# Removal of natural organic matter in a typical south-China source water during enhanced coagulation with IPF-PACl

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**Abstract:** Systematic investigation on enhancing removal of natural organic matter(NOM) using inorganic polymer flocculant(IPF), polyaluminum chloride(PACl) and polyacrylamide(PAM) was performed in a typical south-China source water. Enhanced coagulation and applying polymer flocculant-aid were compared through jar tests and pilot tests. Raw water and settled water were characterized and fractionated by resin adsorption. The results show that DOC composes major part of TOC. The DOC distribution keeps relatively stable all around the year with typical high amounts of the hydrophilic matter around 50%. The distribution between HoB, HoA and HoN varies and undergoes fluctuation with the year round. During the summer season, the HoN becomes gradually the major part in hydrophobic parts. PACl with the species being tailor-made shows little pH effect during coagulation. The enhanced coagulation dosage for PACl could be 4.5 mg/L for the typical source water. The highest TOC removal achieved 31%. To be economically, 3 mg/L dose is the optimum dosage. Although hydrophilic fractions of NOM of both treatment strategies are removed about 30%, NOM causing $UV_{254}$ absorbance were well removed(about 90%). Hydrophobic bases and acids fractions are much more removed under enhanced conditions. The hydrophilic fraction could be better removed using PAM, the polymer coagulant aid.
**Keywords:** enhanced coagulation; PACl; PAM; NOM fractionation

## Introduction

Requirement of organic matter removal, which is generally regarded as precursor of disinfection by-products (DBPs), in water treatment was improved gradually(Edzwald, 1990; Krasner, 1995). Coagulation plays a critical role in water treatment processes for natural organic matter (NOM) removal. Enhanced coagulation is recently proposed to give emphasis on removal of NOM and DBP accordingly. It is obvious that traditional coagulation could also partially remove NOM, while enhanced coagulation is to optimize the conditions of coagulation in order to maximize NOM removal to improve water quality(Edzwald, 1999; Volk, 2000; Exall, 2000).

Water treatment technique level in China is still quite different among various areas because of extremely different economic development situation. Generally speaking, there are still few cases of enhanced coagulation being carried out in China. Meanwhile, with the rapid development of regional economy, environmental pollution becomes more and more serious problem in China. Many of the source water suffer from the micro-polluted water quality problems such as synthetic organic matters, algae bloom, N/P problem etc. Recently, a national 863 project entitled "safe drinking water program" was proposed since 2003 by choosing three typical regional areas as research objectives. One of the subject source water is located in the city of Shenzhen City, south-China, and it supplies drinking water for about 6 million people. The enhanced coagulation feature, optimized technology and performance rule accordingly are one of the main targets.

In this study, the enhanced coagulation conditions of local water were determined by using the well-developed inorganic polymer flocculant(IPF)-PACl as main coagulant. Both enhanced coagulation and poly-electrolyte coagulant aid were compared. Turbidity and organic matter removals, residue aluminum, algae removal and economical costs were investigated to compare the two strategies. The DOC was fractionated into four parts as hydrophobic base (HoB), hydrophobic acid (HoA), hydrophobic neutral (HoN) and hydrophilic fractions (Hi). Differences of organic matter fraction removals between the above two strategies were examined to get further insight of the mechanisms.

## 1 Materials and methods

### 1.1 Materials

The main coagulant used was PACl, which was made by a QY Flocculant Factory, China containing 10% of $Al_2O_3$ and the basicity being about 55%—65%. Laboratory tailor-made PACl with B (OH/Al ratio) of 2.5(equals basicity of 83.3%) was also prepared as described in the literature(Wang, 2002) for a comparison. Cationic polyacrylamide(PAM) was a kind of organic polymer provided by DH Water Plant, China. A 0.1% solution of PAM was made and was used as coagulant aid in this study.

Water samples were taken from the plant reservoir in south China. The same sample of raw water was taken and kept in a tank to be carried out in comparison experiments.

### 1.2 Jar tests and analysis

For the coagulation characterization, a modified jar test procedure was applied by using an apparatus made in China containing four jars. 800 ml of raw water was transferred to each beaker. And the stirring conditions were kept at 250 r/min for 2 min, followed by 10 min at 40 r/min. Then kept still for 10 min sedimentation. Coagulant was dosed by a pipette being calibrated before each experiment and all of the experiments were carried out at a room temperature between 22—25℃. And in some cases, PAM was dosed after major coagulant was added and was continued with 250 r/min stirring for 1 min, and then 40 r/min for 10 min and sedimentation as described above. After sedimentation, a sample was taken from 2.0 cm below the surface. Turbidity, $TOC/COD_{Mn}$, $UV_{254}$ and algae count were measured. The TOC/DOC was analyzed by the Pheonix 8000 TOC system using the method of sodium peroxydisulphate/orthophosphoric acid wet oxidation and UV radiation. UV absorbance at 254 nm was measured by UV-Vis 8500 Spectrophotometer. Turbidity was measured using 2100N Turbidimeter, Hach.

### 1.3 NOM fractionation

Organic matter was fractionated by resin XAD-8

according to the method described by Chang(Chang, 2001). The processes followed some modification as described below:

Certain amount of raw water was filtered through 0.45 $\mu$m pretreated membrane; got DOC of the water; then pass the flow slowly at about 200 ml/h through a column (3.5 cm diameter 50 cm long) filled with certain amount (80 ml) of XAD-8 resin; and hydrophobic base and hydrophobic neutral parts of organic matter (HoB + HoN) were adsorbed on the XAD-8 resin; the effluent was collected and adjusted to pH 2.0; then flowed through another XAD-8 column; on this resin hydrophobic acid (HoA) were absorbed; the effluent was collected as hydrophilic part(Hi) and the first XAD-8 column was back washed by 0.033 mol/L $H_3PO_4$, the washed solution was also collected(HoB) and all the volumes of the influents and effluents were recorded and then DOC of all samples were detected by TOC analyzer.

## 2　Results and discussion

### 2.1　Characterization of the raw water

The typical characteristics of the local source water are low turbidity, high algae and micro-contaminant polluted. Algae concentration is always larger than $10^6$—$10^7$/L throughout the year. As the source of the water becomes gradually well protected, turbidity is always below and around 10 NTU and TOC is quite low which is around 2 mg/L for most time of the year. The water temperature in local area ranges between 15—32℃. And the pH was about 6.5—7.6 for most time of the year. Alkalinity and hardness are both relatively low, averaging about 40 mg/L as $CaCO_3$. The traditional treatment process of the water plant involves pre-chlorination, coagulation, flocculation, sedimentation, and sand filtration, disinfection etc. And the normal coagulant is PACl produced in a local factory. The DOC distribution of the raw water is analysed and shown in Fig. 1. The TOC for the raw water taken is 1.90 mg/L. The results show that DOC composes major part(95%) of TOC. The hydrophobic and hydrophilic parts are almost equal in DOC. Contents of HoB, HoA, HoN and Hi parts are 18.47%, 10.76%, 14.08% and 52.23% respectively. The DOC distribution keeps relatively stable all around the year with typical high amounts of the hydrophilic matter around 50% more. However, the distribution between HoB, HoA and HoN varies and undergoes fluctuation with the year round. During the summer season, the HoN becomes gradually the major part in hydrophobic parts (data not shown).
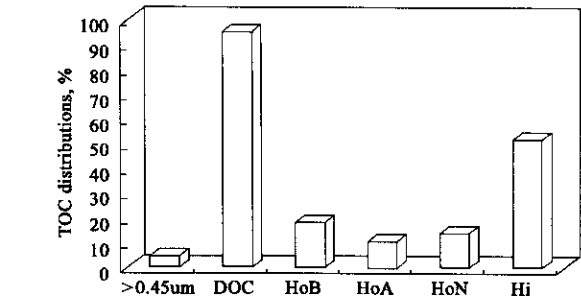
Fig.1　Fractions of organic matter in raw water

### 2.2　Characteristics of coagulation

The general feature of enhanced coagulation with industrial PACl and with PAM as coagulation aid on the source water is shown in Fig.2. It can be seen that the PACl exhibits efficient coagulation with the source water. The residual

turbidity(RT) decreases quickly with increase of coagulant dose. At dosage of 2 mgAl/L($7.4 \times 10^{-5}$ molAl/L), the RT reached gradually the lowest value. Further increase of dosage, no significant removal of turbidity could be obtained. At dosage of 3.6 mg/L, the particle restablization occurs. Then RT becomes increased at higher dosage. It needs to note that the pH maintains the same around 7.0 also. The raise of dosage decreases pH slightly.
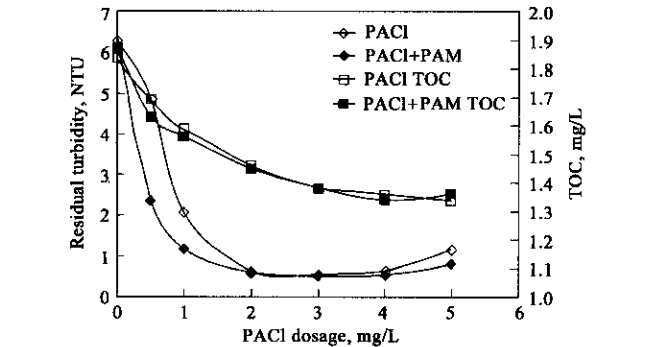
Fig.2　Characteristics of enhanced coagulation using IPF-PACl with and without PAM aid

The change of TOC with PACl dosage exhibits also a rapid decrease initially and then reaches a plateau gradually at PACl dosage of 4—5 mg/L. However, the platform reached is markedly at higher dosage than RT. Therefore as the Enhanced Coagulation rule(Exall, 2000) indicates, the dosage could be 4.5 mg/L for the source water. The highest TOC removal could be achieved at 31%. To be economically, 3 mg/L dose is the optimum dosage for PACl.

When PAM is used as coagulation aid, turbidity removal is increased at relatively low PACl dose (less than 2.0 mg/L as observed) and the effects become less detectable with further increase of PACl. At much higher PACl dose, where the particle becomes restabilized, the bridge effect of PAM shows some positive effect. However, the removal patterns of TOC seem little affected by PAM especially in the large PACl dosages. It indicates that the PACl-NOM interactions dominate the removal of TOC. With the aid of PAM, the formed PACl-NOM precipitates become more easily aggregated into large tight flocs and to be removed after sedimentation. The results correspond well with the other researches(Exall, 2000).

Pilot experiments were performed to compare flocculant aid effects with enhanced coagulation. The dosage of normal coagulation was kept at about 2.2—2.5 mg/L, which was decided through jar tests described above. The combination coagulation dosages were 1.2—1.5 mg/L PACl and 0.06—0.10 mg/L cationic PAM. The results are summarized in Table 1.

Table 1　Pilot test results of two treatment strategies

| | Turbidity, NTU | | COD, mg/L | | TOC, mg/L | | UV | Resid. Al,mg/L |
|---|---|---|---|---|---|---|---|---|
| | Aver. | Rate, % | Aver. | Rate, % | Aver. | Rate, % | Aver. | Aver. |
| Raw | 7.46 | | 1.38 | | 1.94 | | 0.020 | 0.370 |
| Settled | 1.63 | 78.17 | 0.75 | 45.20 | 1.60 | 17.53 | 0.013 | 0.366 |
| Filtered | 0.17 | 97.69 | 0.56 | 59.08 | 1.50 | 22.68 | 0.012 | 0.009 |
| Raw* | 6.93 | | 1.48 | | 2.05 | | 0.020 | 0.370 |
| Settled* | 1.12 | 83.85 | 0.74 | 49.82 | 1.62 | 20.98 | 0.012 | 0.168 |
| Filtered* | 0.16 | 97.72 | 0.63 | 57.65 | 1.59 | 22.68 | 0.012 | 0.007 |

Note：　* Parameters of combination coagulation

Compared with the enhanced coagulation, by which TOC removal is only about 18%, polymer aid coagulation in this study could achieve removal of TOC about 21%, and

more than 40% of $UV_{254}$ is removed in both process. Coagulation plays a critical role in removing organics. It could be found from the above data that the major parts of TOC, $COD_{Mn}$ and $UV_{254}$ are decreased after coagulation process. Residual aluminum is also determined which indicates that combination coagulation would dramatically decrease the concentration of aluminum in the sedimentation stage with a concentration 0.168 mg/L against enhanced coagulation of 0.366 mg/L. The turbidities of the finished water are relatively low, so both of the new methods have no harm on turbidity removal.

Full-scale experiments lasted for one week, which were taken on two lines of tanks with about 1800 t/h each line. Coagulants and flocculant aid were chosen just as the pilot scale tests while the controlled tank using as basic condition at a dosage of 1.5 mg/L. Coagulants were dosed by three pumps, one for controlled tank and the other two for combination tank. The detected parameters were the same as mentioned above. The results were similar to those of pilot-scale experiments. It indicated that combination coagulation dramatically decreases turbidities of the settled water compared to normal coagulation. Removals of TOC, $COD_{Mn}$ and algae are only slightly increased. Fractal dimension and diameter of the coagulated flocs were also tested, which show PAM increases about 10% in floc diameter and increases the density of the flocs. All of these results indicate that cationic PAM used in the experiments improves flocs formation and settling abilities, and increases the clarity performance of coagulated water. But its effect on organics is not remarkable.

The effect of pH on coagulation was also investigated in this work as shown in Fig. 3. It shows from the PACl data that decreasing pH less than 6.0 increased the removal of organic matter, and at pH 5.5 reached the largest removal. However, the difference in the weak acidic region is small. While turbidity removal becomes worse for flocs being difficult to settle down at lower pH ( < 6.0) and the flocs formed become small and loosen. Because of the most hydrolysed species in PACl adsorpted directly and reacted with the organics and particulates, the flocs formed are small especially for the nano-scale primary particles. Increasing the solution pH, the hydrolysed species in PACl become aggregated to form large precipitates after dosing. As shown in Fig. 3, it is indicated that at pH below 6.0 charge-neutralization-precipitation is the major mechanism. While at higher pH 6.0—8.0, sweep precipitation and increasing adsorption of nano-scale primary particles at the formed hydroxide precipitates become dominating. If pH is increased further > 8.0, the precipitation would be weaken and organics would be more hydrophilic and soluble. The use of lab-made coagulant B = 2.5 would be somewhat better as showed above. According to former researches(Chang, 2001) on the basicity effects of coagulants, it was concluded that with higher B ( 1.8—2.5 ), coagulant would take major polymeric states with high charge, moderate polymerization. And such kind of PACl had the ability of high charge-neutralization and bridge ability being essential to particle destabilization. From the results shown above, it is not a good choice to be taken for decreaing pH to achieve more NOM removal, although some reports showed that pH of coagulation was the marked factor for removal of TOC (Kimberly, 2000). In the case of PACl, the decrease of pH seems not a good choice because it deteriorates turbidity

removal. PACl with the species being tailor-made shows little pH effect.
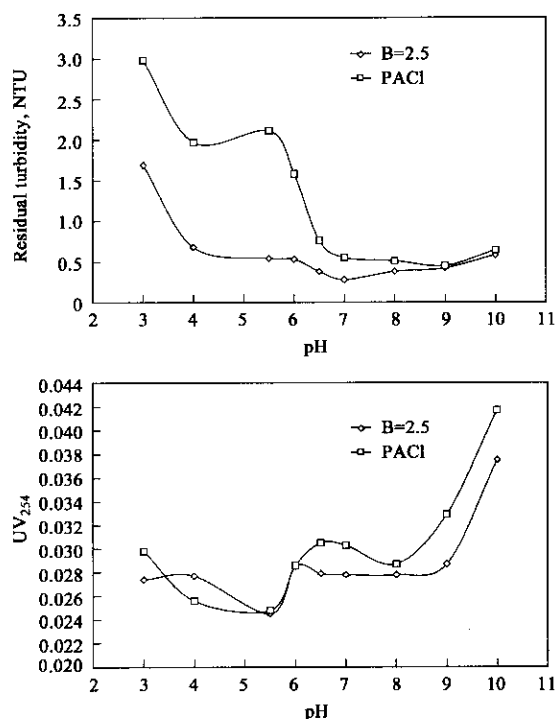


Fig.3  Effects of pH on coagulation

## 2.3  DOC fractionation after enhanced coagulation

The removal of DOC in the two-strategy coagulation was further examined in the pilot test. Total removals of DOC and $UV_{254}$ for the two methods of coagulation, enhanced coagulation with PACl or with PAM coagulant aid, show similar results. Since the TOC of raw water is relatively small, the enhanced coagulation at higher dose improved only limited removal of NOM. Fig.4 is the results of DOC fraction for the water sample taken before sand filtration for the two processes. It seems that the enhanced coagulation with PACl provides better removal of hydrophobic fractions(HOM). The interaction of HOM with PACl is enhanced at higher dosage. The hydrophilic fractions(Hi) are much more soluble. In the presence of PAM, the loose flocs can be aggregated in an efficient way and yield better removal. It can also be seen that at enhanced dosage the HoN and HoB fraction can be removed at highly rate(40%—68%). It indicates that the NOM can be removed selectively. By using the fraction method, the feature of NOM remove can be characterized. Further combination of other methods such as particle size distribution analysis and THMFP measurement will yield more information.

UV absorbance at 254 nm is an excellent surrogate parameter for estimating the raw water concentrations of organic carban ( NPTOC-nonpurgeable total organic carbon) and THM precursors(TTHMFP-total trihalomethane formation potential; Edzwald, 1985). It is a useful surrogate measurement of selected organic constituents in fresh waters, salt waters, and wastewater( Andrew, 1995 ). $UV_{254}$ is closely related to THMFP and is used as an indicator of THMFP during undergoing treatment series. The details of fraction for the two processes by using DOC and $UV_{254}$ are shown in Fig. 5 and 6. It is noticeable that UV absorbance of hydrophilic organic matters ( Hi ) is almost completely removed ( above 90% ), however the DOC results show only about 30%. It
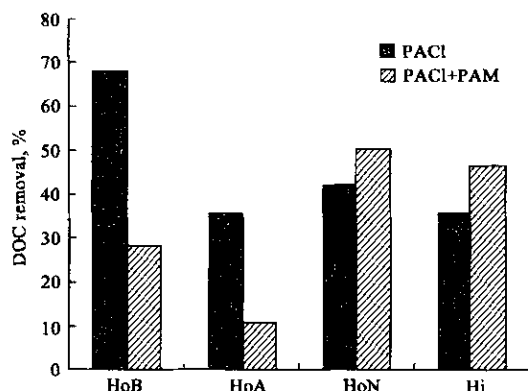
Fig.4　Comparison of fraction removals by PACl with and without PAM aid

indicates that there are some Hi that causes $UV_{254}$ in the water could be almost entirely removed by enhanced coagulation. But there remains significant part of Hi difficult to be removed, as mentioned also by other researchers. Although $UV_{254}$ provides simple way to characterize the NOM, there exists significant limitation.
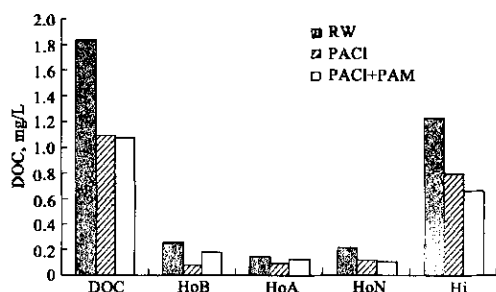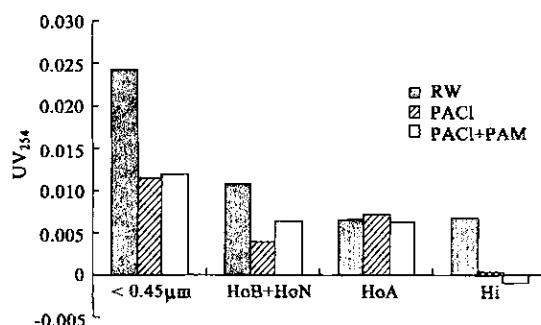


Fig.5　Fraction removals of DOC



Fig.6　Fraction removals of $UV_{254}$

## 2.4　Specific ultraviolet absorbance(SUVA) characterization

SUVA was used as an operational indicator of the nature of the NOM and the effectiveness of coagulation for organic matter removals( Edzwald, 1999; 1985). It represents THM formation potential of aquatic DOC. The results of change of SUVA before and after treatment are shown in Table 2. From Table 2, the SUVA of raw water was 2.21, which indicates the NOM is composed by mixture of aquatic humics and other NOM with various hydrophilicity and molecular weights. NOM in raw water could be removed partially by enhanced coagulation. And based on fraction data, the SUVA of HoB + HoN fraction was 4.32. It could be presumed that HoB + HoN fraction consists mostly aquatic humics with high hydrophobicity and high molecular weights. HoB + HoN should be removed through coagulation more readily as shown in Fig.4, 5 and 6. Little difference of total TOC/DOC and

$UV_{254}$ is shown in both of the two coagulation processes, although there exist certain difference in fraction removals. It needs to note that after enhanced coagulation the SUVA decreases to 1.1, a value acceptable by the enhanced coagulation rule for the low TOC and low alkalinity source water. However, the SUVA for the HOM fractions becomes increased after treatment. Further characterization by THMFP would be needed to give further indication on the behavior of the residual NOM.

Table 2　SUVA of raw water and fractions after treatment

| SUVA | Raw water | Enhanced | PAM aid |
|---|---|---|---|
| Total | 2.21 | 1.1 | 1.1 |
| HoB + HoN | 4.32 | 5 | 3.6 |
| HoA | 1.8 | 3.27 | 2.6 |
| Hi | 0.56 | 0.05 | 0.12 |

## 3　Conclusions

NOM in the raw water is relatively low. The hydrophobic OM in the raw water is about the same as hydrophilic parts. According to SUVA, OM in the raw water is composed of mixture of humics and other organic matters, and it could be largely removed through enhanced coagulation. The increase of SUVA for the HoM after enhanced coagulation indicates further attention on the residual NOM is needed.

The enhanced coagulation dosage could be 4.5 mg/L for the typical source water. The highest TOC removal could be achieved as 31%. To be economically, 3 mg/L dose is the optimum dosage. With PAM used in coagulation, it decreases the dosage of main coagulant without reducing turbidity removal. But the results show little improvement of TOC removal.

All fractions could be removed to some extent by enhanced coagulation and combined coagulation with removal rates about 28%—68%. The Hi dominates the residual DOC. PAM enhances the removal of Hi.

It is noticeable that $UV_{254}$ in Hi fraction is almost completely removed. There might exist two major sorts of Hi in the source water. One that causes $UV_{254}$ easily to be removed by coagulation. The other being the major parts of this fraction without $UV_{254}$ response is difficult to be removed by coagulation.

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