Coagulation behavior and floc characteristics of a novel composite poly-ferric aluminum chloride–polydimethyl diallylammonium chloride coagulant with different OH/(Fe$^{3+}$ + Al$^{3+}$) molar ratios

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**ABSTRACT**

In this paper, flocculating performance and mechanisms of a new composite coagulant, poly-ferric aluminum chloride–polydimethyl diallylammonium chloride (PFAC-PD) with different OH$^-$/(Fe$^{3+}$ + Al$^{3+}$) molar ratios, were investigated for humic acid (HA)–kaolin synthetic wastewater treatment. The impact of OH$^-$/(Fe$^{3+}$ + Al$^{3+}$) molar ratios on the removal efficiencies of turbidity and dissolved organic carbon, specific UV absorbance, coagulation mechanisms and dynamics was explored during the coagulation process using composite coagulants. The coagulation experimental results revealed that the composite coagulants with lower OH$^-$/(Fe$^{3+}$ + Al$^{3+}$) molar ratio exhibited better coagulation efficiency. When OH$^-$/(Fe$^{3+}$ + Al$^{3+}$) molar ratio of the composite coagulant was 1.5, adsorption-bridging played a dominant role in coagulating HA–kaolin synthetic wastewater. The floc growth rate and floc size, increased with increasing OH$^-$/(Fe$^{3+}$ + Al$^{3+}$) molar ratio and the highest peak height of the size distribution was obtained by PFAC-PD with OH$^-$/(Fe$^{3+}$ + Al$^{3+}$) = 1.5. Also, the composite coagulants with higher OH$^-$/(Fe$^{3+}$ + Al$^{3+}$) molar ratio formed more compact flocs, as reflected by the higher fractal dimension value. The flocs coagulated by PFAC-PD with basicity value of 1.0 gave strong strength and good recoverability.

**Key words** | basicity, composite coagulant, floc breakage and regrowth, floc strength and recoverability, fractal dimension

**INTRODUCTION**

Humic substances, which can aggregate with organics and heavy metals, are considered as the important precursors of disinfection by-products (DBPs) after chlorination because of their negative charge (Sadiq & Rodriguez 2004). DBPs have been reported to be harmful to humans (Guo & Lin 2009). Therefore, humic substances (DBP precursors) removal in water treatment has been paid increasing attention (Pramanik et al. 2015). To remove DBP precursors, coagulation has been widely applied in drinking water and wastewater treatment. In the coagulation process, destabilized dissolved and colloidal particles are aggregated into large flocs, which are then effectively removed by subsequent sedimentation/filtration processes (Metcalfe et al. 2015).

By far, the most widely used inorganic polymer coagulants are iron and aluminum salts, such as poly-ferric chloride (PFC), poly-ferric sulfate (PFS) and poly-aluminum chloride (PAC). To avoid the disadvantages and improve coagulation efficiency of iron and aluminum salts, a new composite coagulant, poly-ferric aluminum chloride (PFAC), has been developed (Lan et al. 2013; Sun et al. 2015).

Due to their higher sedimentation rate, less pH dependence and lower sludge volume, synthetic organic polymer coagulants have been extensively used in many industries and water treatment (Yang et al. 2015). One of the synthetic organic coagulants commonly used is polydimethyl diallylammonium chloride (PDMDAAC), which has high molar mass and is highly charged. Nevertheless, the high cost
and small flocs formed have been the limiting factor in the use of PDMDAAC (Sun et al. 2011).

In order to overcome the above limitation, a composite coagulant, produced by combining inorganic coagulant with organic coagulant, has been developed (Yan et al. 2007). A new composite coagulant was prepared using PFC and epichlorohydrin–dimethylamine by Gao et al. (2007, 2008) and used for treating synthetic reactive dying wastewater. Moussas & Zouboulis (2009) have developed a new composite coagulant combining PFS and non-ionic polyacrylamide, which exhibited a superior coagulation performance. A novel PAC–chitosan composite coagulant was investigated for natural organic matter removal (Ng et al. 2012).

Nevertheless, very limited work has been reported on coagulation performance of composite coagulants constituted of PFAC and PDMDAAC. In this study, a new composite inorganic–organic coagulant, poly-ferric aluminum chloride–polydimethyl diallylammonium chloride (PFAC-PD), was prepared. It is well known that coagulation performance depends on the key characteristics of coagulant, such as zeta potential and nature of the used coagulant. Various factors, such as OH⁻/(Fe³⁺ + Al³⁺) or OH⁻/Al³⁺ molar ratios (B, basicity values) and pH, affect the nature of the coagulants (Moussas & Zouboulis 2009). The effluence of B on coagulation effect has been reported. However, the combined investigations of floc size, strength, regrowth, and fractal dimension using composite coagulant with different B has not been well developed. Therefore, this work aimed to investigate the effect of B values on coagulation behavior, floc size, floc fractal structure, breakage, regrowth, strength and recoverability.

MATERIALS AND METHODS

Experimental materials

Deionized ultra-filtered water was used in all experiments. FeCl₃·6H₂O, AlCl₃·6H₂O and Na₂CO₃ were of analytical grade (Sinopharm Chemical Reagent Co. Ltd, Beijing, China). High density polyethylene bottles (250 mL) were used to collect samples, which were preserved with 1 + 9 HNO₃ (one portion of acid and nine portions of water) for 12 h and then rinsed with deionized water.

Preparation of composite coagulants

PFAC-PD coagulants were synthesized at room temperature through a composite method. Analytically pure grade of FeCl₃·6H₂O (CAS No. 10025-77-1), AlCl₃·6H₂O (CAS No. 10124-27-3) and Na₂CO₃ (CAS No. 497-19-8) reagents and deionized water were used in all the prepared experiments. Firstly, PFAC was prepared by slowly adding Na₂CO₃ powder into a solution of FeCl₃·6H₂O and AlCl₃·6H₂O under a slow stirring condition. The amount of Na₂CO₃ depended on the desired B values (0.5, 1.0 and 1.5). In the PFAC products, the concentration of (Fe + Al) was 10 g/L and B values were 0.5, 1.0 and 1.5. Then, an amount of PDMDAAC (the molar ratio of Fe and Al to PDMDAAC was 4:1) solution (100% charge density, 40% w/w aqueous solution, intrinsic viscosity was 1.21 dL/g) was added to the above PFAC solution under slow stirring conditions. Finally, the mixture was then aged for 24 h. The prepared composite coagulants of PFAC-PD were transparent and homogeneous. It should be pointed out that the dosage of coagulants was calculated as (Fe + Al) (mg/L) in all coagulation experiments.

Synthetic water

Kaolin and dissolved humic acid (HA) were used to prepare the synthetic water. The stock kaolin and HA solutions were firstly prepared in deionized water. Their concentrations were determined to be 5 g/L and 1 g/L, respectively. The synthetic wastewater was prepared by diluting the stock solutions with tap water to an HA concentration of 10 mg/L. The general water quality of the test waters was shown as following: HA content = 10 mg/L, UV₂₅₄ (ultraviolet absorbance at 254 nm) = 0.138–0.148 cm⁻¹, dissolved organic carbon (DOC) = 3.28 ± 0.30 mg/L, pH = 8.5 ± 0.10, turbidity = 14.00 ± 0.50 NTU, zeta potential = −14.6 ± 0.2 mV.

Coagulation experiments and analytical methods

All coagulation experiments were conducted using a jar-test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd, China) with six mixing paddles at a room temperature of 20 ± 1°C. The tested coagulants were the composite PFAC-PD coagulants with different B (0.5, 1.0 and 1.5).

Jar tests were carried out in 1,000 mL treated synthetic water with plexiglass beakers (1,400 mL). After addition of the coagulants, the test procedures were as follows: rapidly mixed at 200 rpm for 2 min, followed by a slow mixing at 40 rpm for 17 min and settled for 20 min. After sedimentation, samples were withdrawn at 2 cm beneath the surface for turbidity, UV₂₅₄, DOC and zeta potential.
measurement. In all coagulation experiments, the average values of three replicated measurements were the results.

The residual turbidity and zeta potential of unfiltered sample were measured using a 2100P turbidimeter (Hach, USA) and a Malvern Zetasizer 3000HSa (Malvern Instruments, UK), respectively. Samples were filtered with a 0.45 μm pore size membrane via syringe before DOC and UV254 analysis. UV254 was measured using a 754 UV-visible spectrophotometer (Jinghua Scientific Instrument Co. Ltd, Shanghai, China) at 254 nm. DOC was quantified using a total organic carbon analyzer (TOC-VCPH, Shimadzu, Japan). In this work, the ratio of the residual UV254 to DOC was explored to evaluate specific UV absorbance (SUVA), which represented the characterization of hydrophobic/hydrophilicity of DOC in the water samples.

Floc size, breakage and regrowth analysis

At a room temperature of 20 ± 1 °C, the dynamic floc size was measured using a photometric dispersion analyzer (PDA, Zetasizer2000, Malvern Instruments, UK) throughout the coagulation progress. With the help of a peristaltic pump (LEAD-1, Longer Precision Pump, China), the suspension sampled was introduced through the 5 mm diameter plastic cell of the PDA and flowed back into the jar with a flow of 2.0 L/h. In order to prevent the floc breakage, the pump was positioned downstream of the analyzer. The outflow and inflow tubes were designed to be opposite and just above the impeller. The floc sizes were measured every 0.5 min and recorded on a PC. The change of floc size with time and the floc size distribution were analyzed in this study.

A jar-test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd, China), which was equipped with a six-paddled stirrer and six 2.0 L plexiglass beakers, was used to conduct the experiments. The test water (pH = 8.31 ± 0.10) of 1.00 L was transferred into a beaker. Then, 9 mg (Fe + Al)/L of coagulant was added into the water. In the floc formation process, rapid mixing of 200 rpm was introduced, followed by slow mixing of 40 rpm for 17 min. Breakage and regrowth steps were investigated by improving mixing speed to 150 rpm for 5 min and another slow stirring of 40 rpm for 15 min for floc formation.

Floc fractal structure analysis

Light scattering method was applied to determine floc fractal dimension. The scattered light intensity (I) is measured as a function of the scattering wave vector (Q), where Q is defined as the difference between the incident and scattered wave vectors of the radiation beam in the medium. I and Q can be calculated by Equations (1) and (2):

\[ I \propto Q^Df \]  
\[ Q = \frac{4\pi n \sin (\theta/2)}{\lambda} \]

where \( \lambda, n \) and \( \theta \) are the radiation wavelength in vacuum, the medium refractive index, and the scattering angle, respectively. Based on Equation (1), the fractal dimension \( D_f \) can be determined by the slope of a linear region on the logI-logQ plot. Generally, \( D_f \) has been applied to estimate the compaction degree of the flocs. High \( D_f \) values suggest that the flocs have a compact structure. Low ones suggest that the flocs have a loose structure (Moussas & Zouboulis 2009).

RESULTS AND DISCUSSION

Impact of B on coagulation behavior

The turbidity and DOC removal efficiencies were investigated by using the composite coagulant PFAC-PD (intrinsic velocity = 1.21 dL/g) with various B values (0.5, 1.0 and 1.5) and the results are shown in Figure 1. Figure 2 presents the SUVA value (the ratio of the residual UV254 to DOC) and the zeta potential of flocs under different B values as a function of coagulant dosage. PFAC-PD dosages were 2–12 mg/L as (Fe + Al).

In Figures 1(a) and 2(b), it can be seen that the coagulant (B = 1.5) with lower charge neutralization ability achieved higher turbidity removal. Therefore, the charge neutralization ability of coagulant with B = 1.5 was not the sole coagulation mechanism, and the adsorption-bridging and entrapment was also an effective coagulation mechanism for turbidity removal. From Figure 1(a), it was can be seen that the turbidity removal of PFAC was higher than that of PFAC-PD, which is attributed to the more effective Fe(III)/Al(III) component of PFAC. PDMDAAC presented a lower turbidity removal efficiency than PFAC and PFAC-PD. Moreover, Figure 1(a) showed that the turbidity removal efficiency was slightly affected by B of PFAC-PD and it was increased with B increasing. It could be ascribed to the different content of the Al/Fe hydroxide species. Although the details are not well understood, it seems clear that growing hydroxide precipitate can enmesh colloidal and
suspended particles and thus result in turbidity removal. It is indicated that the content of Al/Fe hydroxide species increased gradually when B value increased to 1.5. Therefore, the turbidity removal is primarily relevant to the content of Al/Fe hydroxide species, which is consistent with other research (Yang et al. 2014).

As demonstrated in Figure 1(b), PFAC-PD presented better DOC removal than just PFAC and PDMDAAC, indicating that PDMDAAC can be combined with PFAC to increase the floculation efficiency. For PFAC-PD with B of 0.5 and 1.0, DOC removal efficiency increased gradually when coagulant dosages increased from 0 to 6 mg/L (zeta potential of flocs was close to zero at a dose of 6 mg/L) and it approximately remained in a stable condition when the coagulant dosages further increased. However, PFAC-PD with B of 1.5 gave improved DOC removal efficiency with coagulant dosage increasing across the whole dosage range. For PFAC-PD with lower B values of 0.5 and 1.0, dissolved and positively charged monomers and polymeric species were the major Al/Fe species. Al/Fe monomers and polymeric species reacted electrostatically with negatively charged colloids and organic matter and thus resulted in the formation of the insoluble Al/Fe-HA precipitates. At lower B (0.5 and 1.0), the charge neutralization was the dominant mechanism and the absorption-bridging and enmeshment did not effectively work for organic matter removal. When B increased to 1.5, more Al/Fe hydroxide precipitates were formed, and organic matter and suspended particles were removed by adsorption onto and enmeshment into the precipitated floc particles. Thus, adsorption-bridging and enmeshment effectively worked and became dominant for organic matter removal at higher B (1.5).

SUVA was defined as UV absorbance of a water sample per mg/L of DOC and represents a simple characterization
of hydrophobicity/hydrophilicity of DOC. Water samples with low SUVA (2 L/(mg·m) or less) contained lower contents of hydrophobic and high molecular weight organic matter. Water samples with high SUVA (4 L/(mg·m) or more) had relatively higher contents of hydrophobic and high molecular weight organic matter (Zhao et al. 2011). In this work, SUVA of the raw water was 3.50–4.00 L/(mg·m). The effect of B on SUVA and zeta potential of flocs formed by PFAC-PD is shown in Figure 2.

As shown in Figure 2(a), SUVA of the effluent decreased with coagulant dosage increasing at all B values, which indicated that PFAC-PD preferentially removed hydrophobic and high molecular weight organic matter. SUVA of the purified water was in the order of \( B = 0.5 > B = 1.0 > B = 1.5 \), which suggested that the hydrophobicity in effluent decreased with B increasing. It can be concluded that PFAC-PD with higher B value was more appropriate to remove hydrophobic organic matter.

Licsko (1997) reported that Al/Fe salt coagulants dosed to treated water were immediately hydrolyzed and rapidly formed Al/Fe-hydroxide precipitates and other dissolved Al/Fe species. The basicity of the coagulants affected the amount of Al/Fe-hydroxide precipitates and dissolved Al/Fe species and resulted in different degrees of neutralization (Leprince et al. 1984). Figure 2(b) shows the variation of zeta potential of the flocs formed by PFAC-PD with different B values (0.5, 1.0 and 1.5). Up to B of 1.0, the higher B gave the stronger charge neutralization ability of the coagulant. However, further increase of B to 1.5 lowered the charge neutralization ability of the coagulant. This can be explained as follows. B values affected the amount of polymeric species present. For PFAC-PD with B of 0.5, the polymerization degree of Al/Fe in PFAC-PD was lower and the Al/Fe hydrolysate was mainly monomers or less polymeric species. With the increase of B from 0.5 to 1.0, the Al/Fe polymerization degree was improved and more highly charged polymeric species were formed and became dominant Al/Fe species. The polymeric species has a larger positive charge than monomers. Thus, charge neutralization ability of PFAC-PD increased when B increased from 0.5 to 1.0. When the B value of PFAC-PD increased from 1.0 to 1.5, the Al/Fe hydroxide precipitate was formed and increased with the increase in B value. Therefore, charge neutralization ability of PFAC-PD decreased with the B increasing when B was over 1.0.

**Influence of B on floc size**

The floc growth curves during 0–17 min at raw water pH are shown in Figure 3, where the floc size was represented by the median equivalent diameter \( (d_{50}) \). The curves can be divided into three specific parts: destabilization phase of the particles, growth phase and steady phase (Zhao et al. 2014; Huang et al. 2015). During the coagulation process, the floc size is a balance between formation of the flocs and the breakup of the flocs’ internal bonds due to mixing conditions. When the balance between aggregation rate and breakage rate is obtained, the floc size reached a steady phase.

PFAC-PD with \( B = 1.5 \) reached a highest \( d_{50} \) of about 459 \( \mu m \) in the steady phase. For PFAC-PD with \( B = 1.5 \), the zeta potential of flocs was close to the isoelectric point when dosage was 9.0 mg/L as \( (Fe + Al) \). The interior repulsive force among the flocs was weak. Therefore, they aggregated quickly to form larger flocs, whereas for PFAC-PD with \( B = 0.5 \) and \( B = 1.0 \), the stronger repulsive force between the microflocs with more positive charge prevented them from contacting one another.

The floc size distribution formed by PFAC-PD with different B values is shown in Figure 4 at 5 and 17 min. The coagulant dosage was 9 mg/L (as \( (Fe + Al) \)).

It can be observed that the size distribution peak slightly shifted to a higher size as coagulation time increased. This result suggested that the microflocs were adsorbed and entrapped by large flocs in the coagulation period, which led to the gradual growth of floc size. PFAC-PD with \( B = 1.5 \) gave the highest peak height of the size distribution and the largest floc growth rate, which contributed to the difference in the coagulation mechanism. For PFAC-PD with \( B = 1.5 \), the zeta potential was very close to zero at dosage of 9.0 mg (Fe + Al)/L. Therefore, the microflocs formed aggregated quickly to larger flocs because of the weak repulsive force between each other.
Influence of B on floc fractal structure

To better understand the change of the floc structure, a study on the variation of fractal dimension in the coagulation process was carried out. In this work, 9 mg/L (as (Fe + Al)) was added to evaluate the effect of B value on floc structure. Figure 5 shows the variation of the fractal dimension of flocs formed by PFAC-PD with different B values at 3, 5, 7, 9, 11, 13, 15, and 17 min of coagulation.

It was observed that $D_f$ gradually increased with the increase of coagulation time for composite coagulant with different B values, which implied that the floc structures become more compact during the entire coagulation process. An explanation for the results was that the fracture of weak points under exposure to prolonged mixing or shear condition resulted in restructuring and rearrangement into a denser floc structure (Amjad et al. 2015; Li et al. 2015; Yu et al. 2015). The composite coagulant PFAC-PD with $B = 0.5$ and $B = 1$ generated flocs with looser structures, as reflected by the lower $D_f$ value. It was due to the higher positive charge of the flocs, which led to the strong repulsion between particles within the aggregates and thus resulted in loosely packed flocs.

Influence of B on floc breakage and regrowth

After the slow stir phase, the flocs were exposed to an increased shear force (150 rpm) for another 5 min followed by the regrowth phase at 40 rpm. The variation of $d_{50}$ is shown in Figure 6.

At the moment when the increasing shear was applied, $d_{50}$ immediately decreased and then gently decreased.
When the shear was reintroduced for another 15 min, the flocs began to reaggregate. However, the floc size did not reach the previous size after the 15 min regrowth period. Meanwhile, different breakage extents and regrowth potentials of flocs were observed using the composite coagulants with different B. Consequently, the floc aggregation was also affected by B.

**Influence of B on floc strength and recoverability**

The floc strength and recoverability can be indicated by strength factor (S_f) and recovery factor (R_f), respectively. They can be calculated by the following equations (Yukselen & Gregory 2004; Wei et al. 2010).

\[
S_f = \frac{d_2}{d_1} \times 100(\%) \tag{3}
\]

\[
R_f = \frac{d_3 - d_2}{d_1 - d_2} \times 100(\%) \tag{4}
\]

where \(d_1\) (μm) and \(d_2\) (μm) represent the stable floc size before and after breakage, and \(d_3\) represents the floc size after regrowth to the new steady step. A higher strength factor suggests that the flocs are stronger. Meanwhile, a higher recovery factor implies that the flocs have better regrowth after breakage. Table 1 shows the strength and recovery factors. The orders of the strength factor and the recovery factor were observed as follows: B = 0.5 > B = 0.75 > B = 1.0. The flocs of PFAC-PD with B = 1.0 were strongest and gave the best regrowth capability.

Floc strength and recoverability are related to the coagulation mechanism and determined by the number of the bridging bonds within the flocs (Zhao et al. 201b). The flocs formed by bridge-sweeping flocculation are considered weaker in comparison with charge neutralization. However, the flocs formed by charge neutralization have better recoverability after breakage (Chaignon et al. 2002). For PFAC-PD with B = 1.5, the destabilized particles aggregated into large flocs through both charge neutralization and polymer bridge-sweeping. When the shear force is larger than the floc bonding strength, the flocs will be broken into smaller sizes. Therefore, the flocs of PFAC-PD with B = 1.5 showed much weaker shear-resistant ability and worse regrowth capability.

**CONCLUSIONS**

The performance and floc characterization of PFAC-PD with different B were investigated. The best DOC removal was achieved by PFAC-PD with B = 1.0. However, PFAC-PD with higher B value was appropriate for removing the hydrophobic fraction of organic matter. Comparing with charge neutralization, adsorption-bridging and enmeshment was more effective for PFAC-PD with B = 1.5. For PFAC-PD with B = 0.5 and 1.0, the charge neutralization was the dominant mechanism. PFAC-PD with higher B formed larger flocs and PFAC-PD with B = 1.5 reached a highest \(d_{50}\) (459 μm) in the steady phase. Moreover, the flocs generated by PFAC-PD with B = 1.5 were more compact and the flocs generated by PFAC-PD with B = 1.0 were stronger and more recoverable.

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