



Distinct coagulation mechanism and model between alum and high Al_{13} -PACl

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Abstract

The conventional alum and polyaluminum chloride (PACl) with high content of Al_{13} were selected to study the interaction between coagulants and particles in suspension. Particulate silica microspheres were used for the investigation with emphasis on the surface adsorption behavior at a constant pH of 6.5. Residual turbidity (RT), zeta potential and fractional surface coverage (θ) were studied as functions of aluminum dosage (C). Differences in the coagulation behavior between alum and PACl were illustrated graphically as $\log C$ -RT and $\log C$ - θ , respectively. It was demonstrated that some distinct mechanisms existed between alum and PACl in their adsorption and coagulation with silica particles owing to their different speciation. The results suggested that, to accomplish destabilization and aggregation, alum interacted with silica particles mainly via monomers and $Al(OH)_3(am)$ flocs, while PACl interacted via the Al_{13} polycations. As a result, charge-neutralization, electrostatic patch coagulation and sweep-flocculation, bridge-aggregation may be included during the coagulation process. The main mechanisms for alum were charge-neutralization/sweep-flocculation while electrostatic patch coagulation and bridge-aggregation may be both involved for PACl besides charge-neutralization. Langmuir and Freundlich isotherm models were used to describe the adsorption process of PACl and alum on silica particles, respectively. Monolayer adsorption was observed for PACl with $\theta < 0.5$ whereas multilayer adsorption occurred for alum with θ value reaching above 1. It was concluded that different adsorption mechanisms occurred for PACl and alum. The predominant driving force in the adsorption process of PACl was of electrostatic origin, whereas for alum was mainly through chemical precipitation.

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1. Introduction

Earlier studies considered that hydrolyzing iron and aluminum metal coagulants were efficient in forming enormous flocs which can be separated eventually by sedimentation and filtration [1,2]. Later, chemical aspects of coagulation demonstrated that the hydrolysis products of polynuclear hydroxyl complexes were the main active species responsible for charge neutralization and aggregation in particle removal [3,4]. Despite various progressive viewpoints in understanding interactions between particles and coagulants [5–8], four primary mechanisms were commonly recognized, i.e. double layer compression, charge-neutralization, sweep-flocculation and bridge-aggregation.

Significance of adsorption by hydrolyzed metal ions during coagulation was first proposed in the 1960s showing the influence of adsorption on the destabilization and also on the surface concentration of solid phase [4]. The proposed adsorption model therein can depict the stoichiometric relationship of coagulation between surface concentration and applied metal ion concentration. Later in the 1980s, three models were put forward based on the surface complexation model to describe the coagulation mechanisms with emphasis on the traditional alum [9–11]. It can be suggested that all the three models described the coagulation behavior between amorphous precipitates and particles, but this may not apply to PACl, although Dentel's model [10] suggested otherwise. Recently, a quantitative model of PACl proposed by Wang et al. distinguished coagulation behavior of different species by ferron-assay and zeta potential [12]. However, the coagulation mechanism of PACl has not been discussed yet and further studies are needed to find out the characteristic features between interactions of PACl and particles which

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may in turn guide the design and operation in water treatment plants.

As one of the most common conventional coagulants, alum has been widely used for years. However, tailor-made polymeric coagulants such as PACls have been used increasingly nowadays due to their high efficiency and relatively lower cost [13]. Previous studies showed that inherent difference in the coagulation behavior and particle removal mechanism existed between traditional coagulants and inorganic polymer flocculants (IPFs) [14]. In recent years, NMR and SAXS investigations revealed that polycation Al_{13} was the dominant polymeric species in PACl and accounted for its considerable effectiveness in the coagulation process [15]. Evidence also showed that IPFs exhibited intermediate destabilization features between the traditional coagulants and organic polymer flocculants [16]. Nevertheless, coagulation mechanism of PACl was not clear although precipitation charge neutralization (PCN) and electrostatic patch coagulation (EPC) have been proposed [10,17]. It is therefore of importance to differentiate their behaviors in the adsorptive destabilization and the subsequent coagulation process between traditional coagulants and polymer flocculants both from theoretical point of view and in the practical applications. In this paper, we focus on the characteristic features of PACl 2.2 with high content of Al_{13} and alum in the adsorptive destabilization of particulate silica to demonstrate the differences in the coagulation mode and mechanism between the two kinds of coagulants.

2. Materials and methods

2.1. Particles and coagulants

All chemicals used in this study were of analytical grade except those being specifically mentioned, and solutions were prepared with deionized water.

Silica microspheres with 3 μm average diameter (Wuhan Shuaier Company, China) were used as model particles in this study because of their strong negative charge in suspension, homogeneity and simple morphology as can be clearly seen in the SEM image (HITACHI S-570) in Fig. 1. A BET method was applied to measure the specific surface area of silica particles, and acid–base potentiometric titration was performed to determine their surface adsorption sites. The major characteristics of the silica microspheres are shown in Table 1. In order to further investigate their electrokinetic features with and without the adsorptive coating of coagulants, ζ -potentials were also measured as a function of pH in suspension.

Two types of coagulants—traditional alum and polymeric flocculants (PACl) were used in this investigation. Alum was prepared as a 0.1 M solution of $Al_2(SO_4)_3$. PACl 2.2 was pre-

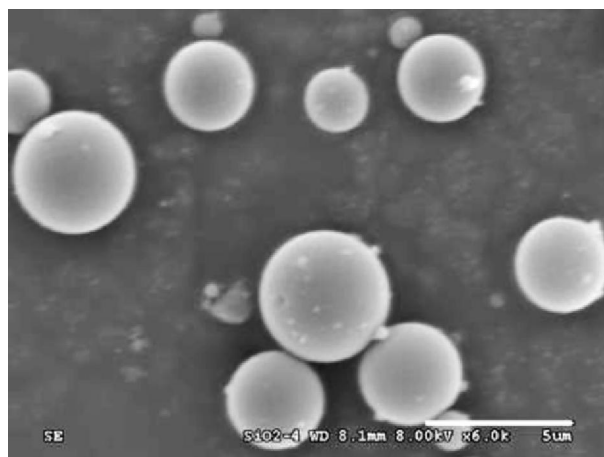


Fig. 1. SEM image of silica microspheres (mean diameter: 3.0 μm).

Table 1
Main characteristics of silica microspheres

Item	Description
Structure	Amorphous
Mean diameter	3 μm
BET surface area	1.3 m ² /g
N_s^a	3.736×10^{-5} mol/m ²

^a Measured by potentiometric titration in 0.01 M $NaNO_3$ with 1 g/L silica concentration.

pared by the slow micro-titration of 0.5 mol/L $AlCl_3$ solution with 1.0 mol/L NaOH resulting in the OH/Al ratio of 2.2 to gain high content of Al_{13} . Speciation of coagulants by ferron assay and ^{27}Al NMR spectroscopy were carried out after 1 week aging, and all the coagulants were stored at 4 °C before use.

The result of ferron assay and ^{27}Al NMR are given in Table 2 and Fig. 2. It is clear that the major species of alum is monomer (Al_1), while for PACl 2.2 tridecamer (Al_{13}) is the dominant.

2.2. Ferron assay and ^{27}Al NMR spectroscopy

The ferron assay was used to characterize the Al species distribution of coagulants. Based on different kinetic rates between reactions of ferron and Al species, three type species denoted as Al_a , Al_b and Al_c , were operationally defined with each kind attributed to a certain category of species, namely the mononuclear (instantaneously reacted species), the intermediate polynuclear (slower-reacting species) and the large polynuclear species (non-reacting or with a imperceptible reaction rate) [15,18]. The detailed operational protocols can be found elsewhere [18].

Table 2
Speciation of the two typical coagulants by ferron assay and ^{27}Al NMR

Coagulants	Al_T (mol/L)	Ferron assay			^{27}Al NMR	
		Al_a (%)	Al_b (%)	Al_c (%)	Al_{13} (%)	Al_1 (%)
Alum	0.108	96.3	2.0	1.7	0	79.2
PACl 2.2	0.101	9.4	83.8	6.8	76.7	5.9

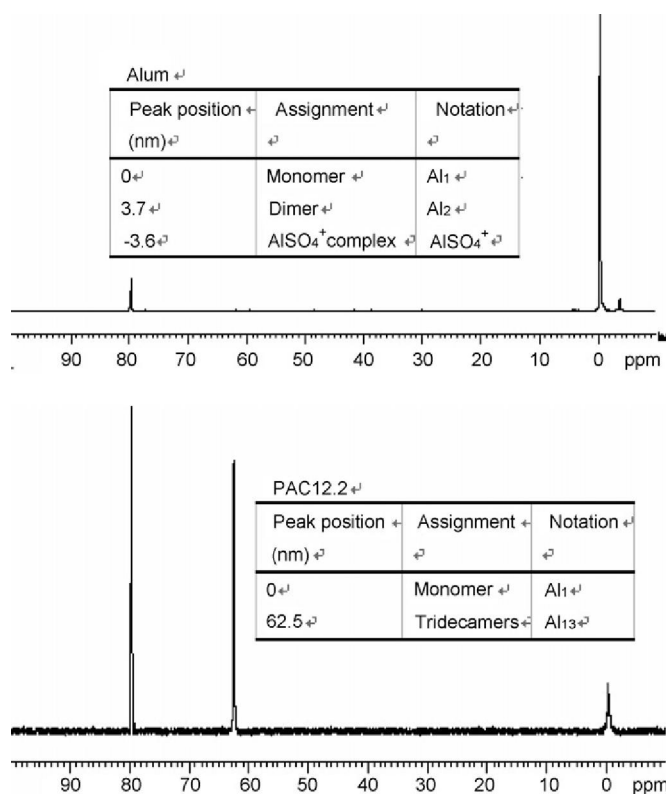


Fig. 2. ²⁷Al NMR spectra of alum and PACI 2.2 after 1 week aging of freshly prepared solution.

The 500 MHz ²⁷Al NMR spectroscopy (Brookhaven Co., U.S.A.) was used to characterize the coagulant speciation, and instrumental settings and experimental conditions were the same as Feng's report [18]. The internal standard was 0.05 M NaAlO₂ with its chemical shift at 80 ppm downfield. The signals near 0, 62.5 ppm represent mononuclear Al (Al₁) and Al₁₃, respectively [19]. The amount of undetectable species in the ²⁷Al NMR spectra was not considered in this investigation.

2.3. ζ-Potential measurements

It is difficult to directly determine the ζ-potential of coagulants because of the variation in their speciation and particle size distribution. Therefore, we performed the coating of silica microspheres with both the alum and PACI 2.2 for ζ-potential measurement to retrieve the electrical properties of coagulants and their interaction with silica particles. Hundred milligrams per liter of silica suspension was used as the carrier and excess coagulants of 10⁻⁴ mol/L in the total aluminum concentration (Al_T) were added to ensure completely coverage of particles. After coating, zeta potentials (Malvern, Zetasizer 2000, U.K.) were measured with the particles under different pH.

2.4. Jar test for the adsorptive coagulation

The traditional jar test was applied to study the effect of adsorption on coagulation mechanism. Aliquots (500 mL) of silica suspension in both concentration levels of 500 mg/L and

5 g/L were dosed with coagulants on a JTY laboratory stirrer (Daiyuan Company, Beijing). The 0.01 M NaNO₃ and 0.001 M NaHCO₃ provided the ionic strength and pH buffers. Experimental procedure included 2 min rapid mixing (200 rpm) after coagulant dosing and 30 min settling, which is enough to reach the adsorption equilibrium according to preliminary experiments and literature [20,21]. The pH of silica suspension was adjusted to 6.5 with diluted HNO₃ or NaOH. Zeta potential (by Malvern, Zetasizer 2000, U.K.) and residual turbidity (by HACH2100N turbidimeter, U.S.A.) were measured both after rapid mixing and sedimentation. The supernatant of suspension was filtered through 0.45 μm membrane and then acidified to analyze the residual aluminum by ICP-OES (Perkin Elmer, Optima 2000, U.S.A.).

3. Results and discussion

3.1. Changes of ζ-potentials

The measured ζ-potential of silica particles with and without coagulant coating at different pH conditions are presented in Fig. 3. It can be seen that silica microspheres alone were strongly negative charged at the pH range investigated. The isoelectric point of silica was lower than pH 3 according to Fig. 3. However, the silica particles coated with alum and PACI behaved differently with its isoelectric point being pH 8.5 and 10.2, respectively, and charge reversal occurred at the common range of pH. The highly positive zeta values and wider positive charged range of PACI 2.2 in relation to alum further suggests that stable polycation coating exists constantly almost at the whole pH range because of the dominant preformed Al₁₃ species. Comparing with the uncoated negative silica microspheres, the positively coated particles performed differently at the same pH range. With increasing pH values, zeta potential of coated particles did not decline but increase before pH 6.5 and then decrease in the basic range. It can be suggested that zeta value curves in Fig. 3 can reflect the charge characteristics of silica microspheres, PACI 2.2 and alum, respectively, and their interfacial interaction processes as well.

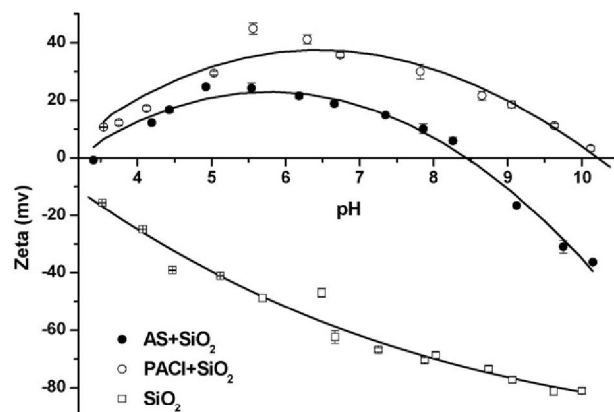


Fig. 3. The ζ-potential curves of silica microspheres with or without coating of alum and PACI 2.2 as a function of pH in 0.01 M NaNO₃ as ionic strength. Particle concentration: 100 mg/L; total aluminum concentration [Al]_T: 10⁻⁴ mol/L.

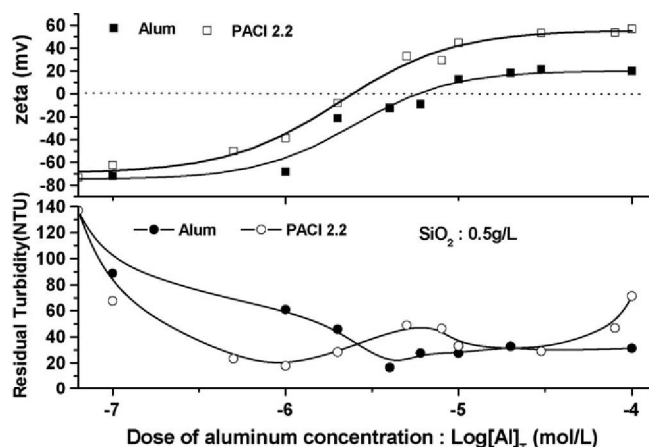


Fig. 4. The ζ -potential and residual turbidity curves as a function of aluminum dosage during coagulation of 0.5 g/L silica microsphere suspension by alum and PACI 2.2 (pH 6.5; NaNO₃: 0.01 M; NaHCO₃: 0.001 M).

3.2. Adsorptive coagulation of silica microspheres

Fig. 4 shows the jar test results for the ζ -potential and residual turbidity of 0.5 g/L silica suspension. Similar results were also found with the high concentration level of 5 g/L which does not show in this regard. It can be seen clearly that the ζ -potential values of PACI were much higher than that of alum in the whole dosage range. For alum, with increasing dosage, the ζ -potential increased and residual turbidity declined to the lowest around isoelectric point and maintained the lower turbidity within the dosage range. On the contrary, after PACI dosing, the residual turbidity declined sharply at the very low aluminum concentration and the lowest occurred far before the isoelectric point but then increased. The corresponding optimum coagulant dosages were 10^{-6} and 4×10^{-6} mol/L for PACI and alum, respectively.

Hydrolysis products of metal coagulants such as $Al(OH)^{2+}$ or Al_{13}^{7+} can readily adsorb onto the negatively charged-surfaces of particles and decrease the original charge on the surface within microseconds to give destabilization of particles [9,22]. It has been considered that negative colloidal particles can be neutralized by aluminum hydrolysis products or also $Al(OH)_3$ precipitates formed in situ under certain conditions [23,24]. As indicated in Fig. 4, the interactions of alum and PACI on destabilization and aggregation of silica particles are different. For alum, the residual turbidity declined slowly to the minimum around zero ζ -potential with increasing dose. At the condition of pH 6.5, charge-neutralization of alum could be interpreted mainly with the freshly formed precipitates of low positive charge. Based on the solubility diagram of $Al(OH)_3$ [25], the amorphous aluminum hydroxide formed when $pH > 6$ ($Al_T = 1 \times 10^{-6}$ to 1×10^{-4} mol/L). As far as this study is concerned, the pH value was constant at 6.5 and aluminum dosage ranged from 1×10^{-6} to 1×10^{-4} mol/L, which means amorphous precipitates playing a major role in the interaction between alum and silica particles. Once the maximum turbidity removal arrived, re-stabilization did not occur at high aluminum concentration. It can be demonstrated that the adhesion of low

charged amorphous precipitates coated on the surface and destabilized particles, which corresponded well with the study of Letterman and Vanderbrook [24].

Compared with alum, however, PACI behaved differently owing to the preformed stable Al species like Al_{13} . It can be understood that the rapidly adsorbed species may aggregate, rearrange and finally form 'electrostatic patches' over portions of particle surface [17]. The positively charged patches could attract negative silica particles and improve the particle collision frequency leading to efficient particle aggregation. Accordingly, the lowest residual turbidity can be observed at the very low dosage when the particle was weakly neutralized [17]. Furthermore, Al_{13} not only on the surface, but also in the solution will rearrange and form Al_{13} -aggregates larger than ~ 2 nm because of increasing alkalinity. This kind of Al_{13} aggregates attracted and connected silica particles by highly positive charge and larger size similar to the organic polymer. In this regard, the electrostatic patch coagulation and bridge-aggregation can be used to explain the effective turbidity removal of PACI. As the dose of PACI increased further, re-stabilization appeared after the maximum turbidity removal. It was implied that particles repelled to each other due to the strong electrostatic repulsion forces caused by adsorbed polycations. However, with further addition of PACI, the residual turbidity declined again. It can be understood that some amorphous precipitates formed for PACI giving sweep-flocculation by which hydroxides improved the turbidity removal. Therefore, different coagulation mechanism could be assigned to alum and PACI in this respect.

3.3. Surface coverage and adsorption isotherm models

To differentiate interaction mode and mechanism of alum and PACI 2.2 in the coagulation process, the fractional surface coverage were calculated by Eq. (1) according to the adsorption test results:

$$\theta = \frac{\Gamma}{\Gamma_{\max}} \quad (1)$$

where $\Gamma_{\max}$ is the full sites adsorption capacity of silica particles in suspension (mol/m²) which is equal to the specific surface site ($N_s = 3.736 \times 10^{-5}$ mol/m²) based on the acid–base titration results. It is assumed that the fractional surface coverage θ is estimated by the stoichiometry with 1:1 (mol/mol) ratio of hydrolysis aluminum species versus occupied surface sites for both polycations and amorphous $Al(OH)_3$ and the bond difference was neglected.

The fractional coverage curves presented in Fig. 5 indicate that adsorption behaviors of alum and PACI 2.2 on silica particles are quite distinct. The maximum surface coverage of PACI was around 0.4 whereas surface coverage of alum varied enormously. The surface coverage obtained for both 0.5 and 5 g/L silica suspensions were well beyond the monolayer coverage as the increase of aluminum concentration, indicating a surface precipitation aggregation for alum. It was the precipitates that adsorbed on the surface sites of particles and built up adhesive multilayer coverage with further increase of Al_T . On the other hand, with predominant species of Al_{13} for PACI 2.2, highly

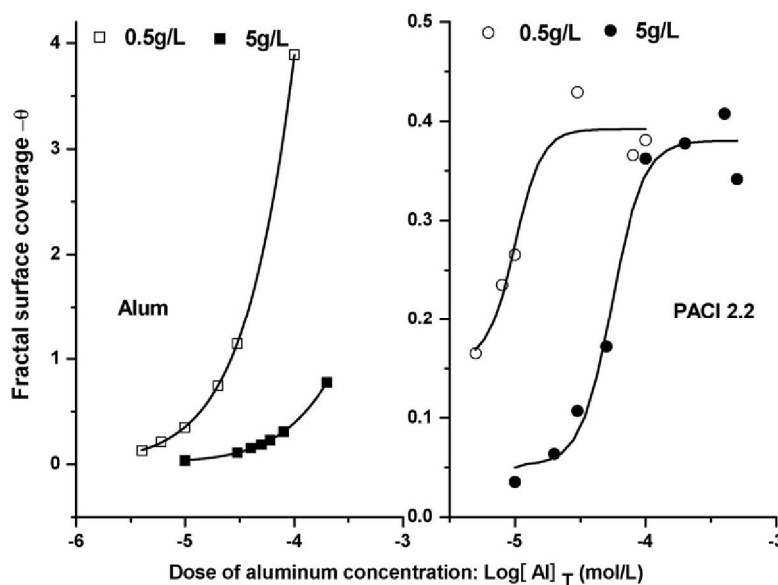


Fig. 5. Comparison of the Al fractional coverage on silica microspheres as a function of $\log [Al]_T$ in the coagulation by alum and PACI 2.2, respectively. Silica suspension: 0.5 and 5 g/L as indicated in the curve.

positive polycations would adsorb on the surface sites at pH 6.5 as monolayer but only to some extent.

Based on the above discussion, two isotherm models of Freundlich and Langmuir were further applied to the adsorption of alum and PACI 2.2 on the silica microspheres in the coagulation process. The adsorbed amount of aluminum on silica microspheres was calculated as follows:

$$\Gamma = \frac{C_t - C_e}{SC_p} \quad (2)$$

where Γ is the adsorbed amount (mol/m^2), C_t , C_e and C_p are the concentrations of total added aluminum, residual equilibrium aluminum (mol/L) and silica suspension (g/L), respectively, S is the specific surface area of silica microspheres (m^2/g). As indicated in Fig. 5, the surface coverage of alum and PACI on silica microspheres represents two distinct adsorption isotherm models. For alum, heterogeneous surfaces may be formed due to its fast hydrolysis and chemical precipitation deposited on the particles' surface, which means the energy of sorption for solute cannot be the same and independent of surface coverage as Langmuir model assumed. Therefore, Freundlich model is used in this case, whereas a single layer of solute on the surface of silica microspheres is developed for PACI 2.2 and the Langmuir model is applied consequently.

3.3.1. The Freundlich isotherm model for alum

Generally, the Freundlich model has the form as in the following equation:

$$\Gamma = kC_e^{1/n} \quad (3)$$

where Γ is the amount adsorbed (mol/m^2) and C_e is the equilibrium aluminum concentration (mol/L). The parameters k and n relate to sorption capacity and sorption intensity, respectively [26]. To determine these empirically derived coefficients, data

are often fitted to the logarithmic form as Eq. (4) and the results are shown in Table 3 and Fig. 6:

$$\log \Gamma = \log k + \frac{1}{n \log C_e} \quad (4)$$

As can be seen from Table 3 and Fig. 6, adsorption of alum on silica fits well with the Freundlich isotherm model. From Table 3, it is obvious that the model parameters of $\log k$ that determine sorption capacity are quite different for both initial silica concentrations. It implied different dominating adsorbate species for alum under two conditions, which were a series of aluminum hydrolysis products that underwent speciation transformation and precipitation in the solution. For both low and high initial silica concentration, optimum coagulation was caused by adsorption of amorphous precipitates on the negative particles and probably also by the sorption of SO_4^{2-} on the coated particles to form $\equiv\text{AlSO}_4^-$ surface complex. For the low initial silica concentration, relatively more precipitates induced infinite deposition on the particle from which high surface coverage can be seen in Fig. 5. Therefore, the maximum adsorbed amount represented by $\log k$ is higher than and nearly as twice as that of high initial silica concentration. Although the adsorption energy can be separated into chemical bonding and electrostatic interaction, there exist difficulties to distinct them especially when the adsorbent transformed during the process. Compared with the ζ -potential values of PACI, it can be suggested that the electrostatic interaction was weaker and chemical

Table 3
Results for the Freundlich isotherm model fitted for alum in the coagulation of silica suspensions

Silica concentration (g/L)	$\log k$	$1/n$	R^2
0.5	5.0787	1.6873	0.9841
5	2.5770	1.4308	0.9608

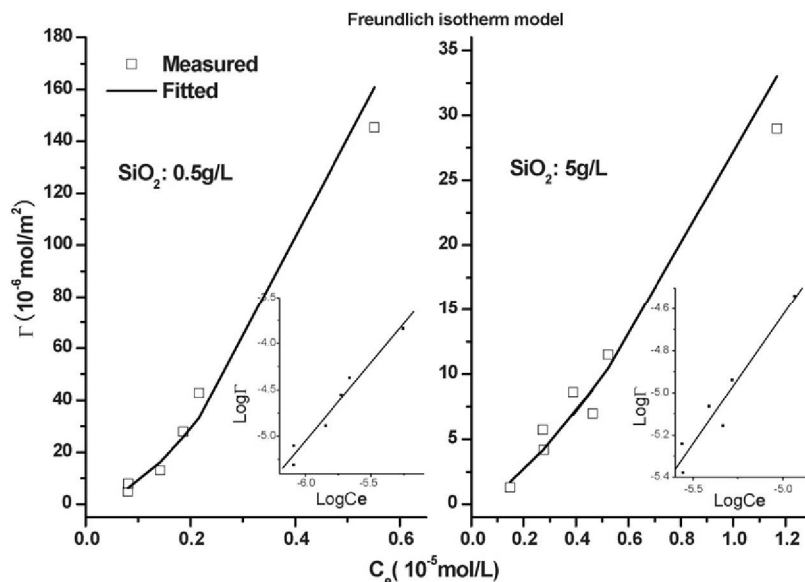


Fig. 6. The Freundlich isotherm model fitted to the sorption data of alum by silica microspheres in the coagulation process (pH 6.5; NaNO_3 : 0.01 M; NaHCO_3 : 0.001 M; $T = 22^\circ\text{C}$).

bonding would dominated the adsorption process of alum on silica.

3.3.2. The Langmuir isotherm for PACI 2.2

The common expression of the Langmuir model is written as the following equation:

$$\frac{1}{\Gamma} = \frac{1}{\Gamma^0} + \left(\frac{1}{K\Gamma^0} \right) \left(\frac{1}{C_e} \right) \quad (5)$$

where Γ is the amount adsorbed (mol/m^2), Γ^0 represents the actual maximum adsorbed amount in the experiment (mol/m^2), K the adsorption coefficient presenting the equilibrium aluminum concentration C_e (mol/L) in solution when half Γ^0 has reached. Calibration of the model to a set of experimental data can be accomplished by linear regression as illustrated in Table 4 and Fig. 7. As we can see the calculated isotherms fit very well to the experimental data at lower aluminum concentration, which means the surface complexation between polycation and silica can be represented by one-site-one model. At higher aluminum concentration, however, amorphous aluminum hydroxides formed in the coagulation process may contribute much to the uptake of aluminum. This assumption was confirmed by the decrease of the residual turbidity after re-stabilization in the high aluminum dosage in Fig. 4, which suggested somehow that amorphous $\text{Al}(\text{OH})_3$ caused the particle aggregation as was in the case of alum.

Table 4
Results for the Langmuir isotherm model fitted for PACI 2.2 in the coagulation of silica suspensions

Silica concentration (g/L)	Γ^0 ($\times 10^{-5}$ mol/m ²)	K ($\times 10^5$)	R^2
0.5	1.4744	7.0357	0.9707
5	1.6105	0.6427	0.9631

It can be seen that the actual maximum adsorbed amounts Γ^0 under the different silica concentrations are very close at $1.4\text{--}1.6 \times 10^{-5}$ mol/m² but much less than the theoretical adsorption capacity Γ_{max}^0 (3.736×10^{-5} mol/m²) according to the full specific surface sites. If divide the Γ^0 by Γ_{max}^0 , the fractional surface coverage can be obtained as 0.37 and 0.43 for both silica concentrations, respectively, by which a complete re-stabilization has occurred. The optimum coagulation of silica suspension after PACI adding occurred when surface coverage was less than 0.1 according to Figs. 4 and 5, which suggest a faster aggregation occurred. The strong charge-neutralization of Al_{13} and the bridging ability with its aggregated species make PACI an efficient coagulant in destabilizing and aggregating suspended particles and colloids. It is therefore very reasonable to suggest that for PACI, the electrostatic interaction is the main driving forces for the adsorption process forming ‘electrostatic patches’ to induce electrostatic patch coagulation and highly charged larger size aggregated polycations can also attract particles through electrostatic forces and bridging.

Using the stoichiometric model proposed by Stumm and O’Melia [4], the applied coagulant concentration can be calculated by the following equation:

$$C_{t\theta} = \left[\frac{\theta}{K(1-\theta)} \right] [1 + K\Gamma^0(1-\theta)] \quad (6)$$

where $C_{t\theta}$ is the concentration of coagulant necessary to produce a certain fractional surface coverage (θ), K the equilibrium constant in the Langmuir model, Γ^0 the actual maximum adsorption amount (mol/m^2), and S is the surface area of dispersed phase (m^2/L). From the jar test results, the minimum residual turbidity was obtained at the very low dosage with the fractional coverage lower than 0.1, when particles were partially covered with positive species. Assuming $\theta = 0.04$ then the theoretical coagulant concentrations in the low (0.5 g/L) and high (5 g/L) silica dispersions can be calculated as 1.0×10^{-6} and 1.2×10^{-5} mol/L,

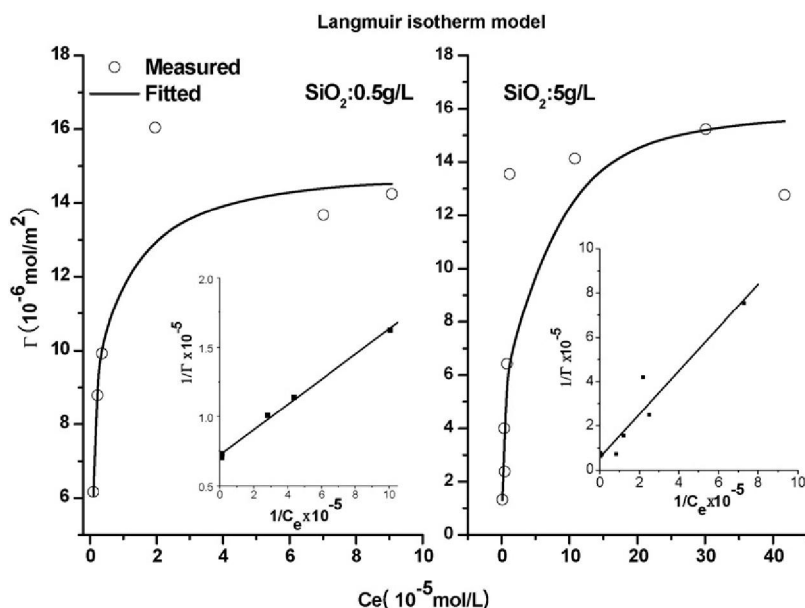


Fig. 7. The Langmuir isotherm model fitted to sorption data of PACI 2.2 by silica microspheres in the coagulation process (pH 6.5; NaNO_3 : 0.01 M; NaHCO_3 : 0.001 M; $T = 22^\circ\text{C}$).

respectively. These values are in accordance with the actual optimum aluminum dosages as shown in Figs. 4 and 8, and are proportional to the concentration of silica suspension. Therefore, it can be concluded that an inherent stoichiometric relationship exists in the coagulation and re-stabilization induced by adsorption of PACI 2.2.

3.3.3. Comparison of coagulation mode and mechanism

Based on the surface coverage and adsorption isotherms discussed above, different coagulation behaviors of alum and PACI 2.2 as given in Fig. 4 were explained. The residual turbidity and corresponding surface coverage of silica as a function of aluminum concentration in the coagulation of 5 g/L silica suspension were further shown in Fig. 8.

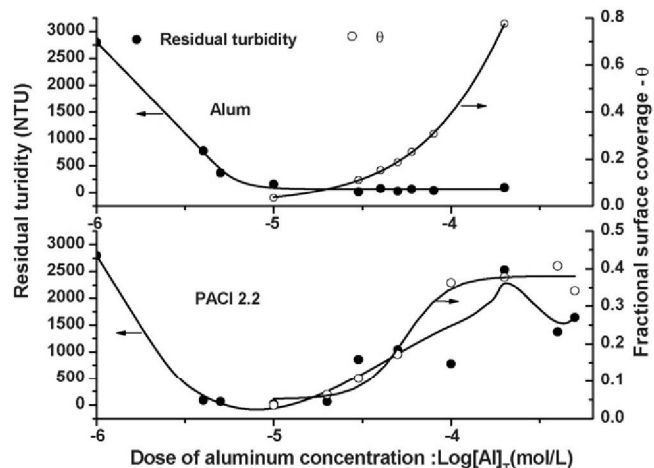


Fig. 8. The residual turbidity and the surface coverage as a function of aluminum dosage in the coagulation of silica suspension of 5 g/L, showing the sorption effect of different Al species of the coagulants (pH 6.5; NaNO_3 : 0.01 M; NaHCO_3 : 0.001 M).

It can be seen that for alum, with the increasing surface coverage, the residual turbidity of silica suspension lowered to the minimum at 3×10^{-5} M and maintained the optimum coagulation area with increasing dose. However, optimum coagulation appeared at the lower dosage at 1×10^{-5} M and re-stabilization occurred with further dose for PACI. The surface coverage increases with the aluminum dosage and reaches the plateau when re-stabilization is completed. These different behaviors are presumably due to the different adsorbed species on the particles. For alum, hydrolysis species like monomers and $\text{Al}(\text{OH})_{3(\text{am})}$ with low positive charge may adhere onto the particle surface to destabilize the silica suspension and then sweep the destabilized particles away by amorphous precipitates. However, with high content of Al_{13} , PACI 2.2 exhibited strong charge-neutralization ability due to fast adsorption process due to high positive charge. The maximum turbidity removal does not correspond to the zero ζ -potential and optimum destabilization occurs when only very small portion of silica surface are covered. The destabilized particles are likely to be removed by both the electrostatic patch coagulation induced by adsorption of Al_{13} on the silica surface and also bridge-aggregation of the aggregated Al_{13} on the particles which tend to strongly repel each other for their high positive charge with the increasing dosage. Therefore, saturation phenomena on surface coverage may occur because of the strong repulsion between polycations and of a monolayer adsorption, leading to the presence of re-stabilization and the maximum adsorbed amount as was demonstrated by Figs. 4 and 8.

4. Conclusion

The coagulation modes and mechanisms of alum and PACI 2.2 are distinct according to the $\log C$ -RT and $\log C$ - θ results in this study. Sweep-flocculation and electrostatic patch coagulation are suggested to be main coagulation mechanisms for

alum and PACl 2.2 respectively besides charge-neutralization owing to their different species. Rapid adsorption of PACl on silica microspheres and stable species lead to particle destabilization and electrostatic patches coagulation. Aggregated Al_{13} enhanced the particles aggregation by efficient bridging. Nevertheless, precipitate hydroxide formed by aluminum hydrolysis is the predominant species both in the adsorption and flocculation process. With much higher efficiency in the low aluminum dosage than alum, PACl should perform effectively in the adsorptive coagulation process which differs from conventional alum treatment. However, due to the stoichiometric relationship between coagulant dosage and surface concentration of dispersion (particle concentration), more precise control of dosage of PACl is required for efficient operation. Considering the promising application of PACl in the drinking water industry, further study on the coagulation mode and mechanism are still needed.

Acknowledgements

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