



Effect of $\text{OH}^-/\text{Al}^{3+}$ and Si/Al molar ratios on the coagulation performance and residual Al speciation during surface water treatment with poly-aluminum-silicate-chloride (PASiC)

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ABSTRACT

Coagulation performance, mechanism of poly-aluminum-silicate-chloride (PASiC) and residual Al speciation in the effluent with respect to a specific surface water treatment in China were comprehensively investigated in this study. The impact of $\text{OH}^-/\text{Al}^{3+}$ and Si/Al molar ratios on the coagulation performance, mechanism and residual Al speciation of PASiC in surface water treatment was discussed as a function of coagulant dosage. It was intended to provide an insight into the relationship between coagulation performance and residual Al. Experimental results revealed that when $\text{OH}^-/\text{Al}^{3+}$ molar ratio = 2.00 and Si/Al molar ratio = 0.0500 in PASiC coagulant, PASiC exhibited beneficial coagulation property and relatively lower content of residual Al. Surface bridging and entrapment was more effective compared with charge neutralization during the specific surface water treatment. The majority of residual Al in the effluent existed in the form of insoluble suspended or particulate Al. Dissolved organically bound Al was almost the major speciation in dissolved Al and dissolved inorganically bound monomeric Al was the only component in dissolved monomeric Al. Al in PASiC remained abundant at lower dosages and residual Al concentration could be effectively reduced at the dosages of 12.0–15.0 mg/L as Al.

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1. Introduction

Aluminum (Al) is among the trace inorganic metals in drinking water. Because of its ubiquity in environment and presence in living organisms, Al can react with various ligands (e.g., humic and fulvic acids, low mass organic compounds and some inorganic ions) and organic molecules in living beings to form some complexes, which can result in certain toxicity [1,2]. In addition, although Al-based coagulants such as $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (known as alum) or polyaluminum chloride are effective in the removal of particulate and natural organic matters (NOM) [3], higher concentrations of Al in treated water often exist when Al-based coagulants are used in water treatment [4]. For many years, the occurrence of Al in water has been regarded as an undesirable aspect of treatment practice and it is mainly attributed to two reasons [5,6]. First, acid rain has caused the increase of Al level in many freshwater sources. A high (3.60–6.00 mg/L) concentration of Al gives rise to turbidity and pipe wall deposition, reduces disinfection efficiency, and may precipitate as $\text{Al}(\text{OH})_3$ in the distribution process. Secondly, it has been verified by recent studies that Al is a suspected causative agent of neuropathological diseases such as Alzheimer's disease,

Parkinson's disease, dialysis encephalopathy and presenile dementia [7–9]. In China, the total Al limits in drinking water should not exceed 0.200 mg/L.

During water treatment process, Al undergoes various transformations (called 'speciation' of Al) influenced by turbidity, water temperature, pH and organic or inorganic ligands. So Al is present in various forms in the environment and its adverse effect on water distribution system and human is highly related to specific species [3,10]. High concentrations of dissolved Al indicate incorrect coagulant added, inefficient coagulant use or problems in treatment process chemistry, while high concentrations of particulate Al may lead to problems in solid–liquid separation of post-precipitation of Al [11]. Accordingly, Al speciation should be considered in the evaluation of its influence on drinking water distribution system and human health. However, most researches were aimed at the control of content of total Al alone in drinking water [9]. Fractionation of various Al forms in raw water and treated water was rarely performed. Thus, it seemed necessary to carry out Al fractionation studies in order to provide operators with valuable information about the various aspects of plant performance as well as to protect human health and ecological system.

Coagulation performance of poly-aluminum-silicate-chloride (PASiC), one of forms of inorganic polymer coagulants, in water and wastewater treatment was already studied by some researchers [12,13]. However, little attention has been given to the observa-

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Table 1
Raw water characteristics and methods of measurement.

Parameter	Value	Measuring methods
Dissolved organic carbon (DOC)	1.47–1.98 mg/L	Prefiltered sample measured on a TOC analyzer (Shimadzu, Japan)
Ultraviolet light absorption at 254 nm (UV ₂₅₄)	0.0510–0.0630 cm ⁻¹	Prefiltered sample measured on a UV-754 UV/VIS spectrophotometer (Jinghua Precision Scientific Instrument Co., Ltd., China)
Turbidity	0.580–2.00 NTU	Portable turbidimeter 2100P (Hach, America)
Total dissolved solid (TDS)	515–594 mg/L	Gravimetric method at 103–105 °C
Total suspended solid (TSS)	17.0–26.0 mg/L	Gravimetric method at 103–105 °C
pH	8.27–8.38	pH analyser
Zeta potential	–13.6 to –11.2 mV	Zetasizer 3000HSa (Malvern Instruments, UK)
Specific UV absorbance (SUVA)	2.60–3.73 L/(mg m)	SUVA = UV ₂₅₄ /DOC × 100
Total Al	0.153–0.164 mg/L	Chrome azurol S spectrophotometer according to GB/T5750.6-2006
Total dissolved Al	0.0710–0.0980 mg/L	Chrome azurol S spectrophotometer according to GB/T5750.6-2006
Dissolved monomeric Al	0–0.0130 mg/L	Chrome azurol S spectrophotometer according to GB/T5750.6-2006
Dissolved organically bound Al	0.0630–0.0750 mg/L	Chrome azurol S spectrophotometer according to GB/T5750.6-2006

tion and explanation of Al fractionation studies on the effluent and residual Al ratio of the coagulant itself. Systemically studying the coagulation property and the law of residual Al species distribution can provide an important practical guideline for the synthesis of a high efficient coagulant. In this study, Al characterization (speciation) studies were conducted with respect to the coagulation of a low turbidity and low dissolved organic carbon (DOC) concentration surface water using several PASiC samples with various OH⁻/Al³⁺ molar ratios (basicity, *B*) and Si/Al molar ratios as a function of coagulant dosage. Comparative investigation was developed in terms of concentrations of different residual Al species together with residual Al ratio of PASiC itself. The content and variation of different residual Al speciation in the effluent after coagulation with reference to the specific surface water treatment were systematically examined and analyzed.

2. Materials and methods

2.1. Experimental materials

Nitric acid and Al sheet (guaranteed reagent, >99.9%) were used for the separation and measurement of residual Al speciation. Strongly acidic styrene type cation exchange resin (hydrogen form, 20.0–40.0 mesh) was used for the separation of organically and inorganically bound Al speciation. In addition to the chemically pure cetyl pyridinium bromide and emulsifier (Triton X-100), other reagents used were analytically pure reagents. Polyethylene bottles with high density were used for the collection of water samples. All devices used were stored in HNO₃ solution for 12.0 h and then rinsed with deionized water.

2.2. Preparation and synthesis of poly-aluminum-silicate-chloride (PAsiC) coagulants

Water glass containing 30.0% SiO₂ was first diluted to 0.500 mol/L SiO₂ solution with deionized water and then was neutralized to pH 1.50 with 0.500 mol/L HCl under magnetic stirring [13]. The final polysilicic acid solution contained 10.0 g/L SiO₂.

Na₂CO₃ solution was initially added to AlCl₃ solution at rapid stirring and room temperature to prepare 10.0 g Al/L of PAC products with various *B* values [14], which was homogeneous and transparent. And then appropriate amount of polysilicic acid was introduced to achieve PASiC products with desired Si/Al molar ratio [15]. At fixed Si/Al ratio of 0.0500, PASiC products with *B* values of 1.50, 2.00 and 2.30 (denoted as PASiC₁₅, PASiC₂₀ and PASiC₂₃) were selected to investigate the effect of *B* value on the coagulation performance and residual Al speciation of PASiC in surface water treatment. In addition, at fixed *B* value of 2.00, PASiC products with Si/Al ratio of 0.0200, 0.0500 and 0.100 (denoted as PASiC₂, PASiC₅

and PASiC₁₀) were selected. Actually, PASiC₂₀ and PASiC₅ were the same product. Different PASiC dosage was calculated as the content of Al (mg/L) during all the experiments.

2.3. Coagulation experiments

All experiments were carried out on raw water collected from a reservoir in Ji'nan in eastern China with water quality shown in Table 1. The raw water was characterized by low turbidity, low DOC content and low SUVA (defined as UV₂₅₄ per DOC content in mg/L). Standard jar tests were performed using a program-controlled jar test apparatus with six flat impellers at a room temperature of 18.0–20.0 °C. The test water of 1.00 L was transferred into each 2.00 L plexiglass beakers. The solutions were stirred rapidly at 200 rpm for 1.50 min during coagulant addition, followed by slow stirring at 40.0 rpm for 15.0 min and quiescent settling for 30.0 min. After deposition, water samples were collected from 2.00 cm below the solution surface for subsequent measurements. PASiC dosages ranged from 3.00 to 18.0 mg/L as Al.

2.4. Separation and measurement of different residual Al speciation

The Al fractionation was a modification of a previously developed method [11,16]. The digestion procedure involved reducing sample pH < 1.00 using HNO₃ and heating for 1 min after it was boiled at pH < 1.00. 1.00 mol/L HCl, NaOH and NaCl were used for pretreatment of exchange resin as stated in previous research [16,17]. Water samples passed through exchange column at 13.0–14.0 mL/min. Discarding initial 10.0 mL filtrate, filtrated substance was then collected for subsequent analysis to prevent pollution due to filters [16,18].

The content of different residual Al speciation was measured by chrome azurol S spectrophotometer according to the Chinese national standard [19]. Precision of measurement as relative standard deviation of 10 samples was within 10.0% and the detection limit was 0.00800 mg/L. Residual Al content could be calculated as follows:

$$C = (0.3165E - 0.0002)n \quad (1)$$

where *C* was the residual Al content of test water (mg/L), *E* was the absorbance of different water sample and *n* was the dilution multiple. 0.3165, –0.0002 was the slope and intercept of Al content-absorbance standard curve, respectively.

2.5. Residual Al ratio of PASiC coagulant

In general, residual Al ratio represents the residual Al induced by coagulant itself and it is an important parameter of various coagu-

lants in practical application [17,20]. It can be calculated according to the following equation:

$$\text{residual aluminum ratio (\%)} = \frac{\text{residual total Al in the purified water (mg/L)} - \text{total Al in raw water (mg/L)}}{\text{coagulant dosage (mg/L)}} \times 100\% \quad (2)$$

3. Results and discussion

3.1. Evaluation of coagulation behaviors of PASiC under different B values as a function of coagulant dosage

The coagulation performance and mechanism of PASiC₁₅, PASiC₂₀ and PASiC₂₃ were studied under raw water condition. The variation of residual turbidity, UV₂₅₄ and DOC removal efficiencies of PASiC with different B values along with zeta potential were displayed in Fig. 1. SUVA and pH of the effluent were shown in Table 2.

Fig. 1(a) partially suggested that PASiC₂₀ and PASiC₂₃ had better turbidity removal performance than PASiC₁₅, especially at higher dosages. As indicated in Fig. 1(a), for PASiC₁₅, when zeta potential was close to zero, the residual turbidity was also the lowest. Both zeta potential and residual turbidity increased with PASiC₁₅ dosage increasing. The inferior performance of PASiC₁₅ could be attributed to the fact that surface of colloid particles was positively charged (Fig. 1(a)) which was directly related to the repulsion between coagulant and destabilized Al-NOM complex and particulates [21,22]. However, in the case of PASiC₂₀ and PASiC₂₃, residual turbidity still decreased when zeta potential increased or changed slightly at higher dosages. This indicated that bridging and entrapment exhibited superior effect to remove turbidity for PASiC₂₀ and PASiC₂₃, particularly at higher dosages. At a lower B value, since coagulant pH was lower, polysilicic acid with a lower polymerization degree was the preponderant form. The hydrolysate of Al appeared mainly in form of dimer, monomer or lower polymerization degree coordination of Al³⁺ with hydroxyl [23]. As also stated by others, with increasing OH⁻/Al³⁺ ratio, the polymerization degree of Al in PASiC was improved and the content of larger polymeric Al species also increased [24]. Similarly, Gao et al. [13] suggested that the combination of PAC and polysilicic acid could be enhanced in aggregating efficiency due to high molecular weight but weakened charge effect in the coagulation process. As a consequence, surface bridging adsorption and entrapment were more effective in turbidity removal for treating this surface water, compared with charge neutralization. Although the details are not fully understood, it seems clear that impure particles are enmeshed in growing hydroxide precipitate and are effectively removed from suspension [25].

As shown in Fig. 1(b) and (c), DOC and UV₂₅₄ removals demonstrated the same tendency: the removal efficiency increased gradually with increasing coagulant dosages and further increase in coagulant dosages did not cause further increase in the percentage of removal of DOC and UV₂₅₄. Additionally, PASiC₂₀ manifested the best UV₂₅₄ removal and PASiC₂₃ showed optimal DOC removal. At low PASiC dosages, Al and its hydrolysate interact electrostatically with anionic NOM and subsequently formed insoluble particulates. Charge neutralization was the major and effective mechanism for this removal phase of colloids and NOM [21]. When the dosage was high enough to cause rapid hydroxide precipitation, NOM could be removed by sweep flocculation [22]. Additionally Al reacted with NOM to form complex which remained in solution until binding capacity of NOM was saturated or the complex solubility was exceeded [25,26]. Another explanation is that pH could influence physical and chemical properties of NOM in water and the weakly acid ambience was favorable to NOM removal [27]. Table 2 demonstrated that effluent pH dropped towards weakly acidic range

as coagulant dosages increased which was correlated well with the considerable removal of NOM at higher dosages. The superior coagulation properties of PASiC₂₀ and PASiC₂₃ for NOM removal were thought to be due to the different mechanisms. For PASiC₁₅, charge neutralization was the major removal mechanism which

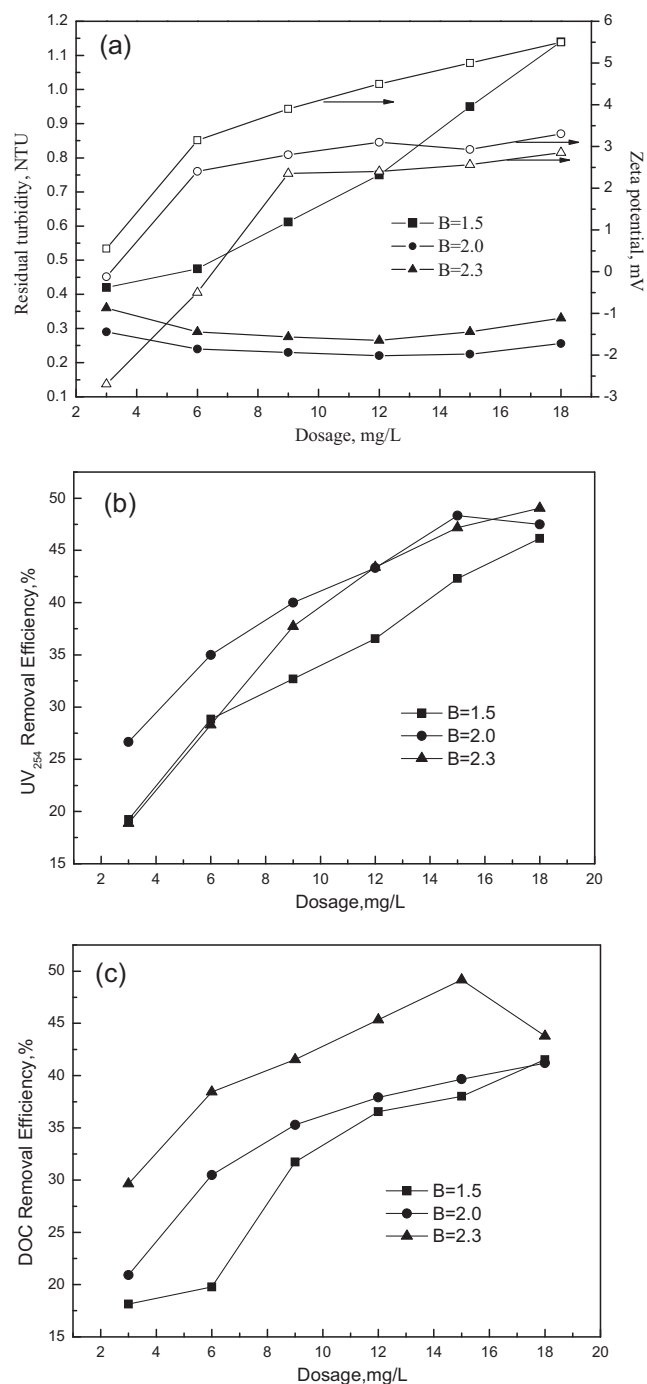


Fig. 1. Coagulation performance of PASiC₁₅, PASiC₂₀ and PASiC₂₃ as a function of coagulant dosage and B value: (a) residual turbidity along with zeta potential of formed flocs, (b) UV₂₅₄ removal efficiency and (c) DOC removal efficiency.

Table 2
Effluent pH, SUVA and residual aluminum ratio of PASiC under different *B* values as a function of coagulant dosage.

Water samples	Coagulant dosage (Al, mg/L)					
	3.00	6.00	9.00	12.0	15.0	18.0
Effluent pH						
Purified water after coagulation with PASiC ₁₅	8.01	7.79	7.65	7.53	7.42	7.33
Purified water after coagulation with PASiC ₂₀	8.14	7.98	7.85	7.73	7.67	7.60
Purified water after coagulation with PASiC ₂₃	8.22	8.09	8.05	7.96	7.92	7.83
Effluent SUVA						
Purified water after coagulation with PASiC ₁₅	3.49	3.13	3.48	3.53	3.28	3.25
Purified water after coagulation with PASiC ₂₀	3.41	3.44	3.41	3.35	3.35	3.33
Purified water after coagulation with PASiC ₂₃	3.56	3.60	3.29	3.20	3.21	2.80
Coagulant type		Residual aluminum ratio of PASiC coagulant (%)				
PASiC ₁₅	18.4	8.41	7.97	7.79	7.20	6.56
PASiC ₂₀	12.7	3.98	2.08	1.21	1.18	0.960
PASiC ₂₃	14.4	6.22	1.50	0.720	1.27	1.47

played a minor role in NOM removal. PASiC₂₀ and PASiC₂₃ in contrast removed NOM depending mainly on bridging adsorption and entrapment prior to charge neutralization. On the other hand, SUVA was an index of hydrophobicity/hydrophilicity of DOC [28]. In this study, SUVA of raw water was less than 4.00 L/(mg m) which indicated that DOC was hydrophilic, low molecular weight, and difficult to be removed [28,29]. Similarly, as shown by the results of Table 2, SUVA of treated water was about 3.00–3.60 which suggested that effluent DOC was still hydrophilic. Meanwhile, SUVA after PASiC₁₅ and PASiC₂₃ flocculation decreased with increasing coagulant dosages while SUVA with PASiC₂₀ coagulation varied little. It can be concluded that the increase of PASiC₂₀ dosages did not change the hydrophobicity/hydrophilicity of DOC present in purified water.

3.2. Effect of *B* values of PASiC on the concentration of different residual Al speciation in the effluent

The actual physicochemical species of an element found in exposure media and in different body compartments, are often determinant in evaluating its toxicity [30]. Thus fractionation and measurement of Al speciation were carried out in this study, in which the Al content was subdivided into several different fractions. The results of the fractionation procedure were provided in Fig. 2(a)–(d), respectively.

It can be seen that different Al speciation in the effluent after PASiC coagulation showed quite different trends with dosages variation. Total dissolved Al, dissolved monomeric Al and dissolved organically bound Al species almost decreased straightly within the whole dosage range investigated. For PASiC₂₀ and PASiC₂₃ coagulation, total reactive concentrations of Al in the effluent still declined within the whole dosage range while total reactive Al after coagulation with PASiC₁₅ increased significantly at higher dosages. There existed no dissolved organically bound monomeric Al in purified water treated with three PASiC samples. In addition, PASiC₂₀ showed relatively lower concentration for each kind of residual Al species except for the dissolved organically bound Al speciation.

Comparing Fig. 1(a) with Fig. 2(a), it can be seen that residual turbidity and total Al concentration in effluent showed the same tendency, which indicated that suspended or particulate Al was the main component in total Al and comparatively higher residual turbidity led to higher total Al in purified water for PASiC₁₅. The organic matter can combine Al and the formation of organic matter–Al complexes allows Al to be maintained in soluble forms despite unfavorable physicochemical conditions. The speciation and fate of dissolved Al in treatment process are determined by competition of Al cation with ligands such as hydroxyl ion, flu-

oride, sulfate and functional groups of NOM. The colloidal and organic materials with a high Al complexation capacity was partially removed in the coagulation progress and residual organic matter exhibited different Al-binding capacity [31]. As seen in Fig. 1(c) and Fig. 2(d), PASiC₂₃ showed the highest DOC removal efficiency and relatively lower DOC concentration was related to comparatively lower content of dissolved organically bound Al. For PASiC₁₅ and PASiC₂₀, DOC removal efficiency and dissolved organically bound Al content showed the same trend. That was due to the hydrophobicity/hydrophilicity of DOC present in purified water as indicated in Table 2. SUVA of finished water with PASiC₁₅ coagulation was relatively lower which suggested that the more hydrophilic DOC present in purified water had a comparatively higher capacity of complexing with metal ions such as Al³⁺. This was in agreement with the comparatively higher content of dissolved organically bound Al after PASiC₁₅ coagulation. Apart from this, it could be also identified from Fig. 1 and Table 2 that PASiC₁₅ and PASiC₂₃ showed inferior coagulation performance and high residual Al ratio which well illustrated the fact that the two coagulants were only partially removed after reacting with the pollutants during coagulation process. In addition, among various Al forms in water solution, the predominant toxic forms were known to be the dissolved monomeric ones [e.g., Al³⁺, Al(OH)²⁺, Al(OH)₂⁺, Al(OH)₄⁻] [6,9,32]. It was clear from the results as expressed in Fig. 2 that PASiC especially PASiC₂₀ could effectively reduce concentration of total dissolved Al and dissolved monomeric Al which had comparatively higher toxicity.

Judging from the results listed in Sections 3.1 and 3.2, it could be concluded that PASiC (*B* = 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.

3.3. Evaluation of coagulation behavior of PASiC under various Si/Al values as a function of coagulant dosage

The addition of polysilicate in PAC could react with Al and its hydrolysate, and thus decreased the positive charge and increased molecular weight in PASiC coagulant [12,24]. The removal efficiencies of monitored parameters with increasing coagulants dosages for PASiC₁₀, PASiC₅ and PASiC₂ (*B* = 2.00) coagulation were given in Fig. 3(a)–(c), respectively. The experiments were conducted at room temperature and at the initial pH of raw surface water. In Table 3, the pH and SUVA of effluent within the whole dosage range were given for each coagulant.

Fig. 3(a) partially validated that PASiC₁₀ and PASiC₅ showed better turbidity removal ability than PASiC₁₅. Furthermore, as indi-

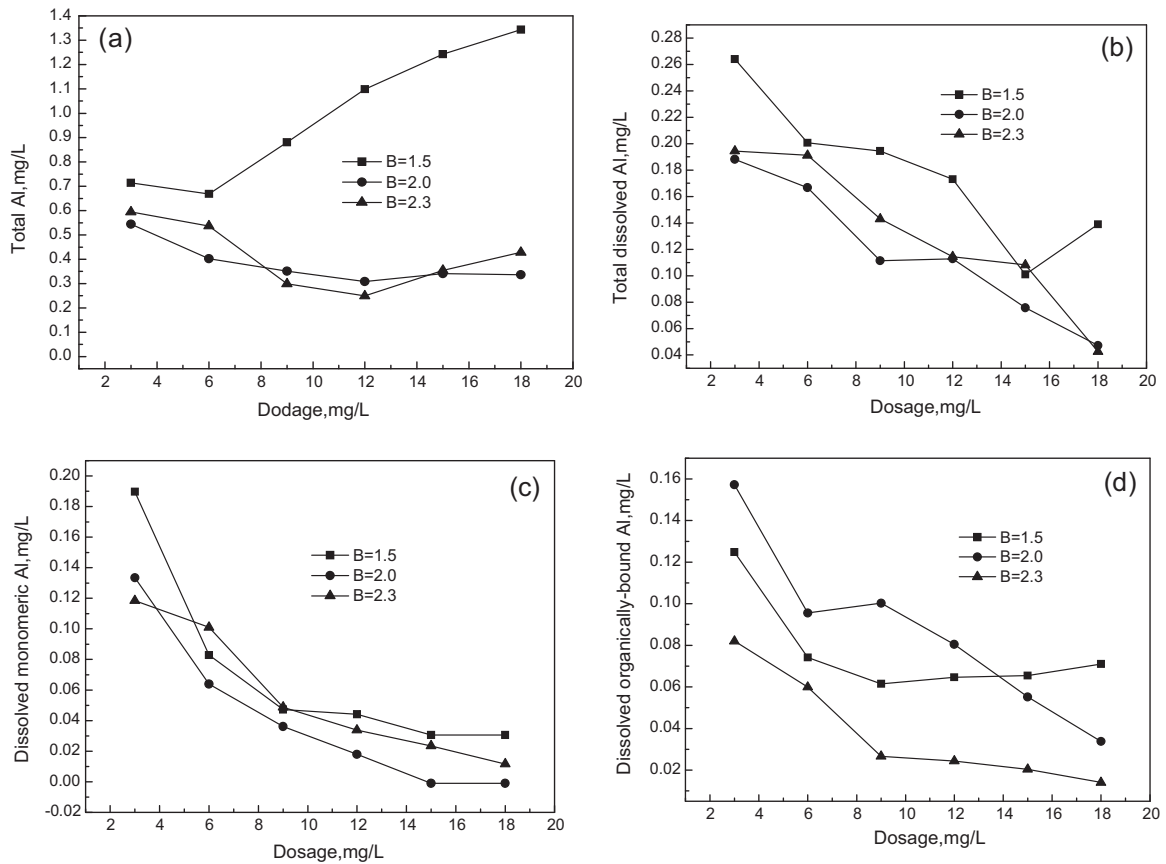


Fig. 2. Concentration of different residual aluminum speciation in the effluent as a function of coagulant dosage and B value: (a) total Al, (b) total dissolved Al, (c) dissolved monomeric Al and (d) dissolved organically bound Al.

Table 3

Effluent pH, SUVA and residual aluminum ratio of PASiC under different Si/Al ratios as a function of coagulant dosage.

Water samples	Coagulant dosage (Al, mg/L)					
	3.00	6.00	9.00	12.0	15.0	18.0
Effluent pH						
Purified water after coagulation with PASiC ₁₅	8.32	8.21	8.11	7.99	7.92	7.81
Purified water after coagulation with PASiC ₂₀	8.14	7.98	7.85	7.73	7.67	7.60
Purified water after coagulation with PASiC ₂₃	8.24	8.10	8.02	7.98	7.84	7.64
Effluent SUVA						
Purified water after coagulation with PASiC ₁₅	2.99	3.02	2.91	2.82	2.73	2.69
Purified water after coagulation with PASiC ₂₀	3.14	3.03	3.11	3.09	2.85	2.96
Purified water after coagulation with PASiC ₂₃	3.09	3.33	3.23	3.26	3.74	4.01
Coagulant type	Residual aluminum ratio of PASiC coagulant (%)					
PASiC ₁₅	14.0	4.68	2.44	1.89	1.31	1.79
PASiC ₂₀	12.7	3.98	2.08	1.21	1.18	0.960
PASiC ₂₃	14.4	4.75	2.98	1.89	1.18	1.17

cated in Fig. 3(a), for PASiC₂, zeta potential varied from negative to positive region with increasing dosages and residual turbidity reached the lowest when zeta potential was close to zero at 15 mg/L. When zeta potential changed to the positive region, residual turbidity increased significantly which was attributed to the electrostatic repulsion. So charge neutralization was the main mechanism in turbidity removal for PASiC₂. In the case of PASiC₅, variation of residual turbidity was similar to that with PASiC₂ coagulation but residual turbidity increased very slowly when the dosages were higher than 15 mg/L. Thus charge neutralization and bridge adsorption worked together and neither played a main role in turbidity removal for PASiC₅. Nevertheless, in the case of PASiC₁₀, residual turbidity did not reach the lowest when zeta potential was close

to zero and it decreased straightly with zeta potential variation which verified that bridging adsorption and entrapment functioned well in removing turbidity for PASiC₁₀. Additionally, for a given B value, an increase in Si/Al ratio would increase the content of larger polymeric coordination [23] which played crucial role in particle adsorption. It also validated that bridging entrapment was more effective in turbidity removal for this specific surface water which was in agreement with the results in Section 3.1.

It can also be observed from Fig. 3(b) and (c) that DOC and UV₂₅₄ removal efficiency increased gradually as dosages increased except for UV₂₅₄ removal when PASiC₂ was used at dosages higher than 12.0 mg/L. PASiC₂ presented better UV₂₅₄ removal at lower dosages, while PASiC₅ showed the best UV₂₅₄ removal at higher dosages

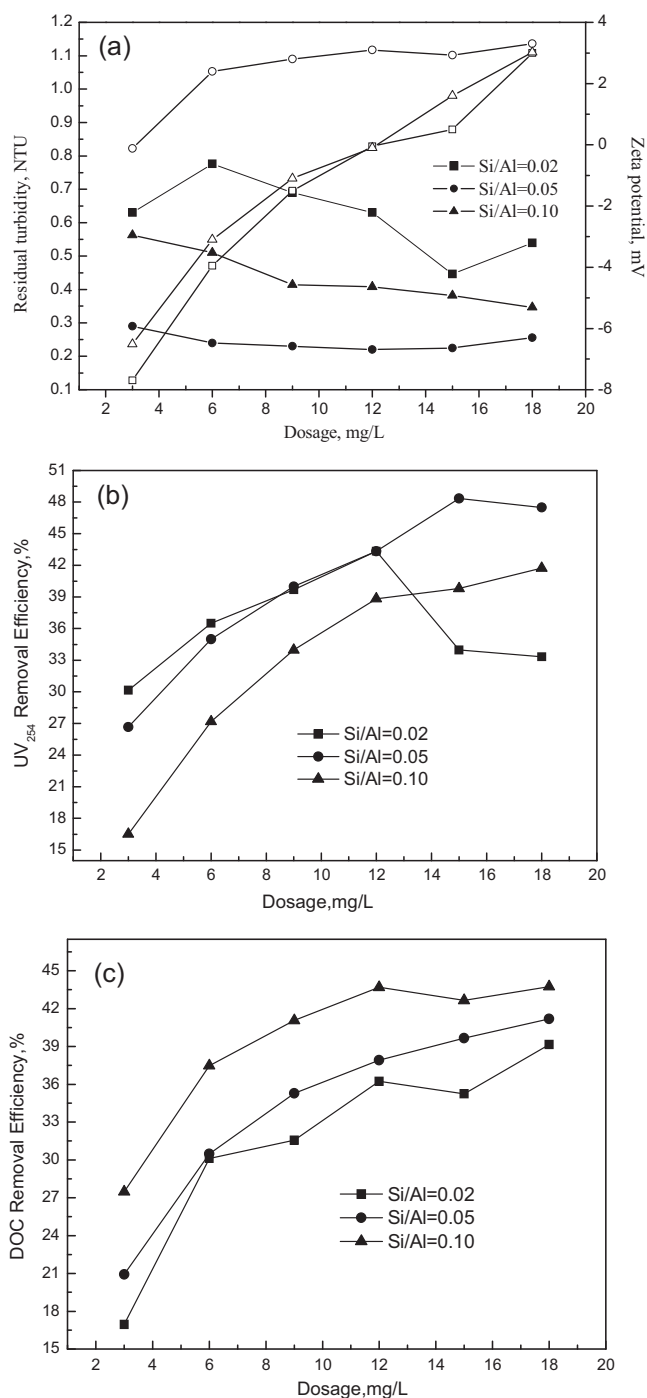


Fig. 3. Comparison of coagulation performance of PASiC as a function of coagulant dosage and Si/Al ratio: (a) residual turbidity along with zeta potential of formed flocs, (b) UV₂₅₄ removal efficiency and (c) DOC removal efficiency.

and PASiC₁₀ manifested optimal DOC removal within whole dosage range. NOM removal was also related to solution pH (as shown in Table 3). NOM removal effect of PASiC₁₀ and PASiC₅ was better than that of PASiC₂ especially at higher dosages. The fact that Si/Al ratio in PASiC affected coagulation performance can be explained by the interaction between hydrolyzed Al species and polysilicic acid. The polysilicic acid could combine with Al and its hydrolysis product by Al–O–Si bonds to form hydroxylaluminosilicate, which could retard the hydrolysis-polymerization of Al to some extent. The polysilicic acid, a negative polymer due to terminal oxygen atoms, could neutralize positive charge in polyaluminum and also polymerize with

Al and its hydrolysis products to form silica–aluminum hydrolyzed species complexes which possibly favored the formation of polymers with larger size and subsequently improved bridge adsorption effect of PASiC [12,24]. The lower Si/Al ratio in PASiC produced higher positively charged but smaller molecular sized product, and higher Si/Al ratio produced lower positively charged but larger molecular sized product. This meant that the charge neutralization effectiveness of PASiC in coagulation progress was weakened by the interaction between hydrolyzed Al species and polysilicic acid [13]. Thus charge neutralization was the major mechanism which played a minor role in NOM removal for PASiC₂. NOM removal for PASiC₁₀ and PASiC₅ depended mainly on bridging and entrapment which might be more effective. Furthermore, SUVA (2.70–4.00, Table 3) as a function of PASiC dosage also indicated that effluent DOC was hydrophilic and SUVA with PASiC₁₀ coagulation was considerably lower than that with PASiC₂ and PASiC₅ coagulation. The above results suggested that when PAC and polysilicate were properly combined together, higher coagulation efficiency of the composite coagulant PASiC was achieved.

3.4. Effect of Si/Al ratio of PASiC on the concentration of different residual Al speciation in the effluent

A major concern about Al in aquatic environment is its potential toxicity in freshwater systems [32]. Al in coagulant and in raw water was transformed into various forms during water treatment and these various forms accounted for different percentages in effluent. Specially, the various Al speciations exhibited quite various toxicities to aquatic organisms [32,33]. Fractionation and measurement of different Al speciation were carried out in this part in order to investigate the evolution of Al as a function of PASiC coagulants and to better characterize the risk of toxicity to aquatic life. The concentrations of various Al speciations in the finished water after PASiC coagulation under different Si/Al ratios were listed in Fig. 4.

As seen in Fig. 4, different residual Al speciation in the effluent after coagulation with PASiC₂, PASiC₅ and PASiC₁₀ showed quite various evolution trends with dosages variation. Total Al in purified water after coagulation with three coagulants and total dissolved Al treated with PASiC₁₀ decreased first and then increased at higher dosages. Dissolved monomeric Al and dissolved organically bound Al mostly decreased straightly within the whole dosage range for PASiC₂, PASiC₅ and PASiC₁₀, as well as total dissolved Al in effluent after coagulation with PASiC₂ and PASiC₅. Dissolved organically bound monomeric Al was always undetectable in the water treated using three PASiC products. PASiC₅ showed relatively lower concentration for each kind of residual Al species except the dissolved organically bound Al.

Comparing Fig. 3(a) with Fig. 4(a), it can be seen that residual turbidity and total Al in effluent manifested the same tendency, which indicated that most of Al was in suspended or particulate form and that relatively higher residual turbidity led to higher total Al for PASiC₂. In addition, because Si/Al ratio in PASiC₂ was relatively lower, it showed poor bridging capacity and exhibited impoverished coagulation performance (Fig. 3) which in turn led to higher content of residual Al. For PASiC₁₀, the reason why total dissolved Al in effluent was higher was that particulate Al was quite lower due to the relatively lower turbidity. The variation of dissolved organically bound Al concentration could be attributed to the fact that the residual organic matter in treated water exhibited a different Al-binding capacity among the three coagulants compared with that in raw water. As seen in Fig. 2(c) and Table 3, although effluent DOC concentration for PASiC₂ coagulation was the highest of the three, effluent SUVA was significantly high which indicated that effluent DOC with PASiC₂ coagulation had a comparatively lower complexing capacity. This was correlated with the low dissolved organically bound Al content. For PASiC₁₀, effluent SUVA was notably low, so

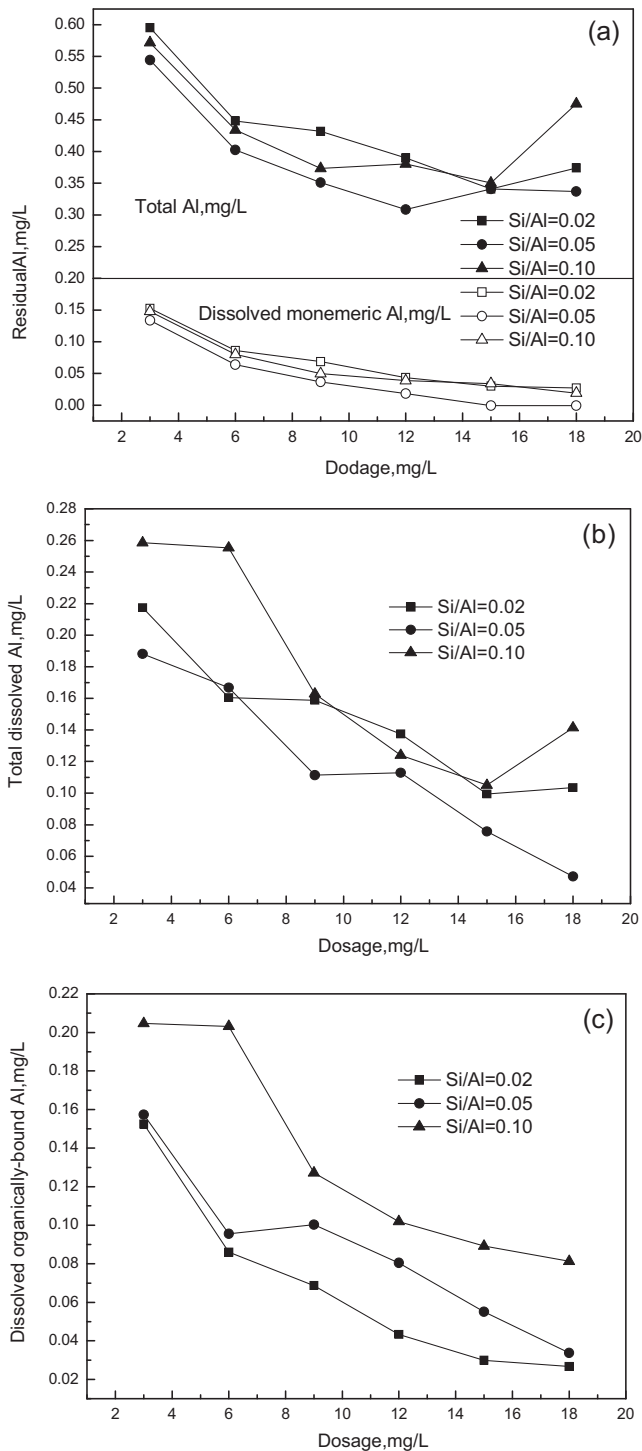


Fig. 4. Comparison of different residual aluminum speciation content in the effluent as a function of coagulant dosage and Si/Al ratio: (a) total Al together with dissolved monomeric Al, (b) total dissolved Al and (c) dissolved organically bound Al.

effluent DOC had comparatively higher complexing ability and it would result in high content of dissolved organically bound Al. Additionally, under different Si/Al ratios, PASiC particularly PASiC₅ could also effectively reduce concentrations of total dissolved Al and dissolved monomeric Al (Fig. 4). According to the literature, the free Al³⁺ or the sum of concentration of Al³⁺, Al(OH)²⁺, Al(OH)₂⁺ and Al(OH)₄⁻ are considered as toxic Al forms for aquatic life [32].

In comparison with the aforementioned results (Sections 3.3 and 3.4), it could be noticed that PASiC (Si/Al = 0.0500) exhibited

superior coagulation–flocculation performance, achieving sufficient removal of contaminant, such as turbidity, UV₂₅₄ and DOC, as well as resulting in the comparatively lower content of residual Al. As indicated, the residual turbidity (<1.00 NTU), effluent pH (6.50–8.50), total suspended solids (TSS, 9.00–13.0 mg/L), total dissolved solids (TDS, 534–676 mg/L), color (<5.00) and the organic matter content (<2.00 mg/L) of treated water could basically meet the requirements of the drinking water quality of China (GB 5749-2006). The total Al limits in drinking water should not exceed 0.200 mg/L in China. The relatively higher total residual Al concentration (>0.200 mg/L in some cases) in treated water can be explained by the high Al concentration in the raw water (particle materials containing Al₂O₃ component as well as some possible impurities in the Yellow River water) together with the fraction caused by the Al-based coagulants. Additionally, the water treatment units utilized in this research only included coagulation–flocculation and sedimentation. However, the subsequent flotation, filtration (sand filter or membrane filter), adsorption and disinfection units are generally used in practical water treatment plants. Application of these units can notably reduce the residual Al concentration furthermore and the effects of subsequent treatment units on the residual Al concentration need to be further studied.

3.5. Residual Al ratio of PASiC and proportion of different residual Al speciation in total residual Al

Al-based coagulants may either increase or decrease Al concentration in purified solution, depending on Al speciation in source water, Al species in coagulants, in situ Al species transformation and treatment conditions [33]. Tables 2 and 3 showed residual Al ratio of PASiC at various coagulant dosages. It was observed in Table 2 that residual Al ratio of PASiC with various *B* values decreased first and then changed slightly in higher dosage range. When the coagulant dosages were higher than 9 mg/L, residual Al ratio of all the tested coagulants was relatively low and varied slightly. Residual Al ratio varied in the following order: PASiC₁₅ > PASiC₂₃ > PASiC₂₀, which indicated that Al speciation in PASiC₁₅ remained abundant in the purified water. Similarly, residual Al ratio of PASiC₁₀, PASiC₅ and PASiC₂ decreased first and then changed slightly at higher dosages (Table 3). And the residual Al ratio varied in the following order: PASiC₁₀ > PASiC₂ > PASiC₅. Specifically, the Al speciation in all silica-enriched coagulants examined in these studies remained readily at relatively lower coagulant dosages, which was attributable to the fact that PASiC could not react sufficiently with particulate and organic material in raw water. However, the addition of PASiC coagulant at 12.0–15.0 mg/L could effectively reduce the residual Al content.

These results also revealed that, for all the several composite PASiC coagulants, the majority of total residual Al existed in insoluble suspended or particulate Al (about 63.7–92.3% for PASiC₁₅, 59.2–85.8% for PASiC₂₀, 54.7–90.4% for PASiC₂₃, 64.3–73.1% for PASiC₂ and 42.2–70.8% for PASiC₁₀), which could be attributed to the residual turbidity of finished water as shown in Fig. 1(a) and Fig. 3(a). Most of the dissolved Al in effluent was strongly bound or polymeric colloidal (about 31.2–64.1% for PASiC₁₅, 56.9–89.7% for PASiC₂₀, 17.8–42.1% for PASiC₂₃, 25.3–70.4% for PASiC₂ and 56.7–84.2% for PASiC₁₀). In addition, dissolved inorganically bound monomeric Al was the only speciation in dissolved monomeric Al for all PASiC samples. Among the dissolved Al speciation, inorganically bound Al was almost 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 stable and could not easily be removed through conventional coagulation process [11,33].

4. Conclusions

Comparing with charge neutralization, surface bridging and entrapment was more effective for this surface water treatment. The addition of PASiC at dosages of 12.0–15.0 mg/L could effectively reduce residual Al concentration.

The majority of residual Al was in the insoluble suspended or particulate form. In the dissolved fraction, organic forms were present at higher content and inorganically monomeric Al was the only component in dissolved monomeric Al.

PASiC with $\text{OH}^-/\text{Al}^{3+} = 2.00$ and $\text{Si}/\text{Al} = 0.0500$ had favorable coagulation performance and meanwhile residual Al in purified water denoted comparatively lower concentration. In particular, residual Al ratio of PASiC was comparatively lower and Al in PASiC remained rare in treated water under this condition.

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