



Alkalinity effect of coagulation with polyaluminum chlorides: Role of electrostatic patch

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Abstract

The coagulation behavior of polyaluminum chloride (PACl) with various basicities ($B = \text{OH}/\text{Al}$ values) was investigated under different alkalinities. It is aimed to get better insights into the coagulation mechanisms involving interactions between hydrolyzed Al(III) products and particles. Jar tests were used to evaluate the coagulation efficiencies, including zeta potentials, residual turbidities (RT) and pH values. An optical monitoring technique of photometric dispersion analyzer (PDA) was utilized to observe the coagulation dynamics. The experimental results show that the traditional coagulant such as alum evolves a rapid hydrolysis after dosing and the in situ formed hydrolysis products can destabilize the kaolin particles by precipitation charge neutralization (PCN). The preformed polymeric species in PACls exhibit a relatively high stability after dosing and can form “electrostatic patches” on clay particle surfaces. These patches play a crucial role in “electrostatic patch coagulation” (EPC). Increasing alkalinity extends both PCN and EPC zones. Under the low alkalinity, EPC with high Al_b contained in PACls works better than PCN coagulation; increased alkalinity improves the efficiency of traditional coagulant due to sweep flocculation. Under the higher alkalinity, more coagulant is required to achieve complete charge neutralization. The stoichiometric relationships between the dosage and alkalinity are different depending on the B values of PACls.

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1. Introduction

Coagulation is one of the most important steps during the conventional water treatment trains. Traditionally, the primary purpose of coagulation is to remove turbidity from water. With the recognition of disinfection by-products, natural organic matter (NOM) removal through enhanced coagulation is being widely adopted in the world [1–3].

The most common coagulants used are aluminum and iron salts, such as ‘alum’ (aluminum sulfate) and ferric chloride. Once added into water, the metal salts can experience a series of hydrolysis processes and form many kinds of hydrolyzed products. Alum is effective in treating a wide range of water types and

the costs are relatively low [4]. However, alum can be subject to significant deterioration of treatment efficiency in some waters, especially in certain ranges of pH and temperature. Within the past decades, a new generation of coagulants-inorganic polymer flocculants (IPFs) has been becoming more and more popular. The IPFs, such as polyaluminium chloride (PACl) and polyiron chloride (PICl), are a category of partially neutralized metal salts with significant polymeric fraction present in some circumstances. Preformed polymerized species have the advantages of being more effective under a variety of water quality conditions, especially at lower temperatures and a broader pH ranges relative to alum [5–11].

The traditional coagulants and IPFs perform differently due to their features of chemical speciation. Under the condition of commonly encountered pH ranges of natural waters, the hydrolysis of aluminum salt could produce a series of products ranging from monomers, oligomers to polymeric hydroxyl complexes. Most of them, such as $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}_2(\text{OH})_2^{4+}$,

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$\text{Al}_3(\text{OH})_4^{5+}$ and $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ (tridecameric polymer or 'Al₁₃'), are positively charged and can interact with the negatively charged colloids, and consequently cause destabilization and aggregation of colloidal particles. PACls are commonly prepared by controlled neutralization of aluminum chloride. PACls usually contain significant amounts of polynuclear aluminum hydrolysis products [12,13] including Al₁₃, which is considered to be among the more important species [14,15]. However, the coagulation mechanisms of PACl are not fully understood to date. Klute [16] found that the preformed species in PACls are more stable than those formed in situ after alum addition; Matsui assumed that those preformed species could destabilize particles faster [17]. It has been reported that the water characteristics, especially alkalinity can affect the hydrolysis processes of many coagulants and have profound influences on coagulation efficiency [18]. Previous studies paid most attention to the effect of alkalinity on the coagulation behaviors of traditional coagulants, and little study has been focused on the effect of alkalinity on coagulation with PACls. It has been observed that demand for alum increases linearly with increased alkalinity [19,20], and turbidity is hard to remove when alkalinity drops below 30 mg/L as CaCO₃ [21]. Alkalinity also plays a key role in the enhanced coagulation to remove NOM, since it tends to keep coagulation pH higher and reduce NOM removal [1]. PACls could be less affected by alkalinity than alum, particularly those PACls with higher basicity [22], but the mechanisms involved in this phenomenon have not been elucidated.

The general mechanisms of coagulation have been summarized in Duan and Gregory's review in detail [23]. Colloidal destabilization can be achieved by adding alum, and the corresponding mechanism involved is called charge neutralization. Due to the extremely low solubility of aluminum, with increase of alum dosage, rapid and excessive aluminum hydroxide precipitation can form and fine particles in water can be enmeshed in the hydroxide precipitate, and thus efficient turbidity removal is achieved. This process is the so-called 'sweep flocculation' mechanism since particles are 'swept out' of water by an amorphous hydroxide precipitate. Chowdhury and Amy [24] claimed that precipitation is the main mechanism in the coagulation of alumina colloids with alum. According to the 'sweep flocculation' model, the incorporation of colloids into precipitate follows two pathways: one is the heterogeneous nucleation involving charge neutralization and subsequent growth of precipitate at low pH values, and the other is homogeneous nucleation involving precipitation and subsequent particle aggregation at high pH values. In this study, the former pathway is regarded as charge neutralization and the latter one as sweep flocculation. With respect to the coagulation/flocculation mechanisms of PACls, most current studies focused on the mode of charge neutralization [13,17,25,26]. Dentel [27] tried to explain the coagulation mechanisms of different kinds of coagulants by a combined model of precipitation charge neutralization (PCN). Recently, 'electrostatic patch coagulation' (EPC) was proposed by Wang et al. [28] to interpret the coagulation behaviors of PACls, but it has not been examined systematically using controlled experiments in detail.

In this paper, the coagulation/flocculation mechanisms of PACls with various basicities were studied. The effect of alkalinity was investigated. Besides jar tests, the flocculation dynamics monitoring technology, photometric dispersion analyzer (PDA) was adopted to observe the flocs aggregation processes. This monitoring technique involves the measurement of transmitted light fluctuations in a flowing suspension, and it is very sensitive to the aggregation state of particles. It was aimed to provide better insight into the role of electrostatic patch on coagulation/flocculation with PACls under different alkalinity levels.

2. Materials and methods

2.1. Preparation of PACl

PACls were prepared by slow base injection into Al solution at room temperature. Analytical grade of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and NaOH reagents and deionized water were used to prepare original solutions. NaOH was added into Al solution using a peristaltic pump under a rapid stirring condition. The amount of NaOH varied with the target basicity ($[\text{OH}]/[\text{Al}]$ molar ratio, *B* value). The chosen *B* values of four PACls were 0, 1.0, 2.2, and 2.5. The resulting products were denoted as PACl₀, PACl₁₀, PACl₂₂, and PACl₂₅, respectively. The final concentrations of all PACls were adjusted to 0.1 M and their species distribution was shown in Table 1. The speciation was determined by ferron assay (ferron reagent was from Sigma, Donset, UK) after 1 week of aging. Ferron assay can differentiate aluminum species into three categories: monomeric species, denoted as Al_a; polymeric species which can react with ferron rapidly, denoted as Al_b; high polymerized or colloidal species which cannot react with ferron, denoted as Al_c. The detailed procedures of ferron assay were described elsewhere [29]. It should be pointed out that the speciation of PACl₀ was due to its self-hydrolysis since no base was added.

2.2. Preparation of working suspensions

A stock kaolin suspension was prepared using deionized water and its concentration was determined to be 66.7 g/L. The kaolin particle size distribution was obtained using a Mastersizer 2000 analyzer (Malvern Co. UK). The particles were mostly below 5 μm in size, with a mean size of about 2 μm. Zeta potentials of the particles were measured by a zeta potential analyzer (Zetasizer 2000, Malvern Co. UK).

Three working suspensions with various alkalinities were prepared by diluting the stock suspension to a concentration of 50 mg/L. NaNO₃ was added to provide a fixed ionic strength of

Table 1
The speciation distribution and pH value of PACl samples

PACls	<i>B</i> value	Al _a (%)	Al _b (%)	Al _c (%)	pH
PACl ₀	0	93.03	4.29	2.68	3.05
PACl ₁₀	1.0	59.75	35.86	4.39	3.66
PACl ₂₂	2.2	19.18	75.36	5.46	4.55
PACl ₂₅	2.5	7.76	77.73	14.51	5.30

Table 2
Characteristics of three working suspensions

Suspensions	Alkalinity (mg/L as CaCO_3)	Alkalinity (mol/L as HCO_3^-)	RT (NTU)	Zeta (mV)	pH
1#	25	0.5	53.2	−49.7	9.51
2#	50	1.0	52.6	−50.2	9.89
3#	100	2.0	53.0	−52.5	10.05

5×10^{-4} M. Calculated amount of NaHCO_3 solution was added according to three target alkalinities: 25, 50, and 100 mg/L as CaCO_3 , and if expressed as bicarbonate concentration, the corresponding values were 0.5, 1.0, and 2.0 mM. The alkalinities of working suspensions were also confirmed using standard acid titration method [30]. Some of the working suspensions parameters were presented in Table 2. It was found that the pH values of three working suspensions were all higher than 9.5, which primarily resulted from the pH increase of NaHCO_3 solution during storage period. The exclusion of CO_2 and consequent pH increase and species transformation was unavoidable even if the storage bottle was sealed after each use.

2.3. Jar test experiments

Batch coagulation experiments were conducted in 500 ml glass beakers using a conventional jar-test apparatus fitted with overhead mixing paddles (40×50 mm rectangular, stainless-steel material). To initiate an experiment, a total amount of 400 ml working suspension was transferred to a beaker. After coagulant addition, the operation procedures were as follows: the suspensions were rapidly mixed at 300 rpm for 1 min after coagulant addition, followed by 10 min of slow mixing at 40 rpm, and the flocs were allowed to settle for 10 min before samples were taken for residual turbidity measurement. After the rapid mixing period, sample (20 cm^3) was withdrawn immediately for zeta potential measurement. After sedimentation supernatant samples were withdrawn for turbidity and pH measurements. The residual turbidity and pH measurements were conducted using a turbidimeter (Hach, Loveland, Co., USA) and a pH meter (MP220, Metler Toledo, Switzerland), respectively.

2.4. PDA

The flocculation dynamics were observed using a continuous optical flocculation monitor (PDA 2000, Rank Brothers, Bottisham, UK). Before the addition of coagulant, working suspension was continuously introduced into the PDA for 30 s to establish a baseline reading, and then after coagulant was added, the coagulation progress was monitored for another 16 min. The PDA apparatus measures transmitted light fluctuation intensities as particles passing through a flow-through cell. The ratio of the root mean square of the fluctuating intensity (AC value) to the average transmitted light intensity (DC value) was a measurement termed as flocculation index (FI). FI was sensitive to particle size and was effectively utilized to describe the aggregation progress of fine particles, such as the initial aggregation, breakage, and re-aggregation behaviors of particles [28,31–33].

A detailed description of the instrument was provided elsewhere [34].

3. Results and discussion

3.1. Coagulation behaviors of PACls under condition of low alkalinity

3.1.1. Charge neutralization capability of PACls

At alkalinity of 0.5 mM as NaHCO_3 , the turbidity of the working suspension was 53.2 NTU. Fig. 1 showed the effect of aluminum dosage on zeta potential, residual turbidity and pH. For all PACls, a general trend was that with increase of dosage, zeta potential changed from negative value to positive and then reached a relatively stable value (Fig. 1a). The curves of different PACls were greatly separated at lower dosage phase depending on the B values. The zeta potential increased quickly for the high B ($B = 2.2$ and $B = 2.5$) PACls, situating significantly above those with small B values ($B = 1.0$ and 0). In other words, with increase of dosage, the negative charge of particles was reduced more rapidly by PACls with higher B values than by PACls with lower B values. It can be seen that increasing the

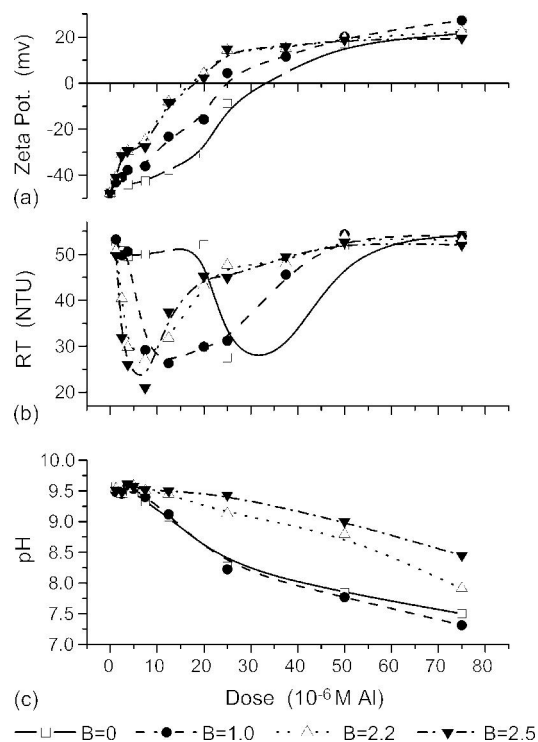


Fig. 1. Effect of dosage on coagulation of 50 mg/L kaolin suspension with alkalinity of 0.5 mM as NaHCO_3 concentration: (a) zeta, (b) residual turbidities, (c) pH vs. dosage.

dosage to a certain level could lead to particles charge reversal. The dosage at which the charge reversal occurs was defined as iso-electrical-dosage (IED) in this paper. The charge neutralization capabilities of coagulants can be compared with their IED data obtained from Fig. 1a. The IED values for PACl₂₅, PACl₂₂, PACl₁₀ and PACl₀ are 17.5, 17, 24 and 33 μM , respectively, indicating the charge neutralization capability order is: PACl₂₅ $\cong$ PACl₂₂ > PACl₁₀ > PACl₀.

Since the charge neutralization capability of coagulants was associated with the positive charge of their corresponding species, the four coagulants could be divided into three types according to their charge neutralization capabilities: high positive charge type such as PACl₂₅, PACl₂₂, denoted as type H; low positive charge type PACl₀, denoted as type L and medium positive charge type PACl₁₀, denoted as type M. The charge neutralization capabilities of different PACls depended quite well on their chemical speciation (Table 1): those with more Al_b/Al₁₃ species possess consequently higher charge neutralization capability.

3.1.2. Residual turbidities and pH variations after sedimentation

Fig. 1b showed the residual turbidities of four PACls after coagulation and sedimentation. With increase of dosage, the sequence of coagulation zone appears in the PACl order of H, M and L type. The optimum dosages (the dosage corresponding to maximum turbidity removal) for L, M, and H type were 30, 13 and 7 $\mu\text{molAl/L}$, respectively. It can also be observed that except for the case of PACl₂₅, the maximum turbidity removals of all other PACls were almost at the same level (about 25 NTU). PACls with higher charge neutralization capabilities could spend less amount of aluminum to make coagulation occur. Taking into account of the zeta potential data, it indicated that charge neutralization was the primary coagulation mechanism under low alkalinity condition.

Fig. 1c showed the pH changes of suspension system after coagulation with different PACls. The pH was decreased after coagulant addition but the extent was much dependent on the *B* value of the coagulant used. The pH associated with H type PACls was clearly situated above that of M and L type PACls, which indicates that PACls with lower *B* values could consume more alkalinity and cause more pH depression. With higher content of Al_b species, PACl₂₂ and PACl₂₅ had less influence on the pH. It can be inferred that the coagulants with low *B* values of 0 and 1.0 experienced significant hydrolysis after dosing, whereas the PACls with high *B* values were more stable and result in less alkalinity consumption. The pH corresponding to optimum dosage also varies with the *B* value of coagulant. For PACl₀, the maximum turbidity removal occurred at the pH range of 7.6–7.9. Combined with Fig. 1a, it can be found that this pH range contained the point of zero charge (PZC, the pH value at which the particles charge is neutralized to zero). For other PACls, the pH values associated with optimum dosages were much higher than the corresponding PZCs, which indicated that the particles were not well neutralized at the point of optimal dosage. On the other hand, within the coagulation zone of PACl₀, the charge of particles was almost neutralized completely (Fig. 1a and 1b),

which was consistent with the findings of a number of investigators [35–37]. However, the optimal dosages of PACl₂₂ and PACl₂₅ were interestingly much below the respective IEDs, with the zeta potential value of -30 mV . Therefore, another coagulation mechanism other than the traditional charge neutralization mechanism may be involved in this case. EPC [28,38] might be applicable to explain the results: after addition of PACls with high *B* values, the preformed Al species can be adsorbed to surfaces of kaolin particles quickly, and the adsorbed species could aggregate, rearrange and finally form ‘electrostatic patches’ over portions of the surface. The attractive force between the positively charged patches and negatively charged surfaces of other kaolin particles could lead to increased collision frequency and efficient aggregation of fine particles. According to this coagulation mechanism, relative high turbidity removal efficiency could be observed even if the particle charge is weakly neutralized at an overall level.

EPC is much dependent on the amount and sort of species in PACls. Different species have different pathways to form electrostatic patches. A schematic diagram about the formation of electrostatic patches by traditional salt (mainly Al_a species) and preformed species is illustrated in Fig. 2. Al_a species (aluminum mononuclear species) is not stable after dosing and will finally form colloidal or amorphous hydroxide precipitate via a series of hydrolysis processes. This kind of precipitate is usually positively charged and able to neutralize the negative charges on clay particles. The precipitation can occur on clay particle surfaces (surface precipitation) or in bulk water [24]. The precipitate on clay particle surfaces (either formed on or adsorbed to clay surfaces) can function as electrostatic patches to induce coagulation/flocculation. In the case of preformed polymeric species of Al_b, due to its much high stability, it cannot be further hydrolyzed and transformed into hydroxide precipitate within the coagulation/flocculation time scale. The electrostatic patches could be formed through its rapid adsorption onto clay particles and subsequent aggregation and rearrangement as mentioned above. With respect to Al_c, its electrostatic patch formation mode should be similar as that of Al_b since it is also a kind of preformed and relatively stable species. However, compared with Al_b species, Al_c have much larger size and lower charge, which is more liable to aggregate and form patches on clay particles once dosed into water. Undoubtedly the electrostatic patches formed from different species should have different characteristics, such as the density of positive charge, the affinity to particle surfaces, and the tendency of self-aggregation. Moreover, the relative importance of different aluminum species changes with coagulation conditions, i.e. the alkalinity of water, which will be addressed later in the following sections. According to Fig. 1b. It was obvious that the turbidity removal efficiency was positively correlated to the content of Al_b species in PACls. It indicated that charge neutralization was the dominant coagulation mechanisms under the condition of low alkalinity.

3.1.3. Floc formation dynamics of PACls under low alkalinity

The FI value increased after the rapid mix period. Under the slow stirring conditions, the particles were allowed to grow

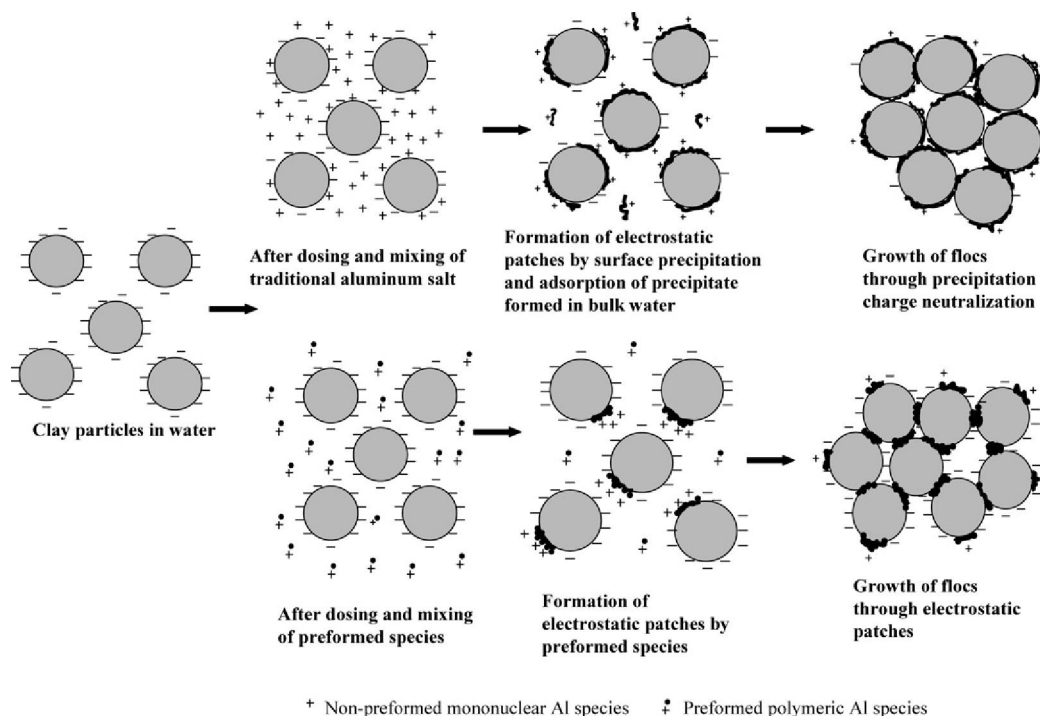


Fig. 2. Schematic diagram of electrostatic patch coagulation.

gradually and form large flocs. Different PACl exhibits quite different FI curves (Fig. 3) for a series of coagulant doses (5, 12.5, 25, 37.5, 75 μM as Al). In the case of PACl_0 , only under the dosage close to IED (30 μM $\sim$ 38 μM), significant aggregation (Fig. 3a) was observed. While in the case of type H coagulants, rapid FI increase and high FI values are detected even at the lowest dosage of 5 μM . As discussed previously, charge neutralization plays the major role in this coagulation process. Further

dosage increase of type H PACls leads to FI value decrease due to the particle restabilization. It is interesting to find that the FI curves are obviously different between PACl_{22} and PACl_{25} under high dosages. With dosages of 38 and 75 μM , FI values of PACl_{25} are greater than those of PACl_{22} , which indicates that the re-stabilization phenomenon is more serious for PACl_{22} than for PACl_{25} . It is likely that the relatively higher concentration of Al_c species in PACl_{25} could experience further hydrolysis

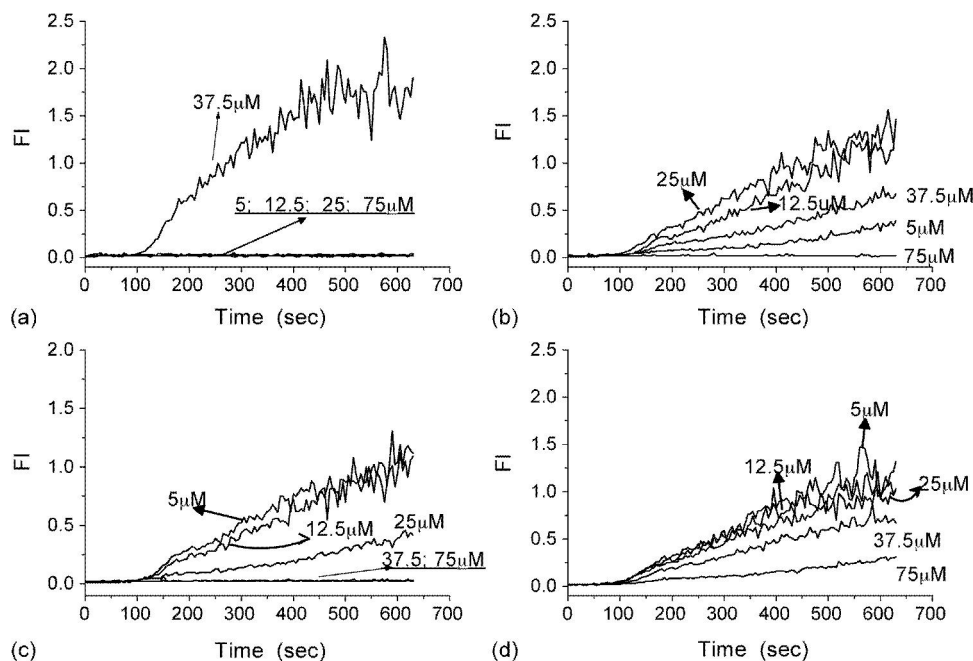


Fig. 3. Effect of coagulant dosage (μM as Al) on the flocculation index for the same systems as in Fig. 1 (with alkalinity of 0.5 mM as NaHCO_3): (a) PACl_0 ; (b) PACl_{10} ; (c) PACl_{22} ; (d) PACl_{25} .

and form hydroxide precipitate; consequently the electrostatic repulsion between positively charged particles is mitigated to some extent. Type M coagulant of PACl_{10} flocculates in a much broader region in terms of dosages. The maximum FI value is obtained under medium high dosage of $25 \mu\text{M}$, which is in agreement with its medium high content of Al_b species.

3.2. Coagulation behaviors of PACls under high alkalinities

Parallel with the experiments carried out under low alkalinity, the coagulation behaviors of PACls with different B values were examined under increased alkalinities. Figs. 4 and 5 demonstrated the coagulation behaviors under alkalinity levels of 1.0 and 2.0 mM, respectively. A glimpse of these plots provided that the general changing trends of the three observed parameters were similar as those under low alkalinity. However, compared with the scenarios under low alkalinity, significant differences were found in many aspects under increased alkalinities, such as IED values, coagulation zones, and maximum turbidity removals. Increasing the concentration of alkalinity magnified the coagulation behavior differences among PACls with various B values. Comparisons were presented in the following aspects.

3.2.1. Comparison of coagulation zones

Based on the experimental data shown in Figs. 1b, 4b and 5b, a schematic representation of coagulation zones (the shaded areas), defined as the range of dosage where no less than half

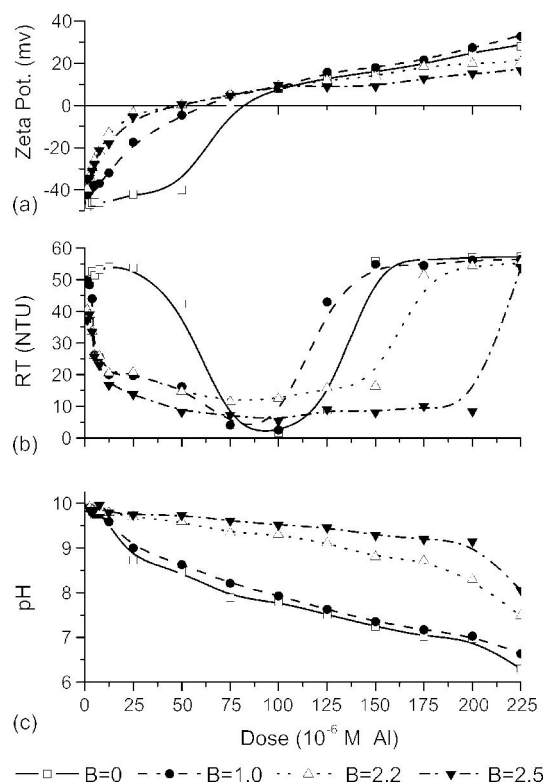


Fig. 4. Effect of coagulant dosage on coagulation of 50 mg/L kaolin suspension with alkalinity of 1 mM NaHCO_3 : (a) zeta potential; (b) residual turbidity; (c) pH vs. dosage.

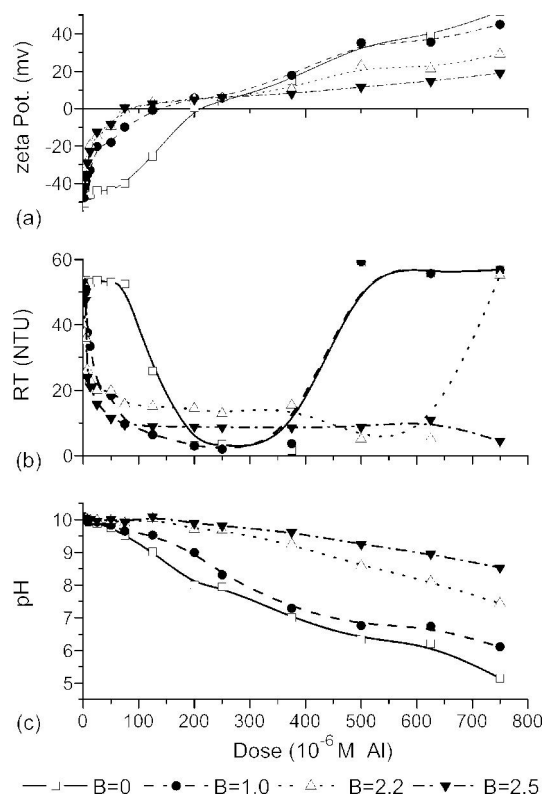


Fig. 5. Effect of coagulant dosage on coagulation of 50 mg/L kaolin suspension with alkalinity of 2 mM NaHCO_3 : (a) zeta potential; (b) residual turbidity; (c) pH vs. dosage.

of the maximum turbidity removal is achieved, for different PACls is illustrated in Fig. 6 (the horizontal axis is alkalinity, the vertical axis is the dosage). With increasing alkalinity, the coagulation zone increases for all PACls. That is to say, higher dosage of coagulant is required to make the suspension system be restabilized under higher alkalinity. However, the shapes of coagulation zones are different with respect to the coagulants used. As aforesaid, precipitate formation is necessary for coagulation with PACl_0 despite the specific mechanism is charge neutralization or ‘sweep flocculation’. However, as to PACls with higher B values, the electrostatic patches could be formed by self-aggregation of preformed species. Obviously, the coagulation zone resulted from precipitate formation is much smaller than the zones resulted from preformed species aggregation. For PACl_0 , the coagulation zone extends from $23 \mu\text{M}$ under alkalinity of 0.5 mM– $80 \mu\text{M}$ and $225 \mu\text{M}$ under alkalinity of 1.0 and 2.0 mM, respectively. As to PACl_{25} , the coagulation zone is so wide that restabilization could not occur under 2 mM of alkalinity. In the case of PACl_{10} , due to its relative abundance of Al_a and Al_b , both precipitate formation and preformed species aggregation played certain roles in coagulation, and consequently resulted in medium large coagulation zone.

Optimal dosages also increased with alkalinity increasing. Under high alkalinity, increasing the dosages of type L and type M PACls might shift the coagulation mechanisms from traditional ‘charge neutralization’ to ‘sweep flocculation’. The former mechanism involves heterogeneous precipitation nucleation and the latter involves homogeneous precipitation [24]. It

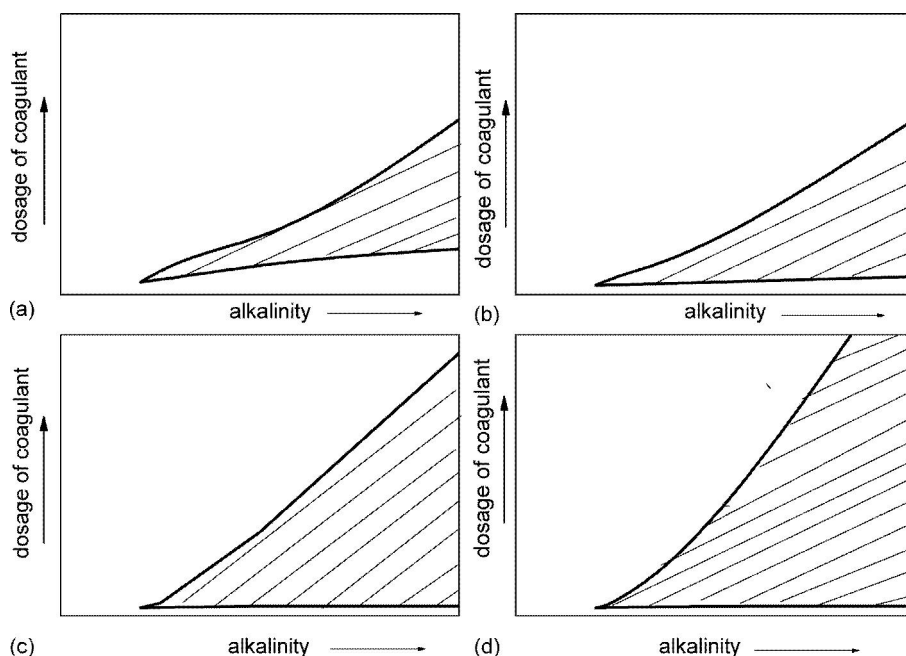


Fig. 6. Schematic representation of coagulation zones (the shadow areas) for different PACl samples: (a) PACl₀; (b) PACl₁₀; (c) PACl₂₂; (d) PACl₂₅.

is interesting to address the possible differences between them. For the traditional coagulants such as alum, the precipitation of aluminum hydroxide act as charge neutralization species. When the precipitation forms in large quantities, colloidal particles would be effectively removed by sweep flocculation rather than by traditional “charge neutralization”. For type L PACl, sweep flocculation is generally more effective and hence is considered as the common mechanism, which functions obviously at high alkalinity and high dosage. At low alkalinity, precipitation formation can be accelerated in presence of sulfate. However, charge neutralization is involved in the sweep flocculation. Therefore, both the traditional charge neutralization and sweep flocculation could be classified into one more general mode of precipitation charge neutralization. Type H PACls might undergo “sweep flocculation” under high alkalinity, but whether and how it would take place is still not clear.

3.2.2. Relative importance of two coagulation modes

As shown in Fig. 1b, under low alkalinity of 0.5 mM as NaHCO₃, charge neutralization was the dominant coagulation mechanism for all PACls, and the electrostatic patches formed by aggregation of preformed aluminum species were more effective than those formed by precipitation of mononuclear aluminum species in terms of maximum turbidity removal. Whereas Figs. 4(b) and 5(b) showed the opposite trend under increased alkalinity: for PACl₀, the maximum turbidity removal could reach as high as 99%, while for PACl₂₂ and PACl₂₅, the average turbidity removal was no more than 90%. It could be inferred that under the condition of high alkalinity, PCN or sweep flocculation was more effective than EPC induced by electrostatic patches of preformed species. As for PACl₁₀, there exist different phases of turbidity removal under the high alkalinity condition: when dosages were relatively low, the coagulation induced by electro-

static patches of preformed species played the major role, and the turbidity removal was about 90%; at high dosages, with particles charge well neutralized, PCN could overtake EPC to remove particles, and consequently turbidity removal reached a higher level of 99%; when the dosage beyond IED, re-stabilization occurred, just like the case with PACl₀.

It can be deduced that PACls might not be always superior to traditional aluminum salts in terms of turbidity removal. However, due to the special characteristics of preformed aluminum species, such as high charge neutralization ability and the high affinity to some filtration media, PACls are expected to have advantages in direct filtration or flotation applications, where limited particle destabilization and aggregation are desired. In addition, PACls could be used to improve NOM removal under some circumstances [39].

3.2.3. Effect of alkalinity on PZC

The coagulation PZC values corresponding to each PACl under different levels of alkalinity were listed in Table 3. It can be seen that when PACl₀ (AlCl₃) was used, the PZC value was not affected by alkalinity and remained at 7.9. At this pH, aluminum hydroxide precipitate was the final hydrolysis product, which served as the particle destabilizer, and PCN was the only coagulation mechanism. On the contrary, alkalinity obviously changed the PZC values of other PACls. Preformed aluminum species was adsorbed on kaolin particles and simultaneously made them destabilized. Due to the relative speciation stability of PACls, the PZC could vary depending on the raw suspension pH values. On the other hand, further hydrolysis and/or structure rearrangement of preformed aluminum species might also occur under high alkalinities, and this kind of species evolution could change its apparent charge neutralization ability.

Table 3
PZC, IED and width of coagulation zone of PACls samples at various alkalinities

Alkali	PACl ₀			PACl ₁₀			PACl ₂₂			PACl ₂₅		
	PZC	IED	Width	PZC	IED	Width	PZC	IED	Width	PZC	IED	Width
0.5	7.9	33	23	8.3	24	25	9.3	17	12	9.5	17	10
1	7.9	75	80	8.5	60	100	9.6	50	155	9.7	50	206
2	7.9	205	225	8.7	130	430	9.8	80	680	9.9	71	–

3.2.4. Flocculation index under high alkalinity

Fig. 7 shows the flocculation dynamics of all coagulants under alkalinity of 2.0 mM as NaHCO₃. When PACl₀ was used, the FI did not increase until dosage reached 150 μM. In the cases of other PACls, FI curves started to increase at the very low dosage of 5 μM, and higher dosages led to more rapid increase of FI and larger flocs. It should be noted that at the highest dosage of 250 μM, the curves for all coagulants exhibit the same increasing rate, but the locations of plateaus are different. PACls with higher *B* values had smaller plateau FI values, indicating the flocs formed by sweep flocculation were larger than those formed by EPC. It confirms that the coagulants in PCN coagulation mode is more inclined to form large flocs under high alkalinity condition and is more suitable for traditional coagulation–sedimentation water treatment facilities.

3.3. Stoichiometric relationship between IED and alkalinity

IED is the dosage where the particles are zero charged. IED can reflect the charge neutralization capability of coagulants, but it is not the exact dosage required to achieve optimal turbidity removal. The IEDs are plotted as a function of the alkalinity (mM as bicarbonate concentration) in Fig. 8. It shows that there

is a stoichiometric relationship between IED and alkalinity. The equations for each PACl derived from linear regression are as follows:

$$\text{For } B = 0 \quad \text{IED} = 116.86 * (\text{Alkalinity}) - 32 \quad R^2 = 0.99$$

$$\text{For } B = 1.0 \quad \text{IED} = 70.57 * (\text{Alkalinity}) - 11 \quad R^2 = 1.0$$

$$\text{For } B = 2.2 \quad \text{IED} = 40.29 * (\text{Alkalinity}) + 2 \quad R^2 = 0.95$$

$$\text{For } B = 2.5 \quad \text{IED} = 33.57 * (\text{Alkalinity}) + 7 \quad R^2 = 0.90$$

The high correlation coefficients for *B*=0, 1.0 suggest the better linear relationship between alkalinity and IED when PCN coagulation is involved. Under PCN mode, the kaolin particles are completely destabilized at the dosage of IED or at the pH of PZC, which is well consistent with Tseng's findings [20]. When *B* increases, the coagulation zones extended much beyond the IED, and smaller correlation coefficients between IED and alkalinity were obtained. Besides, the slopes of the above equations can be used as a parameter to quantify the neutralization capability of different coagulants. For example, with a unit increase of alkalinity, the increments of dosage to maintain the state of zero

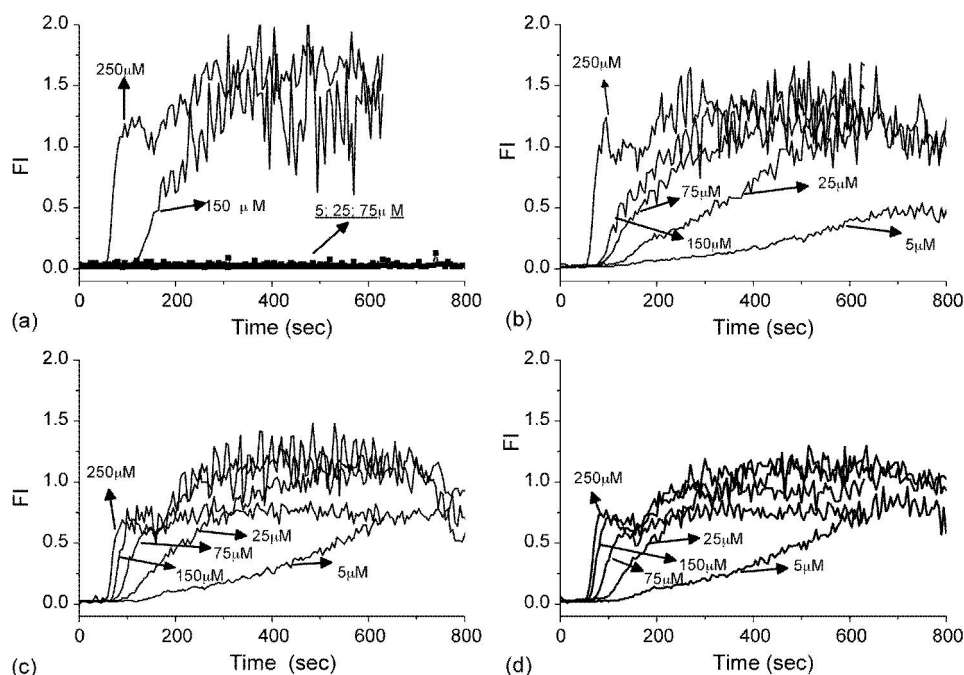


Fig. 7. Effect of coagulant dosage (μM as Al) on the flocculation index for the same systems as in Fig. 4 (with alkalinity of 2.0 mM as NaHCO₃): (a) PACl₀; (b) PACl₁₀; (c) PACl₂₂; (d) PACl₂₅.

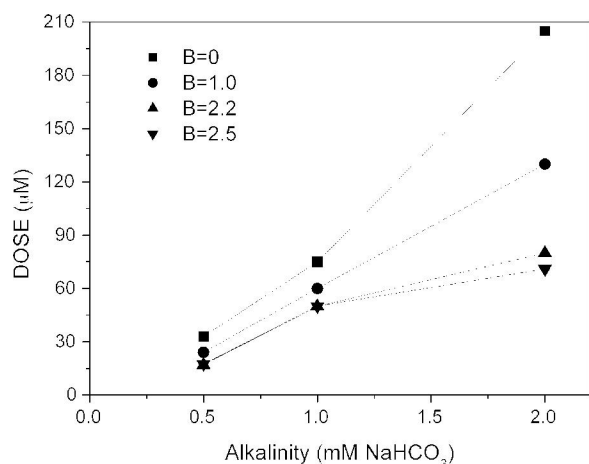


Fig. 8. Changes of IED (μM as Al) with suspension alkalinity (mM as NaHCO_3).

charge are 116.9 mM for PACl_0 , 33.6 mM for PACl_{25} , respectively.

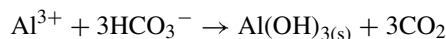
3.4. Further discussion of PCN and electrostatic patch coagulation of preformed species

Once aluminum chloride is added into water, a series of aluminum species will form in situ through progressive hydrolysis. The primary aluminum species are thought to be monomeric, low polymerized and short lived, which are inclined to precipitate in the form of amorphous aluminum hydroxide, $\text{Al}(\text{OH})_{3(s)}$ [13]. The adsorption of these kinds of aluminum hydrolysis products results in destabilization of the kaolin particles—charge neutralization. In most cases, the aluminum hydroxide amorphous solids form so rapidly (1–2s) that they are responsible for the charge neutralization of natural particles [40]. The pH has influence on the charge of amorphous species, and the species is not negatively charged until pH 8.0. In this study the maximum turbidity removal was achieved at PZC of 7.9. The PCN coagulation mode resulted in a relatively narrow coagulation zone, which could limit the application of traditional aluminum coagulant under some circumstances.

Heterogeneous nucleation may take place more rapidly on particle surface than in solution at low saturation ratio. In such case, the solid surfaces act as catalyst to accelerate the aluminum hydrolysis processes [41]. Adsorption of soluble aluminum hydroxide results in a layer of amorphous aluminum hydroxide precipitate, and this process is called surface precipitation [42]. The surface precipitation on the particles is different from the amorphous aluminum hydroxide colloids formed in the bulk—homogeneous nucleation. If large amount of amorphous aluminum hydroxide forms in the bulk water, sweep flocculation becomes the dominant action mode and large flocs are more likely to form. The flocs formed by this way are more suitable for solid–liquid separation in sedimentation.

In most cases there is no clear distinction between those two modes. Raw water physical and chemical parameters, such as particle surface properties, alkalinity and the presence of other ligands, may influence the aluminum hydrolysis progress

greatly. It was confirmed in this study that alkalinity could play a significant role in the coagulation with traditional aluminum salt (AlCl_3). Under low alkalinity condition, the turbidity removal is achieved by adsorption of soluble aluminum hydroxide species and the accompanying charge neutralization. Addition of traditional aluminum salt consumed the alkalinity dramatically, which could be observed from the significant decrease of pH. The consumption of the alkalinity could be simply expressed as:



In this study, the alkalinity and pH conditions of three suspension systems are sufficient to allow for aluminum precipitate formation. However, the precipitate forms less and slower under low alkalinity than under high alkalinity, and the sweep flocculation is more efficient under high alkalinity. It demonstrates that increasing alkalinity can improve the turbidity removal as traditional aluminum coagulant is used.

When PACls are used, the preformed polymeric species (Al_b and Al_c) is rapidly adsorbed on the surfaces of kaolin particles and can resist to further hydrolyzation. The preformed species absorbed on particles can be regarded as positively charged patches on the negatively charged particle surfaces. The electrostatic attractive forces among the patches on one particle and the “naked” surfaces of other particles joint those particles together, and subsequently large flocs would form in this way. Although Al_b species can also be observed by ferron assay after aluminum chloride addition [29,43], they might differ from the preformed Al_b species in PACls in terms of the apparent speciation stability and charge neutralization capability. According to the dual hydrolysis model suggested by Tang and Luan [44], the former Al_b formed in situ via self-hydrolysis is labile to transform into colloidal or amorphous hydroxide precipitate; the Al_b formed via forced hydrolysis in preparation is quite stable [16,44], and will consume less alkalinity once added into water [45]. The preformed Al_b species has been proved to be mainly consisted of Al_{13} , which can be detected by ^{27}Al NMR spectra [46,47].

Alkalinity has little effect on the adsorption of Al_b species; however, it can extend the coagulation zone significantly. At low alkalinity, electrostatic patch coagulation takes place with very low dosage even the overall particles are negatively charged; at high alkalinity, patch coagulation zone extends to the region where the overall particle charge is reversed. The PZC increasing with alkalinity may imply that there exist further hydrolysis or rearrangement of Al_{13} subunits [48,49], which is likely to reduce their neutralization ability.

The preformed aluminum species induced coagulation in essence. It is worthwhile pointing out that EPC involves precipitation charge neutralization, sweep flocculation and bridging flocculation. When PACls with high content of preformed species are used, the complete charge neutralization of clay particles is not required due to electrostatic patch formation. However, if the dosage is lower (or higher) than IED value, the repulsion forces among the overall charged flocs inhibit further growth of the flocs and thus limit the turbidity removal efficiency.

4. Conclusions

When traditional coagulant such as alum is used, the intermediate Al_6 and eventual amorphous precipitate form in situ quickly through self-hydrolysis and exhibit charge neutralization capability. PCN coagulation is the main mechanism for turbidity removal in this case. The preformed polymeric species contained in PACls are fairly stable and highly positively charged and these species can be adsorbed on partial surfaces of clay particles and experience aggregation and rearrangement to form electrostatic patches. The electrostatic patches of preformed species play a vital role in coagulation with PACls.

Alkalinity increased the coagulation zones for all coagulants. The IED value is a linear function of alkalinity. The PZC value of traditional aluminum salt is not influenced by alkalinity, and efficient turbidity removal could be obtained by increasing water alkalinity. The alkalinity has slight influences on the electrostatic patch coagulation resulting from preformed polymeric aluminum species. It is expected that the electrical patch coagulation of PACls might be more suitable for separation processes involving micro-surface interactions, such as direct filtration and flotation instead of traditional coagulation–sedimentation–filtration processes.

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