Experimental research on the poly-aluminum chloride for treating the Pi River water in winter and summer

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Abstract: In the beaker experiments that the disposal of low turbidity water, we observed the influence of some factors, such as the dosage of poly-aluminum chloride coagulant, the pH value of raw water, in disposing the high natural organic matters of low turbidity water in winter and summer. We discussed the removal of residual aluminum and UV254 in summer. The experimental results show that when the turbidity is less than 10 NTU, the optimum dosage are 14.4 mg.L\(^{-1}\) and 8.2 mg.L\(^{-1}\) respectively in winter and summer. No matter in winter or summer, the effect of pH value on coagulation treatment is very significant, the best pH value is about 8.1. In summer, with the increase of dosage of poly-aluminum chloride, residual aluminum increased slowly after decrease, turbidity and UV254 after precipitation is similar removal trend. Finally, according to the current market price of poly-aluminum chloride economic analysis, daily differences in pharmaceutical costs about 1600 yuan in summer and winter in the second water plant in Lu'an.

1. Introduction
The second water plant undertakes the task of water supply for living and some industrial enterprises in Lu'an. The raw water is from Foziling reservoir, Xianghongdian reservoir, the average turbidity is generally lower than 10 NTU, the organic pollutants is a natural organic matter, including humus, microbial secretions, dissolved plant tissue and animal wastes [1]. At present, the removal of natural organic matter are mainly: enhanced coagulation, granular activated carbon adsorption and membrane filtration, in which the enhanced coagulation is recommended by the U.S. Environmental Protection Agency (USEPA) in water control [2]. Over the years, there is no strict seasonal change in dosage of poly-aluminum chloride in the second water plant in Lu'an. So we investigated the effect of poly-aluminum chloride coagulation on low turbidity and high natural organic matter in winter and summer, which provide scientific basis on the treatment of in raw water for the second water plant in Lu'an.

2. Experimental part

2.1. Raw water quality
The raw water is from the Jiefang South Road Bridge intake, the water quality as shown in table 1.
Table 1. Raw water quality in the river.

|                | winter       | summer      |
|----------------|--------------|-------------|
| temperature (℃)| 2.4~6.4      | 21.2~25.4   |
| pH             | 7.2~8.1      | 7.3~7.8     |
| turbidity (NTU)| 2~5          | 1.3~         |
| UV254 (1/cm)   | 0.015~0.046  | 0.032~0.064 |

2.2. Experimental instruments and reagents

Instruments: T6 new century UV spectrophotometer (Beijing Purkinje General instrument Co.Ltd.); MY3000-6F intelligent coagulation test mixing equipment (Wuhan Mei Yu instrument Co.Ltd.); WGZ-200 turbidity meter (Shanghai Xin Rui Instrument Co.Ltd.); portable pH meter (Zhejiang Li Chen instrument technology Co. Ltd.).

Reagents: poly-aluminum chloride, its performance parameters are shown in table 2\[3\]. Other reagents are analytical pure.

Table 2. Performance parameters of poly-aluminum chloride.

| project poly-aluminum chloride | place of origin | character | poly-aluminum chloride |
|--------------------------------|-----------------|----------|------------------------|
|                                | Gongyi, Henan province, China | solid    |                        |
| alumina (Al₂O₃)/%              | 30              |          |                        |
| iron oxide (Fe₂O₃)/%           | 0               |          |                        |
| salt degree /%                 | 40~90           |          |                        |
| pH(1% aqueous solution)        | 3.5~5.0         |          |                        |

2.3. Experimental method

The coagulation sedimentation process of water plant was simulated by MY3000-6F intelligent coagulation test apparatus. The procedure for coagulation sedimentation test is shown in table 3\[3\].

Table 3. Coagulation test procedures.

| segment number | speed(r.min⁻¹) | time (s) | dosing conditions | velocity gradient (G/s⁻¹) | ∑ GT |
|----------------|----------------|----------|-------------------|---------------------------|------|
| 1              | 300            | 30       | dosing            | 232.2                     | 696  |
| 2              | 150            | 300      | no dosing         | 82.0                      | 3196 |
| 3              | 80             | 600      | no dosing         | 32.0                      | 5096 |
| 4              | 00             | 1200     | no dosing         | 0.0                       | 0    |

3. Test results

3.1. Determine the optimum dosage

The effect of poly-aluminum chloride dosage on treatment is shown in table 4\[3\] and table 5.

Table 4. Effect of poly-aluminum chloride dosage on coagulants in winter.

| raw water quality | the turbidity of the supernatant was measured 35 minutes later (NTU) | poly-aluminum chloride dosage (mg.L⁻¹) |
|-------------------|---------------------------------------------------------------------|----------------------------------------|
| Turbidity (NTU)   | Temperature (℃) | pH | 4 | 8 | 12 | 16 | 20 | 24 |
| 3.20              | 4.4            | 7.6 | 3.30 | 0.54 | 0.24 | 0.39 | 1.13 | 1.56 |
| 3.34              | 5.9            | 7.5 | 2.30 | 0.90 | 0.42 | 0.85 | 1.24 | 1.70 |
| 4.25              | 2.4            | 7.8 | 2.97 | 0.41 | 0.31 | 0.39 | 0.76 | 1.28 |
| 4.74              | 3.8            | 8.0 | 3.34 | 0.46 | 0.28 | 0.36 | 0.78 | 1.18 |
Table 5. Effect of poly-aluminum chloride dosing on coagulants in summer.

| raw water quality | the turbidity of the supernatant was measured 20 minutes later (NTU) |
|-------------------|-------------------------------------------------|
| turbidity (NTU)   | temperature (°C) | pH | poly-aluminum chloride dosage (mg.L⁻¹) |
|                   |                   |    | 5     | 7     | 9     | 10    | 11    | 13    |
| 2.84              | 25.0              | 7.2 | 1.73  | 1.34  | 1.49  | 1.41  | 1.53  | 1.86  |
| 3.99              | 24.4              | 6.9 | 3.80  | 3.15  | 3.03  | 2.35  | 2.64  | 2.77  |
| 7.78              | 22.0              | 7.6 | 3.38  | 1.83  | 1.64  | 1.07  | 1.55  | 1.83  |
| 7.98              | 24.1              | 7.5 | 1.76  | 1.32  | 1.08  | 1.17  | 1.23  | 1.46  |

From Table 4 and 5 can be seen that coagulation effect by only adding poly-aluminum chloride in winter and summer are very good, but in winter, the dosage of the coagulant dosage is more than in summer, when the turbidity of raw water is less than 1.5NTU, dosage is about 8mg.L⁻¹ in winter, while in summer the dosage is 7mg.L⁻¹, and the sediment time in winter increase at least 10 minutes or more than in summer, when more than 7.5 pH , precipitation effect 30 minutes later is the best in winter, in summer 20 minutes will be able to meet the requirements. This is because in winter the particle concentration is low, and there is a strong dynamic stability and cohesion stability, often with a small colloidal dispersion dissolved in water, the collision probability is very small [4]. In addition, the zeta potential of the colloidal particles in water is higher, the water viscosity coefficient increases, the particle movement kinetic energy is small, the particle motion is not active, the agglomeration effect is not good; and the low temperature influences the coagulation rate of the coagulant, so the low temperature and low turbidity water formation of flocs fine, less, light, difficult to precipitate [5]. Repeated coagulation beaker experiment, and finally the winter and summer two times the best amount of aluminum chloride polymerization, as shown in figure 1 [3] and figure 2 shows.

Figure 1. Determination of the optimal dosage of poly-aluminum chloride in winter

Figure 2. Determination of the optimal dosage of poly-aluminum chloride in summer

It can be seen from figure 1 and figure 2 that the optimum dosage of poly-aluminum chloride in winter is 14.4 mg.L⁻¹, and the turbidity of supernatant is the smallest and the minimum can reach 0.7NTU. The best dosage of poly-aluminum chloride is 8.2 mg.L⁻¹ in summer, the minimum can reach 0.8NTU.

3.2. Determination of optimum pH value

The pH value of the raw water was adjusted with hydrochloric acid and sodium hydroxide. The optimum dosage of poly-aluminum chloride was 14.4 mg.L⁻¹ in winter and the optimum was 8.2 mg.L⁻¹ in summer. The experimental results are shown in table 6 [3] and table 7.
Table 6. Effect of pH value on poly-aluminum chloride coagulation in winter.

| raw water quality | pH | supernatant turbidity (NTU) | raw water quality | pH | supernatant turbidity (NTU) |
|------------------|----|----------------------------|------------------|----|----------------------------|
| turbidity (NTU) | temperature (℃) | pH | turbidity (NTU) | temperature (℃) | pH | turbidity (NTU) |
| 3.2 | 5.36 |
| 3.6 | 5.18 |
| 7.6 | 1.46 |
| 8.2 | 0.18 |
| 10.1 | 0.24 |
| 10.8 | 0.40 |
| 3.86 | 4.4 | 8.1 |
| 4.64 | 6.4 | 7.8 |
| 3.8 | 5.24 |
| 6.3 | 4.40 |
| 6.8 | 2.15 |
| 8.9 | 0.44 |
| 9.7 | 0.50 |
| 10.1 | 0.64 |

Table 7. Effect of pH value on poly-aluminum chloride coagulation in summer.

| raw water quality | pH | supernatant turbidity (NTU) | raw water quality | pH | supernatant turbidity (NTU) |
|------------------|----|----------------------------|------------------|----|----------------------------|
| turbidity (NTU) | temperature (℃) | pH | turbidity (NTU) | temperature (℃) | pH | turbidity (NTU) |
| 2.17 | 21.9 | 6.9 |
| 6.4 | 1.87 |
| 6.7 | 1.62 |
| 6.9 | 1.18 |
| 7.2 | 1.15 |
| 7.5 | 1.08 |
| 8.4 | 1.23 |
| 8.05 | 22.9 | 7.7 |
| 6.4 | 4.21 |
| 7.1 | 2.51 |
| 7.7 | 1.66 |
| 7.9 | 0.87 |
| 8.1 | 0.60 |
| 8.7 | 0.71 |

| 5.37 | 24.6 | 7.5 |
| 4.1 | 5.54 |
| 4.3 | 5.48 |
| 7.5 | 0.86 |
| 8.1 | 0.60 |
| 8.6 | 0.74 |
| 9.0 | 1.14 |
| 8.24 | 22.3 | 7.4 |
| 6.0 | 4.88 |
| 6.9 | 4.67 |
| 7.4 | 1.69 |
| 7.7 | 1.21 |
| 8.1 | 0.96 |
| 8.8 | 1.41 |

It can be seen that the effect of water pH value on the flocculation effect is very significant in winter and summer. When the pH value is less than 6, the treatment effect is not good. With the decrease of the pH value, the turbidity increased significantly, while the removal rate decreased, the supernatant color more, and it is difficult to hierarchical; when the pH value is 6 ~ 9, coagulation treatment effect is good, the removal rate of turbidity increases. This is because aluminum hydroxide is an amphoteric compound, when the raw water tends to be neutral, it is mainly in the form of precipitation [6], further analysis showed that when pH=8.1, coagulation effect is the best, so the optimum pH value was about 8.1.

3.3. The change of residual aluminum after precipitation of poly-aluminum chloride

Some studies have shown that the use of aluminum salt coagulant is the main reason for the increase of aluminum content in drinking water [7]. At present, the harm of residual aluminum in drinking water to ecosystem and human body has aroused great attention [8,9]. The provisions in drinking water in
China aluminum residues must be less than 0.2mg.L\(^{-1}\). As can be seen from fig. 3, With the increase of the amount of poly-aluminum chloride, the residual amount of aluminum decreased first and then increased slowly. When the poly-aluminum chloride dose was 8.2 mg.L\(^{-1}\), the residual amount of aluminum was 0.094mg.L\(^{-1}\), which was lower than the required requirement. It is shown that poly-aluminum chloride is an inorganic macromolecule coagulant, and it can be hydrolyzed and precipitated even if the dosage of poly-aluminum chloride is less, and the residual aluminum concentration decreases with the removal of turbidity. When the dosage is high, the untreated precipitate coagulant content increased, making the remaining aluminum was on the rise\(^{[10]}\).

3.4. UV254 removal
UV254 reflects the presence of naturally occurring humus macromolecules and the amount of aromatic compounds containing C = C double bonds and C = O double bonds in water\(^{[11]}\), and these natural macromolecules are the precursor to the production of disinfection by-products in water substance. From figure 4 shows that with the poly-aluminum chloride dose increases, after precipitation turbidity and UV254 removal rate are increasing, they have a similar removal trend, when the dosage is greater than 9mg.L\(^{-1}\), turbidity and UV254 removal rate increased slowly. When the poly-aluminum chloride dose is 8.2mg.L\(^{-1}\), UV254 removal rate is 50% or more, turbidity removal rate is 85% or more. The experimental results show that the coagulation and precipitation of poly-aluminum chloride has a good effect on the removal of NOM, especially for aromatic organic substances, because the coagulation process relies on positively charged hydrolyzate through electrical neutralization and adsorption to remove organic matter. This type of organic matter is characterized by a functional group containing negatively charged groups such as carboxylic acid groups and hydroxyl groups, so coagulation is effective in removing such organic compounds\(^{[12,13]}\).

4. Analysis of economic benefit
It is understood that the second water plant in Lu'an city currently added dosing of poly-aluminum chloride mainly rely on experience, there is no strict seasonal change in dosage, and sometimes in order to precipitate the separation of relatively large flocs, usually used method is Increase the dosage of coagulant to meet the water quality requirements of the factory, but excessive coagulants will inevitably lead to increased processing costs and sludge\(^{[14,15]}\). This paper mainly analyzes the cost of pharmaceuticals, according to the poly-aluminum chloride current market price for a simple analysis as shown in table 8.

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Figure 3. Effect of poly-aluminum chloride dosage on the turbidity, aluminum residual change efficiency

Figure 4. Effect of poly-aluminum chloride dosage on the turbidity, UV254 removal efficiency
Table 8. The cost of the agent when the coagulant is added separately in winter and summer.

|          | Winter |          |          | Summer |          |          |
|----------|--------|----------|----------|--------|----------|----------|
| optimum dosage (mg/L) | unit water requirement (mg/L) | current price of Pharmacy (yuan/ton) | unit water agent fee (m3/yuan) | optimum dosage (mg/L) | unit water requirement (mg/L) | current price of Pharmacy (yuan/ton) |
| 14.4     | 14.4   | 2400     | 0.035    | 8.1    | 8.1      | 2400     | 0.019 |

As shown in table 8, the poly-aluminum chloride was added separately, and the unit cost of the unit water body in winter was 0.016 yuan less than that in summer unit. If it is divided into seasons to add poly-aluminum chloride in the second water plant, according to the current 100 thousand tons per day of water supply, the summer and winter each day pharmaceutical cost difference is about 1600 yuan, the economic benefit is obvious.

5. Conclusion
(1) The poly-aluminum chloride dosage in summer can be reduced by 30% ~ 40% compared with winter, which can greatly reduce the cost of water in the water plant. In summer, the coagulation effect of poly-aluminum chloride is better than that of winter. To achieve the same turbidity removal effect, take time to reduce at least 10 minutes or more. In winter, the best dosage of poly-aluminum chloride were 14.4mg.L⁻¹ and in summer were 8.2 mg.L⁻¹.

(2) The effect of pH value on the coagulation effect is very significant. When the pH value of the raw water is acidic or acidic, the coagulation treatment effect is very poor. When the pH value of the raw water is neutral or alkaline, the mixing of poly-aluminum chloride coagulation treatment is better, and the best pH value is about 8.1.

(3) The NOM in the pihe river is mainly aromatic organic matter and the main organic matter removed during the deposition process. At the optimum poly-aluminum chloride dose, the residual aluminum content in drinking water is as low as 0.094 mg .L⁻¹. Through this study, it can be seen that poly-aluminum chloride is an effective treatment of low turbidity, high NOM inorganic polymer coagulant.

(4) If poly-aluminum chloride dosage varies with season, the unit water costs is difference of 0.016 yuan in summer and winter in the second water plant. According to the current 100,000 tons per day water supply, daily differences in pharmaceutical costs about 1600 yuan in summer and winter.

In summary, in winter and summer only adding poly-aluminum chloride on the pi river water coagulation treatment, the effect is more significant. The experimental results provide scientific reference for the treatment of low turbidity and high natural organic matter raw water in the second water plant and similar water plant.

Acknowledgement
This research was funded by the natural science research project of West Anhui University . No. WXZR201617.

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