Mechanism of natural organic matter removal by polyaluminum chloride: Effect of coagulant particle size and hydrolysis kinetics

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ABSTRACT

The mechanism of natural organic matter (NOM) removal by $AlCl_3$ and polyaluminum chloride (PACl) was investigated through bench-scale tests. The fraction distributions of NOM and residual Al after coagulation in solution, colloid and sediment were analyzed as changes of coagulant dosage and pH. The influence of NOM, coagulant dose and pH on coagulation kinetics of $AlCl_3$ was investigated using photometric dispersion analyzer compared with PACl. Monomeric Al species (Al_a) shows high ability to satisfy some unsaturated coordinate bonds of NOM to facilitate particle and NOM removal, while most of the flocs formed by Al_a are small and difficult to settle. Medium polymerized Al species (Al_b) can destabilize particle and NOM efficiently, while some flocs formed by Al_b are not large and not easy to precipitate as compared to those formed by colloidal or solid Al species (Al_c). Thus, Al_c could adsorb and remove NOM efficiently. The removal of contaminant by species of Al_a, Al_b and Al_c follows mechanisms of complexation, neutralization and adsorption, respectively. Unlike preformed Al_b in PACl, in-situ-formed Al_b can remove NOM and particle more efficiently via the mechanism of further hydrolysis and transfer into Al_c during coagulation. While the presence of NOM would reduce Al_b formed in-situ due to the complexation of NOM and Al_a.

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1. Introduction

After the discovery of potentially toxic halogenated organics as by-products produced in drinking waters after chlorination (Rook, 1974), research on coagulation in drinking water shifted from the removal of particle toward the removal of natural organic matter (NOM) and disinfection by-products precursors (Semmens and Field, 1980). According to the classical theory of coagulation for colloid removal, destabilization could be achieved by *compressing double electric layers*, *neutralizing*, *adsorption* and *bridging or sweep flocculation* (Duan and Gregory, 2003). The presence of NOM would complicate the process of coagulation because of its complex structure such as high negative charge and wide molecular weight

range. Part of the NOM is dissolved and is unlikely to provide nuclei for precipitate formation as particle. Two mechanisms of NOM removal most commonly referred to are charge neutralization and adsorption (Hundt and O'Melia, 1988; Randtke, 1988; Van Benschoten and Edzwald, 1990b; Gregor et al., 1997; Edzwald and Tobaison, 1999). Charge neutralization is the mechanism used to explain the precipitation of NOM in operational regions where aluminum hydroxide precipitation is minimal. Cationic aluminum interacts electrostatically with anionic NOM to form insoluble charge-neutral products. This mechanism applies mainly to the removal of colloidal and higher molecular weight NOM, which can act as nuclei for precipitate formation. In the operational regions where insoluble aluminum hydroxide forms, NOM can be removed by surface adsorption. The concentration of coagulant has to be high enough to cause rapid precipitation of $Al(OH)_3$. A third mechanism, complexation is also occasionally alluded, is the chemical interaction of soluble NOM with soluble coagulant metal ions such as aluminum (Van Benschoten and Edzwald, 1990b; Gregor et al., 1997). The complex of metal cation and NOM remains in solution until either the binding capacity of the NOM has been saturated or the solubility of the metal–NOM complex is exceeded. The operational conditions for charge neutralization, adsorption and complexation are not the same, and mechanisms involved under different operational conditions are still not clear. It would be determined not only by NOM characteristics but also by hydrolysis chemistry of coagulant.

When alum is added to water, Al^{3+} rapidly undergoes hydrolysis reactions to form other dissolved Al species or Al-hydroxide precipitates, including monomeric Al species $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$, dimmer ($Al_2(OH)_2^{4+}$), trimer ($Al_3(OH)_4^{5+}$), tridecamer ($Al_{13}O_4(OH)_{24}^{7+}$) and amorphous precipitate $Al(OH)_{3(am)}$ (Van Benschoten and Edzwald, 1990a). A large number of investigations and practical applications show that the $AlO_4Al_{12}(OH)_{24}^{7+}$ (simplified as Al_{13}) is the most efficient species for contaminant removal because of its high stability and positive electric charge (Van Benschoten and Edzwald, 1990a; Duan and Gregory, 2003). Polyaluminum chloride (PACl), the intermediate products during the hydrolysis–polymerization–precipitation process of Al^{3+} ions under specifically controlled conditions was developed to enhance the content of Al_{13}.

Various chemical and physical methods have been applied in monitoring the Al(III) hydrolysis/polymerization processes and the species in PACl stock solution (Wang and Tang, 2001). However, the performance of coagulant is determined by the species present during the coagulation process. The Ferron reaction is the only one which can be used to determine the speciation of Al under water treatment conditions (generally at concentrations in the sub-millimloar range, 10^{-4}–10^{-5} M). Based on the kinetic difference of reactions between Ferron reagent (8-hydroxy-7-iodo-5-quinoline sulfonic acid) with different hydrolyzed species, hydrolyzed Al species can be divided into three types: monomeric Al species (Al_a), medium-polymerized Al species (Al_b) and colloidal or solid Al species (Al_c). It is found that dilution has little effect on the species distribution of PACls after dosing in the range of dilution factors of 200–2000 times if the solution alkalinity is not too high, while pH has significant effect on further species

transformation of PACl. The Al_a fraction in the primary coagulants is the most unstable species. After dosing, these species would transform into Al_b, and finally Al_c within minutes depending on the reaction conditions. The polymeric and colloidal species, once preformed, are quite stable. There is a great difference between the stability of the preformed Al_b species and that formed in-situ after dosing. The higher the B (OH/Al molar ratio) value of PACls, the less the Al_a species, and the more stable the Al speciation after dosing (Wang et al., 2004; Yan et al., 2008b).

However, the presence of strongly complexing anions such as citrate, tartrate or oxalate results in the formation of complexes with Al that do not readily react with Ferron (Jardine and Zelazny, 1987a, b). The Ferron method cannot provide enough information in the study of natural water sources directly.

The removal of NOM is also affected by the kinetics of coagulant hydrolysis and of reaction between coagulant and contaminants. Precipitates of $Al(OH)_{3(S)}$ induced by turbidity formation can be formed in 1 s under certain conditions (Letterman et al., 1973). Since both precipitation and polymerization have dimerization as an intermediate step, dimerization must happen at the same speed as precipitation or polymerization. Some researchers estimated the dimerization rate constant of 10^2–$10^3 M^{-1} s^{-1}$ in water at 25 °C when Al^{3+} is the predominant monomeric species (Holmes et al., 1968; Owens and Eyring, 1970). This result suggests that dimerization of aluminum may be partially completed in about 1 s (at 10^{-3} M Al_T). Langford and Khan (1975) provided indirect evidence that complexation between NOM and monomers of aluminum appeared to be several orders of magnitude slower than conversion among monomeric forms of aluminum, as well as adsorption–destabilization reactions between Al and particle (Hahn and Stumm, 1968), and the process of the destabilized NOM and particle to aggregate to form larger floc in the settling process is relatively slower, and depends on the collision frequency and efficiency of the particle (Hahn and Stumm, 1968). Whether the dimerized and monomeric Al species would further hydrolyze to form larger polymer and precipitate in minutes depends upon pH condition (Wang et al., 2004; Yan et al., 2008b).

In general, although the interactions between coagulants and NOM are well understood via the broad reaction principles, there are still some uncertainties regarding the nature of the aqueous chemistry of metal coagulant, the polymer type (preformed and in-situ formed), and the effectiveness of particle size of hydrolyzed species, beyond the charge density parameters, for their application. A clear picture of the coagulation process has been limited by the complexity and diversity of both NOM and aqueous Al species. In this paper, the mechanism of NOM removal with typical PACls is investigated.

2.   Materials and methods

2.1.   Materials

All the reagents used were of analytical grade, except for those being specified. Three aluminum chloride-based coa-

gulants, AlCl$_3$, PACl$_I$ and PACl$_{20}$, were used in the study. PACl$_I$, commercial PACl product, was provided by a local factory in the form of liquid containing 10% of Al$_2$O$_3$, which was diluted into 0.1 mol/L Al before use. The coagulant, PACl$_{20}$ (OH/Al molar ratio of 2.0), was prepared by the base titration method in laboratory at room temperature (Wang et al., 2002). A brief description of the preparation is as follows: an aliquot of 0.5 mol/L AlCl$_3$ solution was transferred into a 300-mL glass reactor. Under rapid stirring and purging with nitrogen gas, 0.5 mol/L NaOH was titrated slowly into the Al solution using a peristaltic pump (BT00-100 M, Lange CO., China). The amount of NaOH added varied with the target OH/Al molar ratio (simplified as B values), with the final concentration of aluminum being 0.1 mol/L. Meanwhile, the 0.1 mol/L AlCl$_3$ solution used in this study was considered as a special PACl with B value of 0 as reference. The Al species distribution in the PACls and AlCl$_3$ samples was analyzed by the Ferron (Sigma, UK) assay after 1 week aging (Wang et al., 2002). The chemical species of hydrolyzed Al(III) can be divided into three types according to their reaction kinetics: monomeric Al species (Al$_a$) (instantaneous reaction), medium-polymerized Al species (Al$_b$) (reaction within 120 min) and species of colloidal or solid (Al$_c$) (no reaction in 120 min). The results are shown in Table 1.

2.2. Raw water

Source waters for coagulation performance examination were collected from the Luan River (located in Tianjin, China). The experiment for coagulation kinetics was carried out by using synthetic water, which was based on tap water with predetermined amount of kaolin and humic acid addition to obtain TOC concentration of 4.0 mg/L and to obtain turbidity of 8.08 NTU. The quality of the source waters, tap water and synthetic water is presented in Table 2.

2.3. Jar tests

Jar tests were performed on a programmable jar test apparatus (Daiyuan Jar Test instruments, China). The operation procedures were as follows: 1.0 L of raw water was transferred into a 1.4-L square beaker with sampling port 3 cm below water surface; the jar tester was started at rapid mixing of 300 rpm; after 30 s coagulant was added followed by mixing speed of 250 rpm for 2 min; 40 rpm for 10 min; and then after 20 min of quiescent settling, samples were taken for water quality measurement. Predetermined amount of HCl and NaOH were dosed 15 s before adding coagulant during rapid mixing period for pH adjustment. Coagulants as well as acid and base reagents for pH control were all dosed by pipettes, which were calibrated before each experiment.

2.4. Analysis

Total organic carbon (TOC) was analyzed by the TOC Analyzer (Phoenix 8000 system, Tekmar-Dohrman Co., USA) using the method of sodium peroxydisulfate/orthophosphoric acid wet oxidation and UV radiation. Dissolved organic carbon (DOC) was analyzed by the TOC Analyzer after filtration through 0.45 μm membrane, and the filtration was carried out immediately after sample. Colloidal organic carbon (COC) was TOC subtracted from DOC. TOC in the sediment was determined by TOC in raw water subtracted from the TOC after coagulation. UV$_{254}$ was measured by a spectrophotometer (UV-VIS8500, China) using a quartz cell with 1 cm path length after filtration through 0.45 μm membrane. Turbidity was measured using the Hach 2100N Turbidimeter. pH was measured by the pHS-3C (Shanghai, China) pH meter, which was calibrated daily using pH 4.01 and pH 7.01 buffers. The pH, UV$_{254}$ and turbidity were measured immediately. The TOC and DOC were measured within 3 days after being acidified and stocked in refrigerator.

Metal elements were analyzed by ICP-OES. Total Al and dissolved Al concentrations were measured before and after sample filtration through 0.45 μm membrane. Prior to analyzing the total Al, samples were digested by nitric acid. Colloidal Al was the difference between the total and dissolved Al concentrations. Residual Al in the sediment was determined as the total Al of raw water and coagulant addition subtracted by total Al in water after coagulation.

The velocity of floc formation was detected with the photometric dispersion analyzer (PDA, PDA2000, Rank Brothers Ltd.). The output from the PDA, the flocculation index was

Table 1 – Speciation of PACls as characterized by the Ferron assay

Coagulant	Basicity	Al$_a$ (%)	Al$_b$ (%)	Al$_c$ (%)
AlCl$_3$	0	91.9	8.1	0
PACl$_I$[a]	1.6	40.0	38.5	21.5
PACl$_{20}$	2.0	25.6	70.5	3.9

[a] I: commercial industrial PACl product.

Table 2 – Water quality characteristics of water samples

Source water	pH	Alkalinity (mg/L)	Hardness as CaCO$_3$ (mg/L)	Turbidity (NTU)	DOC (mg/L)
Luan River water I	8.3	125	170	8.26	4.25
Luan River water II	8.6	135	150	0.92	4.52
Tap water	7.0	145	152	0.95	2.01
Synthetic water	7.0	145	152	8.08	4.00

recorded from 30 s before the beginning of rapid mixing to the end of slow mixing.

3. Results and discussion

3.1. Effect of coagulant dosage on PACls performance

NOM and turbidity removal by three coagulants, $AlCl_3$, $PACl_I$ and $PACl_{20}$, in the dose range of 0.02–0.33 mM, are investigated and results are shown in Fig. 1. NOM removal under the consideration of three fractions, dissolved NOM (D-NOM), colloidal NOM (C-NOM) and NOM in sediment (S-NOM) are separately assessed. The distribution of organic carbon (dissolved, colloidal and in sediment) after coagulation is affected by the speciation of PACl (data are presented in Table 1). The DOC fraction (D-NOM or DOC) is removed more efficiently by PACl with higher content of Al_b species at the dosage commonly used in treatment practice. The efficiency of DOC removal is in the order of $PACl_{20}$ followed by $PACl_I$ and then $AlCl_3$. It is believed that the high neutralization ability of Al_b species contributes to the effective removal of DOC (Yan et al., 2008a). While the dosage is increased to 0.33 mM, $AlCl_3$ shows the best DOC removal performance. It is worth noticing that the solution pH drops to acidic range with high dosage of $AlCl_3$ and only slight pH changes are observed for the high B value PACls (Fig. 1e). The relatively high DOC removal of $AlCl_3$ could be attributed to the in-situ formation of Al_b species, as reported earlier in Wang et al. (2004) and Yan et al. (2008b).

COC or C-NOM in water after coagulation is shown in Fig. 1b, and it decreases with the increase in dosage. Water treated by $AlCl_3$ has the highest residual COC concentration followed by $PACl_{20}$ and $PACl_I$. Compared with the content of Al_c in Table 1, it could be found that PACl with higher content of Al_c corresponds to the lower percentage of COC present in the treated water. Although PACl with higher content of Al_b is more efficient in DOC removal, its TOC removal ability is not as efficient as DOC removal. The flocs of Al_b–NOM cannot be removed efficiently using the coagulation test protocol. The content of Al_c in $PACl_I$ is higher than that in $PACl_{20}$, and the residual COC after coagulation by $PACl_I$ is lower than that in $PACl_{20}$. As shown in Fig. 1c, the percentage of NOM in the sediment (S-NOM or source water TOC subtracted by treated water TOC) varies with the coagulant dosage. At low dosage, NOM is removed most efficiently by $PACl_I$; at moderate
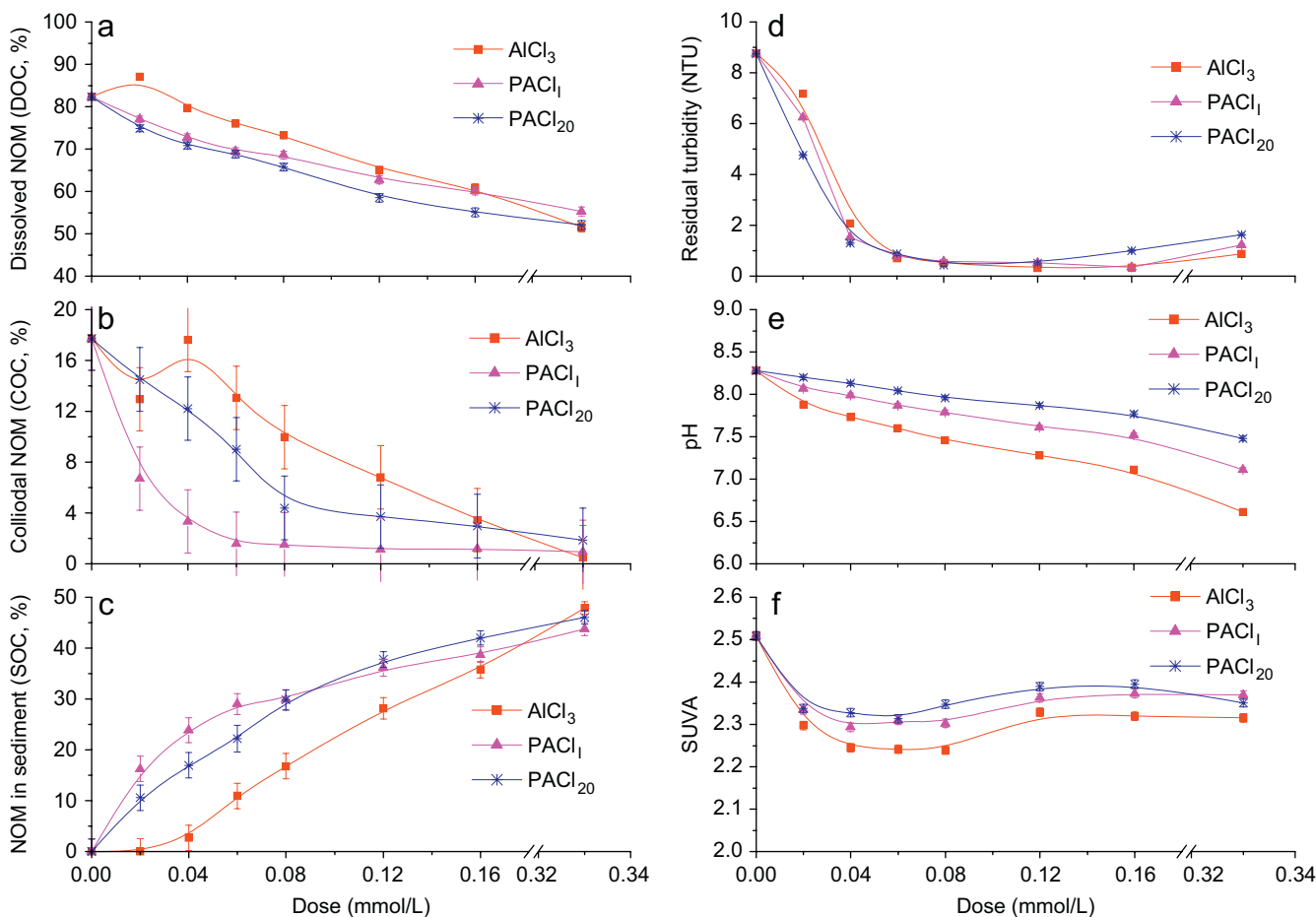

Fig. 1 – The dose response and removal performance of different coagulants with the Luan River water I. (a) Percentage remains of dissolved NOM; (b) percentage remains of colloidal NOM; (c) percentage of NOM in sediment; (d) turbidity removal; (e) pH after coagulation; (f) residual SUVA.

dosage, $PACl_{20}$ is the most efficient coagulant; and at high dosage $AlCl_3$ becomes the most efficient one.

At low dosages, the flocs of $AlCl_3$ and NOM are in colloidal state, which are not easily precipitated out of the solution, and thus the percentage COC is relatively high. With higher dosage, the flocs become easier to precipitate and the percentage of COC decreases. It could be explained by the transformation of Al_a into Al_b, and further into Al_c in the case of $AlCl_3$.

Turbidity removal with various PACls is also worth further discussion. At low dosage, the mechanism of turbidity removal is mainly through charge neutralization. The higher the content of Al_b, the more efficient the turbidity removal. With the increase of dosage, the particle begins to restabilize due to the formation of positively charged small flocs by PACls with high content of Al_b. Although there is a large portion of Al_b formed in-situ at high dosage for $AlCl_3$, it could transfer into Al_c and make the flocs more easy to settle.

NOM is complex in nature and changes from water to water and also season to season. Specific UV absorbance (SUVA) is used to estimate the chemical nature of the DOC. SUVA is calculated as one hundred times UV_{254} divided by the DOC concentration. High SUVA waters are generally enriched in hydrophobic and high molecular weight NOM, such as humic substances. This portion of NOM is more readily

removed by coagulation (Edzwald et al., 1985; Weishaar et al., 2003).

As shown in Fig. 1f, the SUVA of the residual DOC decreases gradually at low dosages and increases at moderate dosages for all three PACls. It shows that the NOM with high SUVA is more easily removed at low dosages, and then NOM with low SUVA is removed at moderate dosages. For the three PACls, the one with lower B value has less hydrolyzed species, and the corresponding SUVA of the residual DOC is lower, which indicates that PACl of lower B value is inclined to remove NOM of higher SUVA (hydrophobic and higher molecular weight).

3.2. Effect of pH on PACls performance

The jar test results of the effect of pH control on NOM and turbidity removal by three PACls at dosage of 0.06 mM are shown in Fig. 2.

Considering the Al_b distribution at different pH, DOC is removed most efficiently at around pH 6.0 for the PACls with high content of Al_b (Wang et al. (2004) and Yan et al. (2008b)), and the percentage DOC (D-NOM) is the lowest at that pH (Fig. 2a). With further change in pH (decrease or increase) from 6.0, DOC removal efficiency decreases with the decrease of Al_b content, especially for PACl with low B value. DOC is removed more efficiently by the higher B value PACl in the
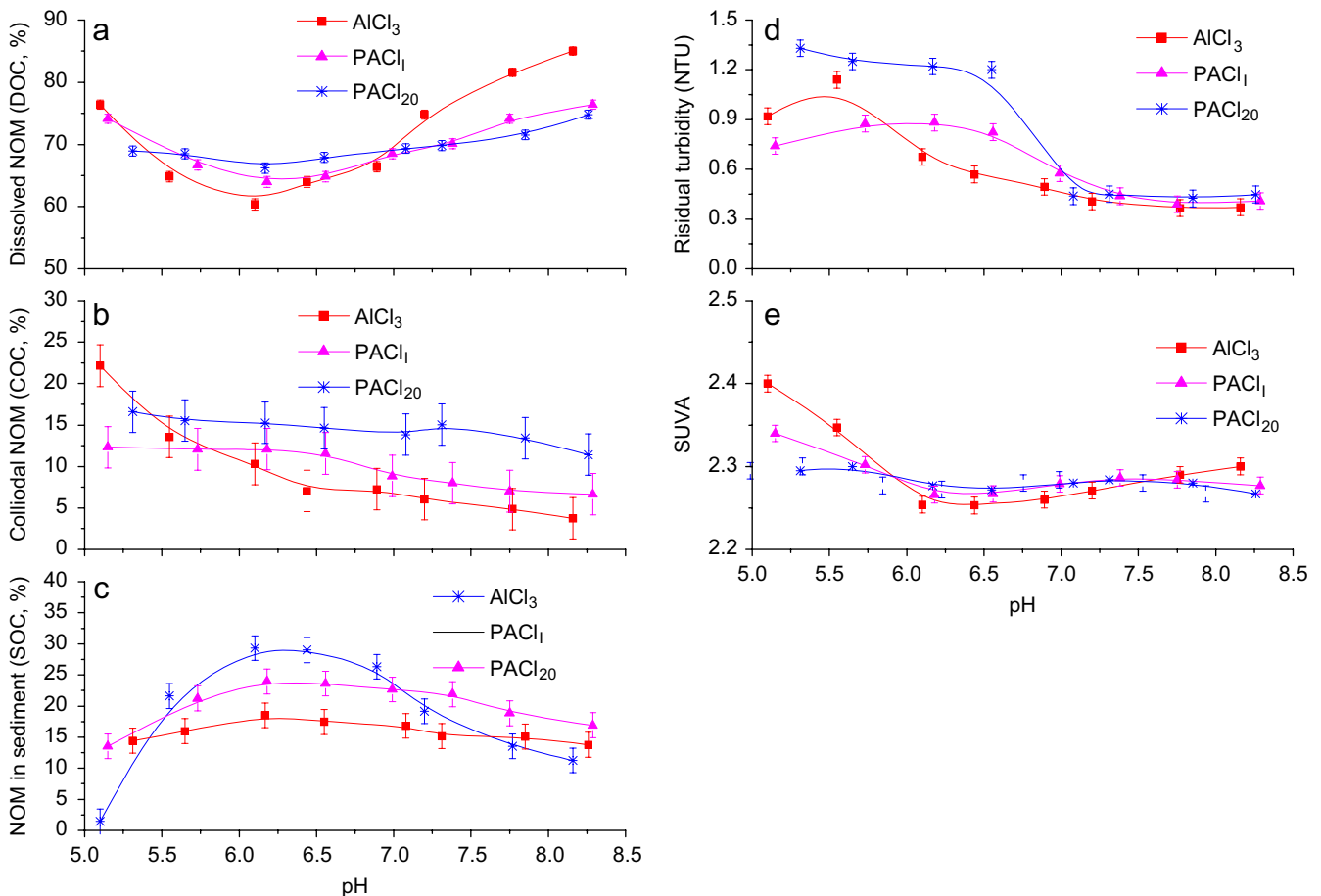

Fig. 2 – The performance of coagulants with pH change with the Luan River water II at dose of 0.06 mM. (a) Percentage of dissolved NOM; (b) percentage of colloidal NOM; (c) percentage of NOM in sediment; (d) turbidity removal; (e) residual SUVA.

acid and basic pH range due to the high content of preformed Al_b species; the situation is reversed by more Al_b formed in-situ at pH about 6.0. DOC removal is more stable for the PACl with higher B because the preformed Al_b species is more stable.

The percentage of colloidal NOM or COC in water after coagulation by the three PACls is shown in Fig. 2b. The percentage of COC decreases with the increase of pH, especially for $AlCl_3$. At pH below 5.5, the COC is the highest for $AlCl_3$, followed by $PACl_{20}$ and $PACl_I$. While with pH up to 6.0, COC is the highest for $PACl_{20}$, followed by $PACl_I$ and $AlCl_3$. The flocs of $AlCl_3$ are small and are not easy to settle at low pH. With the increase in pH, Al hydrolyzed further to form larger polymer and sol, the flocs become larger, and the percentage COC decreases gradually. For the PACls with higher content of Al_b, the residual COC is higher. It shows that the flocs of preformed Al_b and NOM are not amenable to sedimentation. Therefore, although $PACl_{20}$ removes DOC more efficiently than $PACl_I$ at high pH range, $PACl_{20}$ is less efficient than $PACl_I$ for NOM removal, the NOM in sediment (S-NOM) for $PACl_I$ is higher (Fig. 2c).

The change of residual turbidity by three PACls at a dosage of 0.06 mM is shown in Fig. 2d. Turbidity is removed most efficiently at basic pH range, above 7. The pH range for efficient turbidity removal expands to the acid region with the decrease of B value of the PACl. With the decrease of pH, turbidity rises for PACls with high B value. It could be seen that the colloidal Al is particularly high at pH about 6.0 (Fig. 4b). It shows that Al_b could destabilize particle efficiently to form aggregates. However, it could not form flocs large enough to settle down efficiently, and remain mostly in colloidal form. For PACl with lower B value, more efficient turbidity removal could be achieved at neutral and acidic pH region. It may be due to further hydrolyzing of Al_a into Al_b and Al_c to form larger flocs.

From Fig. 2e, it could be seen that SUVA in coagulated water at slightly acidic and neural pH region is lower than that at higher pH region for $AlCl_3$, indicating DOC with higher SUVA is easier to remove at acid pH. That portion of NOM with high molecular weight and hydrophobic is more easy to be removed at acidic pH by low molecular hydrolyzed Al_a species. NOM with low SUVA is more hydrophilic, has lower molecular weight and is more negatively charged, is amenable to removal by coagulation through adsorption onto larger polymer, Al_b and Al_c. Then PACl with high B value is less efficient in NOM with high SUVA reduction, and SUVA is more stable through the pH range (Fig. 2e).

3.3. The impact of dosage on residual Al

The distribution of residual Al in water and sediment after coagulation by three PACls is shown in Fig. 3. Considering the speciation of the PACls (Table 1), the higher the content of Al_a in PACl, the higher the residual dissolved Al at low dosages, while it reverses at high dosages. The dissolved Al decreases with the dosage increase for $AlCl_3$. While the trend of $PACl_I$ and $PACl_{20}$ is different, it increases first, and then decreases with dosage increase. The dissolved Al reaches a concentration higher than 0.4 mg/L, and is greater than the theoretical value calculated based on the solubility of $Al(OH)_3$ (Van

Benschoten and Edzwald, 1990a). It implies that Al_a is able to form soluble complexes with NOM until the functional groups of the unsaturated NOM have been saturated (Gregor, 1997). The flocs of Al_b and Al_c are large enough to be removed by the 0.45 μm membrane.

At low dosage (0.02 mM), most of Al from $AlCl_3$ is in the form of dissolved Al–NOM complex (Gregor et al., 1997); the residual colloidal Al is minimum. For PACl with higher B value, the residual colloidal Al is higher due to the higher content of Al_b, while at moderate dosage, the residual colloidal Al is highest for $AlCl_3$, followed by $PACl_{20}$ and $PACl_I$. At high dosage, the residual colloidal Al increases more significantly and the PACl with higher B exhibits higher residual colloidal Al.

Residual Al in sediment is shown in Fig. 3c. At low dosage, for PACl with higher B value, residual Al in the sediment is lower. While at high dosage, residual Al in the sediment is higher for PACls with lower B value.

3.4. Effect of pH on residual Al

The effect of pH on the distribution of Al in water and sediment after coagulation by three PACl is shown in Fig. 4. The dissolved Al is higher for PACl with lower B value at acidic and basic pH. The residual dissolved Al of $AlCl_3$ and PACl with low B value rises at acidic and basic pH due to their high content of Al_a.
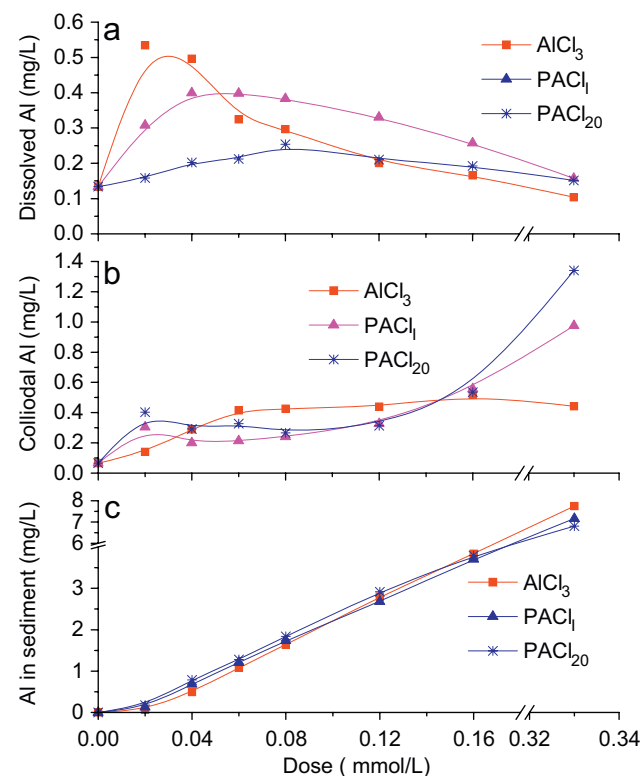
Fig. 3 – The distribution of residual Al after coagulation with dosage increase with the Luan River I. (a) Residual dissolved Al; (b) residual colloidal Al; (c) residual Al in sediment.

Fig. 4b shows that the colloidal Al is particularly high for the PACl with high B value at pH about 6.0. $PACl_{20}$ has the highest content of preformed Al_b and it has the widest pH range for colloidal Al, which corresponds to its deterioration for turbidity removal.

The residual Al in sediment increases with the increase in pH, which is in accordance with the turbidity removal results (Fig. 2d).

3.5. Coagulation kinetics of PACls

Floc formation kinetics is investigated using synthetic water based on tap water with predetermined amount of kaolin and humic acid. The results are shown in Fig. 5. The influence of NOM on the coagulation kinetics was carried out with or without humic acid addition to obtain the final TOC concentration of 4.0 mg/L in synthetic water. The result at the dosage of 0.02 mM is shown in the Fig. 5a. It shows that for $AlCl_3$ and $PACl_{20}$, the presence of NOM would increase the velocity of floc formation, the flocs of Al and NOM are formed faster than that of Al and particle.

The coagulation kinetics of $AlCl_3$ and $PACl_{20}$ was compared at pH about 7.0. Two dosages were exploited, 0.03 and 0.06 mM. The result is shown in Fig. 5b. It shows that the prehydrolyzed $PACl_{20}$ reacts more quickly than $AlCl_3$ due to the preformed polymer Al species in $PACl_{20}$. The flocs are

formed more quickly at higher dosage, especially for $AlCl_3$ compared with $PACl_{20}$.

The effect of pH on coagulation kinetics for $AlCl_3$ and $PACl_{20}$ was also investigated, and only the results of $AlCl_3$ at low dosage (0.03 mM) and high dosage (0.06 mM) are shown in Fig. 5c and d, respectively. It is shown that flocs are formed faster at higher pH. This is more obvious at low dosage. It indicates that hydrolysis and precipitation at high pH is quicker than the further polymerization process of Al_b formed in-situ at acidic pH, this process is relatively slow and normally occurs within minutes (Wang et al., 2004; Yan et al., 2008b).

Although the complexation between NOM and monomers of aluminum appears to be several orders of magnitude slower than conversion among monomeric forms of aluminum (Langford and Khan, 1975), it would still be faster than further polymerization and precipitation. This is supported by the result in Fig. 3a, the PACl with higher content of monomeric Al (Al_a) has higher residual Al at low dosage. It shows that the monomeric Al complex firstly with NOM to form dissolved Al–NOM complex. It cannot form large polymer until it reacts with the un-reacted sites of the NOM. If PACl has a higher content of prehydrolyzed polymer, the flocs are formed more quickly (Fig. 5b).

Further hydrolysis of polymer would be favorable for growing of flocs and to enhance particle removal, as shown in the Figs. 1d and 2d. PACl with lower B is more efficient in turbidity removal. Further hydrolysis leads to the formation of polymer bridges between particle, this bridges the small region between the particle and destabilized NOM–Al complex and caused the particles to repel each other and reduce floc breakage by acting as a binder (O'Melia, 1987; Gregory, 1989).

As discussed, the prehydrolyzed process is very important in NOM removal due to the special characteristic of NOM together with coagulation kinetic and the particulate size effectiveness of preformed Al species.

3.6. Model of NOM removal by PACl

Natural water contains a very wide variety of organic compounds. Generally, it is divided into two categories: (1) particulate/colloidal organic matter and (2) dissolved organic matter (DOM). The particulate/colloidal organic matter includes various organic colloids and microbes such as viruses, bacteria, protozoa and algae and some organic matter coated on particle by organic functional groups. These kinds of NOM are negatively charged and can be destabilized and aggregated only if fully or partly neutralized. The DOM is defined artificially by filtration through 0.45 μm pore filtration membrane. DOM could be divided further into two categories: one is small (lower than about 1000 Da) and hydrophilic, which is difficult to remove by coagulation (Owen et al., 1995; Dennett et al., 1996); the other is larger and more complicated functional groups, the molecular weight is from several kDa to several hundred kDa, and is more hydrophobic.

Coagulation of NOM is defined as the transformation from dissolved to a separable solid phase. In this paper, the floc was divided into three categories: (1) precipitated floc, which could settle down in the jar test apparatus at experiment condition, (2) colloidal floc, which cannot settle down in the
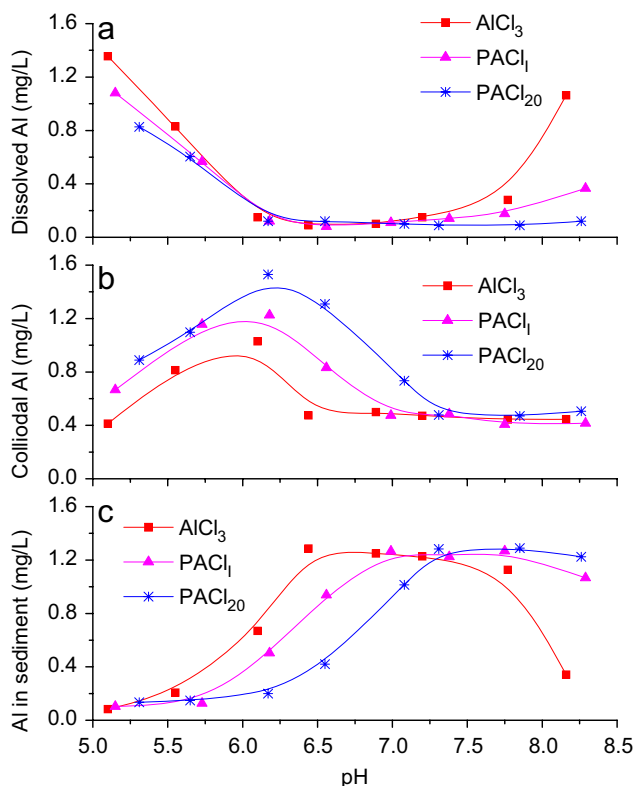
Fig. 4 – The distribution of residual Al after coagulation with pH change with the Luan River water II at dose of 0.06 mM. (a) Residual dissolved Al; (b) residual colloidal Al; (c) residual Al in sediment.
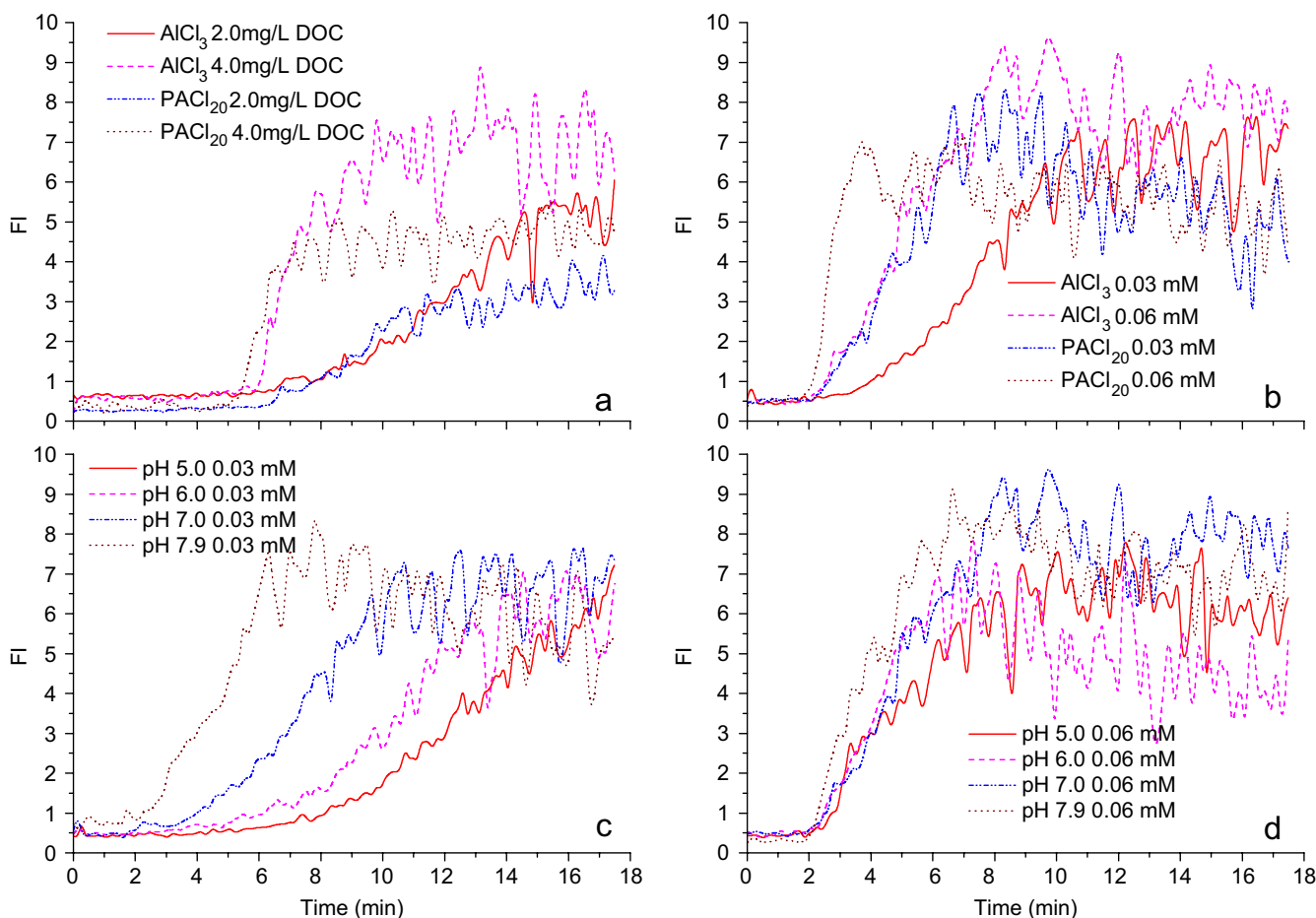
Fig. 5 – Floc formed kinetics of AlCl₃ and PACl₂₀ with synthetic water. (a) Effect of humic acid at dosage of 0.02 mM Al; (b) effect of dosage; (c) effect of pH at low dosage (0.03 mM); (d) effect of pH at high dosage (0.06 mM).

jar test apparatus, but it can be filtered off by filtration through 0.45 μm filtration membrane and (3) NOM–Al floc, which is not large enough to be removed by filtration through 0.45 μm filtration membrane.

To summarize the results in the paper and other researchers (Hundt and O'Melia, 1988; Randtke, 1988; Van Benschoten and Edzwald, 1990b; Gregor et al., 1997; Edzwald and Tobaison, 1999), the coagulation model for NOM removal by AlCl₃ and PACls could be rendered as Fig. 6. Eleven typical floc states were formed as a result of the complicated chemical–physical process after coagulant addition.

Monomeric Al species (Al_a) is mainly composed of Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_4^-$, dimer ($Al_2(OH)_2^{4+}$), trimer ($Al_3(OH)_4^{5+}$) and some small polymers. It complex with negative functional groups, and neutralize some large NOM and particle to form insoluble $Al–NOM_{(s)}$. While most of the NOM in natural water is not large enough to provide nuclei for floc formation with Al_a, the complex of Al_a–NOM is soluble and is not large enough to settle down. The role of complexation should not be under estimated. As discussed above, with the dose increase, the soluble Al_a–NOM complex would aggregate with further hydrolyzation and polymerization of Al, and the residual DOM and dissolved Al decreases with increase in dose, especially for AlCl₃ (as shown in the Figs. 1a and 3a). Additionally, the reaction of complexation

could decrease the negative charge of NOM, which would be in favor of collision frequency and efficiency. Although the charge of Al_a is not as high as Al_b, the charge of per Al ion in Al_a is higher than that in Al_b. It has high complexation ability.

Medium-polymerized Al species (Al_b) is the intermediate polymer formed during aluminum hydrolyzation. A lot of experimental results have ascertained that the content of Al_b is correlative to the tridecamer ($Al_{13}O_4(OH)_{24}^{7+}$, often denoted by Al_{13}) (Duan and Gregory, 2003), which is a high-charged cluster with seven positive charges. It not only shows high effectiveness in neutralizing the negative charge of colloids and NOM in water, but can also act as nuclear to form floc with soluble NOM to produce colloids and precipitate efficiently. If PACls have higher B value, higher Al_b and, also zeta potential (Yan et al., 2008b), then particle and NOM are removed more efficiently (shown in Fig. 1). At pH about 6.0, more Al_b is produced in-situ, the zeta potential is also higher, NOM is removed more efficiently. Floc formed by Al_b is small, and Al_b can make colloids and NOM reverse charge and restabilize at over dosage; thus, the flocs of Al_b–NOM cannot be removed easily by settling (shown in Figs. 1b, 2b, 3b and 4b). But they can be removed by filtration.

Colloidal or solid Al species (Al_c) is the large polymer formed during aluminum hydrolysis. There are positive charges on its surface and it can adsorb negatively charged
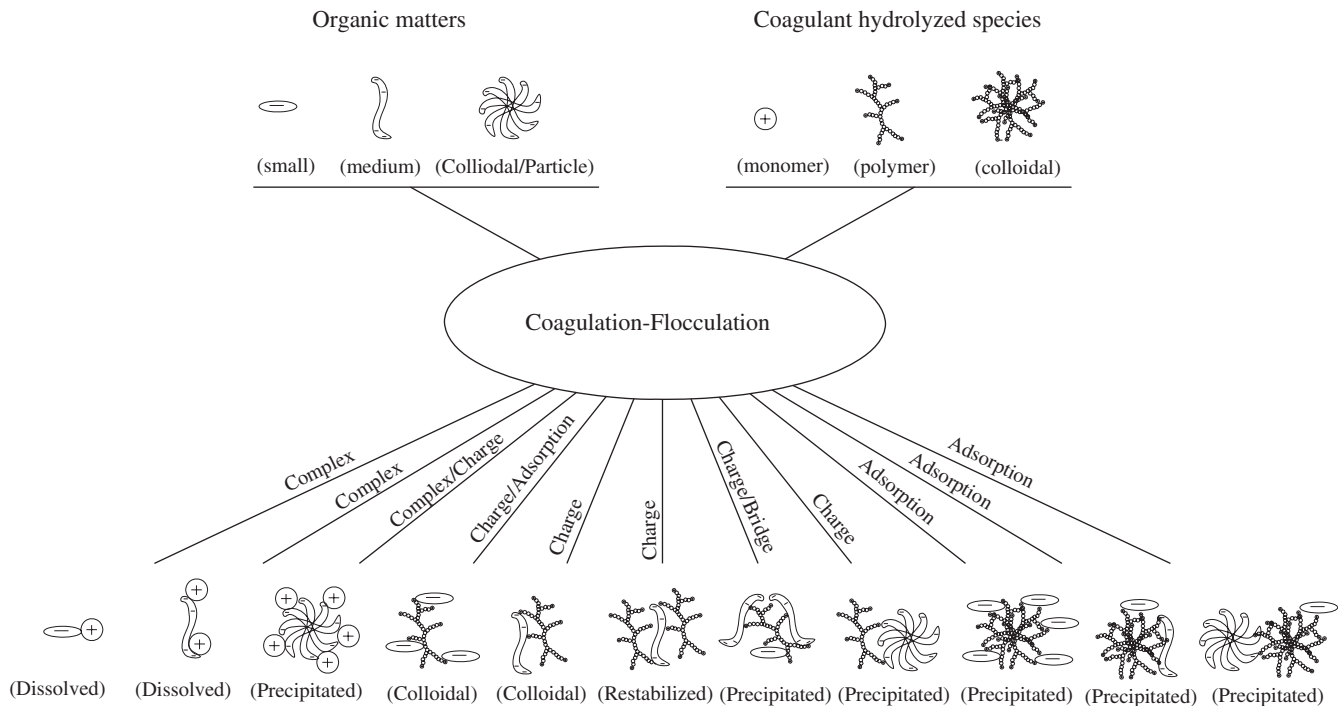
Fig. 6 – The model of interaction of coagulant hydrolyzed species and organic matters.

colloids and NOM in water efficiently. The molecular weight of Al_c is always large. It can precipitate easily in coagulation when it adsorbs particle and NOM, even small DOM. For $PACl_I$ with higher content of Al_c, the COC is lower (shown in Figs. 1b and 2b).

In addition, Al species would further hydrolyze to form larger polymer and sol after dosing, especially for monomeric Al. As shown in the literature (Wang et al., 2004; Yan et al., 2008b), the unstable Al_a species transforms into Al_b, and finally transfer into Al_c and after aging depending on the reaction conditions, which would then facilitate the growth of floc through bridging, and make soluble Al–NOM flocculate and become more easily removable.

Although flocs of preformed Al_b are hardly removed by settlement, combining PACl with coagulation aids such as large composite polymers (e.g., active silicates and organic polymers) can take advantage of the high charge neutraliza-tion ability of Al_b and improve the settlement performance of floc formed by preformed Al_b (Yan et al., 2008a).

4. Conclusions

The following conclusions can be drawn:

(1) The mechanism of contaminants removal is governed by the particle size of the coagulant species. Al_a shows high ability to complex with the unsaturated coordinate bond of NOM to facilitate particle and NOM removal, while most of the flocs formed by Al_a are small and difficult to settle. Al_b could destabilize particle and NOM efficiently, while some flocs formed by preformed Al_b are not as large as those formed by colloidal or solid Al species (Al_c) to settle

down efficiently. The Al_c could adsorb and remove NOM efficiently.

(2) The efficiencies of NOM and particle removal are greatly affected by hydrolysis kinetics. NOM in natural water would complex with Al_a and reduce Al_b formed in-situ during further hydrolysis. Preformed Al_b in PACl will be stable after dosing and can react with NOM directly. Unlike the preformed Al_b in PACl, in-situ formed Al_b can remove NOM and particle more efficiently via the mechanism of further hydrolysis and transfer into Al_c during coagulation.

(3) The removal mechanism of contaminants by species of Al_a, Al_b and Al_c follows the mechanism of complexation, neutralization and adsorption, respectively. A coagulation model for NOM removal by PACl could be rendered based on particle size of coagulant and NOM.

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