Enhanced coagulation with polyaluminum chlorides: Role of pH/Alkalinity and speciation

Mingquan Yan a,b, Dongsheng Wang b,*, Jianfeng Yu b, Jinren Ni a, Marc Edwards c, Jiuhui Qu b

a Department of Environmental Engineering, College of Environmental Sciences and Technology, The Key Laboratory of Water and Sediment Sciences, MOE, Peking University, Beijing 100781, China
b State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, CAS, P.O. Box 2871, Beijing 100085, China
c Department of Civil Engineering, Virginia Tech., Newark, VA 24061-0246, USA

Received 31 August 2007; received in revised form 9 January 2008; accepted 10 January 2008
Available online 6 March 2008

Abstract

Enhanced coagulation is considered to be among the best available techniques (BAT) for disinfection by-product (DBP) precursor removal in water treatment. Improving existing understanding requires further consideration of nuances of chemical speciation relative to source water chemistry. In this paper, the effect of alkalinity/pH and speciation on inorganic polymer flocculants, polyaluminum chlorides (PACls) for enhanced particle and natural organic matter (NOM) removal was investigated. Three kinds of well-characterized typical source waters in China with low, moderate, and high alkalinity were selected. Performance of coagulants is controlled not only by preformed species but also by those formed in situ. At neutral and basic pH values, PACls with higher basicity (ratio of OH /C0 /Al), which have more stable preformed Al (the rapid reacted species as in ferron assay), are more efficient for turbidity and NOM removal. At slightly acidic pH, PACls with lower basicity are more efficient since more Al can be formed in situ. Optimal NOM removal was achieved at pH 5.5–6.5 for all PACls. Basicity, speciation, and dosage of coagulant should be optimized based on raw water alkalinity to enhance the removal efficiency of NOM.

© 2008 Elsevier Ltd. All rights reserved.

Keywords: Alkalinity; pH; Polyaluminum chloride (PACl); Natural organic matter (NOM); Enhanced coagulation

1. Introduction

Natural organic matter (NOM) can cause odor, taste, color, and bacterial regrowth problems in water supplies. Furthermore, NOM also can lead to the formation of disinfection by-products (DBPs) and increase chlorine demand during disinfection processes. Obtaining low-cost and reliable removal of NOM is a major challenge in modern drinking water treatment, since the US Environmental Protection Agency (USEPA) mandated that water supply plants remove NOM (DBP precursors) to control disinfection by-products (USEPA, 1998). Enhanced coagulation has been identified as a best available technology (BAT), with mandated percentage total organic carbon (TOC) removal based on the raw water TOC and alkalinity levels (USEPA, 1998). The higher the alkalinity levels the lower the requirement for TOC removal. It is highly desirable to gain an ability to predict percentage NOM removal without trial and error methods such as jar testing (Edwards, 1997).

Alkalinity and pH affect the interactions of coagulant–NOM–particle (Amirtharajah and Mills, 1982; Tseng et al., 2000). Previous studies showed that the traditional coagulants (alum and ferric salt) provide optimal organic matter removal at low pH values (pH < 6.0). TOC removal for high alkalinity water is generally obtained by acidifying...
the raw water with $\text{H}_2\text{SO}_4$ or by applying increased dose of hydrolyzing coagulants (USEPA, 1998; Crozes et al., 1995; Tseng and Edwards, 1999). Unfortunately, both of these methods can increase the corrosivity of water, or the dose of base required to counter the corrosive tendency of water before water distribution (Carlson et al., 2000). In some waters, the extent of pH depression from the coagulant can be minimized by using pre-hydrolyzed coagulants such as polyaluminum chloride (PACl).

Pre-hydrolyzed coagulants are formed by the forced hydrolysis of a simple coagulant, such as alum or aluminum chloride. The degree of pre-hydrolysis is expressed as a hydroxide-to-aluminum ratio expressed in terms of basicity ($B$). PACl has been found to be superior to the traditional Al-based coagulants (e.g., AlCl$_3$ and alum) for particulate and/or organic matter removal under some conditions in which significant amounts of high-charged polynuclear aluminum hydrolysis products (Al$_b$) are present (Bottero et al., 1982; Dempsey et al., 1985; Pasrthasarathy and Buffle, 1985; Edzwald, 1993; Matsui et al., 1998). In other cases, PACI does not demonstrate superior performance (Odegaard et al., 1990; Van Benschoten and Edzwald, 1990; Lind, 1994; Sinha et al., 2004) and the chemical processes determining the relative benefits are not well known.

In this research, PACls with various $B$ and AlCl$_3$ ($B = 0$) were examined for three typical surface waters with low, moderate, and high alkalinity, to investigate the effect of alkalinity/pH on performance of PACls in particle and NOM removal. Effect of pH on the Al speciation and charge property was investigated using the ferron method and Micro-Electrophoresis. The results provide further insight into the understanding of coagulation mechanisms with PACI and help define the sub-set of waters in which relative benefits versus traditional coagulants might occur.

2. Materials and methods

2.1. Materials

All the reagents used were of analytical grade except as mentioned otherwise. The coagulants, PACI$_{10}$ and PACI$_{20}$ (OH/Al molar ratio of 1.0 and 2.0, respectively), were prepared by base titration method in a laboratory at room temperature (Wang et al., 2004). A brief description of the preparation is as follows: a certain amount of 0.5 M AlCl$_3$ solution was transferred into a 300-ml glass reactor. Under rapid stirring and purging with nitrogen gas, 0.5 M NaOH was titrated slowly into the Al solution using a peristaltic pump to achieve the targeted $B$ values (BT00-100M, Lange Co., China). The final concentrations of all PACI solutions are 0.1 M. A control solution of 0.1 M AlCl$_3$ solution was applied as a control in this work with a $B$ value of 0.

The commercial PACI products were provided by chemical suppliers. One was produced by dissolving Al(OH)$_3$ solids (denoted as PACI$_1$) and diluting to 0.1 M Al before use. Speciation of the different solutions (Table 1) was determined by the ferron method (Bertsch, 1989; Wang et al., 2004). The chemical species of hydrolyzed Al(III) can be divided through the different reaction rates into three types: monomeric species (Al$_a$) (instantaneous reacted), medium polymer species (Al$_b$) (reacted less than 120 min), and species of sol or gel (Al$_c$) (no reaction).

Raw waters were from three typical rivers in China. Water 1 and 2 were collected from the Yellow River (YW) and had high alkalinity and high pH. Water 3 was a moderate alkalinity water taken from the Luan River which runs through industrial estates and residential areas in the North-China. Water 4 is a South-China water with low alkalinity and pH collected from the Pearl River (PW). Basic water quality parameters were shown in Table 2.

To examine the effect of pH on the speciation transfer of PACls, synthetic water containing 5 × 10$^{-4}$ M NaHCO$_3$ and NaNO$_3$ was made up by adding 1 M NaHCO$_3$ and NaNO$_3$ to distilled water. A pre-determined amount of 0.20 or 0.05 M NaOH/HCl solution was used and added first into the synthetic water to control the final pH. Under rapid stirring at 250 rpm, coagulants at a dose of 2.0 × 10$^{-4}$ M Al were then dosed. After 2.0 min aging, the solution was subsequently analyzed by ferron assay.

2.2. Jar tests

Jar tests were performed using a programmable jar test apparatus (Daiyuan Jar Test instruments, China). One liter of raw water was transferred into a 1.4-l square beaker with a sampling port 3 cm below water surface. Coagulant was added to the container while mixing at 300 rpm for 30 s. Thereafter the mixing speeds were 250 rpm for 2 min, 40 rpm for 10 min and 20 min of quiescent settling. A small sample was taken immediately after the 1 min rapid mix period for the determination of electrophoretic mobility. The pH was adjusted using predetermined amounts of HCl and NaOH dosed 30 s before adding the coagulant during the rapid mix period.

2.3. Analytical methods

Dissolved organic carbon (DOC) was analyzed by a TOC Analyzer (Phoenix 8000 system, Tekmar-Dohrman Co., USA) using the method of sodium peroxysulphate/orthophosphoric acid wet oxidation and UV radiation after filtration through a 0.45 μm pore size mem-
brane. UV$_{254}$ was measured by a spectrophotometer (UV– 
VIS8500, China) after filtration through a 0.45 μm pore 
size membrane. SUVA is calculated as UV$_{254}$ divided by 
the mg l$^{-1}$ DOC concentration. Turbidity was measured 
using a Hach 2100N Turbidimeter. Solution pH was mea-
sured by a pHS-3C pH meter (Shanghai, China), calibrated 
daily. Zeta potential (ZP) was measured by a Particle 
Micro-Electrophoresis Apparatus (Rank Brothers, Appa-
ratus Mark II, UK). DOC was characterized using resin 
absorption and ultrafiltration (UF) fractionation methods 
described elsewhere (Yan et al., 2006).

3. Results and discussion

3.1. Raw water characterization

The characteristics of dissolved organic matter (DOM) 
in the three rivers were determined by resin absorption 
and UF fraction (Fig. 1). It is revealed that the YW is pro-
tected best among the three waters, the LW is polluted 
most seriously by hydrophilic and low molecular weight 
DOC, and the PW is polluted by hydrophilic DOC slightly. 
Although the characteristics of DOM in the three river 
waters differ greatly, none of them is too extraordinary 
compared to the water examined in other studies (O’Melia 
et al., 1987; Jacangelo et al., 1994). These representative 
micro-polluted waters were used to study organic matter 
removal by enhanced coagulation.

3.2. Coagulation efficiency of various PACls

Coagulation was examined with a range of doses of 
PACls with various $B$ values (Figs. 2–4). For the PW with 
low alkalinity, final pH after coagulation was controlled at 
target 5.5 and 7.0 by addition of acid or base before coag-
ulation as necessary.

For the high alkalinity YW, UV$_{254}$ and turbidity are removed more efficiently by PACls with high $B$ value; that 
is, the removal efficiency was highest for PACI$_{20}$, followed 
by PACI$_{1}$ and AlCl$_{3}$. At low dose, PACls with the high $B$ 
value exhibit immediate coagulation efficiency, while no 
obvious removal occurs for the low $B$ value PACls. The dif-
ference in performance among PACls with different $B$ value 
becomes smaller with the increase of dosages.

For the moderate alkalinity LW, the same trend in 
UV$_{254}$ and turbidity removal by three PACls as that of high 
alkalinity YW is observed at low coagulant dosages. As the 
dose increases above 0.120 mM, the relative performance is 
reversed, as shown that UV$_{254}$ and turbidity are removed 
more efficiently by PACls with lower $B$ value. This is most 
likely due to the lower coagulation pH values achieved 
using the PACls with lower $B$ value.

For the low alkalinity PW at pH 7.0, UV$_{254}$ and turbid-
ity are removed more efficiently by PACls with higher $B$ 
value, the same trend as that of YW. Unlike YW, signifi-
cant difference in coagulation efficiency occurs with the 
increase of dosages. Particles begin to restabilize at the dos-
age of 0.060 mM and the residual turbidity is highest for 
PACI$_{20}$. At pH 5.5, it is of interest that UV$_{254}$ and turbidity

<table>
<thead>
<tr>
<th>Water</th>
<th>$T$ ($^\circ$C)</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
<th>DOC (mg l$^{-1}$)</th>
<th>UV$_{254}$</th>
<th>SUVA</th>
<th>Alkalinity (mg l$^{-1}$ as CaCO$_3$)</th>
<th>Hardness (mg l$^{-1}$ as CaCO$_3$)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water 1</td>
<td>22.5</td>
<td>8.49</td>
<td>5.46</td>
<td>5.95</td>
<td>0.139</td>
<td>2.34</td>
<td>194</td>
<td>354</td>
<td>YW</td>
</tr>
<tr>
<td>Water 2</td>
<td>18.0</td>
<td>8.60</td>
<td>4.90</td>
<td>4.90</td>
<td>0.126</td>
<td>2.57</td>
<td>200</td>
<td>340</td>
<td>YW</td>
</tr>
<tr>
<td>Water 3</td>
<td>25.6</td>
<td>8.18</td>
<td>4.76</td>
<td>3.75</td>
<td>0.069</td>
<td>1.84</td>
<td>115</td>
<td>170</td>
<td>LW</td>
</tr>
<tr>
<td>Water 4</td>
<td>25.0</td>
<td>6.90</td>
<td>20.00</td>
<td>3.50</td>
<td>0.101</td>
<td>2.89</td>
<td>50</td>
<td>100</td>
<td>PW</td>
</tr>
</tbody>
</table>
are removed more efficiently by low value \( B \) PACls at both moderate and high dosages; \( \text{AlCl}_3 \) is the most efficient, followed by \( \text{PACl}_1 \) and \( \text{PACl}_{20} \).

Fig. 4 shows the change of solution pH after coagulation with various PACls for PW and YW. The change of solution pH occurred because the metal coagulants are acidic and they can consume large amounts of raw water alkalinity, dependent on the coagulant type. Higher alkalinity means more \( \text{OH}^- \) could be provided to meet the consumption of coagulant hydrolysis; solution pH is then more stable as coagulant was added. For water with lower alkalinity, pH decreases more obviously with dose increase.

Alkalinity consumption is also related to the basicity of PACls. Higher \( B \) PACls will consume less alkalinity relative to low and medium \( B \) ones. The lower the \( \text{PACl}_B \) value, the more obvious decreases of solution pH. Solution pH also determines the hydrolyzed speciation of coagulant after dosing. Then the pH/alkalinity would affect the performance of coagulant significantly, as will be discussed in more detail in the later sections.

### 3.3. Effect of pH control

In order to get more insight into the mechanism of the effect of alkalinity/pH on coagulation, jar tests with different pH control were further carried out. Although the particle and NOM removal efficiency were different for YW and PW, they show similar trends when plotted versus pH (Fig. 5).

The efficiency of \( \text{UV}_{254} \) removal increases with decrease of pH from 10.0 to 6.0. Maximum removal is achieved around pH 6.0 or so for all PACls. As pH decreases below 5.5, \( \text{UV}_{254} \) removal efficiency also decreases. In the basic pH region, \( \text{UV}_{254} \) is removed more efficiently in the order \( \text{PACl}_{20} > \text{PACl}_1/\text{PACl}_{10} > \text{AlCl}_3 \). As pH decreases to about 6.0, \( \text{UV}_{254} \) removal efficiency for PACls becomes reversed. The most efficient \( \text{UV}_{254} \) removal coagulant becomes \( \text{AlCl}_3 \), and \( \text{PACl}_1/\text{PACl}_{10} \) is more efficient than \( \text{PACl}_{20} \). \( \text{UV}_{254} \) removal is much more stable for PACls with higher value \( B \). Even at pH 10, \( \text{UV}_{254} \) removal by \( \text{PACl}_{20} \) decreases only slightly.

Turbidity is reduced most efficiently at neutral and basic pH regions. The higher the \( B \) value, the more efficient turbidity removal exhibits. The pH range for efficient turbidity removal extends to the acid range with decreasing \( B \) of PACls. As pH decreases, turbidity rises obviously for PACls with high \( B \) at the acid pH region. As pH is decreased to about 6.5–5.8, turbidity increases obviously for PACls with high value \( B \). It seems that particle restabilization occurs for high \( B \) PACls resulting in the decrease of DOM...
removal. The species preformed and formed in situ play different roles in this pH region as will be discussed in the later section in detail. It is also observed that the residual turbidity increases greatly when the pH is increased up to 10. Such phenomenon can be attributed to calcium carbonate precipitate, especially for the YW source water with high hardness (Ca 70 mg l\(^{-1}\); Mg 30 mg l\(^{-1}\)).

The influence of pH on NOM removal can be interpreted from two aspects. One is that pH affects the balance between the reactions of organic functional groups with hydrogen ions or hydrolyzed Al(III) products. At lower pH, hydrogen ions could out-compete the metal hydrolysis products for organic ligands. Thus, the amount of unsatisfied organic ligands decreased and the DOC could be removed more efficiently. In this way, the influence of pH is relevant to the characteristics of NOM. It shows that change of UV\(_{254}\) removal with pH is more significant for PW than that for YW because the NOM in PW is more hydrophilic. The other aspect is that pH would affect the speciation distribution of coagulants. The paper focuses on the latter.

3.4. Effect of pH on speciation stability and transformation

Dilution has little effect on the species distribution of PACls after dosing in the range of dilution factors of 200–2000 times if the alkalinity is not too large, while pH has a significant effect on further species transformation of PACI. The effect of pH on speciation transformation of the various PACls after dosing was characterized by adjusting pH in the range of 3–11 with 0.20 or 0.050 M NaOH or HCl solution. The results of speciation
It can be seen that pH has a significant effect on further speciation transformation of PACls, corresponding with OH/Al values. For AlCl$_3$ in the acidic region, Al$_a$ decreases rapidly as pH is raised, and reaches a minimum in the near neutral pH about 6.5. Upon increase of pH to the alkaline portion of the figure, Al$_a$ species increase sharply again. In contrast, a rapid increase of Al$_b$ species can be observed in the acidic pH region. The Al$_b$ maximum occurs at pH about 6.5. In the alkaline portion, a rapid decrease occurs as pH is raised. The distribution of Al$_c$ is similar to that of Al$_b$, but the scale of change is smaller.

Similar trends of the change in Al$_a$, Al$_b$, and Al$_c$ species are also observed for the other PACls at higher OH/Al ratio. However, the scale of change decreases largely with increasing OH/Al. For PACl$_I$, the decrease of Al$_a$ with large yield of Al$_b$ occurs obviously under the weak acidic conditions. Note that the decrease of Al$_a$ is not so significant, as the original fraction of Al$_a$ in PACl$_I$ is only 40% prior to dosing. Increasing the OH/Al ratio to 2.0, the trend becomes less obvious for PACl$_{20}$. There is little difference in the speciation distribution throughout the pH range investigated. At the acidic pH region for PACl with lower $B$ value, more Al$_b$ is formed in situ. It becomes reversed at neutral and basic pH. For PACl with high $B$ value, more Al$_b$ was preformed and remained.

The results shown above indicate that the Al$_a$ fraction in the primary coagulants is the most unstable species. After dosing, these species would quickly transform into Al$_b$, and finally into Al$_c$ depending on the reaction conditions. No matter in the commercial products or laboratory tailor-made PACls, the polymeric and colloidal species, once they were preformed, they were quite stable.

### 3.5. Effect of pH on Zeta potential

The change of ZP of three PACls at various pH and dose of 0.200 mM is shown in Fig. 7. The ZP changes with pH and coagulant speciation distribution. On one hand, the ZP increases with pH decrease for an increase of H$^+$. On the other hand, the ZP increases with the content of Al$_b$. Although ZP is higher for the PACls with higher $B$ at neutral and basic pH range, it reverses at pH 5.5, where the ZP is higher for the PACls with low $B$. At higher pH, the Al$_b$ in the AlCl$_3$ is less than PACl$_{10}$ and PACl$_{20}$, while at acidic pH region, more Al$_b$ has been formed in situ for PACls with lower $B$. As pH decreases to about 6.0, the ZP of AlCl$_3$ is highest, followed by PACl$_{10}$ and PACl$_{20}$.
The ZP by PACls with various $B$ at pH 5.5 and 7.0 are shown in Fig. 8. It is seen that for PACls with high $B$, i.e., high $A_{lb}$ preformed, the ZP is higher at pH 7.0. At pH 5.5 it is reversed; the ZP is higher for PACls with lower $B$, since more Alb is formed in situ. It needs to be noted that at low dosage, for PACls with higher $B$, the ZP is higher. This is because the content of monomeric Al in PACl with low value $B$ is not enough to satisfy the unsaturated complexation bonds of DOM under low dosage, and most monomeric Al is in the form of soluble aluminum-DOM complexes after dosing. Little $A_{lb}$ is formed in situ, thus the ZP is low.

4. Discussion

4.1. Mechanism of the effect of alkalinity/pH on coagulation

Solution pH during coagulation affects the chemistry of the coagulant. The traditional coagulants, alum and ferric salts, undergo rapid, uncontrolled hydrolysis reactions upon their addition to water, forming a series of products, e.g., monomers, oligomers, and polymeric hydroxyl complexes. Various chemical and instrumental methods have been used in monitoring the hydrolysis/polymerization process and characterizing the chemical species distribution. Each of these methods, however, has its specialty and shortcomings (Tang, 1990; Parker and Bertsch, 1992; Wang and Tang, 2001). Nevertheless, in recent years, the ferron timed complexation spectrophotometry method has become the main popular characterization method (Hsu and Cao, 1991; Wang et al., 2004).

With ferron assay, through the different reaction rates, the chemical species of hydrolyzed Al(III) can be divided into three types: $A_{la}$ (instantaneous reaction) is mainly composed of monomers, $Al_2(OH)_4^{2+}$ (dimer), and $Al_3(OH)_4^{3+}$ (trimer), normally under 1000 Da; $A_{lb}$ (reaction less than 120 min) is the intermediate polymer formed during hydrolysis, in the range from 1000 to 3000 Da; and species of sol or gel ($A_{lc}$) (no reaction).

Fig. 6 indicates that not only the alkali pre-added would affect the speciation of PACls, but also the pH of the coagulated water. Obviously, further transformation of species after dosing at the various conditions depends largely on the original PACl composition. PACls at low OH/Al ratio show a significant change of speciation under the various conditions. The $A_{la}$ fraction in the primary coagulants is the most unstable species. After dosing, these species would quickly transform into $A_{lb}$, and finally into $A_{lc}$ depending...
on the reaction conditions. The polymeric and colloidal species, once they were preformed, remained quite stable.

Fig. 7 shows that the Al₆₀ is highly charged. The charge capacity of PACls depends on the amount of Al₅₀. At high pH, the ZP is higher for PACl with high B, while at acidic pH, there is more Al₅₀ produced in situ; the ZP is higher for the PACl with low B.

Coagulation performance relates closely to the distribution of aluminum species in PACls (shown in Fig. 5). The effectiveness of coagulant is significantly affected by coagulant speciation. The Al₅₀ is highest at pH about 6, therefore, the UV₂₅₄ was removed most efficiently at this condition. As pH increases, the Al₅₀ decreases which resulted in the decrease of UV₂₅₄ removal. At the acidic region, more Al₅₀ is produced in situ for PACl with low B, which removes UV₂₅₄ more efficiently. At basic pH, PACl with high value B, i.e., Al₅₀ preformed is stable, removes UV₂₅₄ more efficiently.

It is interesting to note that the Al₅₀ preformed shows significant difference with Al₅₀ formed in situ in particle removal (Yan et al., 2007). It shows that Al₅₀ formed in situ rearranges in structure after dosing and tends to transform into Al₅₀ with aging. Under the basic pH range, PACl with high B value removes turbidity more efficiently. At the acidic pH range, PACl with high B value restabilizes the particles. Therefore, the residual turbidity increases for pH < 7.0.

Water with high alkalinity means more OH⁻ could be provided to meet the consumption during metal coagulant hydrolyzing. Alkalinity/pH would therefore affect the speciation distribution of the coagulant after dosing.

For high alkalinity water, the pH after coagulation is still above 7.0. High alkalinity waters (highly buffered) may require high coagulant additions to depress the pH to values favorable for coagulation (Fig. 4). For high B PACls with more Al₅₀ preformed, the UV₂₅₄ and turbidity removal are higher (Fig. 3). For moderate alkalinity water, the pH decreases more quickly with low B PACl. As dosage increases to a certain degree, it more easily reaches the acidic pH range, and much more Al₅₀ would be then formed in situ. PACl with high B becomes much more efficient. For low alkalinity water, PACl with low B would consume most of the OH⁻ and the pH decreases very quickly to favorable pH.

PACl preformed by adding alkali is a very useful method to produce high efficiency Al-species. The species preformed are quite stable after dosing and very efficient in NOM and particle removal. There is little influence by alkalinity and pH in water.

4.2. Guideline for IPF application

The performance of a coagulant is affected not only by the species preformed but also by that formed during coagulation. There are many factors to be considered together with the application of coagulant, including pH and alkalinity in raw water, pre-hydrolyzing degree of coagulant—PACl and coagulation target. Effective results cannot be reached unless they are optimized together. Coagulant basicity should be matched to raw water alkalinity, so that coagulation pH is as close as possible to the favorable pH.

For high alkalinity and pH water, most hydrolyzed products of AlCl₃ after dosing is sol (Al₅₀); although it may remove particles efficiently, it is inefficient in UV₂₅₄ removal. Pre-hydrolyzed PACl would enhance the UV₂₅₄ and particle removal with preformed Al₅₀. Adding acid before coagulation to decrease the pH after coagulation may increase UV₂₅₄ and particle removal efficiently, but the cost for chemicals and facility reform will be increased. It would also increase the difficulty of operation.

For moderate alkalinity and pH water, pH decreases only slightly at low dosage with AlCl₃. The pH may remain above 7.0, therefore coagulation is less efficient. PACl may still be more efficient at the same dosage than AlCl₃ for its high content of preformed Al₅₀. As dosage increases, AlCl₃ could consume most of the alkalinity and the pH decreases significantly. Most hydrolyzed products of AlCl₃ after dosing become Al₅₀. The Al₅₀ formed in situ result in very efficient particle and NOM removal. Therefore, at higher dosages, AlCl₃ may be more efficient than PACls. Medium alkalinity waters should be treated with medium or low basicity PACls because the acidity of these coagulants can consume sufficient alkalinity to decrease pH to a favorable pH region for NOM and particles removal at moderate doses.

For low alkalinity water, pH decreases rapidly for AlCl₃, at moderate dosage, most hydrolyzed product of AlCl₃ after dosing is Al₅₀. AlCl₃ may be more efficient than PACls. At pH lower than 5.0, most hydrolyzed product of AlCl₃ after dosing is Al₅₀, and the efficiency of UV₂₅₄ and particles removal deteriorates. Low alkalinity waters are suitable for high basicity PACls because favorable coagulation pH can often be maintained without base addition. An alternative for good NOM and particles removal is to employ low basicity PACls and alum with alkali addition to adjust the coagulation pH.

PACl can enhance the coagulation efficiency more than AlCl₃, especially for waters with low and high alkalinity. The basicity of PACl should be optimized to the characteristics of the raw water, coagulant dosage and coagulation targets. On-site PACl preparation and application techniques would be a good choice for water treatment facilities.

Acknowledgements

The authors are very grateful to the people of the Tianjin water treatment plant who provided full support to this research. The kind suggestions from the anonymous reviewers and editors are greatly acknowledged. This research was funded by the National Key Technology R&D Program of China under 2006BAD01B03 and 2006BAD01B09, the China national 863 projects 2006AA06Z312, CNSF 50578155, and CNSF Program.
for Innovative Research Group (No. 50621804). This project was supported by China Postdoctoral Science Foundation also. Dr. Meiping Tong is also acknowledged for kind assistance in language revision.

References