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Fractionation of residual Al in natural water treatment from reservoir with poly-aluminum-silicate-chloride (PASiC): Effect of OH/Al, Si/Al molar ratios and initial pH

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Abstract

An aluminum fractionation study was conducted for a surface reservoir water treatment to understand the performance of poly-aluminum-silicate-chloride (PASiC) in terms of the residual Al fractions as a function of initial pH. The coagulation performance expressed as turbidity and organic matter removal was established as supporting data. Some extra data were evaluated in terms of the residual Al ratio of the composite PASiC coagulant. The main residual Al sources were the Al fractions derived from the use of PASiC. The turbidity and organic matter removal ability was optimal at initial pH 6.00–7.00, while the concentrations of various residual Al species and the residual Al ratio of PASiC were minimal at an initial pH range of 7.00–8.00. Under the conditions of OH/Al molar ratio = 2.00 and Si/Al molar ratio = 0.05, PASiC had superior coagulation performance and comparatively low residual Al concentrations. The Al fraction in the composite PASiC coagulant seldom remained under such conditions. Experimental data also indicated that the suspended (filterable) Al fraction was the dominant species, and organic-bound or organo-Al complex Al was considered to be the major species of dissolved Al in water treated by PASiC coagulation. Additionally, the dissolved inorganic monomeric Al species dominated the dissolved monomeric Al fraction.

Key words: coagulation performance; OH/Al and Si/Al molar ratio; poly-aluminum-silicate-chloride (PASiC); residual Al speciation; residual Al ratio

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Introduction

Aluminum is one of the most abundant elements in soils and exists in soil solutions as well as in aquatic systems. In addition to natural or anthropogenic origins such as acid rain and atmospheric deposits, the use of Al-based coagulants in water utilities has been identified as responsible for the increase of aluminum concentration in natural or treated water, which leads to problems relating to water quality and supply (Srinivasan et al., 1999; Berthon, 2002; Zhao et al., 2006). A major concern regarding Al in the aquatic environment is its potential toxicity in freshwater systems and its implication in various neurodegenerative processes. Al is a powerful neurotoxicant, and has a potential for skeletal and haematopoietic toxicity, especially for patients on dialysis due to chronic renal failure (Berthon, 2002; Flaten, 2002). Recently, this problem has become more serious, and many countries have enacted limitation criteria on residual Al content in potable water, for example, 0.05 mg/L in the USA, and 0.2 mg/L for the

World Health Organization (Kvech and Edwards, 2002). The maximum permissible content of Al in drinking water in China is 0.200 mg/L.

Dissolved in water, Al exists as different species with varying toxicity (Berthon, 2002; Flaten, 2002; Kvech and Edwards, 2002; Perry and Shafran, 2001). In addition, Al can form complexes with various organic compounds (e.g., humic and fulvic acids, and low mass organic compounds) and inorganic ligands (e.g., fluoride, chloride, sulfate and phosphate), most of which are soluble (Guibaud and Gauthier, 2005; Zhao et al., 2009a). It is generally accepted that low molecular weight Al species, mainly of inorganic nature, are primarily responsible for Al toxicity in waters because they are able to pass through biological membranes (Guibaud and Gauthier, 2003, 2005). Under certain conditions such as low pH, Al tends to form species that are potentially toxic to all living organisms, including humans (Zhao et al., 2009a). Particularly, in spite of established guidelines for the control of Al, most studies only focus on the control of total Al (Wang et al., 2010). Moreover, unlike the coagulation performance of Al-based coagulants, the residual Al speciation and fractionation

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in treated water have rarely been investigated. Thus, the study of Al speciation in water treatment is of interest for water quality assessment, not only because it influences many related environmental processes, but also because the important geochemical and toxicological effects of this element in elevated concentrations depend on existing species (Zhao et al., 2009a).

Polymeric aluminum chloride (PAC) has been extensively used instead of $Al_2(SO_4)_3$ at water purification plants and wastewater treatment plants (Gao et al., 2002). The merits of PAC are reflected in its superior efficiency compared to conventional Al-salts and much lower cost than organic polymeric flocculants (Gao et al., 2003). However, regarding the morphology and coagulation characteristics, the molecular weight and size for aggregating action and its ability to resist further hydrolysis are still much lower than organic polymeric flocculants. These are the main weakness of PAC needing improvement (Zhao et al., 2009b) and more research is merited to develop Al-silicate polymer composite (PASiC) coagulants (Tzoupanos et al., 2009). Al-salts and polysilicate (PSi) can be combined together under certain conditions to prepare PASiC coagulants (Gao et al., 2003). As one of the forms of inorganic polymer coagulants, PASiC can be prepolymerized by hydroxylation individually and each component eventually becomes the polymeric proportion of the composite (Gao et al., 2007; Tzoupanos et al., 2009). However, little attention has been given to the observation and explanation of Al fractionation in the effluent of PASiC coagulation systems or the residual Al ratio of PASiC itself. Systemically studying the coagulation properties and the residual Al species distribution can provide an important practical guideline for the synthesis of a highly efficient PASiC coagulant.

In the present work, to provide insight into residual Al speciation after coagulation and sedimentation treatment using Al-based coagulants, PASiC with different OH/Al and Si/Al molar ratios was used for coagulation treatment of surface water from Quehua Reservoir in Jinan, China. The effect of the OH/Al and Si/Al molar ratios together with the initial solution pH was studied. The results obtained in this work will be useful for the development and application of a new kind of Al-silicate polymer composite coagulant (PASiC).

1 Materials and methods

1.1 Materials

Materials included high purity Al sheet (G.R. (guarantee reagent)), HNO_3 (G.R.), $AlCl_3·6H_2O$ (A.R. (analytical reagent)), HCl (A.R.), NaCl (A.R.), NaOH (A.R.), Na_2CO_3 (A.R.), water glass (C.P. (chemical pure), Na_2O 10%, SiO_2 30%), Chrome azurol S (A.R.), ascorbic acid (A.R.), CH_3CH_2OH (A.R.), 4-nitrophenol (A.R.), ethylenediamine (A.R.), ammonia (A.R.), cetyl pyridinium bromide (CPB, C.P.), and Triton X-100 (OP, C.P.). All reagents were used as received, without any further purification. Deionized water was used for preparation and

dilution of each reagent. High-density polyethylene bottles and containers for sample collection and storage were stored in HNO_3 solution (10% as volume percentage) for 12 hr and then rinsed with deionized water.

1.2 Preparation of PASiC coagulants

Water glass containing 30% SiO_2 was first diluted to a concentration of 0.5 mol/L SiO_2 solution with deionized water. The pH of the diluted water glass solution was adjusted to 1.50 with 0.500 mol/L HCl under intense magnetic stirring to obtain the final polysilicic acid (10.0 g/L SiO_2).

Na_2CO_3 solution was slowly added into $AlCl_3$ solution under rapid stirring using a micro-titration apparatus to prepare value polyaluminum chloride (PAC) products (10.0 g Al/L) with varying OH/Al ratio. Finally, different volumes of polysilicic acid were mixed with appropriate amounts of PAC solution to obtain PASiC coagulant, which had 3.00 g/L (Al) as well as the desired OH/Al ratios and Si/Al molar ratios (Gao et al., 2002, 2007). The selected OH/Al ratios were 1.50, 2.00 and 2.30 (Si/Al ratio was set at 0.05), and Si/Al ratios were of 0.02, 0.05 and 0.10 (OH/Al ratio was fixed at 2.00). The PASiC dosage was 12.0 mg/L of Al content.

1.3 Coagulation/flocculation experiment

The raw surface water collected from Quehua Reservoir, an important drinking water source in Jinan, China, was used to examine the coagulation performance and residual Al fractionation of PASiC. The raw water qualities are summarized as following: turbidity (0.90–1.91 NTU), UV_{254} absorbance (0.0450–0.0510), pH (8.41–8.62). This indicated that the raw surface water was characterized by low turbidity and low DOC content. The raw water initial pH was adjusted to predetermined values with 0.100 mol/L HCl and 0.100 mol/L NaOH solutions.

Standard jar tests for the surface water treatment were conducted using a program-controlled jar test apparatus (Zhongrun Water Industry Technology Development Co., Ltd., China). Each plexiglass beaker contain 1.00 L raw surface water with different pH. The coagulant dosage was determined at 12 mg/L as Al according to the previous studies (Yang et al., 2011) in view of the requirements of the single-factor tests and the optimal coagulant dosage of 12 mg/L for this specific surface water treatment. The fast mixing time after coagulant addition was set to 60 sec at 200 r/min, followed by 15 min of slow stirring at 40 r/min and 30 min of sedimentation. After settling, an unfiltered supernatant was withdrawn for residual turbidity measurements. A sample filtered through 0.45 μm membrane was tested for DOC content (TOC-V_{CPH} analyzer, Shimadzu, Japan) and absorbance at 254 nm wavelength (UV_{254}, via UV-754 UV/Vis spectrophotometer, Shanghai Jinghua Precision Scientific Instrument Co. Ltd., China). The results were the average values from 2–3 replicated jar tests and 3–5 replicated measurements of turbidity, UV_{254}, DOC, pH, and Al speciation concentration for each jar test effluent. Turbidity was measured using a portable turbidimeter, 2100P (Hach, USA).

1.4 Fractionation and measurement of residual Al speciation

The residual Al fractionation method used was a modification of the Benschoten and Edzwald method (Yang et al., 2011; Van Benschoten and Edzwald, 1990). Nucleopore polycarbonate 0.45 μm filters were used for the separation of total and dissolved Al. It need to be stressed that fresh membrane filters should be used and the first 50.0 mL filtrate should be avoided to prevent any contamination due to the filters (Yang et al., 2011; Srinivasan and Viraraghavan, 2002). A strongly acidic styrene type cation exchange resin (hydrogen form, 20–40 mesh) was used for separation of organically and inorganically bound Al. The detailed methods for residual Al separation and exchange resin pretreatment were introduced by Yang et al. (2011). Using this separation procedure, five different residual Al fractions can be obtained: total Al, total dissolved Al, dissolved organically bound Al, dissolved monomeric Al and the dissolved organic monomeric Al. The different residual Al species concentrations were measured by chrome azurol S colorimetric analysis according to the standard (GB/T5750.6-2006) of China. The precision of the method was verified within 10% and the detection limit was 0.008 mg/L.

1.5 Residual Al ratio of PASiC

The residual Al ratio of the PASiC coagulant can be calculated by the subtraction of total Al concentration (mg/L) in raw water from the residual total Al (mg/L) in purified water and then divided by the coagulant dosage (mg/L) (Wu and Chen, 2008).

2 Results and discussion

2.1 Coagulation performance of PASiC

Estimation of the effect of initial solution pH on the coagulation performance of PASIC was comparatively investigated. The results of jar tests are summarized in Fig. 1, and the effluent pH values are summarized in Table 1. It can be clearly seen that the measured values of residual turbidity exhibit a maximum value at initial pH of 6.00, and the residual turbidity of purified water at higher initial pH was low for any of the inorganic and organic hybrid coagulants.

The turbidity removal performance of PASiC with different OH/Al molar ratios varied as follows: OH/Al = 2.30 > OH/Al = 2.00 > OH/Al = 1.50. The residual turbidity in water purified by $PASiC_5$ at Si/Al molar ratio = 0.05 was the lowest (Fig. 1a, b).

With respect to the UV absorbance removal, the most significant removal was observed for OH/Al = 2.00 and Si/Al = 0.05 (Fig. 1c, d). The removal of UV absorbance by PASiC coagulation increased steadily with elevated initial pH in the lower initial pH range from 4.00 to 6.00, while this trend became reversed at higher initial pH ranging from 7.00 to 9.00. The obtained results suggested that the optimum pH range for UV removal was between 6.00–7.00 for each composite coagulant. Similar trends were obtained for the variation of DOC removal under different pH conditions (Fig. 1e, f), and the optimal pH was determined as initial pH = 6.00. However, the removal efficiencies diminished considerably with increasing initial pH above 6.00. Additionally, the highest DOC removal efficiency was attained under the conditions of OH/Al = 2.00 and Si/Al ratio = 0.05. Most notably, the data shown
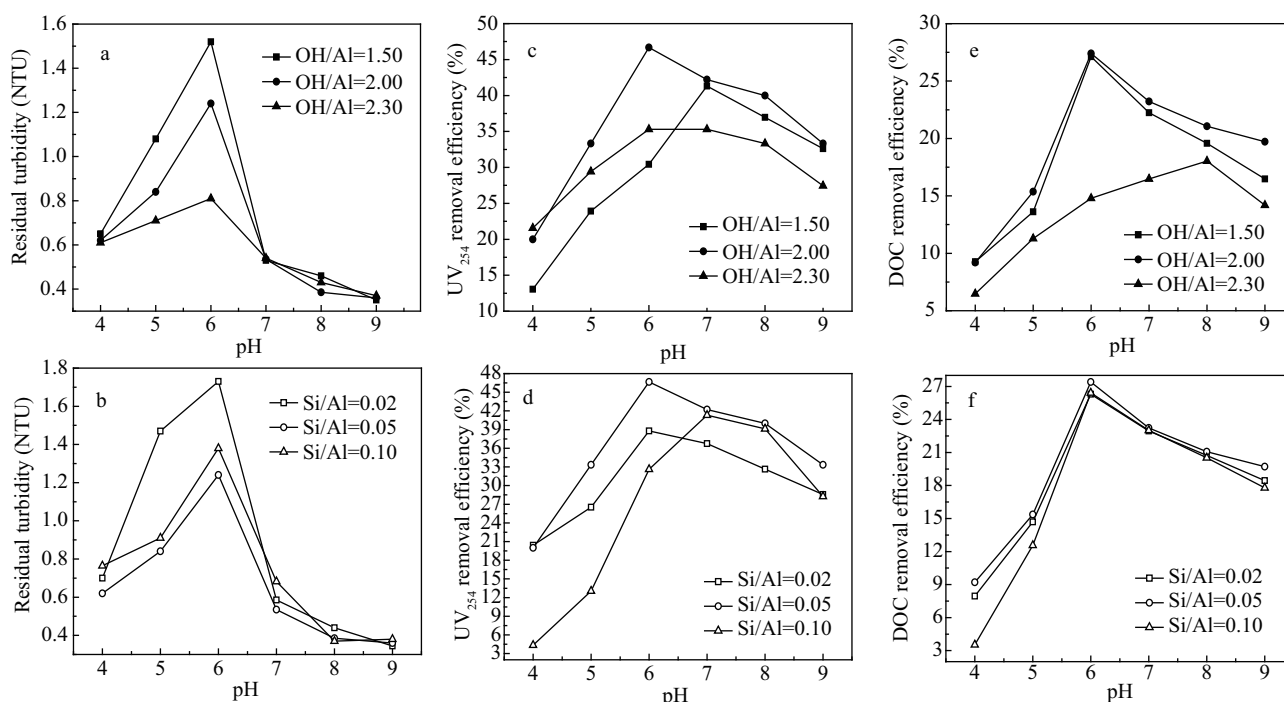

Fig. 1 Residual turbidity (a, b), UV_{254} removal efficiency (c, d) and DOC removal efficiency (e, f) of PASiC at different initial pH. Experimental condition: initial turbidity 1.24 NTU; UV_{254} 0.047; pH 8.45; temperature 20°C.

Table 1 Effluent pH of purified water after coagulation by PASiC with different OH/Al and Si/Al ratios

Initial pH	Effluent pH				
	OH/Al = 2.30	OH/Al = 2.00, Si/Al = 0.05	OH/Al = 1.50	Si/Al = 0.02	Si/Al = 0.10
4.00	4.67	4.59	4.40	4.58	4.45
5.00	6.01	5.23	4.66	5.15	5.09
6.00	7.41	7.34	6.33	7.60	6.83
7.00	8.05	8.10	7.41	8.15	8.31
8.00	8.29	8.13	7.83	8.11	8.38
9.00	8.52	8.30	8.12	8.39	8.66

in Fig. 1 indicated that optimum pH for organic matter removal was 6.00 for hybrid PASiC, no matter what the OH/Al and Si/Al molar ratio were. This was consistent with previous work (Qin et al., 2006; Park et al., 2000), in which the maximum removal efficiency was also achieved in the pH range of 6.00–7.00.

The observed peak value of residual turbidity for PASiC coagulation at initial pH of 6.00 was attributed to the characteristics of the raw water. The raw water had a low turbidity and low DOC content, which would result in smaller flocs during the PASiC coagulation process. These flocs may suspend in treated water and lead to considerably higher residual turbidity. The organic matter removal was strongly related to the Al speciation distribution and transformation of the composite coagulant, and the hydrolysis of Al-based coagulants due to initial pH variation (Zhao et al., 2009a). Compared with the influence of the surface charge of natural organic matter (NOM) molecules, the effect of initial pH on Al hydrolysis in the hybrid PASiC coagulant is the most important and significant aspect for the interpretation of PASiC coagulation performance, and it will in turn affect the interaction between Al and NOM (Zhao et al., 2009a). As indicated by the pH of raw and treated water (Table 1), the effect of initial pH on turbidity and NOM removal was correlated with the hydrolyzates of the Al-based coagulants. It was found that hydrolysis of the coagulant occurred immediately after it was added to water and PASiC could rapidly form dissolved species or hydroxide precipitates (Istv'an, 1993; Zhang et al., 2008). As stated by other researchers, monomeric and dimeric Al species and trimers (with some series of small polymers containing Al_4 and Al_5 cores) were the dominant components at initial pH lower than 5.00 (Zhao et al., 2009a). When pH was raised to 5.00–6.00, monomers and dimeric series diminished, whereas medium and large polymeric Al species containing Al_{13} cores became dominant in the coagulant. In the pH range of 6.00–7.00, the ratio of Al precipitates increased due to the formation of amorphous aggregates of $Al(OH)_3$ at higher pH (Zhao et al., 2009a; Liu et al., 2009). The higher pH (> 7.00) contributed to a more destabilized suspension system and decreased coagulation performance of PASiC, mainly due to the transformation of hydrolyzates into $Al(OH)_4^-$. As a consequence, the weakly acidic conditions of pH from 6.00 to 6.50 were beneficial to the stabilization of the short-lived highly positively charged polymeric intermediates (especially the Al_{13} speciation) and the poorly water-soluble Al hydroxide sols in dilute solutions for the time scales typical in water treatment (Liu et al., 2009). The colloids

and NOM were easily absorbed and co-precipitated by the highly polymeric positive hydrolyzates and $Al(OH)_3$ formed with low solubility and large surface area (Liu et al., 2009). Another factor could be the significant effect of initial pH variation on the physical and chemical characteristics of NOM. The NOM, especially the humic material, was acidic by virtue of ionizable carboxyl and hydroxyl groups, and it exhibited more negative charge with elevated pH under conditions of acidic initial pH from 4.00 to 6.00. As shown in Table 1, all the effluent pH dropped or increased towards the weakly acidic or neutral pH range. The effluent pH at OH/Al = 1.50 was the lowest and declined fastest, which was attributable to the relatively low OH/Al ratio. At one specific pH value, the effluent pH showed only slight difference in the coagulated effluent for PASiC with various Si/Al ratios. In addition, as indicated by the initial pH and the effluent pH (Table 1), a weakly acidic environment was beneficial to the reactions between humic acid and positively charged Al species (Gjessing, 1976).

The influence of the OH/Al ratio on the residual turbidity and NOM removal can be ascribed to the titration of Al salts with base and thus the different Al speciation distribution of the PASiC coagulant. At a lower OH/Al value, since the coagulant pH was lower, the hydrolysate of Al appeared mainly in the form of lower polymerization degree coordination of Al^{3+} with hydroxyl (Kim et al., 2001), which exhibited inferior sweep flocculation for the turbidity and NOM removal. With increasing OH/Al ratio, the polymerization degree of Al in PASiC was improved and large quantities of more highly polymeric Al species could form and become the dominant species, which subsequently strengthened the bridge and adsorption ability of the coagulant (Gao et al., 2002, 2007; Yang et al., 2011). However, with OH/Al ratio further increasing to 2.30, although the polymerization degree of Al was enhanced to form much more extensive polymeric speciation and amorphous $Al(OH)_3$, the positive charge per Al was normally lower, inhibiting the formation of charge neutralized aggregates, which was beneficial to the subsequent sweep flocculation. In this mode, particles and NOM were stabilized by adsorption of $Al(OH)_3$ sols and were enmeshed in sol aggregates.

Additionally, the incorporated polysilicate in PAC could interact with Al and its hydrolysate by Al-O-Si bonds to form silica-aluminum hydrolyzed species complexes (hydroxyaluminosilicate) with larger size and molecular weight (Gao et al., 2002). Thus, for a given OH/Al value, an elevated Si/Al ratio would increase the extent

of polymeric coordination, which was favorable to particle adsorption. The inhibited coagulation of PASiC with molar ratio further increased to 0.10 can be ascribed to the fact that the negatively charged polysilicic acid would largely neutralize the positive charge of poly-Al. These results indicated that when polysilicate and PAC were properly combined, a higher coagulation efficiency composite PA-SiC could be achieved.

2.2 Residual Al speciation under different OH/Al ratios

The OH/Al ratio can be used for expressing the degree of pre-hydrolysis of the PAC utilized for PASiC preparation. With different OH/Al molar ratios, PASiC exhibited varying properties which may result in the difference of concentration and speciation distribution of residual Al in purified water. Apart from this, in various studies, pH was believed to be one of the most important factors affecting Al species present in aqueous solutions (Zhao et al., 2006). The amounts of different residual Al speciation varying with solution initial pH were examined in water treated by PASiC coagulation for different OH/Al molar ratios, and the results are presented in Fig. 2.

The actual physicochemical species of Al in exposure media such as aqueous solution and in different body compartments is highly related to the solution properties. As shown in Fig. 2, different residual Al speciation in the effluent after PASiC coagulation exhibited quite similar trends as a function of solution initial pH. The concentrations of different residual Al species were recorded in descending order and then ascending order with initial pH variation, and residual Al concentrations were minimal for the initial pH 7.00. As surface water pH further increased, the content of various residual Al species showed an increasing trend. This tendency in residual Al concentration can be explained by a twofold effect summarized as

follows: firstly the coagulation performance of PASiC and secondly the Al speciation distribution with solution initial pH variation, while the latter dominated the variation of the residual Al speciation content. Earlier studies have confirmed that Al is entirely soluble in strongly acidic conditions and gel-Al(OH)$_3$ will form in a neutral or weakly alkaline environment, while dissolved Al(OH)$_4^-$ exists in strongly alkaline solutions (Zhang et al., 2008; Kim et al., 2001). This is consistent with the variation pattern of residual Al concentration summarized in Fig. 2. On the other hand, this trend was also evident in data shown in Fig. 1 where PASiC was proven to be more effective in the initial pH range of 6.00–7.00. In this pH range, the Al component in the coagulant itself coagulated with turbidity- and organic matter-causing materials, and subsequently little Al remained in treated water compared to other initial pH values.

Regarding the influence of OH/Al ratio on different residual Al speciation contents, it can be confirmed from Fig. 2 that in the lower pH range, residual total Al and dissolved Al concentrations varied in the following order: OH/Al = 2.30 > OH/Al = 1.50 > OH/Al = 2.00. However, the trend was reversed for residual total Al concentration in OH/Al = 1.50 and OH/Al = 2.30 coagulation systems. The dissolved Al content after OH/Al = 1.50 and OH/Al = 2.30 coagulation was essentially indistinguishable under alkaline conditions. For dissolved monomeric Al, a slight concentration variation was observed between the results obtained with OH/Al = 1.50 coagulated water and those with OH/Al = 2.30. Additionally, the dissolved organically-bound Al concentration was observed to vary according to the following sequence: OH/Al = 1.50 > OH/Al = 2.30 > OH/Al = 2.00. In conclusion, regardless of the residual Al speciation, the minimum content of the corresponding Al fractions was always achievable at
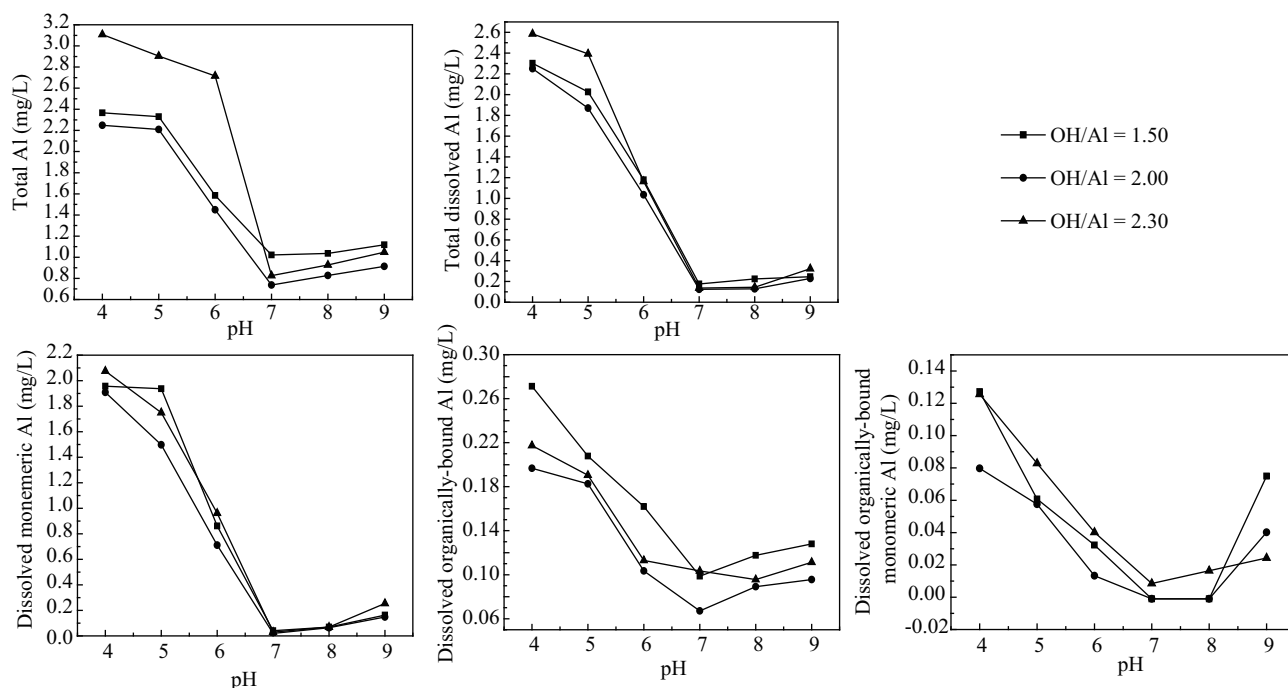

Fig. 2 Effect of OH/Al ratio on the content of different residual Al speciation. Experimental condition: initial turbidity 1.24 NTU; UV$_{254}$ 0.047; pH 8.45; temperature 20°C.

OH/Al = 2.00. This is also related to the coagulation performance of PASiC for different OH/Al ratios as indicated in Fig. 1. The formation of organic matter-Al complexes during the coagulation process allowed Al to be maintained in soluble forms despite unfavorable physicochemical conditions. The reason for the comparatively lower residual Al concentration can be attributed to the superior turbidity and organic matter removal efficiencies.

In addition, the following phenomena can also be observed from Fig. 2. Under neutral or weakly alkaline conditions (7.00 < pH < 8.00) with comparatively lower residual Al concentration, the treated water total Al was predominantly present in suspended or particulate Al for this surface water treatment by PASiC coagulation. However, at pH < 6.0 or pH > 8.00, the finished water total Al was predominantly present in the dissolved Al form rather than suspended or particulate Al. Meanwhile, in the dissolved residual Al fraction, organically-bound forms (organically-bound Al, also known as organic Al complexes) were present with higher concentrations in treated water. The dissolved inorganically bound Al fraction accounted for a large proportion of the monomeric Al fraction. The treated water contained only a small amount of dissolved organically-bound monomeric Al for any PASiC coagulation. This can be interpreted as follows: inorganically-bound Al was mostly the monomeric cation, while organically-bound Al existed mostly in oligomers or complexes formed between Al and NOM or polymeric colloidal materials in the water, which was more non-labile and could not easily be removed through the conventional coagulation process (Srinivasan et al., 1999; Van Benschoten and Edzwald, 1990). In particular, dissolved organically-bound monomeric Al was almost undetectable in the water treated with three PASiC products. Judging

from the results stated in Section 2.1 and 2.2, it could be concluded that PASiC with OH/Al = 2.00 presented advantageous flocculation properties which can be verified not only by the favorable coagulation performance but also by the relatively lower residual Al concentration. The concentrations of different residual Al (especially the more toxic dissolved monomeric Al) can be controlled at the pH range of 7.00–8.00 (Silwood and Grootveld, 2005; Zhao et al., 2006).

2.3 Residual Al speciation for different Si/Al molar ratios

Based on the preliminary experimental results, the influence of three Si/Al molar ratios (0.02, 0.05, and 0.10) on the concentration of five different residual Al species in coagulated water was explored within pH range of 4.00–9.00 (Fig. 3).

Quite similar to the results investigated in Fig. 2, the minimum residual Al concentration can be achieved in the pH range 7.00 to 8.00, and the Al speciation distribution together with its solubility variation with pH was largely responsible for the shift in residual Al content. Furthermore, the residual Al speciation distribution and the proportion of various residual Al species were also similar to the results shown in Fig. 2. The results shown in Section 2.1 and 2.3 indicated that PASiC with Si/Al ratio = 0.05 was effective to remove turbidity- and organic matter-causing materials from reservoir water and subsequently led to relatively lower content of residual Al in purified water.

It was confirmed that the addition of polysilicic acid into PAC had a twofold effect on the characteristics and performance of composite PASiC. Firstly the negatively charged polysilicic acid can weaken the charge neutralization
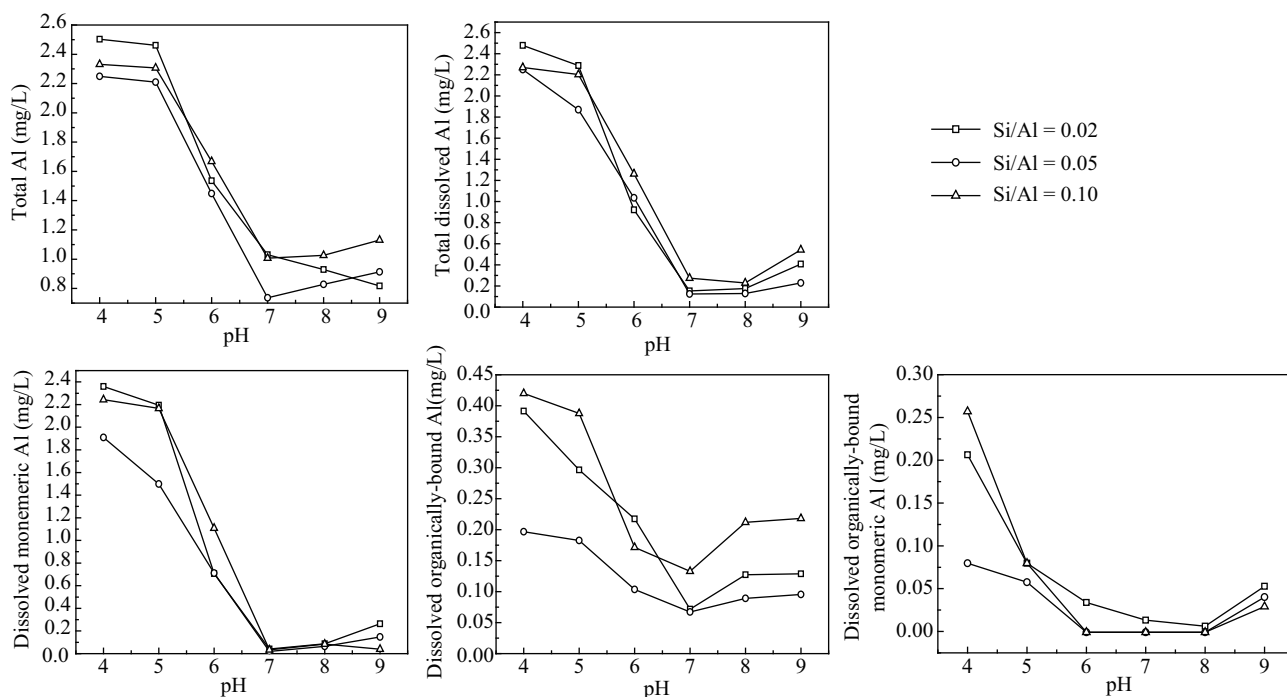

Fig. 3 Effect of Si/Al ratio on the content of different residual Al species. Experimental condition: initial turbidity 1.24 NTU; UV$_{254}$ 0.047; pH 8.45; temperature 20°C.

property of the composite product. Secondly the bridging adsorption and particle flocculation can be improved due to polysilicic acid incorporation (Gao et al., 2002, 2007). On the other hand, particulate and organic material removal from this surface water by composite coagulation is performed primarily by particle-bridging flocculation prior to charge neutralization (Yang et al., 2011). Therefore, due to the relatively lower Si/Al ratio, PASiC$_2$ showed inferior bridging capacity and coagulation-sedimentation performance, which resulted in higher concentrations of residual Al in treated water. Yet, the excessive addition of polysilicic acid in PASiC (with Si/Al molar ratio 0.10) would lead to instability in the composite PASiC coagulant, resulting in an inferior flocculation effect and higher residual Al concentration. Particularly, in accordance with the literature (Wang et al., 2010), polynuclear silicic acid can also increase the concentration of sol-Al and subsequently the total residual Al.

The results shown in Fig. 3 also suggest that PASiC$_5$ could effectively reduce concentrations of total dissolved Al and dissolved monomeric Al, especially in the initial pH range 7.00–8.00. According to the literature, the free Al^{3+} or the sum of the concentrations of Al^{3+}, Al(OH)$^{2+}$, Al(OH)$_2^+$ and Al(OH)$_4^-$ are considered as Al forms toxic for aquatic life (Guibaud and Gauthier, 2003, 2005). The content variation of organic Al complexes fraction is most likely the result of the fact that the residual organic matter in treated water exhibited a different Al-binding capacity among the three composite PASiC coagulants compared to that in raw water (Zhao et al., 2006).

2.4 Residual Al ratio of PASiC coagulant at different solution initial pH

Al-based coagulants may either increase or decrease the Al concentration in a purified solution, depending on the Al speciation in the source water, Al species in coagulants, *in-situ* Al species transformation and treatment conditions (Srinivasan et al., 1999). For a given Al-based coagulant, the residual Al ratio can indicate the residual Al fraction induced by the Al-based coagulant in purified water (Yang et al., 2011). Typically, the residual Al introduced by the Al-based coagulants is the largest proportion of the

residual Al in treated water (Zhao et al., 2006). The effectiveness of the composite PASiC coagulant was also evaluated by measurement of total residual Al in an attempt to investigate the residual Al percentage induced by PASiC itself. A summary of the effectiveness of PASiC in terms of residual Al ratio with increasing solution initial pH (4.00–9.00) for PASiC coagulation with various OH/Al and Si/Al ratios is presented in Fig. 4.

It can be concluded from the results in Fig. 4 that despite the influence of OH/Al molar ratio or the effect of Si/Al molar ratio, the residual Al ratio of PASiC showed quite similar tendency, i.e., decreasing initially with solution pH enhancement and then increasing slightly as solution pH further increased. This trend was also evident in data as depicted in Figs. 2 and 3 (concentration of residual Al species). The residual Al ratio reached the lowest value when the solution initial pH was 7.00–8.00, expressed as 4.30% for OH/Al = 2.00 (Si/Al = 0.05). That is to say, only 4.30% of the Al fraction in PASiC (OH/Al = 2.00 and Si/Al = 0.05) remained as residual Al present in purified water after coagulation in the pH range 7.00–8.00 and at coagulant dosage of 12.0 mg/L.

As noted above, solution pH has in theory an influence on the residual Al speciation distribution and its solubility, and subsequently the diversification of residual Al ratio along with solution initial pH variation can be well explained from the perspective of this theory. Besides, regarding the influence of OH/Al and Si/Al ratio, the residual Al ratio was minimal for the OH/Al = 2.00 and Si/Al = 0.05. Specifically, the residual Al species in all silica-enriched coagulants examined in these studies remained extremely high at relatively low solution pH, which is attributable to the fact that PASiC could not react sufficiently with particulate and organic material in raw water and subsequently the residual Al fraction in PASiC easily remained under these low pH conditions.

The results regarding the influence of OH/Al ratio was in good agreement with the coagulation performance summarized in Fig. 1 (OH/Al = 1.50 and 2.30 showed inferior coagulation performance and high residual Al ratio), and this indicates that the Al fraction at OH/Al = 1.50 and 2.30 were merely removed partially after reacting with the
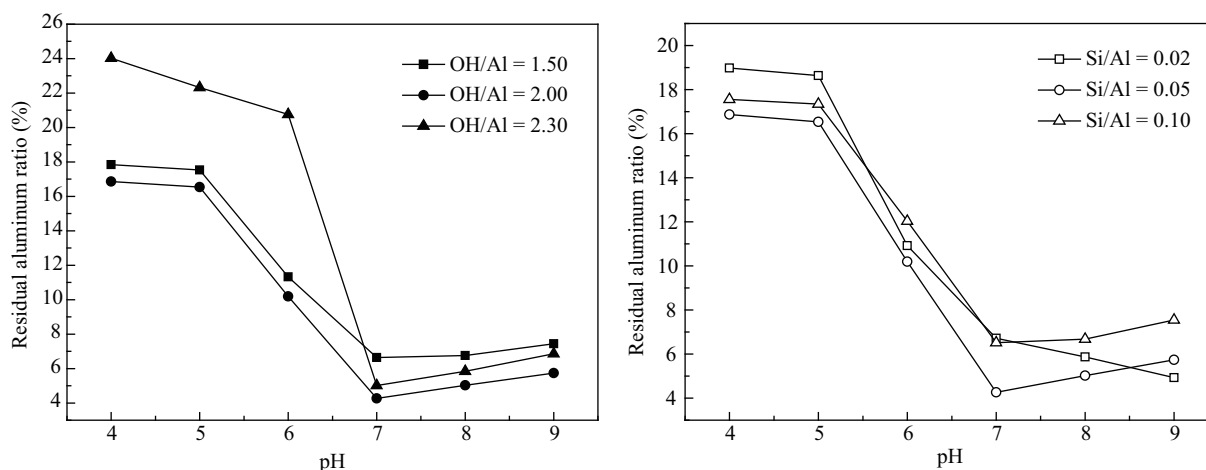

Fig. 4   Residual Al ratio of PASiC coagulant at varying initial pH. Experimental condition: initial turbidity 1.24 NTU; UV$_{254}$ 0.047; pH 8.45; temperature 20°C.

pollutants during the coagulation process. Apart from this, it can also be identified from Figs. 1 and 4 that Al species at Si/Al = 0.02 and 0.10 remained abundant in the purified water after coagulation. A lower residual Al ratio can be reasonably induced for the composite PASiC coagulants at an initial pH range from 7.00 to 8.00.

The high total residual Al concentration (more than 0.5 mg/L) can be explained by the high Al concentration in the raw water (particulate materials containing an Al_2O_3 component as well as some possible impurities in the Yellow River water) together with the fraction caused by the Al-based coagulants (Zhao et al., 2006). Additionally, the water treatment units utilized in this study only included coagulation-flocculation and sedimentation and it is necessary and crucial to investigate the effects of the subsequent treatment units (flotation, filtration, adsorption, disinfection, etc.) on the residual Al concentration for the purpose of reducing residual Al concentration.

3 Conclusions

Characterization of residual Al in water treated by PASiC coagulation showed that the residual Al speciation distribution was highly variable and that the filterable (suspended) form of Al was the dominant species of total residual Al in treated water under conditions of 7.00 < pH < 8.00. However, in finished water total Al was predominantly present in the dissolved Al form at pH < 6.00 or pH > 8.00. Organically bound Al appeared to be the dominant species of dissolved Al and dissolved monomeric Al was mostly present in the form of inorganically Al in treated water. The OH/Al ratio and Si/Al ratio in PASiC and the solution initial pH should be selected appropriately to achieve the optimum coagulation performance and reduce the content of residual Al species.

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