

# Effect of Al(III) speciation on coagulation of highly turbid water

Jr-Lin Lin<sup>a</sup>, Chihpin Huang<sup>a,\*</sup>, Jill Ruhsing Pan<sup>b</sup>, Dongsheng Wang<sup>c</sup>

<sup>a</sup> *Institute of Environment Engineering, National Chiao Tung University, 75, Po-Ai Street, Hsinchu, Taiwan*

<sup>b</sup> *Biotechnology Center, National Chung Hsing University, 250 Kuo Kuang Road, Taichung, Taiwan*

<sup>c</sup> *SKLEAC, Research Center for Eco-Environmental Sciences, CAS, P.O. Box 2871, Beijing 100085, China*

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## Abstract

In Taiwan, the turbidity of raw water for fresh water treatments can sometimes reach as high as 40000 NTU due to intensive rainfall, especially in typhoon seasons. In response, water works often apply large quantities of coagulants such as polyaluminium chloride (PACl). In this study, simulated and natural highly turbid water was coagulated with two PACls, a commercial product (PACl-1) and a laboratory product (PACl-E). The Al species distributions of PACl-1 and PACl-E under various pH conditions were determined, and the corresponding coagulation efficiency was evaluated. The PACl-E has a wider range of operational pH, while the efficiency of PACl-1 peaks at around neutral pH. For simulated water up to 5000 NTU, the PACl-E was superior to PACl-1 at low dosage and in the pH range studied. Similar results were discovered with natural water, except that when the turbidity was extremely high, the coagulation efficiency of PACl-E decreased significantly due to the presence of large amounts of organic matter. The coagulation of PACl-E was closely related to the content of polycationic aluminium ( $Al_{13}$ ) while that of PACl-1 was dictated by the amount of  $Al_c$ . The sludge from PACl-E coagulation had better dewaterability when the optimum dosage was applied. The experimental results suggest that for natural water up to 5000 NTU, PACl containing high  $Al_{13}$  species is recommended for coagulation. In cases when the water contains high organic matter, efficient coagulation depends upon enmeshment by amorphous aluminium hydroxide.

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## 1. Introduction

During typhoon seasons in Taiwan, excessive upstream erosion has substantially raised the turbidity of surface waters. Consequently, the raw water turbidity for water purification is extremely high. Turbidity of the raw water at the pump station can reach over tens of thousands NTU, which can significantly handicap the water treatment plant. Researchers have explored strategies such as full-scale sludge blanket, dissolved air floatation (DAF) and two-stage filtration to treat highly turbid water (Lin et al., 2004; Kwon et al., 2004; Di Bernardo and Di Bernardo, 2006). Unfortunately, the applicable range of

turbidity was substantially lower than what we have encountered in Taiwan. The highly turbid water also occurs annually in the arid zone of western China, where water treatment plants draw raw water from the Yellow River. The river water contains extremely high concentration of solids, which is carried into water treatment plants such as the Langchou water treatment plant. In response, several large pre-sedimentation tanks have been constructed prior to upstream of the conventional water treatment plant. After the sedimentation of great amounts of suspended particles, the supernatant was then delivered to the treatment plant. The coagulant was replaced by polyacrylamide in the coagulation process to enhance turbidity removal (Fang and Fu, 2004). Because of land scarcity in Taiwan, expansion of the sedimentation tank is beyond reach. Most waterworks in Taiwan generously apply polymers such as polyaluminium chloride (PACl)

\* Corresponding author. Tel.: +886 3 5726463; fax: +886 3 5725958.  
E-mail address: [cphuang@mail.nctu.edu.tw](mailto:cphuang@mail.nctu.edu.tw) (C. Huang).

in hopes of bringing down the high turbidity. In the existing facility, however, performance was limited.

Poor performance of PACl has been blamed on its low content of critical hydrolysis products, especially polycationic aluminium ( $Al_{13}$ ).  $Al_{13}$  is a highly charged polymeric aluminium species,  $Al_{13}O_4(OH)_{24}^{7+}$ , which is an effective agent for charge neutralization (Wang and Hsu, 1994). Studies have also confirmed that  $Al_{13}$  is the key to efficient coagulation of particulates and natural organic matter (NOM) by PACl (Wang et al., 2002; Gao et al., 2005; Hu et al., 2006). PACl is an intermediate product during hydrolysis, polymerization and precipitation of aluminium salts. There are different ways to produce PACl. Researchers have shown that the distribution of Al species in PACl varies according to the physical and chemical conditions during PACl production (Bertsch, 1987; Bottero et al., 1987; Klopogge et al., 1992; Qu and Liu, 2004; Hu et al., 2005). A PACl with over 70%  $Al_{13}$  has been produced by an electrolysis process (Liu et al., 1999a). PACl containing over 90%  $Al_{13}$  has also been prepared by sulfate precipitation and nitrate metathesis ( $SO_4^{2-}/Ba^{2+}$  separation method) from a pre-hydrolyzed PACl solution produced by alkaline titration method (Shi et al., 2007). Similar results can be achieved through separation and purification by ultra-filtration (Huang et al., 2006). In addition, the pH of the solution has a profound effect on Al speciation of PACl during coagulation processes, depending mainly on its OH<sup>-</sup>/Al ratio (Wang et al., 2004). Studies have shown that treatment of highly turbid water is affected by rapid mixing and humic acid content (Kan et al., 2002; Annadurai et al., 2004). However, there has been limited research investigating the effects of Al speciation on coagulation for highly turbid water treatments. To determine the effectiveness and optimum conditions of PACl on treating highly turbid water, the Al speciation of PACl in relation to the mechanism of coagulation must be examined thoroughly. In this study, experiments were carried out to investigate the effects of PACl speciation on coagulation efficiency for waters of different levels of turbidity. One commercial and one laboratory PACl product were applied to a range of highly turbid waters.

## 2. Materials and methods

### 2.1. Highly turbid water samples

The sediment for the preparation of the highly turbid water samples was collected from the Shihmen Reservoir located in Taoyuan County, Taiwan. The sediment was mixed with tap water and aerated for 1 h, followed by settling for 30 min. After settling, the supernatant was used as the stock solution, to which deionized water was added to prepare the highly turbid water samples with the desired turbidity. Natural highly turbid water was also collected from rivers of northern, central, and southern Taiwan during heavy rainfalls. The suspension was also settled for

30 min, and the supernatant was collected as the natural highly turbid water sample.

Dissolved organic carbon (DOC) was measured by total organic carbon analyzer (TOC-5000A, Shimadzu, Japan). Particle size distribution and zeta-potential were characterized by particle size analyzer (Mastersizer 2000, Malvern, UK) and laser zeta analyzer (Zetasizer nano ZS, Malvern, UK), respectively. The characteristics of the two natural water (Natural 1 and Natural 2) and one simulated water (Simulated) samples are listed in Table 1. The table indicates that the properties of the simulated water were quite similar to those of the two natural waters, except that the turbidity as well as DOC and volatile solids of Natural 2 were substantially higher.

### 2.2. Coagulants

Two PACl products were used in this study. Reagent-grade PACl ( $Al_2O_3 = 10\%$ ) was purchased from Showa Chemicals Inc., designated as PACl-1. Another PACl ( $Al_2O_3 = 33\%$ ) named PACl-E, for the electrochemical process by which it is made, was received as a gift from the Research Center for Eco-environmental Sciences, Chinese Academy of Sciences in China. The OH<sup>-</sup>/Al ratios,  $\gamma$ , of PACl-1 and PACl-E were 1.4 and 2.1, respectively. Working solutions containing  $1000 \text{ mg l}^{-1}$  as Al were freshly prepared from the solutions before each test. Aluminium concentration was analyzed by inductive coupled plasma atomic emission spectrometry (ICPAES) (JY24, Jobin-Yvon, France).

### 2.3. Jar tests

Standard jar tests were conducted in one-liter beakers to evaluate coagulation efficiencies. An initial rapid mixing was conducted at 200 rpm ( $G = 350 \text{ s}^{-1}$ ) for one min followed by a slow mixing at 30 rpm ( $G = 25 \text{ s}^{-1}$ ) for 20 min. Zeta-potential was measured immediately without dilution after the rapid mixing. The suspension was left undisturbed for 20 min. After settling, the residual turbidity (RT) of the supernatant was measured.

Table 1  
Characteristics of simulated and natural highly turbid water

Parameters	Stock water samples		
	Simulated	Natural 1	Natural 2
Turbidity (NTU)	–	300–7500	35000
Turbidity after 30 min settling (NTU)	4500–5300	200–6500	10000
pH	8.1	7.6–8.2	8.1
Zeta-potential (mV)	–22 to –18	–21.9 to –13.8	–18.1
Size ( $\mu\text{m}$ )	0.8–2.2	0.5–2.3	2.0
Alkalinity ( $\text{mg l}^{-1}$ as $\text{CaCO}_3$ )	100–120	70–200	191
DOC ( $\text{mg l}^{-1}$ )	2.0–3.0	2.1–2.7	8.5
VS of TS (%)	4.5	1.2–3.7	8.3

#### 2.4. Ferron assay

The Ferron colorimetric method has been widely adopted to quantify aluminium species (Smith, 1971). In this study, a slightly modified version of the Ferron method was used (Wang et al., 2004). After the addition of the Ferron agent, the PACl sample was immediately shaken to ensure a complete reaction between the Ferron agent and Al. The aluminium species were quantified by timed absorbance at 366 nm with a UV–Visible Spectrometer (U3010, Hitachi, Japan). Based on the kinetics of the reactions between the aluminium species and Ferron agent, the hydrolyzed Al species can be categorized into three groups: Al<sub>a</sub>, monomeric; Al<sub>b</sub>, the polycations; and Al<sub>c</sub>, the amorphous aluminium hydroxide. The absorbance in the first minute was assigned to Al<sub>a</sub>, and from one min to two hours to Al<sub>b</sub>. Al<sub>c</sub> was obtained by subtracting Al<sub>a</sub> and Al<sub>b</sub> from the total Al. The total aluminium concentration of the solution was maintained at 0.37 mM Al for the duration of the test.

#### 2.5. Aluminium-27 nuclear magnetic resonance (<sup>27</sup>Al NMR)

The distributions of hydrolyzed species of PACl-1 and PACl-E in solution were also determined by 500 MHz <sup>27</sup>Al nuclear magnetic resonance (NMR) (Uniytinova-500, Varian, USA). The operational parameters for the NMR analysis: spectrometer frequency, solvent, and temperature, were set at 130.246 MHz, D<sub>2</sub>O, and 298 K, respectively. A 5-mm sample tube (Wilma 507-pp, SP Industries Inc., USA) containing 3 mL Al solution and a 4.2-mm sample tube (Wilma WGS-5BL, SP Industries Inc., USA) containing 1 mL 50 mM Al(OD)<sub>4</sub><sup>-</sup> solution were co-inserted as the internal standard. The chemical shift of Al(OD)<sub>4</sub><sup>-</sup> was at 80 ppm. The signals in the proximity of 0 ppm, 3–4 ppm, and 62.5 ppm represent monomeric Al (Al<sub>m</sub>), dimeric Al (Al<sub>2</sub>), and tridecamer Al<sub>13</sub>, respectively. The concentration of each species was determined by the ratio of the integrated intensity of the corresponding peak to that of Al(OD)<sub>4</sub><sup>-</sup> at 80 ppm. The amount of the undetectable species (denoted as Al<sub>u</sub>) was obtained by subtracting the sum of the detected Al species from the total Al concentration.

#### 2.6. pH effect on Al species distribution

Solutions contained 1 mM NaOCl<sub>4</sub> and 1 mM Na<sub>2</sub>CO<sub>3</sub> to maintain the conductivity and ionic strength for each test. Various amounts of NaOH and HCl solutions were

added to the solutions to maintain the final pH. After the addition of the coagulant, the solution was stirred at 200 rpm for one min followed by the Ferron assay. The total aluminium concentration of the solution was held at 0.2 mM Al for each pH condition. All the experiments were carried out at 23 ± 1 °C.

#### 2.7. Sludge dewatering test

The dewaterability of the sludge from PACl-1 and PACl-E coagulation was evaluated by specific resistance to filtration (SRF) and capillary suction time (CST). The zeta potentials of PACl-1 and PACl-E sludge were also measured. Natural water samples at 1300 NTU were used to estimate the dewatering characteristics of sludge from the settled sludge after PACl-1 and PACl-E coagulation.

### 3. Results and discussion

#### 3.1. Al speciation of PACl-1 and PACl-E

Al speciation of PACl-1 and PACl-E was identified by Ferron assay and <sup>27</sup>Al NMR method. The results are summarized in Table 2. By Ferron assay, the major Al species of PACl-1 were found to be monomeric Al (Al<sub>m</sub>) and Al<sub>c</sub> (Al(OH)<sub>3</sub>) while the majority of the Al species in PACl-E was found to be Al<sub>b</sub>. The Al<sub>m</sub> and Al<sub>13</sub> by <sup>27</sup>Al NMR measurement correspond to the Al<sub>a</sub> and Al<sub>b</sub>, respectively. Although there was some discrepancy between the composition of Al<sub>b</sub> and Al<sub>13</sub>, both methods confirmed that PACl-E contained much more Al<sub>13</sub>. Other studies have also indicated that Al<sub>13</sub> can be roughly represented by Al<sub>b</sub>. (Parker and Bertsch, 1992; Liu et al., 1999a; Shi et al., 2007). Therefore, the Ferron assay was used to estimate the Al speciation of PACl in further studies.

#### 3.2. pH effect on turbidity removal

Literature has indicated that pH change may have a significant effect on PACl coagulation (Wang et al., 2002; Hu et al, 2006). Because both turbidity and pH of the coagulation suspension can affect the optimum dosages of PACls, the 250 NTU water samples were used to avoid the interference of high turbidity on the coagulation pH effect experiments. Jar tests were performed on both simulated water and natural water without pH control to determine the optimum dosages of PACl-1 and PACl-E. The optimum coagulant dosages for 250 NTU simulated water by PACl-1 and PACl-E were 2.5 mg l<sup>-1</sup>, which were applied

Table 2  
Characteristics of coagulants by Ferron assay and <sup>27</sup>Al NMR method

Coagulant	γ	pH	Ferron assay (Al %)			<sup>27</sup> Al NMR (Al %)		
			Al <sub>a</sub>	Al <sub>b</sub>	Al <sub>c</sub>	Al <sub>m</sub>	Al <sub>13</sub>	Al <sub>u</sub>
PACl-1	1.4	3.8	42.3	8	49.7	38.4	6.8	54.8
PACl-E	2.1	4.06	19	65.8	15.2	16.6	60	23.4

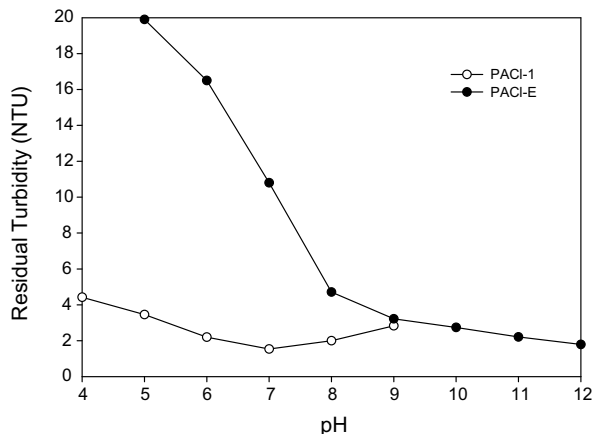


Fig. 1. pH effect on turbidity removal with PACI-1 and PACI-E coagulation at dosage of  $2.5 \text{ mg l}^{-1}$  as Al for the simulated water with 250 NTU.

subsequently in the jar tests to evaluate the optimum pH for both PACI-1 and PACI-E coagulation. The RT of PACI-1 and PACI-E coagulation at various pH values are shown in Fig. 1. A marked difference between the two coagulants was observed. Fig. 1 shows that the optimum pH for PACI-1 coagulation occurred around pH 7, which implies that sweep flocculation (enmeshment) by  $\text{Al}(\text{OH})_3$  was probably the principal coagulation mechanism of PACI-1. For PACI-E coagulation, the RT decreased continuously with increasing pH. Since the coagulation performance is directly affected by the effective Al species, the pH effect on coagulation may be explained by its effect on Al speciation.

### 3.3. pH effect on Al speciation of PACI-1 and PACI-E during coagulation

The hydrolysis products of aluminium coagulants are significantly affected by the pH of the solution. Both Al speciation and solubility of the polyaluminium coagulants vary with pH (Pernitsky and Edzwald, 2003). Al speciation of PACI-1 and PACI-E at various pH values, as measured by Ferron assay, is shown in Fig 2a and b, respectively. A distinct difference was observed. For PACI-1, the  $\text{Al}_a$  dropped sharply in the range of pH 4–5. Very little monomeric Al ( $\text{Al}_a$ ) was detected at neutral pH, but concentrations then rose rapidly at high pH. The disappearance of  $\text{Al}_a$  at neutral pH was compensated by the rise in  $\text{Al}_b$  and  $\text{Al}_c$ , in which the  $\text{Al}_c$  was substantially more than  $\text{Al}_b$ . In contrast, pH had little effect on any of the three species of PACI-E. The most dramatic observation was that the  $\text{Al}_a$  of PACI-E stayed very low, especially at neutral pH, while the  $\text{Al}_b$  content was extremely high, ranging from 60% to 70%. Only a little  $\text{Al}_a$  of PACI-E transformed into  $\text{Al}_b$  at neutral pH. In addition,  $\text{Al}_c$  content of PACI-E decreased slightly in the basic pH region. The study also indicated a discrepancy between the stability of the  $\text{Al}_b$  species pre-formed before the dosing and those formed

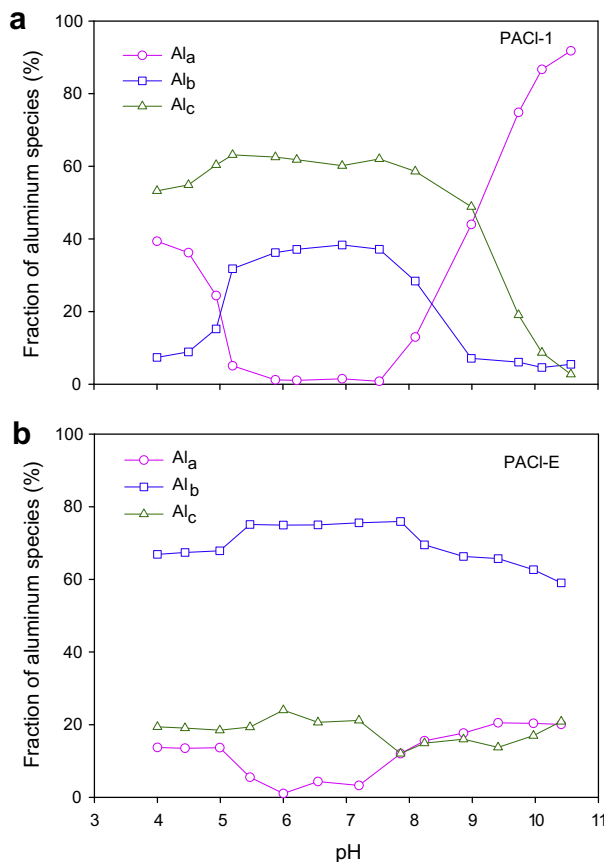


Fig. 2. Al speciation of (a) PACI-1 and (b) PACI-E under various pH conditions at a concentration of  $5.4 \text{ mg Al l}^{-1}$ .

in-situ after dosing, suggesting different  $\text{Al}_b$  structures (Wang et al., 2004). Although the maximum  $\text{Al}_b$  was observed at neutral pH for PACI-1, the in-situ formed  $\text{Al}_b$  species was metastable, and thus probably transformed into  $\text{Al}_c$  or another Al species immediately after dosing (Hu et al., 2006). On the contrary, the pre-hydrolyzed  $\text{Al}_b$  in PACI-E remained stable with varying pH. As a result, PACI-1 and PACI-E responded differently to pH.

Study has reported that aluminium(III) species would be transformed into voluminous aluminium hydroxide ( $\text{Al}(\text{OH})_3$ ) at neutral pH (Duan and Gregory, 2003). Large amounts of  $\text{Al}_c$  formed in the neutral pH region for PACI-1, indicating the formation of significant amount of amorphous aluminium hydroxide ( $\text{Al}(\text{OH})_3$ ), and consequently the occurrence of precipitation. In addition, because the in-situ formed  $\text{Al}_b$  that occurred in the neutral pH region can quickly transform into  $\text{Al}_c$ ,  $\text{Al}_c$  dominated over PACI-1 coagulation at neutral pH. As a result, enmeshment by amorphous aluminium hydroxide was responsible for the turbidity removal by PACI-1 at neutral pH, as seen in Fig. 2. On the other hand, because the  $\text{Al}_{13}$  content of PACI-E consistently exceeded 60% of total Al concentration throughout the entire pH range studied, charge neutralization most likely played a significant role in turbidity removal. However, maximum turbidity removal was observed at alkaline pH, which could be explained

by the effect of Al aggregation on particle-aggregation. Al aggregates formed at various pH values differ in electrophoretic mobility and charge. Studies have suggested that polymeric aluminium species aggregate and precipitate above pH 7.5 (Van Benschoten and Edzwald, 1990; Wang et al., 2004). Although the aggregation and precipitation of  $Al_{13}$  occurred above pH 6, and the charge of aggregated  $Al_{13}$  became weak at such condition (Furrer et al., 1992), previous study has shown that  $Al_{13}$  still has some charge neutralization ability to aggregate particles (Chen et al., 2006). Thus, the PACI-E aggregates containing voluminous  $Al_{13}$  possibly remain weakly positively charged in the basic pH region to induce an electrostatic patch during coagulation (Wang et al., 2002), which promotes more turbidity removal in the basic pH region. As such, the coagulation of PACI-E is mainly dictated by charge neutralization.

### 3.4. Effect of turbidity on PACI-1 and PACI-E coagulation

To examine the efficiency of PACI-1 and PACI-E coagulation on highly turbid water, various dosages of PACI-1 and PACI-E were applied on both simulated and natural water. The turbidity ranged from 50 to 5300 NTU for simulated water and from 450 to 10000 NTU for natural

water. The major Al speciation of PACI-1 and PACI-E at pH 7 and pH 8, is shown in Fig. 2. Coagulation efficiency is strongly dependent on the speciation of aluminium coagulants. Moreover, pH can significantly affect the surface charge of turbid particles as well as the speciation of aluminium coagulants during hydrolysis. In order to understand the effects of major speciation of PACI-1 and PACI-E on the coagulation of high turbidity water, pH values were controlled at 7 and 8 for PACI-1 and PACI-E coagulation, respectively, for the study.

The RT for simulated water and natural water was measured to determine the ability for particle removal, as presented in Figs. 3 and 4, respectively. The variation of zeta potential (ZP) with coagulation dosage was also monitored for simulated water, as shown in Fig. 3. For both PACI-1 and PACI-E, the ZP of the particles and turbidity removals increased with increasing dosage. The increase in ZP by PACI-E was more significant than that of PACI-1. At low turbidity, e.g., 50 NTU, as seen in Fig. 4a, PACI-1 was more effective in particle removal even though PACI-E was more efficient in charge neutralization of the particles. The difference became insignificant when the original turbidity of the water was increased. At 5300 NTU, PACI-E was superior to PACI-1 in turbidity removal,

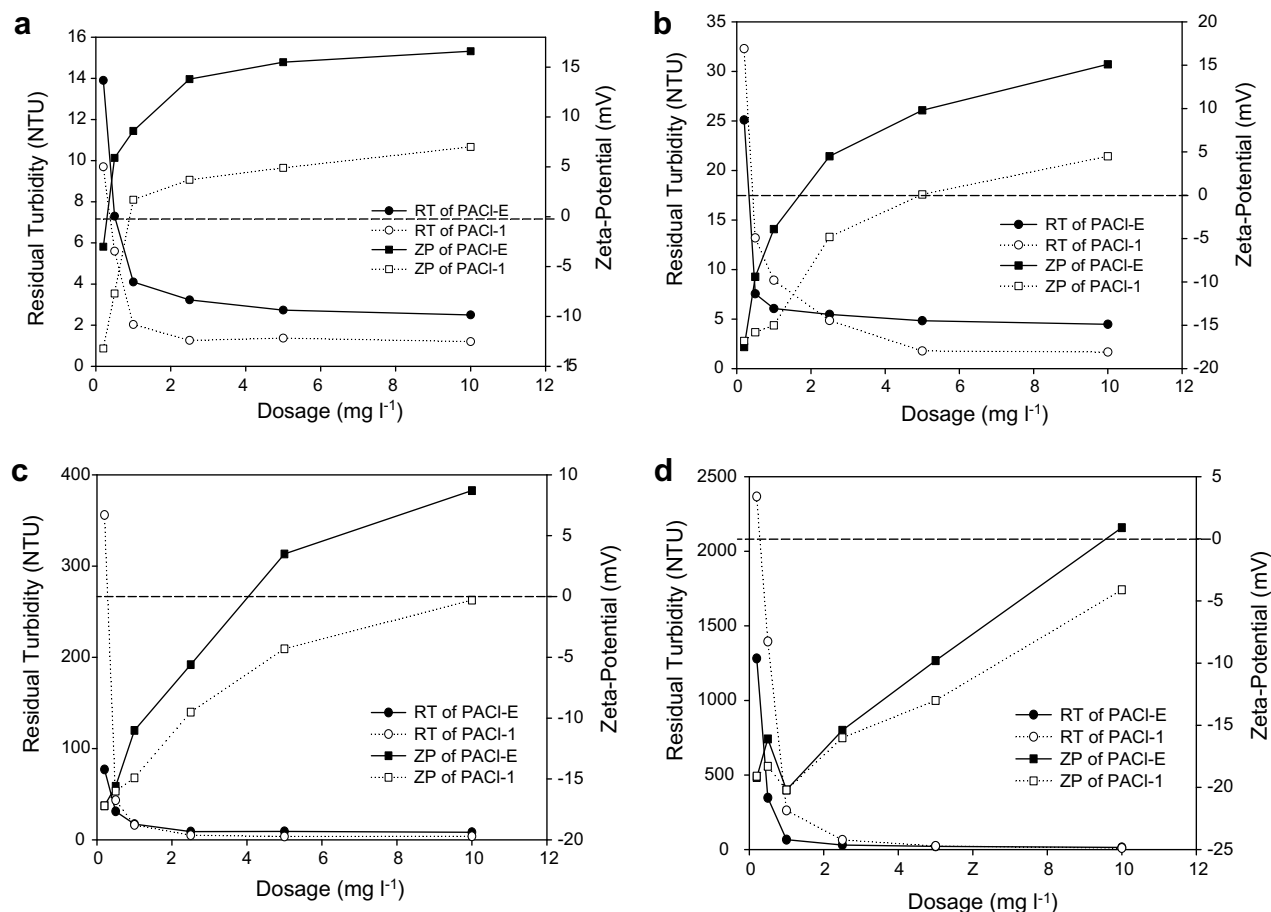


Fig. 3. Residual turbidity (RT) and zeta-potential (ZP) changes of simulated water at various coagulant dosages. The pH was controlled at 7 for PACI-1 and 8 for PACI-E, and the original turbidities were (a) 50 NTU, (b) 1000 NTU, (c) 2500 NTU and (d) 5300 NTU.

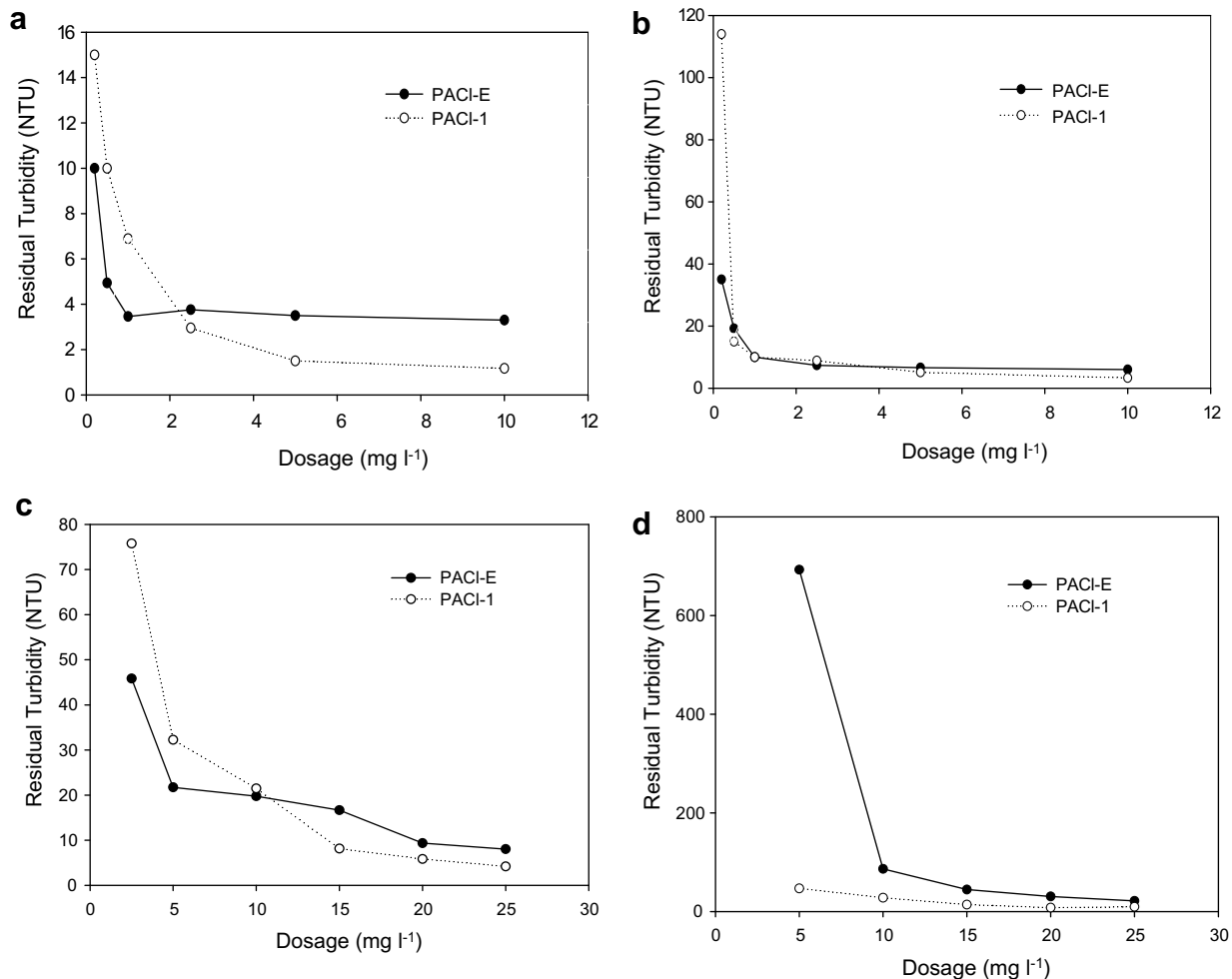


Fig. 4. Variations of residual turbidity of natural water at various coagulant dosages. The pH was controlled at 7 for PACI-1 and 8 for PACI-E, and the original turbidities were (a) 450 NTU, (b) 2550 NTU, (c) 5000 NTU and (d) 10000 NTU.

especially at low dosage. At low turbidity, large particle-aggregation was limited due to an insufficient number of particles, despite the strong charge neutralization of PACI-E. Because of the increase of turbidity, the collision efficiency between particles during the coagulation process will increase. An increase of collision efficiency will improve the particle-aggregation induced by charge neutralization or electrostatic patch (Gregory, 1973). As a result, PACI-E containing a large amount of  $Al_{13}$  can aggregate particles by charge neutralization (or electrostatic patch) at dosage less than  $2 \text{ mg l}^{-1}$  even as turbidity is increased continuously. A similar result was observed with natural highly turbid water.

On the other hand, effective turbidity removal also occurred at high dosage in which the zeta potential of suspended particles was high positive, which is similar to the results of previous research (Chen et al., 2006). Furrer et al. (1992) have suggested that the polymeric aluminium species would aggregate and precipitate above pH 6. Study also has indicated that  $Al_{13}$  could be transformed into linear  $Al_{13}$  aggregates by maintaining a total high aluminium concentration (Bottero et al., 1987). In our study, because

the PACI-E coagulation was conducted at pH 8, the  $Al_{13}$  aggregates can occur when high PACI-E dosage was applied. As a result, PACI-E could induce particle-aggregation by interparticle bridging at a higher dosage even though the zeta potential of suspended particles was high positive.

The results with natural highly turbid water are depicted in Fig. 4, in which the turbidity spanned from 450 to 10000 NTU. For turbidity levels up to 5000 NTU, PACI-E was generally more efficient than PACI-1, particularly at low dosage, similar to the previous result with simulated water (Fig. 3). At 10000 NTU, this advantage was overturned. Studies have reported that the organic matter in water would preferentially react with  $Al_{13}$  and decompose the structure of the cationic polymer  $Al_{13}$  (Vilge-Ritter et al., 1999; Liu et al., 1999b; Mason et al., 2000; Exall and van-Loon, 2003; Kazpard et al., 2006). The strong charge neutralization ability of PACI-E was deprived in the highly turbid natural water at 10000 NTU due to the high organic content, as suggested in Table 1. Because the  $Al_{13}$  species is critical in removing particles from the high turbidity water, as demonstrated in Fig. 3, the occurrence of large amounts

of organic matter in the natural water interfered with the coagulation efficiencies of PACI-E. This phenomenon disappeared when the dosage was increased. Moreover, since coagulation by PACI-1 mostly depends upon enmeshment at neutral pH, extremely high turbidity (10000 NTU) assisted in particle removal by enmeshment, even at low dosage. Studies have suggested that in the presence of organic matter, Al(III) does not hydrolyze into  $Al_{13}$  at neutral pH. Conversely, it transforms into  $Al(OH)_3$ , which then removes organic matter by adsorption and precipitation (Huang and Shiu, 1996). Thus, particle removal during PACI-1 coagulation was somewhat insensitive to dosage at neutral pH for the highly turbid water containing a high organic matter load. Another study has also shown that PACI can simultaneously remove turbidity, as well as humic acid from highly turbid water at neutral pH (Annadurai et al., 2004), which supports the result of Fig. 4d.

### 3.5. Dewaterability of sludge from PACI-1 and PACI-E coagulation

The sludge characteristics depend on the mechanisms of coagulation. Study has suggested that sludge formed from

charge neutralization is more easily dewatered (Wu and Wu, 2001). Capillary suction time (CST) and specific resistance filtration (SRF) were determined to reflect the dewatering of sludge, which is presented in Fig. 5, along with the ZP at various coagulant dosages. Natural water at 1300 NTU was the test water. A marked difference was observed between the dewaterability of PACI-1 and PACI-E sludge. Both CST and SRF indicated that sludge from PACI-E has higher sludge dewaterability due to the coagulation mechanism of charge neutralization, attributed to high  $Al_{13}$  content. The dosages for the optimum dewatering of the sludge from both PACI-1 and PACI-E coagulations coincide with the dosages at which the zeta potentials of the both samples were around zero. Since enmeshment is the predominant mechanism for PACI-1 coagulation, the sludge thus formed was harder to be dewatered.

## 4. Conclusions

Coagulation efficiency of PACI from different preparations may vary substantially. For PACI-E, the coagulation efficiency increases with increasing pH, while the optimum operational pH for PACI-1 remains around neutral. The PACI-E has a higher  $Al_{13}$  content which remains fairly constant at various pH conditions. Al speciation of PACI-1 varies significantly with pH especially the  $Al_a$  (monomeric Al) and  $Al_c$  ( $Al(OH)_3$ ) contents. Coagulation with PACI-E in the basic pH region at low dosage is due to charge neutralization or electrostatic patch, while that of PACI-1 relies mostly on sweep flocculation (enmeshment). PACI-E is superior to PACI-1 in turbidity removal for natural highly turbid water up to 5000 NTU. However, a sufficient number of particles is necessary to promote large particle aggregation during PACI-E coagulation. The presence of high organic content in highly turbid water can disturb the charge neutralization ability of PACI-E. Sludge produced from charge neutralization of PACI-E coagulation is more easily dewatered than that from the enmeshment of PACI-1.

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## References

Annadurai, G., Sung, S.S., Lee, D.J., 2004. Simultaneous removal of turbidity and humic acid from high turbidity storm water. *Adv. Environ. Res.* 8, 713–725.

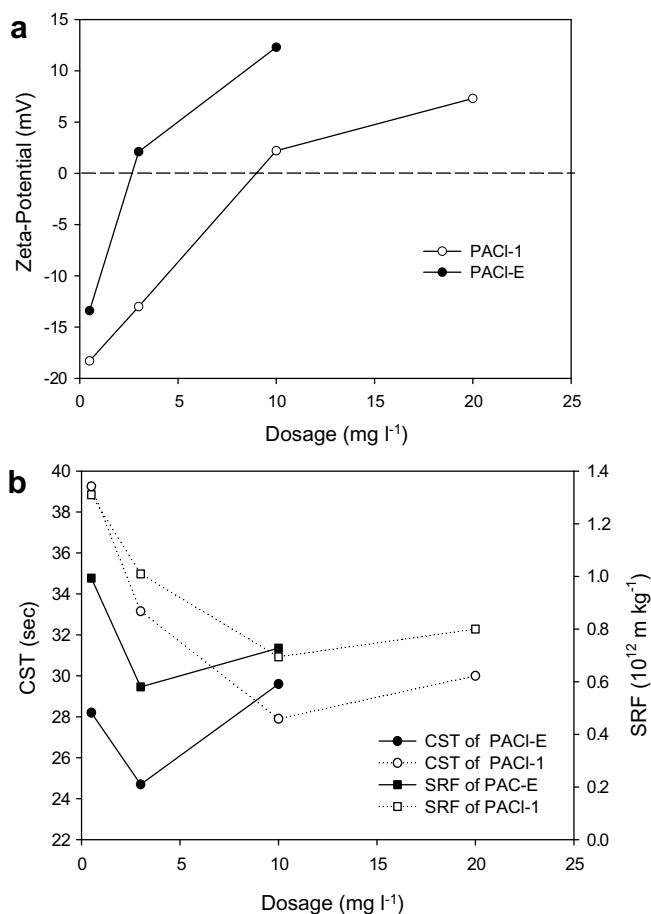


Fig. 5. Dosage effect on the sludge dewaterability of PACI-1 and PACI-E coagulation with natural water at 1300 NTU: (a) ZP and (b) sludge dewaterability.

- Bertsch, P.M., 1987. Conditions for  $Al_{13}$  polymer formation in partially neutralized aluminium solutions. *Soil Sci. Soc. Am. J.* 51, 825–828.
- Bottero, J.Y., Axelos, M., Tchoubar, D., Cases, J.M., Fripiat, J.J., Fiessinger, F., 1987. Mechanism of formation of aluminium trihydroxide form Keggin  $Al_{13}$  polymers. *J. Colloid Interf. Sci.* 117, 47–57.
- Chen, Z.Y., Fan, B., Peng, X.J., Zhang, Z.G., Fan, J.H., Luan, Z.K., 2006. Evaluation of  $Al_{30}$  polynuclear species in polyaluminium solutions as coagulant for water treatment. *Chemosphere* 64, 912–918.
- Di Bernardo, D., Di Bernardo, L., 2006. Performance of two-stage filtration system for treating high turbidity water. *J. Water Suppl.: Res. Technol.-AQUA* 557, 499–515.
- Duan, J., Gregory, J., 2003. Coagulation by hydrolyzing metal salts. *Adv. Colloid Interf. Sci.*, 475–502.
- Exall, K.N., VanLoon, G.W., 2003. Effects of raw water conditions on solution-state aluminium speciation during coagulant dilution. *Water Res.* 37, 3341–3350.
- Fang, S., Fu, L., 2004. *Theory and Technology of High Turbidity Water Supply*. Chemical Industries Publication, Beijing.
- Furrer, G., Ludwig, C., Schindler, P.W., 1992. On the chemistry of the Keggin  $Al_{13}$  polymer. I. Acid-base properties. *J. Colloid Interf. Sci.* 149, 56–67.
- Gao, B.Y., Chu, Y.B., Yue, Q.Y., Wang, B.J., Wang, S.G., 2005. Characterization and coagulation of a polyaluminium chloride (PAC) coagulant with high  $Al_{13}$  content. *J. Environ. Manage.* 76, 143–147.
- Gregory, J., 1973. Rates of flocculation of latex particles by cationic polymers. *J. Colloid Interf. Sci.* 42, 448–456.
- Hu, C.Z., Liu, H.J., Qu, J.H., 2005. Preparation and characterization of polyaluminium chloride containing high content of  $Al_{13}$  and active chlorine. *Colloid Surface A* 260, 109–117.
- Hu, C.Z., Liu, H.J., Qu, J.H., Wang, D.S., Ru, J., 2006. Coagulation behavior of aluminium salts in eutrophic water: Significance of  $Al_{13}$  species and pH control. *Environ. Sci. Technol.* 40, 325–331.
- Huang, C.P., Shiu, H.L., 1996. Interactions between alum and organics in coagulation. *Colloid Surface A* 113, 155–163.
- Huang, L., Wang, D.S., Tang, H.X., Wang, S., 2006. Separation and purification of nano- $Al_{13}$  by UF method. *Colloid Surface A* 275, 200–208.
- Kan, C.C., Huang, C.P., Pan, J.R., 2002. Coagulation of high turbidity water: the effect of rapid mixing. *J. Water Suppl.: Res. Technol.-AQUA* 51, 77–85.
- Kazpard, V., Lartiges, B.S., Frochot, C., d'Espinose de la Caillerie, J.B., Viriot, M.L., Portal, J.M., Görner, T., Bersillon, J.L., 2006. Fate of coagulant species and conformational effects during the aggregation of a model of a humic substance with  $Al_{13}$  polycations. *Water Res.* 40, 1965–1974.
- Klopprogge, J.T., Seykens, D., Jansen, J.B.H., Geus, J.W., 1992. A<sup>27</sup> Al nuclear magnetic resonance study. *J. Non-Cryst. Solid* 142, 94–102.
- Kwon, S.B., Ahn, H.W., Ahn, C.J., Wang, C.K., 2004. A case study of dissolved air flotation for seasonal high turbidity water in Korea. *Water Sci. Technol.* 50 (12), 245–253.
- Lin, W.W., Sung, S.S., Chen, L.C., Chung, H.Y., Wang, C.C., Wu, R.M., Lee, D.J., Huang, C.P., Juang, R.S., Peng, X.F., Chang, H.L., 2004. Treating high-turbidity water using full-scale floc blanket clarifiers. *J. Environ. Eng.* 130, 1481–1487.
- Liu, G.G., Qu, J.H., Tang, H.G., 1999a. The electrochemical production of highly effective polyaluminium chloride. *Water Res.* 33, 807–813.
- Liu, X.Q., Chen, Z.L., Yang, X.H., 1999b. Spectroscopic study of aluminium speciation in removing humic substances by Al coagulation. *Water Res.* 33, 3271–3280.
- Masion, A., Vilge-Ritter, A., Rose, J., Stone, W.E.E., Teppen, B.J., Rybacki, D., Bottero, J., 2000. Coagulation-flocculation of natural organic matter with Al salts: speciation and structure of the aggregates. *Environ. Sci. Technol.* 34, 3242–3246.
- Parker, D.R., Bertsch, P.M., 1992. Identification and quantification of the  $Al_{13}$  tridecameric polycation using ferron. *Environ. Sci. Technol.* 26, 913–914.
- Pernitsky, D.J., Edzwald, K., 2003. Solubility of polyaluminium coagulants. *J. Water Suppl.: Res. Technol.-AQUA* 52, 395–406.
- Qu, J.H., Liu, H.J., 2004. Optimum conditions for  $Al_{13}$  polymer formation in PACl preparation by electrolysis process. *Chemosphere* 55, 51–56.
- Shi, B.Y., Li, G.H., Wang, D.S., Tang, H.X., 2007. Separation of  $Al_{13}$  from polyaluminium chloride by sulfate precipitation and nitrate metathesis. *Sep. Purif. Technol.* 54, 88–95.
- Smith, R.W., 1971. Relations among equilibrium and nonequilibrium aqueous species of aluminium hydroxy complexes. *Am. Chem. Soc. Adv. Chem. Ser.* 106, 250–279.
- Van Benschoten, J.V., Edzwald, J.K., 1990. Chemical aspects of coagulation using aluminium slats-I. Hydrolytic reactions of alum and polyaluminium chloride. *Water Res.* 24, 1519–1526.
- Vilge-Ritter, A., Masion, A., Boulange, T., Rybacki, D., Bottero, J., 1999. Removal of organic matter by coagulation-flocculation: a pyrolysis-GC-MS study. *Environ. Sci. Technol.* 33, 3027–3032.
- Wang, W.Z., Hsu, P.H., 1994. The nature of polynuclear OH-Al complexes in laboratory-hydrolyzed and commercial hydroxylaluminum solutions. *Clay Clay Miner.* 42, 356–368.
- Wang, D.S., Tang, H.X., Gregory, J., 2002. Relative importance of charge neutralization and precipitation on coagulation of kaolin with PACl: effect of sulfate ion. *Environ. Sci. Technol.* 36, 1815–1820.
- Wang, D.S., Sun, W., Xu, Y., Tang, H.X., Gregory, J., 2004. Speciation stability of inorganic polymer flocculant-PACl. *Colloid Surface A* 243, 1–10.
- Wu, C.C., Wu, J.J., 2001. Effect of charge neutralization on the dewatering performance of alum sludge by polymer conditioning. *Wat. Sci. Technol.* 44 (10), 315–319.