polymerization. The synthesized product at this stage was PPAS. Finally, the mixture of tartaric acid and sodium potassium tartrate as a stabilizer at a specific molar ratio was added to stabilize the PPAS. After aging for 24 hours at room temperature, a liquid PPAS was produced.

Characterization of PPAS

The samples of PPAS were dried in an oven at 50°C and ground into powders. The powders were mixed with potassium bromide (KBr) and the respective pellets suitable for FT-IR analysis were prepared. The FT-IR spectrum in the range of $4,000\text{--}400\text{ cm}^{-1}$ was recorded on a Perkin-Elmer Spectrum One B spectrometer. Then, the powders were characterized by SEM to examine their surface morphology, which was obtained on a JEOL JSM-6380LV electron microscope instrument.

Al(III) speciation distribution analysis

The Al(III) hydrolysis species distribution in PPAS solution was measured by timed complexation spectroscopy involving the reaction between Al and the Ferron reagent, following the detailed operational process reported by Hu *et al.* (2001). Visible light absorbance was measured as a function of time at a wavelength of 365 nm to quantify the amount of metal complexes. The Al(III) hydrolysis species

reacting with the Ferron reagent in 1 min is considered to be the Al(III) monomeric species (denoted as Al_a), and the Al(III) species reacting with the Ferron reagent over the next 2 hours is considered to be the Al(III) medium polymeric species (denoted as Al_b). Any Al(III) that remained unreacted after 2 hours is considered to be precipitated Al(III) (denoted as Al_c).

Jar test

The coagulation experiments were carried out using a program-controlled jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd, China) at room temperature. An amount of 1,000 mL of water sample was transferred into a beaker; under rapid stirring of 300 r/min, the predetermined amount of coagulant was dosed. After 1.5 mins, the speed was changed to a slow stirring speed of 70 r/min for 15 mins; after quiescent settling of 30 mins, samples were collected from 2 cm below the surface for water quality analysis.

Analytical method

The dosage of coagulant was calculated in this study by using an effective component of Al(III). The Al(III) was measured using aurintricarboxylic acid triammonium salt by spectrophotometric determination on a TU-1901 spectrophotometer (Puxi Analytic Instrument Ltd of Beijing, China). The turbidity of the supernatant was measured with a turbidity meter (HACH 2100Q, HACH Company, USA). Ultraviolet-visible adsorption at 254 nm (UV254) was also measured. TDN was digested by alkaline potassium persulphate and determined by an ultraviolet spectrophotometric method (Chinese Standard GB 11894-89). For analysis of TDN and UV254, all water samples were filtered through a membrane ($0.45\ \mu\text{m}$).

RESULTS AND DISCUSSION

Characterization of PPAS

FT-IR and SEM instruments were used to analyze and characterize the structure and morphology of PPAS,

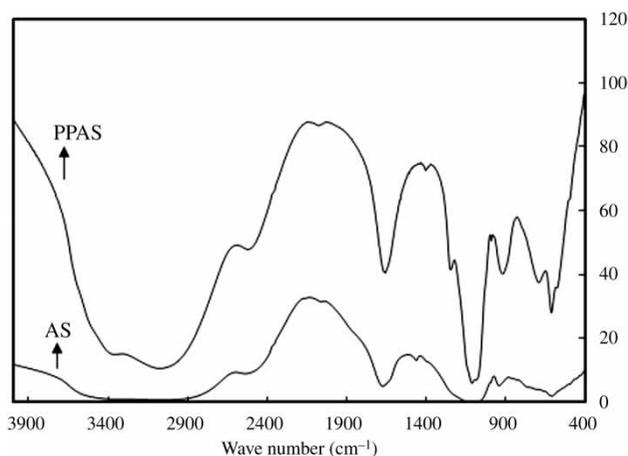


Figure 1 | FT-IR spectra of PPAS and AS.

respectively. In addition, Al-Ferron analysis was employed to examine the Al(III) hydrolysis species distribution.

FT-IR spectra analysis

The possible chemical bonds present in PPAS and AS were examined using FT-IR in the range of 4,000–400 cm^{-1} with KBr as dispersant.

Figure 1 shows that there is a broad absorption peak in the range of 3,200–3,000 cm^{-1} for PPAS, which can be attributed to the stretching vibration of OH groups (Zeng & Park 2009). The medium peak in the range of 1,600–1,700 cm^{-1} (1,654 cm^{-1} for PPAS, 1,670 cm^{-1} for AS) can be assigned to the bending vibration of -OH groups in the water molecule, namely the H-O-H angle distortion frequency, indicating that PPAS and AS may contain structural and adsorbed water (Zeng & Park 2009). The absorption peaks at around 609 cm^{-1} for PPAS and 605 cm^{-1} for AS can result from the bending vibration distortion of the H-O-H bond and Al-OH bonds (Xing *et al.* 2010; Soleimani *et al.* 2014). Therefore, this peak indicates the presence of the hydroxyl functional group in both structures.

Figure 1 shows absorption peaks at 2,072 cm^{-1} for PPAS and 2,065 cm^{-1} for AS, which were assigned to the HSO_4^- group. FT-IR spectral studies have revealed that the characteristic absorption peak for sulphate is evident in the range of 900–1,200 cm^{-1} (Frost *et al.* 2003). The sulphate structure is tetrahedral and it exhibits symmetrical and

anti-symmetrical stretching vibration with IR activity. The characteristic absorption peaks at 914 cm^{-1} for PPAS and 940 cm^{-1} for AS were attributed to SO_4^{2-} symmetrical stretching vibrations. There were other absorption peaks at around 1,110 cm^{-1} for PPAS and around 1,098 cm^{-1} for AS, which are characteristic frequencies for SO_4^{2-} . Figure 1 shows that there was a significant difference in the spectrum of PPAS at wave numbers of 1,244 cm^{-1} and 690 cm^{-1} . The absorptions at these frequencies were assigned to the -P=O, PO_4^{3-} stretching and bending vibrations, which were only present in PPAS. In summary, the IR spectrum indicates that PPAS may generate a number of surface-active substances such as hydroxyl-sulphate. On the other hand, for PPAS the presence of PO_4^{3-} generated a new class of highly charged poly-nuclear poly-hydroxyl complexes.

SEM analysis

The surface morphologies of PPAS and AS were analyzed using SEM. The PPAS used in this experiment was a product with fixed component ratios at $n(\text{P})/n(\text{Al})$ ratio of 0.15, $n(\text{OH})/n(\text{Al})$ ratio of 0.2 and stabilizer dose of 7.5%.

As shown in Figure 2, AS is an orthorhombic crystal structure. However, PPAS has a significantly different morphology from AS. It has an irregular surface with randomly forming aggregates of various sizes and shapes. Apart from the irregular surface, a clustered solid structure of PPAS was observed. With this type of structure, PPAS possesses a large surface area with strong adsorption capacity (Chen 2010; Zhu *et al.* 2011), which is conducive to the adsorption and sweeping of colloidal particles to form flocs.

PPAS coagulation for source water

Effect of $n(\text{OH})/n(\text{Al})$

During preparation of PPAS, the hydrolysis of Al(III) and hydroxyl resulted in a series of multi-hydroxyl polymeric compounds. The hydrolysis and polymeric reactions were both affected by Al(III) concentration and pH value. During the hydrolysis, the increase of pH could promote the hydrolysis and polymeric reaction. However, if hydroxyl content was over-dosed, it would lead to a hydroxyl

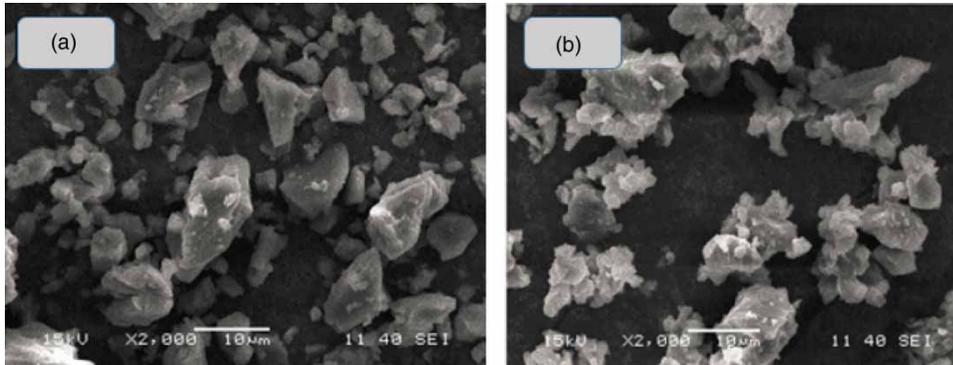


Figure 2 | SEM images of (a) AS and (b) PPAS.

aluminum precipitation. Thus an appropriate amount of $n(\text{OH})/n(\text{Al})$ molar ratio is conducive to the preparation, generating a stable product.

The effect of $n(\text{OH})/n(\text{Al})$ on Al(III) species distribution in PPAS was investigated with the results shown in Table 2. According to the previous report about Al(III) species in AS (Tang 2006), it was mainly composed of Al_a with lesser amounts of Al_b and Al_c . Similar results were found in this study, which indicated that the Al(III) species in AS consists of 90.2% Al_a , 8% Al_b , and 1.8% Al_c , with the increase of $n(\text{OH})/n(\text{Al})$ molar ratio. As a result, most Al_a of the AS was transferred to the Al_b and the Al_c of the PPAS, which showed that a higher $n(\text{OH})/n(\text{Al})$ molar ratio could increase the polymeric degree content of intermediate complex and high molecular compounds.

The effect of PPAS on turbidity removal with various $n(\text{OH})/n(\text{Al})$ molar ratios was investigated in order to obtain an appropriate range of the $n(\text{OH})/n(\text{Al})$ molar ratio to prepare PPAS. The quality analysis of raw water for coagulation showed that the turbidity and pH were 10.70 NTU and 7.62, respectively. The experimental result is shown in Figure 3.

Figure 3 shows that as the $n(\text{OH})/n(\text{Al})$ molar ratio increased in the range of 0.05–0.10, the residual turbidity

at PPAS dosage of 2 mg/L increased and then decreased as the PPAS dosage increased further. The residual turbidity reached the minimum at $n(\text{OH})/n(\text{Al})$ molar ratio of 0.20. At PPAS dosages of 1 mg/L and 4 mg/L, the residual turbidity decreased as the $n(\text{OH})/n(\text{Al})$ molar ratio increased. Therefore, the appropriate $n(\text{OH})/n(\text{Al})$ molar ratio was 0.20, at which the residual turbidity achieved 0.42 NTU. The coagulation–flocculation was affected by the Al(III) species in PPAS. It showed that PPAS at $n(\text{OH})/n(\text{Al})$ molar ratio of 0.20 has the highest Al_c and Al_b values and it could present a better removal of turbidity than others. Al_b is known as the most active coagulant component in aluminum salt coagulants, and is responsible for coagulation performance. Al_c is a mixture of Al(III) high molecular weight polymers and Al(III) colloids, which can absorb more contaminants, and plays an important function in the adsorption-bridging role between the colloids and

Table 2 | Al(III) species distribution in PPAS

$n(\text{OH})/n(\text{Al})$	Al(III) species percentage (%)		
	Al_a	Al_b	Al_c
0.05	59.39	35.68	4.93
0.1	55.73	25.92	18.35
0.20	51.55	26.99	21.46

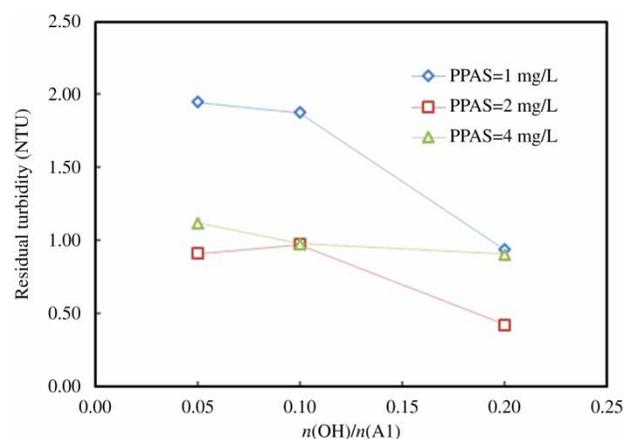


Figure 3 | Effect of $n(\text{OH})/n(\text{Al})$ on turbidity removal.

coagulant molecules, thus improving flocculation efficiency. As shown in Table 2, for the PPAS with $n(\text{OH})/n(\text{Al})$ molar ratio of 0.05, although the Al_b content was relatively higher, the Al_c content was very small, and its coagulation–flocculation performance was not superior to others. Therefore, Al_c played a significant role in the coagulation–flocculation process for turbidity removal.

Effect of $n(\text{P})/n(\text{Al})$

The physico-chemical properties of PPAS and AS were largely affected by their species. Firstly, PPAS has a lower hydrolysis process than AS because during the preparation process, PPAS has been pre-hydrolysed and its species are composed of Al_a , Al_b and Al_c of various content. However, AS species are mainly composed of Al_a with less amounts of Al_b and Al_c (Tang 2006). The hydrolysis of the AS is the process of generating hydroxyl-bridging compounds, which is more rapid than that of PPAS. Under a specific water environment, the hydrolysis of super-saturation would lead to a precipitation of AS species. Therefore, PPAS is more stable than AS. In the transformation of species of AS into PPAS during preparation, the phosphate introduced into AS could change the PPAS species, which would make the PPAS more stable. According to the previous report (Chen 2010), the mechanism for potential species formation generated by the reaction between phosphate and Al(III) can be expressed as shown in Figure 4.

This reaction mechanism indicates that the phosphate is one of the important species components of PPAS by replacing the partial hydroxyl during preparation of PPAS. The presence of phosphate changes the Al(III) species distribution, especially slowing the hydrolysis of Al(III) and thus improving the stability of PPAS. The Al(III) species distribution is shown in Table 3.

Table 3 shows that phosphate could enhance the Al_b content in PPAS, which shows that the Al(III) species

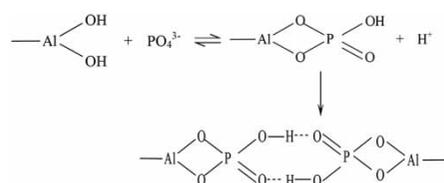


Figure 4 | Possible mechanism for complexation of Al(III) and phosphate.

Table 3 | Al(III) species distribution in PPAS

$n(\text{P})/n(\text{Al})$	Al(III) species percentage (%)		
	Al_a	Al_b	Al_c
0.05	63.79	32.59	3.51
0.1	39.28	36.21	24.43
0.15	48.47	40.39	11.04

distribution in PPAS was changed due to the presence of phosphate, which produced a new class of multi-core phosphate intermediate complex with high charge.

An appropriate amount of phosphate introduced into PPAS to replace partial hydroxyl to attend the polymeric reaction could improve the coagulation–flocculation performance of PPAS and its stability. For example, the presence of phosphate in polymeric aluminum chloride (PAC) could significantly improve PAC performance (Zheng et al. 2011a; Zheng et al. 2011b), whereas there is a need to add an appropriate amount of phosphate. Compared with the PAC, PAS was more unstable. The presence of phosphate would be helpful in improving the stability of PAS.

In order to obtain the appropriate range of the $n(\text{P})/n(\text{Al})$ molar ratio, the effect of PPAS on turbidity removal with various $n(\text{P})/n(\text{Al})$ molar ratios was investigated. The quality analysis of the raw water showed that the turbidity and pH were 20.5 NTU and 7.66, respectively. The experimental result is shown in Figure 5.

Figure 5 shows that as the $n(\text{P})/n(\text{Al})$ molar ratio increased from 0.05 to 0.15, the residual turbidity at PPAS

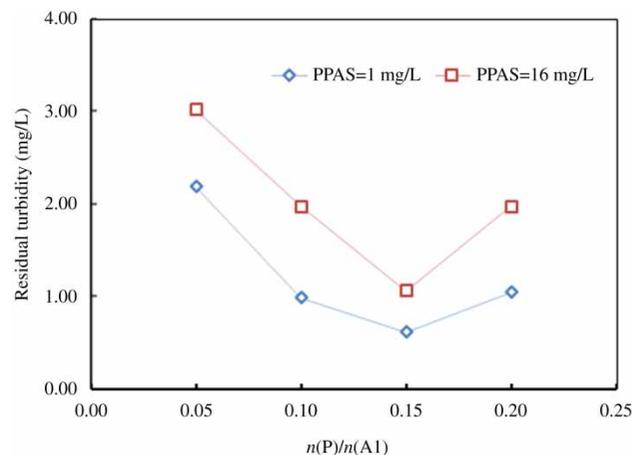


Figure 5 | Effect of $n(\text{P})/n(\text{Al})$ on turbidity removal.

dosages of both 1 mg/L and 16 mg/L decreased and then increased as the dosage increased further. The residual turbidity reached the minimum at an $n(\text{P})/n(\text{Al})$ molar ratio of 0.15. Therefore, the appropriate amount of phosphate was at this $n(\text{P})/n(\text{Al})$ molar ratio. Coagulation–flocculation was significantly affected by the PPAS species. Al(III) hydrolysis species distribution in PPAS (see Table 3) showed that Al_a was the majority in PPAS with the $n(\text{P})/n(\text{Al})$ molar ratio ranging from 0.05 to 0.15. As the $n(\text{P})/n(\text{Al})$ molar ratio increased, Al_b increased significantly with the highest value of 40.39% at an $n(\text{P})/n(\text{Al})$ molar ratio of 0.15. Table 3 shows that the highest Al_c value in PPAS was at an $n(\text{P})/n(\text{Al})$ molar ratio of 0.1. However, the minimum residual turbidity was achieved at an $n(\text{P})/n(\text{Al})$ molar ratio of 0.15. Although the PPAS had a smaller Al_c value (11.04%), its Al_b was relatively high (40.39%) at an $n(\text{P})/n(\text{Al})$ molar ratio of 0.15. This implies that coagulation–flocculation for turbidity removal mainly relied on Al_b . This result combined with the study of the $n(\text{OH})/n(\text{Al})$ molar ratio on turbidity removal indicated that the Al_b and Al_c were both the decisive factors of coagulation–flocculation and Al_b showed a more significant effect than Al_c .

Effect of stabilizer dosage

A higher $n(\text{OH})/n(\text{Al})$ molar ratio could induce hydroxyl aluminum precipitation. The presence of some organic compounds would be able to make PPAS more stable. Compared with previous studies on the stability improvement of PAS, the introduction of phosphate and organic compounds are more convenient and simple. For example, sodium silicate and AS have been mixed to form a polymeric aluminum silicate sulphate under the condition of effective acid control (Wei & Gu 2005). The main drawback for this preparation is that the control of polysilicic acid formation as well as reaction with AS is hard work.

In this study, a mixture of organic tartaric acid and sodium potassium tartrate at a specific mass ratio of 2:1 was introduced in order to improve the stability of PPAS. The stabilizer dosage was added according to the predetermined molar percentage of Al(III). The effect of PPAS on residual turbidity with various stabilizer dosages was investigated in order to obtain the appropriate range of stabilizer dosage to prepare PPAS. The quality analysis of

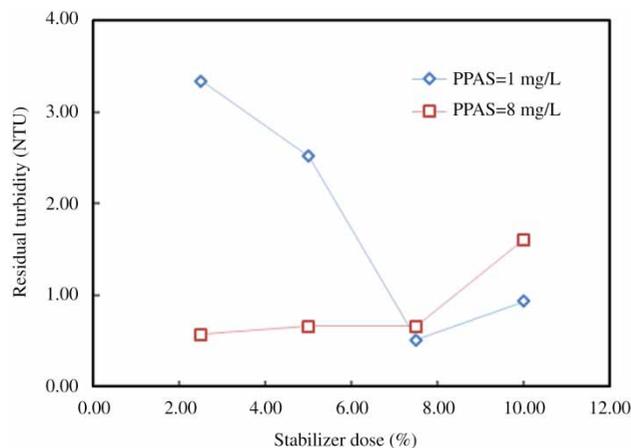


Figure 6 | Effect of stabilizer dose on turbidity removal.

the raw water showed that the turbidity and pH were 11.10 NTU and 7.97, respectively. The experimental result is shown in Figure 6.

Figure 6 shows that as the stabilizer dose increased in the range of 2.5%–7.5% for the PPAS dosage of 1 mg/L, the residual turbidity decreased and then increased as the stabilizer dose increased further. The residual turbidity reached the minimum at a stabilizer dose of 7.5%. With the PPAS dosage of 8 mg/L the minimum residual turbidity of 0.58 NTU was achieved at a stabilizer dose of 2.5%, which was close to the 0.67 NTU value that was obtained at a stabilizer dose of 7.5%. In this study, the stabilizer dose at 7.5% was selected as the optimum preparation condition. The prepared PPAS in the presence of the optimized stabilizer dose and the above $n(\text{P})/n(\text{Al})$ molar ratio of 0.15 and $n(\text{OH})/n(\text{Al})$ molar ratio of 0.20 can be stable at least for 6 months without any precipitation occurring (see Figure 7). Figure 7 indicates that the solution of the optimum PPAS (Figure 7(b)) was not layered, whereas the solution of that with poor stability (Figure 7(a)) easily formed crystalline precipitate.

Effect of coagulant dosage

The effect of PPAS dosage on residual turbidity, UV254 and TDN removal efficiencies were investigated. The PPAS used in this experiment was a product with a fixed $n(\text{P})/n(\text{Al})$ ratio of 0.15, $n(\text{OH})/n(\text{Al})$ ratio of 0.2 and stabilizer dose of 7.5%. The quality of the raw source water indicated that



Figure 7 | Photos of PPAS with (a) poor stability and (b) excellent stability, after storage for 6 months.

the turbidity, pH, UV254 and TDN were 23.90 NTU, 7.29, 0.072 and 5.81 mg/L, respectively. The experimental result is shown in Figure 7.

Figure 8 shows that as the PPAS dosage increased from 0.5 to 6.5, the residual turbidity decreased. However, at an even higher dosage (e.g., 8 mg/L), the residual turbidity increased. The possible reason for the increase of residual turbidity was that the coagulant was able to absorb onto the colloid surface with its long chains where the tails and loops are extended far beyond its surface and can interact with other particles via bridging (Luo *et al.* 2011; Zhu *et al.* 2011). At low coagulant dose, there is insufficient coagulant to form adequate bridging links between particles, while with excess coagulant, there is not enough bare particle surface available for the attachment of segments and the particles become destabilized (Krishnamoorthi *et al.* 2010; Zhu *et al.* 2011), thus there is an optimum polymer dosage for coagulation–flocculation behavior. Figure 8 shows that with a low or high PPAS dosage the coagulation–flocculation efficiencies were

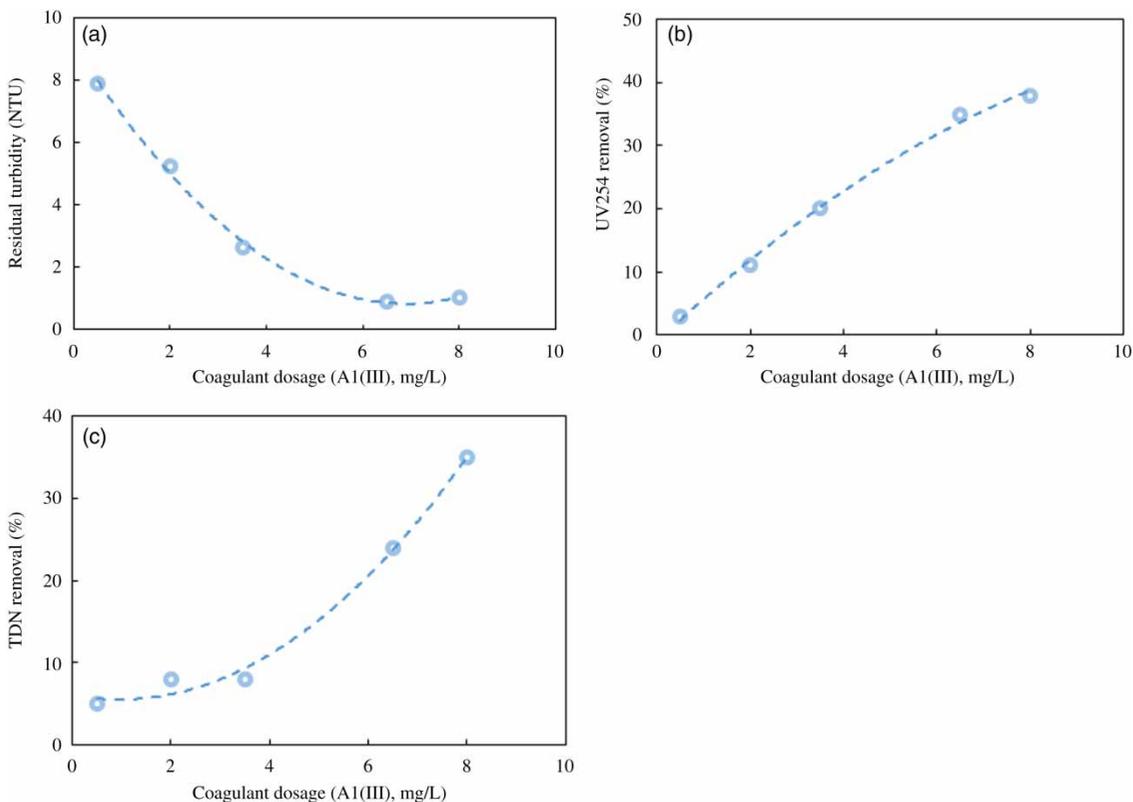


Figure 8 | Effect of PPAS dosage on (a) turbidity removal, (b) UV254 removal percentage, (c) TDN removal percentage.

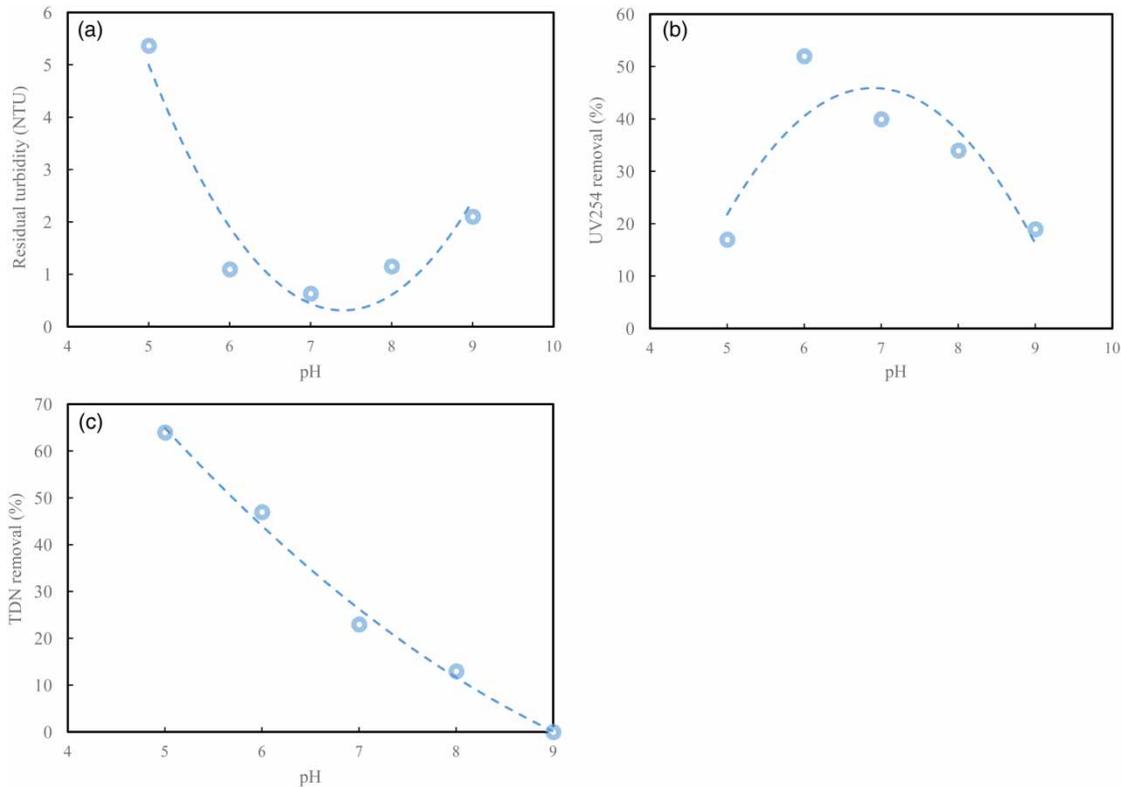


Figure 9 | Effects of pH on (a) turbidity removal, (b) UV254 removal percentage, (c) TDN removal percentage.

both not good, so coagulation–flocculation by the PPAS followed the micro-bridging mechanism, which gave an optimum PPAS dosage at 6.50 mg/L with a lowest residual turbidity of 0.92 NTU.

Inorganic metal coagulant has long been considered as an important phosphorus removal agent. However, for removal of other contaminants such as dissolved organic carbon (DOC) and TDN, removal performance was largely dependent on the type of coagulant, dosage, pH and the specific environmental conditions (Matilainen *et al.* 2010). In this study, the effects of PPAS dosage on the removal of UV254 and TDN were investigated. UV254 was in general linear to the DOC, which was a potential indicator of DOC for rapidly assessing and controlling water quality (Sen Kavurmaci & Bekbolet 2014). TDN was a mixture of dissolved organic nitrogen (DON) and inorganic nitrogen (DIN). It has been known to affect water quality and be a potential threat to human health as a precursor of nitrogenous disinfection by-products, especially DON (Chuang & Tung 2015). The coagulation–flocculation process has been

considered effective for carbon compound removal; however, for nitrogen organic compounds, it has not been as effective as the former is. The results showed that in the investigated PPAS dosage range, the removal efficiencies of UV254 and TDN increased significantly. At a PPAS dosage of 8 mg/L, the UV254 and TDN removal rates could achieve 38% and 35%, respectively.

Effect of pH

Because pH is a critical parameter that controls the coagulation–flocculation efficiency, the effects of pH on turbidity, UV254 and TDN removal efficiencies were investigated. The PPAS used in this experiment was a product with a fixed $n(\text{P})/n(\text{Al})$ ratio of 0.15, $n(\text{OH})/n(\text{Al})$ ratio of 0.2 and stabilizer dose of 7.5%. The quality of the raw source water indicated that the turbidity, UV254 and TDN were 23.90 NTU, 0.07 and 6.92 mg/L, respectively. This experiment was conducted at a PPAS dosage of 6.50 mg/L. The experimental result is shown in Figure 9.

Figure 9 shows that as the pH increased from 5 to 7, the residual turbidity decreased and then increased as pH increased further. The UV254 removal efficiency achieved the maximum at pH 6; it decreased with either increasing or decreasing the pH from there. A better coagulation for UV254 and turbidity was obtained in the pH range of 6–8. For coagulation of TDN, a decrease in the removal efficiency was found as the pH increased from 5 to 9. At pH 9, coagulation was ineffective for TDN. This could be attributed to the depletion of the effective Al(III) species because of the formation of aluminum hydroxide precipitate. At pH 5, TDN removal efficiency achieved the maximum of 64%. However, the removal rates of UV254 and turbidity were not ideal at this pH point. At pH 6, UV254 removal efficiency reached the maximum and the lowest residual turbidity value was achieved. From the above results, it was concluded that the coagulation–flocculation effects on carbon and nitrogen compounds, respectively, were different. In this study, the pH value of 6 was considered as the optimum condition based on the removal efficiencies of turbidity, UV254 and TDN. A further study of the pH effect on TDN removal is needed in the future. Meanwhile, preparing a modified PPAS with its species favorable to the efficient removal of both the carbon and nitrogen compounds under the same environmental condition will be an interesting research direction.

CONCLUSIONS

In this study, a modified coagulant PAS, polymeric phosphate-aluminum sulphate, was prepared. Parameters affecting PPAS performance, such as $n(\text{P})/n(\text{Al})$ molar ratio, $n(\text{OH})/n(\text{Al})$ molar ratio, and stabilizer dose containing a mixture of tartaric acid and sodium potassium tartrate, were examined. The $n(\text{P})/n(\text{Al})$ molar ratio of 0.15, $n(\text{OH})/n(\text{Al})$ molar ratio of 0.2 and stabilizer dose of 7.5% were found to be optimum for stabilization of the PPAS. The PPAS had more morphology compression, which was distinct from the AS product. The influence of PPAS coagulation performance analyzed through the species distribution indicated that Al_b and Al_c in PPAS played a significant role, especially the Al_b . At pH 6, the coagulation

system with PPAS showed excellent removal rates of source water turbidity, UV254 and TDN.

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