Study on the Coagulation Process of Water Treatment under Two Water Source Conditions

Pan Yu¹, Huasheng Wang²

¹ School of Architectural and Surveying & Mapping Engineering, Jiangxi University of Science and Technology, Ganzhou, Jiangxi, 341000, China
² Jiangxi Provincial Key Laboratory of Environmental Geotechnology and Engineering Disaster Control, Ganzhou, Jiangxi, 341000, China

*Corresponding author’s e-mail: precious6y@outlook.com

Abstract. The source water of Ganzhou Sanshui Plant mixes the water of Zhangjiang River and Fengshan Reservoir to change the water quality of the source water, which makes the water treatment more difficult and the sedimentation tank runs away. In order to ensure the water quality of the factory water in the case of changes in water quality, the coagulation effect of three common coagulants was studied by a beaker test, and pre-oxidation was carried out using potassium permanganate. The results show that the organic matter in the source water is mainly humic acid. With the increase of coagulant dosage, the residual turbidity showed a gradual decline. When the dosage exceeded 40 mg/L, the system showed some degree of turbidity. With the increase of potassium permanganate dosage, the turbidity removal rate showed a gradual increase trend. When the dosage reached 0.7 mg/L, the continuous increase of KMnO₄ dosage did not significantly improve the turbidity removal. Under the condition that the coagulation effect is optimal, 0.5 mg/L potassium permanganate can significantly improve the sedimentation of flocs and reduce the turbidity of water after sinking.

1. Introduction
Coagulation is one of the most common and effective operating units in water treatment technology. Good coagulation effect is of great significance for ensuring the water quality of the water purification plant. The third water plant in Ganzhou City is located in Shashi Town, Ganzhou City. The daily water production is about 100,000 tons, and the water source is taken from Zhangjiang. In order to ensure the safety of residents' water, the water purification plant implemented an expansion water source plan. About two-thirds of the water was taken from Zhangjiang, and one-third of the water was taken from Fengshan Reservoir. Due to the different water quality of the two water sources, the coagulation process of the water plant is seriously affected, the water treatment is more difficult, the sedimentation efficiency is low, the water turbidity is high after the sedimentation, and the filter tank faces enormous pressure.

Previous studies have shown that humic substances (HS) in water has an important impact on the coagulation process. HS is derived from the microbial biochemical action of plant or animal residues and accounts for more than 50% of dissolved organic matter (DOM) in surface water [1]. The main components of HS are weakly acidic aliphatics and aromatic compounds containing functional groups (such as -COOH and phenol-OH groups), also known as humic acid (HA) [2]. Many drinking water quality issues are related to HA, Including undesirable color, odors and tastes. Studies have indicated that HA is the main precursor of disinfection-by-products (DPBs) [3]. Under the action of strong
oxidizing agent chlorine, the structure of HA is destroyed, degraded into low molecular weight compounds, and further reacts with chlorine to form a series of carcinogenic halides [4]. In addition, when a large amount of HA is present in the water, the negative charge on the surface of the colloid will increase, and the stability will be enhanced, resulting in steric hindrance between the inorganic colloidal particles or repulsion of the electric double layer, thereby keeping it dispersed and difficult to coalesce [5].

In order to improve the coagulation effect, the raw water may be pretreated by pre-oxidation or activated carbon adsorption. Pre-oxidation is currently the most commonly used method for removing organic matter from raw water. Various oxidants including ozone [6], chlorine dioxide [7] and potassium permanganate [8] can be used for pre-oxidation. Compared with other pre-oxidation methods, potassium permanganate pre-oxidation can largely remove algae, odor and the like in raw water [9]. In addition, since HS contains a large amount of aromatic hydrocarbons and aliphatic residues, it is easily aggregated and precipitated by charge neutralization, and manganese dioxide formed by potassium permanganate reduction has a certain nucleation effect, which can improve flocculation and sedimentation effects, and its strong oxidizing properties make the colloidal particles in the water easy to destabilize, and the formation of larger flocs helps to improve flocculation and filtration [10].

The purpose of this study was to ensure the quality of the effluent in the event of changes in water quality. The coagulation effect of three common coagulants was compared by beaker test, and pre-oxidation was carried out with potassium permanganate. The supernatant under different conditions was examined to determine the optimal coagulation conditions.

2. Materials and Methods

2.1. Sample collection
Water samples from 2 sources were collected, including surface water (water source A) and reservoir (water source B). The concentrations of turbidity, pH, DO, and COD were measured. All the samples were filtered through 0.45 μm membranes to remove any particulates, the concentrations of total organic carbon, and the UV absorbance at 254 nm (UV$_{254}$) were measured. The water properties are summarized in Table 1.

| Water sample  | Temperature °C | Turbidity NTU | PH   | DO mg/L | COD mg/L | UV$_{254}$ cm$^{-1}$ | TOC mg/L |
|--------------|----------------|---------------|------|---------|----------|---------------------|----------|
| Water source A | 19.0-23.0       | 7.0-10.8       | 7.10-7.40 | 3.12-3.96 | 20.10-23.13 | 0.120-0.144       | 14.92-17.62 |
| Water source B | 18.0-25.0       | 15.1-18.5      | 7.13-7.43 | 3.20-4.12 | 41.10-42.50 | 0.140-0.185       | 17.85-28.67 |

2.2. Pre-oxidation experiments
Analytical grade potassium permanganate (KMnO$_4$) was used for the pre-oxidation experiment. The pH of the water sample was adjusted with 0.1 M hydrochloric acid (HCl) or sodium hydroxide (NaOH). Each type of water sample was oxidized with 0.1, 0.3, 0.5, 0.7, 1.0, and 1.5 mg/L KMnO$_4$, respectively. After pre-oxidation for 10 min, coagulant was added for coagulation, and after the coagulation was completed, the supernatant was taken for measurement. This is also to monitor the side effects of oxidation (color and turbidity levels brought about by Mn$^{2+}$). In addition, the time needed for the oxidation was determined by measuring the variation of UV absorbance at 254 nm.

2.3. Coagulation tests
Three commonly used industrial grade coagulants (purity of more than 98%), coagulant A: polyaluminum chloride, coagulant B: polyaluminum sulfate and coagulant C: polymeric aluminum
iron. 1 g of a coagulant was added to 100 ml of pure water to prepare a 1% concentration as a stock solution. The coagulation test was carried out on a ZR4-6 automatic control six-mixer. Take 500 mL of water sample and stir rapidly at 300 r/min for 0.5 min. After mixing thoroughly, add the required coagulant. Then adjust the speed to a medium speed of 200 r / min for thorough mixing. After running at medium speed for 1.5 min, it was quickly adjusted to a low speed of 80 r / min for 10 min to allow the flocs to grow sufficiently. After the coagulation process was finished, after standing for 30 min, the water sample at 2.0 cm below the liquid surface was taken to determine the turbidity of the supernatant.

2.4. Analytical methods
The pH of the water sample was directly measured using a S320 pH meter (Sartorius Scientific Instruments Co., Ltd., Beijing), and the turbidity was directly measured using a 1900C portable turbidimeter (Shanghai Shilu Instrument Co., Ltd.). COD adopts national standard fast closed digestion method. After coagulation, the water sample was filtered through a 0.45 micron microporous membrane and the TOC and TP were measured using a multi N/C® 3100 total organic carbon analyzer (Analytik Jena AG, Germany). The UV absorbance at 254 nm (UV254), after experiments were measured with a UV-1800 spectrophotometer (Persee General Analysis Instrument Co., Ltd., Beijing) with 1 cm quartz cells. All measurements were conducted in triplicate with measurement errors less than 3%.

3. Results and discussion
3.1. Sample water characteristics
The water characteristics were presented in Table 1. The turbidity of the reservoir is significantly higher than the surface turbidity, up to 18.5 NTU, which may be related to geographical location and rainfall. In the temperature, pH and DO indicators, the water quality of the two sources is not much different. However, the COD of reservoir water is an order of magnitude higher than surface water, reaching 42.5 mg / L; while the highest UV254 and TOC are 0.185 cm⁻¹ and 28.67 mg / L, respectively, which reflect the organic content.

3.2. Effect of different coagulant dosage on coagulation performances

![Figure 1. Effect of dosage of coagulant on turbidity and UV254](image)

As can be seen from Figure 1, as the coagulant dosage increases, the supernatant turbidity decreases. However, when the coagulant dosage exceeds 30 mg/l, turbidity occurs. When the coagulant concentration reaches a limit value, the coagulation effect is the best. When the coagulant concentration exceeds the limit value, the coagulation effect decreases. UV254 also shows the same trend as turbidity, but its change is more stable and increases. The large coagulant dose not have much effect on it, and the residual organic concentration is still high. All three coagulants are optimally
treated at 30 mg/L. Comparing the experimental results of the three coagulants, it is known that the treatment effect of polyaluminum chloride is the best. At 30 mg/L, the residual turbidity of Zhangjiang water and reservoir water is 1.18 NTU and 1.65 NTU, respectively, to achieve the best treatment effect. In combination with cost considerations, it is more appropriate to use 30 mg/L of polyaluminum chloride as a coagulant.

3.3. Effect of potassium permanganate dosage on coagulation performances

The pH of the water sample was adjusted to 7.0, and potassium permanganate at a concentration of 0.1, 0.3, 0.5, 0.7, 1.0, and 1.5 mg/L was sufficiently oxidized, and then 30 mg/L of polyaluminum chloride was added for the coagulation experiment. Figure 2 reflects the effect of coagulation of the water sample after oxidation. With the increase of potassium permanganate dosage, the coagulation effect also gradually increased, and the residual turbidity content gradually decreased. When the dosage of potassium permanganate was 0.5 mg/L, the residual turbidity of reservoir water and mixed water were 1.06 NTU and 0.83 NTU, respectively, and the remaining UV$_{254}$ were 0.060 and 0.063, respectively, and the remaining COD were 19.36 and 15.56, respectively. Comparing the experimental data of reservoir water and mixed water, it is found that when the dosage of potassium permanganate is 0.5mg/L, the turbidity removal rate of mixed water is 93%, and the turbidity removal rate of reservoir water is 86%. The turbidity removal rate is high. The reason for the analysis is that the reservoir water contains a large amount of organic matter, and a large amount of potassium permanganate and coagulant are consumed during the coagulation process, so that the turbidity removal rate of the reservoir water is lower than that of the Zhangjiang water. Considering the treatment effect and cost considerations, it is suitable to determine the dosage of potassium permanganate at 0.5 mg/L.

![Figure 2. Effect of KMnO$_4$ dosage on coagulation performances](image-url)
3.4. Effect of pH on coagulation performances

It can be seen from the experimental results that pH has a great influence on the experiment, and good experimental results can be obtained under acidic conditions. When the pH was 6, the residual turbidity of the mixed water and the reservoir water were 0.62 NTU and 0.75 NTU, respectively, and the residual turbidity was 0.73 NTU and 0.95 NTU at pH 7, respectively, and the residual turbidity was 0.91 NTU and 1.12 NTU at pH 8. Since potassium permanganate is acidic, its oxidation is favored under acidic conditions. When the pH of the environment changes to alkaline, potassium permanganate neutralizes the acid ions in the water, accelerates decomposition and weakens the oxidation [11]. At the same time, the turbidity removal rate of the mixed water can reach 80%, while the turbidity removal rate of the reservoir water is only 65%. The reason for the analysis is that the reservoir water contains a large amount of organic matter, which consumes more potassium permanganate, so the coagulation effect is poor, and the turbidity removal rate is not high.

Figure 3. Effects of solution pH on coagulation performances

3.5. Pre-oxidation effect of potassium permanganate under optimal dosage

It can be found from Figure 1 that the coagulation effects of the three coagulants are better at the dosages of 25, 30, and 35 mg / L. To this end, potassium permanganate pre-oxidation test (0.5 mg / L) was carried out under three doses to investigate the improvement of coagulation effect of potassium permanganate pre-oxidation. The results are shown in Table 2.

Table 2. Effect of KMnO4 on coagulation performances

| Project                | Coagulant A/mg*L⁻¹ | Coagulant B/mg*L⁻¹ | Coagulant C/mg*L⁻¹ |
|------------------------|--------------------|--------------------|--------------------|
|                        | 25                 | 30                 | 35                 | 25     | 30     | 35     | 25     | 30     | 35     |
| No pre-oxidation        |                    |                    |                    |        |        |        |        |        |        |
| Turbidity/NTU           | 1.32               | 1.16               | 1.45               | 1.3    | 1.1    | 1.3    | 2.1    | 1.8    | 2.0    |
| UV254/cm⁻¹              | 0.065              | 0.051              | 0.055              | 0.067  | 0.060  | 0.066  | 0.070  | 0.060  | 0.069  |
| Pre-oxidation           |                    |                    |                    |        |        |        |        |        |        |
| Turbidity/NTU           | 0.76               | 0.65               | 0.81               | 1.1    | 0.8    | 1.0    | 1.2    | 0.9    | 1.4    |
| UV254/cm⁻¹              | 0.046              | 0.036              | 0.050              | 0.050  | 0.043  | 0.051  | 0.058  | 0.042  | 0.052  |

According to Table 2, the addition of 0.5 mg / L potassium permanganate can significantly reduce the turbidity of water samples and UV254. The reason is that the organic matter in the natural water body has a strong protective effect on the colloid, and the difficulty of compressing the electric double layer by the coagulant is increased, resulting in poor coagulation effect when the coagulant is separately added. KMnO4 can effectively oxidize the organic layer covering the surface of the colloid, thereby improving the coagulation effect [12]. At the same time, the manganese dioxide formed by the reduction of potassium permanganate has a large specific surface area and a large number of active adsorption sites, which can form dense flocs with hydrated MnO2 as the core and have a certain
"coagulation" effect. The flocculation and precipitation effects can be enhanced by adsorption and catalysis [13, 14].

4. Conclusions
This fundamental study investigated the effects of different water quality conditions on the coagulation effect of water purification plant and the subsequent analysis of the oxidation process of KMnO4. The most effective coagulant was polyaluminium chloride, and it was observed that as the coagulant dosage increased, the residual turbidity showed a gradual decline. KMnO4 has proven to be a potent oxidant for DOM in water. When the operation optimization methods such as KMnO4 dosage change and pH adjustment were carried out, it was found that when the dosage was 0.5 mg / L, the treatment effect was better under acidic conditions. This knowledge is critical to the construction or expansion of water purification plants and provides an adaptive view of ensuring safe water supply when water sources change.

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