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Coagulation of micro-polluted Pearl River water with IPF-PACls

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Abstract: Water samples collected from early March 2001 to the end of April 2002 at the branch of Pearl River around the Guangzhou City were analyzed for its micro-polluted characteristics. The coagulation behavior of polyaluminum chlorides(PACls) was then examined focusing on the effect of primary water quality and speciation distribution. The results showed that PACls exhibit better coagulation efficiency than alum in accordance with the different speciation. The turbidity removal property of PACls is evidently better than alum at low dosage. While in neutral zone(about 6.5—7.5), the turbidity removal of PACls decreases owing to the restabilization of particles at higher dosage. The organic matters in raw water exhibit marked influence on coagulation. In acidic zone, organic matters complex with polymer species and promote the formation of flocs. With an increase in pH, the complexation of organics with polymer species gradually decreases, and the removal of organics mainly depends on adsorption. The effect is evidently improved with the raise of *B* value.

Keywords: PACl; micro-polluted river water; DOC; coagulation efficiency

Introduction

The water quality of natural river is very complex, including various kinds of organic, inorganic and biological matters, such as the soluble molecules, polymeric matters, colloids, and suspended particles such as live bacteria, algae and also protozoan (Tang, 2000). Generally, aquatic particulates are dispersively suspended, or deposit into diverse sediments through adsorption, aggregation and sedimentation. Furthermore, they can be resuspended, transferred and converted under various water fluid conditions. Clearly documented historical trends reveal the response of a natural system to either the unintentional consequences of human activity or the deliberate results of past management(Uri, 1991; Stow, 1998). With the rapid progress both of industrial and agriculture production, the river water suffers serious problems as source water. In the meantime, the knowledge of coagulation process on source river water is still limited, especially on using inorganic polymer flocculants regarding the specific coagulant species.

The objective of this paper was to investigate the coagulation process and mechanism with preformed PACls (polyaluminum chloride), using typical source water from Pearl River, Guangdong Province. The results would provide further information on enhanced and optimized coagulation of polluted river water, and theoretical basis for the advance of PACl production as well.

1 Materials and methods

1.1 Preparation of PACl

The reagents adopted in this paper are all of analytical grade except those being pointed out specifically. The method to prepare PACl is adopted as literature(Wang, 2002). The various PACl samples were prepared by using a slow base titration at room temperature. A solution of $AlCl_3 \cdot 6H_2O$ was titrated slowly with NaOH under rapid stirring conditions. The amount of NaOH added varied with the target [OH]/[Al] ratio(*B* values). The chosen *B* values were 0, 1.0, 2.0 and 2.5, and the resulting samples were denoted respectively as $PACl_0$, $PACl_{10}$, $PACl_{20}$ and $PACl_{25}$. The final concentration of aluminum was 0.1 mol/L. The samples after aging for one week were analyzed by an assay procedure using Ferron reagent(Hsu, 1990; Wang, 2002; Gray, 1995). It needs to point out that the species distributions of PACls depend largely on the preparation methods and conditions such as the concentration of primary materials, titration speed and mixing condition. With the above conditions established as shown in this study, the species distribution of PACls can easily be repeated within difference less then 5%. The typical speciation distribution of PACls by ferron assay is shown in Table 1.

Table 1 The speciation distribution of PACls by ferron assay

PACl	*B*	Al_a, %	Al_b, %	Al_c, %
$PACl_0$	0	90.1	9.90	0.0
$PACl_{10}$	1.0	60.1	38.5	1.40
$PACl_{20}$	2.0	26.1	70.3	3.60
$PACl_{25}$	2.5	7.40	60.5	32.1

Notes: Al_a (monomers), Al_b (oligomers and polymers) and Al_c (colloidal hydroxides)

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1.2 Sample collections from the river water

Water samples were collected once a week from early March 2001 to the end of April 2002 from the four sites: XC, FC, SX and XZ. These four sites are all located at the main branches of Pearl River basin around Guangzhou City. River water temperature was 12℃ in December and 28℃ in August. The water samples were pumped into a big pre-cleaned stainless steel bucket from 30 cm under the surface in the middle of each sampling site, and transferred into several pre-cleaned glass containers (20 L). It was then stored at 4℃ in the refrigerator. All samples were analyzed within 48 h after collection.

1.3 General methods

For the coagulation tests, a modified jar test procedure was applied by using a Flocculator apparatus (HuaDai, Beijing). This allows for different stirring-times and speeds (rapid for mixing coagulant and slow for coagulation) to be preset.

A total of 800 ml of the Pearl River raw water was transferred to a 1 L beaker. The coagulation experiments were conducted at room temperature (23—26℃). Prior to the addition of coagulants, the target pH was adjusted by adding a predetermined amount of NaOH or HCl into the solution with rapid stirring. The coagulant was added using a micropipet. After being dosed, 1 min of rapid mixing at 250 r/min was applied, followed by 15 min of slow stirring at 40 r/min. The flocs were allowed to settle for 15 min, and the residual turbidity (RT) was measured using a Hach Ratio/XR turbidimeter (Hach, Loveland, CO). The pH of the supernatant was also measured. A small sample was taken immediately after the 1 min rapid mix period for the determination of electrophoretic mobility using a Particle Micro-Electrophoresis Apparatus (Rank Brothers, Apparatus Mark II, UK). At the end of the settlement, 30 ml supernatant was taken using a syringe, then it was filtered through 0.45 μm filter membrane for UV determination at 254 nm.

2 Results and discussion

2.1 Characterization of Pearl River raw water

The change of turbidity in the four sites are clearly, the range is from 9 up to 90 NTU. However, the average value is relatively steady at 20—30 NTU. The content of sulfate ion is high in the water, and its range is 20—100 mg/L, average about 40 mg/L. The total phosphorus of the water is less than 0.15 mg/L, average about 0.06 mg/L. Its low concentration is possibily because the phosphate is liable to react with metal ion of the water, and can be removed in the form of precipitation. There is a moderate concentration of silicate (average at 10 mg/L) in the river. And the total hardness and basicity are average at 100 mg/L and 50 mg/L, respectively. Besides the inorganic anions, there are a large content of organic matters in the river, including surfactant and other total organic carbon. To sum up, the main influencing factors during coagulation process are inorganic anions including sulfate and silicate, and DOCs.

The coagulation experiments on the target raw water were then conducted according to the aquatic characteristics. Two typical modes, i.e. coagulation at constant dosage and constant pH, were examined. The XC water samples were chosen for further study in this article.

2.2 Effect of pH on coagulation with PACl

In this experiment, aluminum sulfate (AS) and PACl (*B* values were 0, 1.0, 2.0 and 2.5) were chosen to make a parallel comparison. The coagulant dose was set constant at 5×10^{-5}, 8×10^{-5}, and 2×10^{-4} mol Al/L respectively. The dosage chosen here is just according to the water quality and practical working parameter. Adjust the pH of the system by adding predetermined HCl and NaOH. The charge properties of the particles, residual turbidity (RT) and the removal of NOM were examined. The typical results are shown in Fig.1.

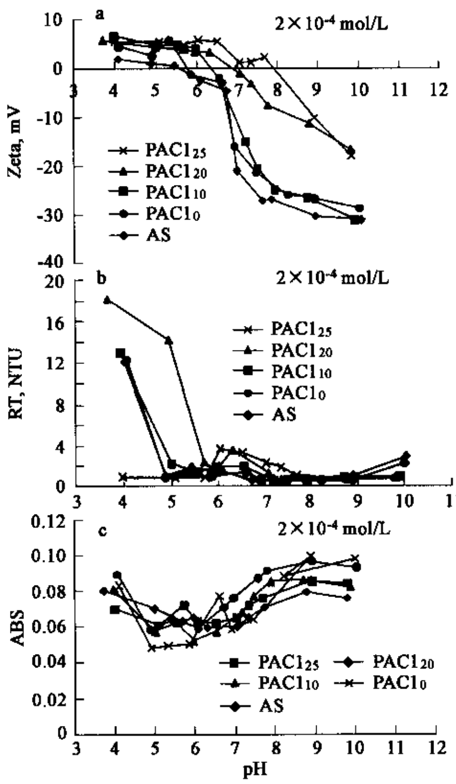

Fig.1 Effect of pH on coagulation of raw water with various PACl
a: zeta potential; b: RT; c: UV_{254}

It can be seen that different coagulants showed significant different coagulation efficiency depending on their speciation distribution and pH condition. With the increase of pH, the charge of the particle decreases rapidly, and various PACls exhibit marked difference in Fig.1a. The larger the *B* value, the much higher the charge of the particle. It illustrates that preformed PACls contain much more positive charged stable polymers, which exhibit notable charge neutralization ability after dosing into water solution, especially when the *B* value at 2.0 and 2.5. When the pH are in the range of 4 to 6, the zeta potential of particles changes only slightly. It showed that PACls are stable in this pH region. As pH rises to about 6.5, the zeta value of particles is reduced quickly. This becomes more significant on the PACls with lower *B* value. And it is in accordance well with the rule of solubility of aluminum hydroxide. The solubility of Al(III) salts rises very fast in basic condition, corresponding well with the rapid drop of its adsorption and charge neutralization abilities. In the raw water, there exist high quantity of anions and organic materials. Their complexation with Al(III) ions shifts the solubility curve to acidic zone. However, the preformed PACls with high *B* values are stable in basic zone, keeping remarkable charge neutralization ability.

The change of RT during the coagulation process showed the relative characters in Fig.1b corresponding well with the change of zeta potential. It can be seen that the PACl with lower *B* value reduce RT quickly as pH is increased in the zone of pH less than 5.5. This indicated that the dissolution nature of Al(III) salts is a controlling factor of coagulation effect. Because the PACl with moderate *B* value contain many polymer species, it can react with NOM and particles of raw water directly. Whereas this reaction is very complicated, and the micro-flocs formed can not be removed by short time settlement. The polymer species tend to aggregate into larger polymer in PACls with higher *B* value. It has superior effect on coagulation for the adsorption and bridge-formation after dosing. Furthermore, it must be point out that the RT rises again for PACl with higher *B* value in neutral pH zone, exhibiting that the NOM in the raw water has an important influence on the coagulation process. In acidic zone, the complexation-precipitation of NOM with the polymer species of PACl functions well, which promotes the formation of flocs. As observed in Fig. 1c, the optimal removal of NOM takes place at pH near 5.5. The complexation-precipitation drops off gradually with the increase of pH. And the removal of NOM mainly depends on adsorption on the aluminum hydroxide formed. Continue raising the pH, though significant RT is still reached, the removal of NOM becomes worse.

2.3 Effect of dosage of coagulation with PACl

At constant pH 5.5 and pH 7.0, the effect of dosage is shown in Fig.2 and Fig.3. From Fig.2a, it can be seen that the surface charge on the particle is quickly neutralized with the increase of dosage. Different PACls showed complicated charge neutralization behavior. At a low concentration of Al (III), the higher the *B* value, the less the charge of the particle. It indicated that the interaction among organic matter and PACls at the acidic pH region is very complicated. The polymers in high *B* value PACl tend to form precipitate with NOM, which results in the low surface charge of flocs formed. However, the turbidity and NOM removal exhibit different trend with zeta potential. It indicated that the charge neutralization becomes less significant after reaching certain value. While the nature of chemical interaction and precipitation formation become then significant role on final turbidity and NOM removal. As shown from the RT curve in Fig.2b, it can be seen that the PACls with high *B* value give better coagulation effect at low dosage.

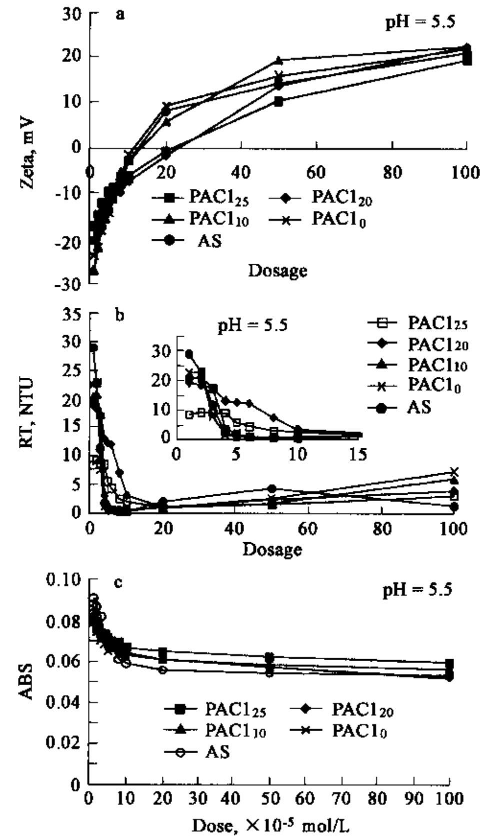

Fig.2 Effect of dosage on coagulation of raw water at constant pH 5.5
a. zeta potential; b. RT; c. UV_{254}

Continue raising the dosage, the reaction process becomes complicated, and the surface charge exhibits little change. It can be illustrated that NOM tends toward complexing intensely with hydrolyzed aluminum species at this pH condition, consequently different PACls have similar effect on the surface charge. On the one hand, dissolved organics and anions induce hydrolyzed aluminum species to form precipitation. On the other hand, they formed complex precipitate with polymer species. Therefore, the difference among charge properties of various flocs disappears. The UV_{254}-ABS curves exhibit no clearly difference in the removal of NOM, as shown in Fig.2c. With the increase of dosage, the removal efficiency rises fast at the beginning, then becomes stable at higher dosage.

Increase the solution pH to 7.0 as shown in Fig.3, the difference among PACls become more evidently. Increase the *B* value of PACl, the charge neutralization ability increase markedly. It indicated the significant effect of preformed polymer species. Once formed, they exhibit quite stable behavior and high charge neutralization ability after dosing into solution. While the traditional salts tend to form amorphous hydroxides and precipitate at the increased pH conditions. Under the neutral pH condition, the polymer species can still react directly with NOM to form complexes and colloidal aggregates. The aggregates formed tend to be restablized at high coagulant dosage and are difficult to settle down at short sediment period. It is therefore turbidity become raised again for high *B* PACls at increased dosages as shown from Fig.3b.

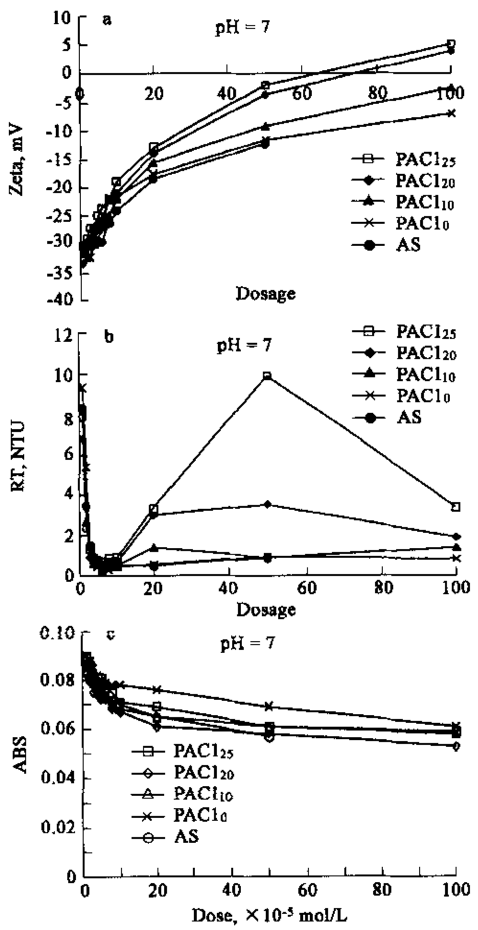

Fig.3 Effect of dosage on coagulation of raw water at constant pH 7.0
a. zeta potential; b. RT; c. UV_{254}

3 Conclusions

The results showed that PACls are better than aluminum salts in coagulation efficiency. While in neutral zone (about 6.5—7.5), with the increase of *B* value, the turbidity removal effect of the PACls decreases in a small degree for the restabilization of particle aggregates. As pH is increased to basic zone, PACls still keep higher charge neutralization ability. While the traditional coagulant tends to hydrolyze and decrease its surface charge. Therefore, pH has a great influence up on coagulation efficiency and removal of dissolved organics as well.

The organic matters in micro-polluted raw water exhibit marked influence on coagulation. In acidic zone, organic matters complex with polymer species and promote the formation of flocs. With an increase in pH, the complexation of organics with polymer species gradually decreased, and the removal of organics mainly depends on adsorption. The optimum pH is near 5.5.

The coagulation efficiency can be improved by the increase of dosage in a limited extent. As compared with traditional flocculants, PACls possess stronger stability and turbidity removal property is evidently better than AS at low concentration, while at higher dosage restablization would appear. And the effect will be improved with the raise of *B* value.

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