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# Optimization of coagulant for raw water in Ganjiang River in winter

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**ABSTRACT**

The paper aims to determine the optimal coagulant for raw water in the Ganjiang River during the winter. To explore their removal effect on turbidity and organic matters, respectively, by using $FeCl_3$, $Al_2$ $(SO_4)_3$, polyaluminum chloride, and polymeric aluminum ferric chloride as coagulant, there has been a total of six-jar test conducted. It was discovered that the removal rates of turbidity and organic maters vary a lot according to different raw water quality.

*Keywords:* Coagulant; Removal efficiency; Organic matters

## 1. Introduction

Since the establishment of the Standards for Drinking Water Quality(GB5749-2006) in China on 1 July 2007, the index number of water quality has increased from the original 35 (GB5749-85) to 106. It lays greater stress on the quality of water in terms of the requirements of organic matters, micro-organisms, and water disinfection. Water pollution and water conservation has become an outstanding issue in their respective fields according to the Communiqué on Environmental Status of China in 2010, published by the Environmental Protection Administration of China. Hence, China's city water supply industry is now facing to struggle against the source of water contamination and improving water quality. Through the study of many scholars, it has revealed that the enhanced coagulation technology is one of the technical means which serve as helpful tools for the current Chinese water industries to increase their water production and improve their water quality.

Nowadays, with a variety of coagulants and uneven water quality in different water sources, poses a great challenge and difficulty in the suitable selection of coagulants for certain raw water. In conventional water treatment process, in the presence of a suitable coagulant and proper dosage, we can achieve a better removal result of organic matters and a better removal of precursor of the disinfection by-products. Through the experiment, we expect to figure out how to achieve a better removal effect of the organic matters by analyzing the changes of different water quality indexes of different coagulants through a six-jar test.

## 2. Experimental materials and methods

### 2.1. Experimental materials

(1) The quality of raw water

The first raw water samples were taken from Ganjiang River, near Shuang Gang road in Nan Chang city between December 2010 and January 2011. A

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Table 1
The first raw water quality

| Turbidity (NTU) | ζ Potential (mV) | TOC (mg/L) | $NH_3$-N (mg/L) | $COD_{Mn}$(mg/L) |
|---|---|---|---|---|
| 42.04–48.06 | −16.24–14.99 | 9.54–11.14 | 4.18–4.66 | 3.59–4.18 |

Table 2
The second raw water quality

| Turbidity (NTU) | ζ Potential (mV) | TOC(mg/L) | $NH_3$-N (mg/L) | $COD_{Mn}$(mg/L) |
|---|---|---|---|---|
| 24.18–26.49 | −16.78–19.70 | 1.76–3.42 | 0.07–0.43 | 2.14–2.74 |

dredge in the river and domestic wastewater surging into the river was polluting the water. Their quality is shown in Table 1.

The second raw water samples were taken from a water point in a water inlet of a water factory in Nan Chang City in the center of the Ganjiang River between December 2010 and March 2011. Their quality is shown in Table 2.

(2) Experimental equipment and instruments

The main test equipment and instruments included a MY3000-6K Flocculator equipped with a programmable mixer made by Wuhan Hengling Technology Ltd., a turbidimeter (TDT-2), a Total organic carbon (TOC) analyzer multi N/C 2100, and a 90 plus zeta potential analyzer.

(3) Experimental reagents

- Ferric chloride ($FeCl_3 \cdot 6H_2O$) is a chemical pure reagent in the form of brownish yellow crystalline block, and the content of $FeCl_3$ is 93.63%.
- Aluminum sulfate ($Al_2(SO_4)3 \cdot 18H_2O$) is a chemical pure reagent in the form of white or off-white crystalline powder or flake, $Al_2O_3 \geq 15.6\%$.
- Polyaluminum chloride (PAC) is an industrial liquid medicine produced by Ganjiang Water Purification Agent Ltd. in Nanchang with density (20 ℃)/(g/cm$^3$) $\geq 1.12$, $Al_2O_3 \geq 29.0\%$.
- Polymeric aluminum ferric chloride (PAFC) is an industrial solid drug in the form of yellow granules with aluminum oxide ($Al_2O_3$) $\geq 29\%$ and ferric oxide ($Fe_2O_3$) $\approx 3$–5%.

Table 3
Water quality monitoring projects and analysis methods

| Testing item | Unit | Analysis method or instrument |
|---|---|---|
| Turbidity | NTU | TDT—2 turbidimeter |
| $NH_3$-N | mg/L | Nessler reagents' spectrophotometer |
| TOC | mg/L | Multi N/C 2100 TOC |
| $COD_{Mn}$ | mg/L | Acidic titration method of $KMnO_4$ |
| Zeta potential | mV | 90 plus Zeta particle size analyzer |
| UV254 | Abs. | Lambda 35 visible spectrophotometer |

### 2.2. Detecting indicators and methods

Detecting indicators and methods in the test are shown in Table 3.

Turbidity is an important index for the evaluation of water quality. Its decline not only meets the sensory requirements, but also has an important role in limiting the content of harmful and toxic substances in the water.

High ammonium content indicates serious micropollution of the raw water. Chlorine molecules react with the organic compounds in the water producing carcinogenic substances as trihalomethanes. We use chloramines for salient point chlorine disinfection because of the large content of disinfection by-products along with large dosage of chlorine.

TOC is a parameter of the total organic compounds in water and a composite index to evaluate the organic pollutants of drinking water.

$COD_{Mn}$ is considered as the comprehensive indicator of the polluted water by reducible organic (inorganic) substances.

Table 4
The operating parameters of coagulation

| | Quick coagulation | Slow coagulation | Static setting |
|---|---|---|---|
| Run speed(r/min) | 350 | 70 | – |
| Time(min) | 0.5 | 15 | 15 |

Zeta (ζ) potential, an important coagulation parameter, reflects the stability of suspensions and colloidal particles in water.

### 2.3. Experimental methods

The test is aimed to find a better method for coagulation of water with different qualities by analyzing different indices through six-jar test. Its operating parameters of coagulation are shown in Table 4.

## 3. Results and discussion

### 3.1. Optimization of coagulant for the first raw water in Ganjiang River in winter

With the increase of coagulant's dosage as shown in Fig. 1, both the turbidity of $FeCl_3$ and PAC showed a downward trend; but the turbidity of $Al_2(SO_4)_3$ and PAFC had an initial downward followed by an upward trend due to the following reasons. The residual turbidity was high with a low dosage owing to the difficulty in forming bigger flocs, because of difficulty in sinking due to similar specific gravity with water. The floc increased in volume as well as in density with the dosage increasing, the settling velocity sped up, and so the residual turbidity decreases accordingly. When the dosage increased to a certain level, the solid particles adsorbed the spare coagulant ions producing a "protective colloid" to restabilize themselves, which in turn led to the increase of residual turbidity [1,2].

In Fig. 1, the coagulation effects of $FeCl_3$, $Al_2(SO_4)_3$, and PAFC were at dosage of 25 mg/L, where the turbidity of raw water decreased from 42.04 to 0.70, 0.68, 0.67 NTU, respectively. Major decreases from the initial water turbidity of $FeCl_3$, $Al_2(SO_4)_3$, and PAFC were also at the dosage of 25 mg/L, respectively. PAC dropped to 1.20 NTU at the dosage of 30 mg/L with a major decrease at the dosage of 35 mg/L. Its turbidity

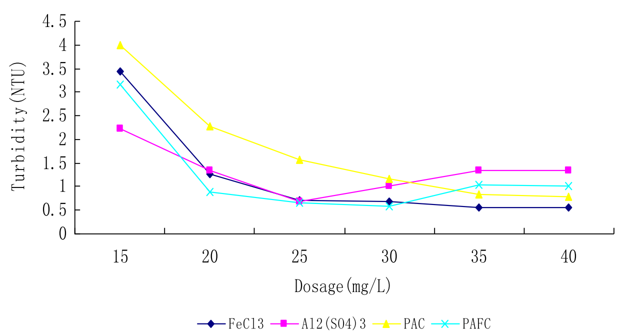


Fig. 1. The removal case of turbidity with increased dosage.

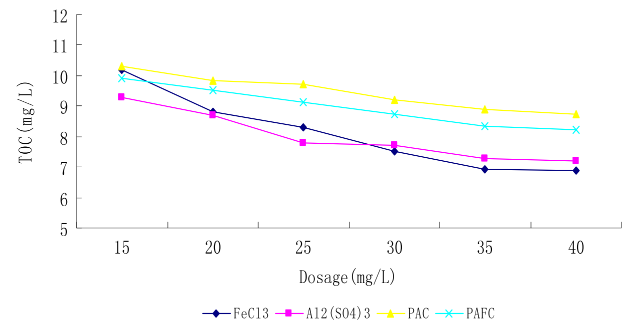


Fig. 2. The removal case of TOC with increased dosage.

was 0.91 NTU, but 30 mg/L was the optimum dosage of PAC after taking into consideration the cost and reduction scale of turbidity. Most waterworks adopt PAC together with PAM to improve the removal rate since their rate of turbidity is lower than other coagulants [3,4]. Although the removal effects of turbidity of all the above four coagulants were poor with a low dosage, the result was just the opposite with the increase in dosage.

TOC, as shown in Fig. 2, showed a clear downward trend with an increase of coagulant dosage. The major decreases in the initial water TOC of $FeCl_3$, $Al_2(SO_4)_3$, PAC, and PAFC were all at the dosage of 40 mg/L. Likewise, the optimum dosage was selected and analyzed after considering the cost and reduction scale of turbidity. $FeCl_3$ and $Al_2(SO_4)_3$ had a better decontamination effect compared with PAC and PAFC. The change of TOC slowed down when the dosage of $FeCl_3$ and $Al_2(SO_4)_3$ reached 35 mg/L. Polymer coagulations contain more intermediate polymers, and $FeCl_3$ and $Al_2(SO_4)_3$ mainly exist as the form of hydroxide in neutral media after being added into water. So it is believed that polymer coagulations have a higher ability of electrical neutralization and trapping role and have a better effect of coagulation. This theory was found to be inconsistent with the change in trend of TOC in our study. The complex quality of water might have affected the morphology of hydrolysis product of coagulation due to petroleum and other macromolecular substances dumped by some docking tankers together mixed with domestic sewage surged into the river. The ability of electrical neutralization and adsorption were therefore reduced [5,6]. $FeCl_3$, $Al_2(SO_4)_3$, PAC, and PAFC made the TOC of raw water fall from 11.14 mg/L to 6.88, 7.165, 8.73, and 8.235 mg/L, respectively. The highest removal rate of TOC reached as high as 38.2% when the dosage of $FeCl_3$ was 40 mg/L.

The decontamination effects of $FeCl_3$ and $Al_2(SO_4)_3$ were different. The TOC removal rate of $FeCl_3$ was higher than that of $Al_2(SO_4)_3$ with a low dosage, but it was reversed with a higher dosage. Combined with Fig. 6, the pH value change of $FeCl_3$ was higher than $Al_2(SO_4)_3$. The pH value decreased at the proper dosage of $FeCl_3$, while improving the positive charge density of hydrolysis product. At the same time, the protonation of organic compounds in water increased with the rapid decline of pH value. It is beneficial for the organic compounds to be adsorbed by hydrolysis product of coagulation. The ability of iron salt for removing organic compounds was high. As for $Al_2(SO_4)_3$, the specific surface of hydrolysis product of aluminum salt ($Al(OH)_3$) was higher from 200 to 400 $m^2/g$ compared to that of the iron salt ($Fe(OH)_3$) from 160 to 230 $m^2/g$. So the removal rate of aluminum salt for organic compounds was higher than iron salt, but the removal rate of iron salt was higher than aluminum salt when the dosage was larger because the effect of the positive charge density of hydrolysis product and increase in protonation of organic compounds in water with iron salt were higher than that of specific surface of hydrolysis product of aluminum salt [7].

Fig. 2 reveals that the removal rate of PAFC was slightly higher than PAC, because PAFC had iron and aluminum cations and possessed advantages over iron and aluminum chlorohydrate. It could overcome not only the weakness of small alum floc and slow settlement of aluminum chlorohydrate, but also the weakness of easy coloring of iron chlorohydrate [8].

In Fig. 3, a downward trend of $NH_3$-N was found with the increase of coagulant dosage. Its removal effect of various coagulants made no significant differences when the coagulant dosage was less than 25 mg/L; but its removal effect of $Al_2(SO_4)_3$ was the highest when the coagulant dosage was greater than 25 mg/L. It dropped from 4.66 mg/L to 2.76 mg/L when the dosage of $Al_2(SO_4)_3$ increased to 40 mg/L, with a removal rate of 40.7%. In this Figure, the removal effect of $FeCl_3$ was found to be the worst. Its decline slowed down after 30 mg/L with the use of $FeCl_3$. Its removal effect by coagulation was not ideal and this result confirmed the conclusion made by other studies. However, biological treatment or advanced oxidation technology could be used to remove $NH_3$-N.

Expressed as mg/L of oxygen, $COD_{Mn}$ is the consumed quantity of oxidant of potassium permanganate in the acid or alkaline medium. Nitrite, ferrous salt, sulfide, and other reducible inorganic and the organic compunds oxidized in such conditions to consume potassium permanganate. So $COD_{Mn}$ represented most reducible organic as well as inorganic compounds. On the other hand, TOC stood for the organic matters in the water, and the removal rate of $COD_{Mn}$ and TOC were different [9,10]. In Fig. 4, $COD_{Mn}$ showed a downward trend with the increase of coagulant dosage. Obviously, the removal effects of PAC and PAFC on $COD_{Mn}$ were ideal. Polymer coagulations play a big role in adsorbing and attaining a high charge when reducible substances are removed. The $COD_{Mn}$ of the raw water declined from 4.18 mg/L to 2.55 mg/L and 2.56 mg/L at the dosage of 20 mg/L with a removal rate of 39.0 and 38.8%, respectively. The removal effects of $FeCl_3$ and $Al_2(SO_4)_3$ on $COD_{Mn}$ were relatively poor, but was better when the dosage increases to 30 mg/L; and the removal effect of $FeCl_3$ was worse than that of $Al_2(SO_4)_3$. The contents of $COD_{Mn}$ of $Al_2(SO_4)_3$ and $FeCl_3$, dropped from 4.18 mg/L to 2.44 mg/L and 2.33 mg/L, respectively, with a removal rate reaching 41.6 and 44.3%, respectively. Afterwards they were followed by a very slow downward trend. This was due to the fact that $FeCl_3$ has a high removal rate of small molecule organic matters, while $Al_2(SO_4)_3$ has a high removal rate of large molecule organic matters. Among the two, the removal rate of hydrophilic organic matters of $FeCl_3$ was higher than that of $Al_2(SO_4)_3$. Coagulation mainly removed large molecule organic matters in water, so the removal rate of $Al_2(SO_4)_3$ was higher than $FeCl_3$ after the dosage of coagulant went up to a certain concentration.

Zeta (ζ) potential is an important indicator used to reflect the stability of colloidal particles and suspen-

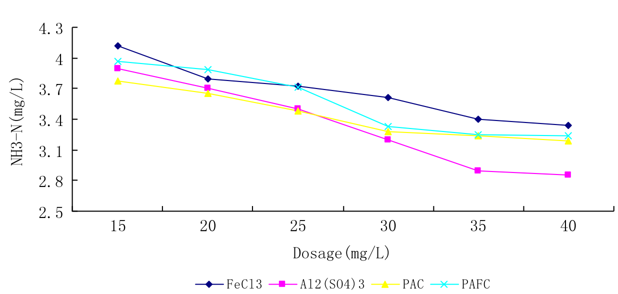


Fig. 3. The $NH_3$-N removal effect with different dosage.

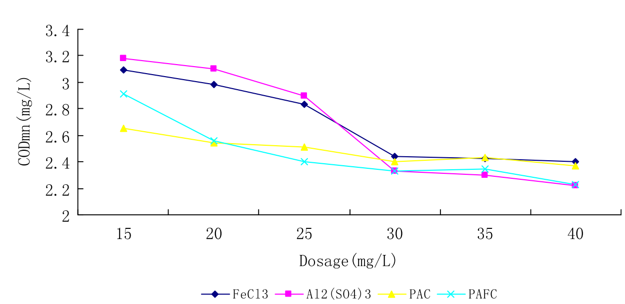


Fig. 4. The $COD_{Mn}$ removal effect with different dosage.

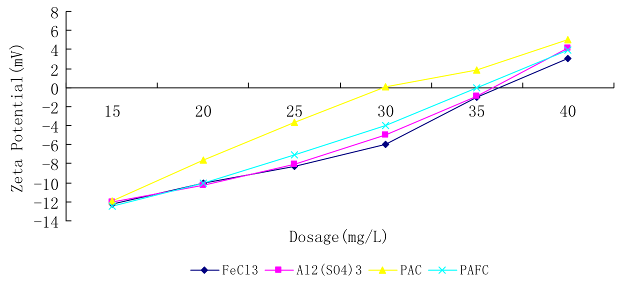


Fig. 5. The removal effect of $\zeta$ potential with different dosage.

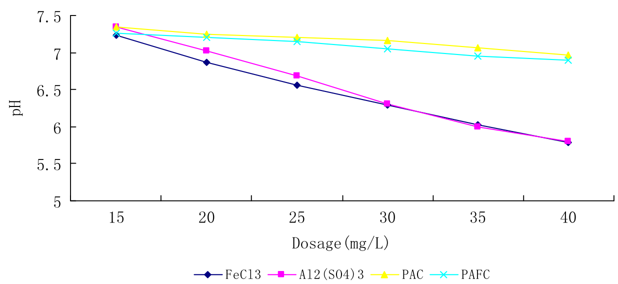


Fig. 6. The removal effect of pH with different dosage.

sions in water. Coagulation mainly depends on compressing electric double layer and reducing the $\zeta$ potential of diffusion layer to achieve the coagulation effect [11]. From Fig. 5, $\zeta$ potential curves increased gradually with the dosage increase of the four coagulants from −15.6 mV of the raw water gradually to about 5 mV. The impact on $\zeta$ potential of the four coagulants was not similar, which was reflected by the slopes of $\zeta$-potential curve. Among the four coagulants, PAC had the highest impact on $\zeta$-potential, followed by PAFC. Zeta ($\zeta$) potential raised rapidly with the PAC dosage increase from −15.6 mV to 4.99 mV, but the optimum $\zeta$ potential was between the dosage of 30∼35 mg/L.

In the first four figures, the PAC reduced the turbidity of raw water to 0.91NTU at the dosage of 30∼35 mg/L, and its removal rates of TOC, ammonia, and $COD_{Mn}$ were all strong. This phenomenon indicated that PAC might have had the effect of coagulation by compressing electric double layer reducing the $\zeta$ potential and adsorbing electric neutralization. Besides, it also had the functions of adsorbing bridge sediments and net rolling-sweeping of hydroxide precipitation, which played a dominant role in its coagulation; but had less effects on the coagulants of $FeCl_3$ and $Al_2(SO_4)_3$.

In Fig. 6, adding of each coagulant resulted in a decrease of pH value with an increasing dosage. The four coagulants caused the pH value to change differently. An increase in the dosage of $FeCl_3$ and $Al_2(SO_4)_3$ may exert apparent influence on the pH value although an increase in the dosage of PAC and PAFC only induced little change of pH value, which was too little to be significant in the experiment. The gradient of curves was large. High dosage made water acidic with pH value up to 5.88 and 5.87 at the dosage of 40 mg/L. Based on this Figure, the dosage of $FeCl_3$ and $Al_2(SO_4)_3$ should be less than 25 mg/L because the pH value of drinking water is generally required to be 7.5∼6.5. Furthermore, the change of $FeCl_3$ was larger than $Al_2(SO_4)_3$ which was consistent with the removal of TOC. There might have been a hydrolysis reaction of the low-molecular weight coagulants, where metal ions and hydroxyl bound and released more protons resulting in higher hydrogen ion concentration, which contributed to the decrease of the pH values.

The two ion flocculants worked better at higher pH values. The pH value in water treatment should be set for optimum flocculation. It will be beneficial to the hydrolysis of flocculants because inorganic ion flocculants can produce hydrogen ion during hydrolysis, while it has less influence on the flocculating effect than ion flocculants when hydrolysis reaction of polymeric coagulants have taken place during preparation stage [12].

The ion flocculants were affected by the pH value in the formation of final hydrolysates. Since iron and aluminum exist mainly in ionic forms in low pH value stage, organic compounds were removed mainly by electrical neutralization, while organic compounds were removed by being trapped with the increase of pH value. Aluminum salt had a better removal effect of organic compounds with a pH value from 5 to 6, whereas, the pH value of 4–5 was required for iron salt. However, polymeric coagulants

Table 5
Result of coagulation of the second raw water in winter

| | Dosage (mg/L) | Turbidity (NTU) | TOC (mg/L) | $NH_3$-N (mg/L) | $COD_{Mn}$ (mg/L) | $UV_{254}$ (Abs.) |
|---|---|---|---|---|---|---|
| $FeCl_3$ | 25 | 0.772 | 1.90 | 0.31 | 1.68 | |
| $Al_2(SO_4)_3$ | 25 | 1.715 | | 0.29 | 1.74 | 0.0171 |
| PAC | 30 | 1.185 | 1.88 | | 1.59 | 0.0141 |
| PAFC | 25 | 1.287 | 1.80 | 0.29 | | 0.0132 |

were affected slightly by the change of pH values [13].

If we want to control the pH value of drinking water, we may have to take into account the different impacts of coagulants on the pH value, select the corresponding coagulants, and then determine the proper dosage of each coagulant for water treatment.

### 3.2. Optimization of coagulant for the second raw water in Ganjiang River in winter

The result of coagulation treatment is shown in Table 5.

As shown in Table 5, the coagulation results varied in water quality. In the second raw water experiment, the removal rate of turbidity of $FeCl_3$ was the best, while $Al_2(SO_4)_3$ was the worst. The macromolecule coagulants had a high removal rate of organic compounds. Besides, the removal trends of every indicator of organic compounds were similar and consistently strong.

## 4. Conclusion

The best dosage of $FeCl_3$, $Al_2(SO_4)_3$, and PAFC was at 25 mg/L and it was at 30 mg/L for PAC. Hydrolyses of $FeCl_3$ and $Al_2(SO_4)_3$ significantly reduced the pH value, while polymers had little effect. The removal effect of ammonia nitrogen by coagulation was not ideal. We therefore needed to consider other methods to reduce ammonia nitrogen. The removal rate of TOC of lower molecular coagulants was higher than that of polymer coagulants for the first raw water, but the removal effect was just opposite for $COD_{Mn}$. Lower molecular coagulants may have a bad removal effect for the reducible organic compounds. Besides, the effect of PAFC was better than PAC because it contained a combined advantage of iron and aluminum chlorohydrate. Finally, for the second raw water of Ganjiang River, every indicator of organic compound had a similar removal trend.

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