The Investigation of Oxidation Flocculation Characteristics of Ferrate Solution

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Abstract. The fresh ferrate solution was prepared by in situ electrolysis method and directly added into the simulated surface micro-polluted water to proceed purification and pretreatment process. To explore the influence on the dosage of ferrate and pH of raw water, the simulated water sample was treated by single factor change coagulation experiment. Combining with turbidity, ammonia nitrogen, humic acid removal rate as the judgment index, and the fractal dimension of floc was calculated by using the platform of floc morphology analysis, the optimal dosage of the ferrate solution and reaction pH range were confirmed. This work revealed profoundly the correlation of turbidity, ammonia nitrogen, humic acid removal rate and flocculation fractal dimension.

1. Introduction
Ferrate is a kind of hexavalent iron compound, which possesses of strong oxidizing properties and has important application prospect in water treatment, oxidative synthesis and electrode materials, etc. [1, 2]. Ferrate possesses of high selectivity for the oxidation degradation of many organic substances when it is used as oxidant. There is no secondary pollution to the environment or the toxic and side effects caused by ferrate itself and the corresponding reduction products, it exhibits the unique environmentally friendly properties [1]. Therefore, ferrate is an ideal safety and efficiency green oxidant for water purification. When ferrate is applied for sewage treatment and water purifying, it possesses of many advantages, such as rapid and efficient, good oxidative decontamination effect, outstanding coagulation effect, excellent sterilization and disinfection effect, high efficiency deodorization function [3]. It will not produce any trivial substance of the treated water body that is harmful to human health, and has no obvious secondary pollution to the water resources environment. It is especially suitable for the comprehensive treatment of micro-polluted surface water and the use of pre-oxidation as well as coagulation, which has exhibited extremely broad research and development prospects in the wastewater purification process.

However, because of the inferior stability and inconvenient in storage, ferrate is always difficult to be fully recognized in the field of water treatment. Therefore, the fresh ferrate solution is prepared by in situ electrolysis method in this work, which is directly added into simulated surface micro-polluted water to flocculate the inorganic impurities and oxidize organic pollutants is a quite simple and effective way. The liquid ferrate synthesized by in suit electrolysis can be directly and continuously applied to supply wastewater treatment, avoiding the complicated purification process of ferrate and the storage problems caused by its own instability [4]. Thus the in suit electrolysis method is an effective measure to give full play to the oxidation and flocculation of ferrate with a broad market prospect.
2. Experimental Section

2.1. Experimental Reagents
Kaolin, humic acid (HA), NH₄Cl, KI, HgI₂, NaKC₈H₄O₆•4H₂O, NaOH and HCl were purchased in analytical grade from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China), and used as received without purification.

2.2. Experimental Instruments
Floc morphology analysis platform, flocculation stirrer, UV-visible spectrophotometer, turbidity analyzer, pH meter, electronic balance and electric mixer.

3. Experimental Design Scheme

3.1. Coagulation Experiment with a Single Change Factor of Ferrate Solution Dosage
The simulated water sample was coagulated by the dosage of ferrate solution as a single variation factor, and the residual content of turbidity, HA and ammonia nitrogen in the supernatant after flocculation precipitation were determined to obtain the removal efficiency, respectively. Thereby the optimum dosage of ferrate solution was obtained, and the oxidation flocculation effect was analyzed. The hydraulic condition was divided into two-stage stirring: first stage, stirring speed of 200 r/min and stirring for 1 min; second stage, stirring speed of 60 r/min and stirring for 5 min. After finished the slow stirring, take a small amount of flocs from the bottom of the beaker and placed on the glass slides, then the images of flocs were captured by image capture device. Finally, utilizing the floc shape analysis platform to analyze and calculate the fractal dimension of flocs, obtaining the fractal dimension of flocs. The correlations between fractal dimension of flocs and turbidity, removal efficiency of humic acid, ammonia nitrogen as well as the addition amount of ferrate solution were obtained.

3.2. Coagulation Experiment with the pH Value of Water as a Single Variation Factor
Under the optimal dosage of ferrate solution and the same hydraulic conditions, the coagulation experiment was carried out with the pH value of raw water as a single variation factor. The effect of raw water pH value on the oxidation flocculation effect of ferrate solution was investigated. According to the chemical reaction progress between impurities in the raw water and ferrate under different pH conditions, determining the effect of ferrate on the oxidizing ability of organic and inorganic pollutants as well as the effect of hydrolysate on the flocculation of suspended solid particles. From the perspective of reaction kinetics, the whole coagulation process was further explored to confirm the optimum pH of raw water. The flocculation morphology analysis platform was used to analyze and calculate the fractal dimension of flocs, thus the correlation between the fractal dimension of flocs and turbidity, humic acid, ammonia nitrogen removal efficiency as well as the pH value of raw water can be obtained.

4. Results and Discussion

4.1. The Dosage of Ferrate Solution on the Effect of Oxidation Flocculation
The simulated water sample was prepared with the turbidity of 100 NTU, the concentration of ammonia nitrogen was 5 mg/L and the concentration of HA was 10 mg/L. Adjusting the pH to 7.0, the initial concentration of ferrate solution prepared by in situ electrolysis method was 0.027 mol/L, changing the dosage of ferrate solution as a single factor and starting the beaker coagulation experiment. The effect of removal rate between ferrate solution dosage and turbidity, ammonia nitrogen and HA was shown in figure 1.
It can be seen that when the dosage of the ferrate solution was in the range of 0.5 mL/L to 1.5 mL/L, the turbidity removal rate rapidly increased as the dosage enhanced. When the dosage was 1.5 mL/L, the removal of turbidity was the highest, and the removal rate was as high as 92.8%. Then the turbidity removal rate decreases as the dosage was enhanced. This was mainly due to the difference in the mechanism of coagulation caused by the dosage of ferrate solutions during the coagulation process. Under low dosage of ferrate solution, different valence of iron ions generated by the spontaneous decomposition of ferrate in water would rapidly hydrolyze to form varieties of cation forms, which could adsorb the negative charge of the neutralized colloid. Eventually, resulting the reduced of charge on the surface of colloid and occurring the destabilization process. During this time, the electrical neutralization was the most likely mechanism of coagulation. As the dosage of ferrate solution enhanced, the suspended solid particles in the water could be wrapped inside the precipitate of Fe(OH)₃ colloid. At this time, the sweeping and flocculation process occurred and causing the turbidity removal rate greatly increased. When the dosage of ferrate solution reached up to a certain value, the turbidity removal rate achieved the highest peak. However, when continuously increased the ferrate dosage, the previously formed flocs might be re-established as stable colloidal particles and forming a re-stable state, thereby causing the turbidity removal rate reduced.

The removal rate of ammonia nitrogen increased with the enhancing of ferrate solution dosage, and the removal rate ranged from 23.6% to 60.4%. The strong oxidizing property of ferrate caused a part of NH4+ oxidizing and forming NO3-N, but no NO2-N was formed. And the rest of NH4+ could be adsorbed and charged neutrality by colloidal Fe(OH)₃ and Fe3+, which were formed by the decomposition of ferrate. At the same time, Fe(OH)₃ formed bridges among the colloidal impurity particles, which was then separated by flocculation and sedimentation, thereby effectively removing the ammonia nitrogen in water.

When the dosage of ferrate was between 0.5 mL/L and 2.0 mL/L, the removal rate of HA showed a sharp increasing tendency with the enhancing of ferrate dosage. When the dosage was 2.0 mL/L, the maximum removal rate of HA reached up to 70.6%, then the removal rate showed a slight decrease. When the ferrate solution was added into water, it would spontaneously decompose to Fe3+ and forming Fe(OH)₃ colloid finally. Since the Fe(OH)₃ precipitate was flocculated in the aqueous solution, which possessed of a relatively large specific surface area and the unique colloidal interface chemistry, making it extremely excellent in adsorption and decontamination. In addition, Fe(OH)₃ was formed during the coagulation process, and the pollutants in water can be effectively removed by its net-sweeping and co-precipitation functions. When the dosage of ferrate was lower, the
iron ions presented could complex with HA to form an insoluble colloidal complex such as iron humate [10]. With the enhancing of ferrate dosage, on the one hand, the iron ion reacted with HA and performed co-precipitation reaction. On the other hand, the positively charged hydrolyzate of iron ions could be electrically neutralized with the surface of negatively charged colloidal particles and forming the destabilization state. At the same time, the adsorption process would further destabilize the colloid which was stable. However, when the dosage of ferrate increased continuously, as most of HA in water had already been removed, the excess charge caused colloidal particles which have already been destabilized occurring re-stabilize phenomenon and reducing the removal rate of HA.

The computational fractal dimension on the ferrate solution dosage of 0.5 mL/L, 1.0 mL/L, 1.5 mL/L, 2.0 mL/L, 2.5 mL/L were Dfa=1.0529, Dfb=1.3287, Dfc=1.7824, Dfd=1.6190, Dfe=1.4337, respectively. The relationship between the dosage of ferrate solution and the fractal dimension of flocs was shown in figure 2. It can be seen from the comparison of figures 1 and 2 that the fractal dimension of flocs varied with the dosage of ferrate, and always related to the change of turbidity, ammonia nitrogen and HA removal rate. When the dosage of ferrate solution was in the range of 0.5 mL/L to 1.5 mL/L, the fractal dimension of flocs gradually increased with the enhancing of dosage. When the dosage was 1.5 mL/L, the fractal dimension reached up the maximum value and the flocs formed a relatively dense structure. When the ferrate dosage was between 1.5 mL/L and 2.5 mL/L, the fractal dimension of flocs began to decrease greatly with the further increasing of dosage. According to figure 2, the morphological structure of flocs experienced a process from densification to loosening with the change of ferrate solution dosage. Therefore, the optimum dosage of ferrate solution (the initial preparation concentration was 0.027 mol/L) can be determined to be 1.5 mL/L which was added into the simulated surface micro-polluted water to proceed purification and pretreatment process, and the corresponding fractal dimension of flocs was determined to be 1.7824.

![Figure 2](image)

Figure 2. Relationship between the dosage of ferrate solution and the fractal dimension of floc.

4.2. Effect of pH Value about Raw Water on the Oxidation Flocculation of Ferrate Solution

The simulated water sample with the turbidity of 100 NTU, the concentration of ammonia nitrogen was 5 mg/L and the concentration of HA was 10 mg/L. Based on the optimum dosage of ferrate solution, changing the pH of raw water to conduct the beaker coagulation experiment. The effect of raw water pH on the removal of turbidity, ammonia nitrogen and HA by ferrate solution was shown in figure 3.
Figure 3. Effect of pH value about raw water on the removal of turbidity, ammonia nitrogen and HA by ferrate solution.

It can be seen from figure 3 that when the pH value was between 3 and 5, the turbidity removal rate gradually decreased with the increase of pH value. However, when the pH value was in the range of 5 to 9, the turbidity removal rate increased with pH value. When the pH value continued to rise and reached up to 11, the turbidity removal rate tended to be stable and with only a slight fluctuation. The change regularity of turbidity removal rate with pH value may be closely related to the form of iron ions ionized by ferrate ions under different pH values and the charge states. The optimum pH value for turbidity removal of ferrate was 9, which could achieve the best flocculation effect.

When the pH value was in the range of 3 to 5, the removal rate of ammonia nitrogen by ferrate solution was inferior. And the ammonia nitrogen removal rate was only maintained at about 30%. In addition, the ammonia nitrogen removal rate gradually decreased with the pH value improved. When pH value was between 5 and 9, the ammonia nitrogen removal rate showed a significant increase tendency with the enhancing of pH value. When the pH value raised to 9, the highest ammonia nitrogen removal rate could be reached up to 59.4%. When the pH exceeded 9, the removal rate of ammonia nitrogen in ferrate solution declined with the increase of pH value. From the above analysis and discussion, it can be determined that the optimum pH value for the removal of ammonia nitrogen by ferrate solution was 9. Under acidic condition with low pH, ferrates were highly oxidizing and its oxidation-reduction potential was about 2.20V. However, the stability of ferrates under acidic condition was inferior, the presence of H+ made it prone to recombine the structure of high iron molecules due to the protonation. The redox reaction occurred rapidly and completed inside its molecules, and releasing Fe3+ and oxygen at the same time. Fe3+ underwent hydrolytic complexation to form Fe(OH)3 colloid, which possessed of outstanding adsorption and flocculation efficiency. Meanwhile, oxygen atom could also effectively oxidize ammonia nitrogen, but the time of contact with ammonia nitrogen was limited. Therefore, removal of ammonia nitrogen in acidic medium was realized by strong oxidation of ferrate. When under alkaline environment, the oxidizing ability of ferrate was weakened and the oxidation-reduction potential was about 0.72 V. As a result, the stability of ferrate was enhanced and the catalytic decomposition rate became slowly, high ferrate concentration could be maintained in aqueous solution. Although the oxidizing ability of ferrate was decreased a little, the oxidation time of ammonia nitrogen could be prolonged, so that the ammonia nitrogen removal rate could be improved.

When the pH value was in the range of 3 to 9, the oxidative removal effect of ferrate solution on HA was significantly enhanced with the increase of pH value. When the pH rose to 9, the HA removal
rate reached a maximum of 70.8%, then gradually decreased as the pH continued to increase. As a consequence, the optimal pH value for oxidative degradation of HA on ferrate was 9. This may be mainly affected by two factors, on the one hand, the improving of pH value was beneficial for the mineralizing of humic acid macromolecule into ionic state and making it easier to be oxidized. On the other hand, a continuous increase in pH value will lead to the gradual decrease in the oxidation-reduction potential of ferrate.

Under different raw water pH conditions, the fractal dimensions of flocs were calculated to be $D_{fa}=1.4771$, $D_{fb}=1.3295$, $D_{fc}=1.6384$, $D_{fd}=1.7608$ and $D_{fe}=1.7073$ for the pH values of 3, 5, 7, 9 and 11, respectively. The relationship between different pH value of raw water and the fractal dimension of flocs was displayed in figure 4. It can be seen from the comparison of figures 3 and 4 that the fractal dimension of flocs changed with the pH value of raw water, and maintaining a high correlation with the changes of turbidity, ammonia nitrogen and HA removal rate. When the pH value was between 3 and 5, the fractal dimension of flocs decreased with the enhancing of pH value, and the removal rate of turbidity and ammonia nitrogen of ferrate solution also presented the same tendency. However, when pH value was in the range of 5 to 9, the fractal dimension of flocs increased sharply with the raise of pH value. Meanwhile, the turbidity, ammonia nitrogen and HA removal rate were also greatly improved. When the pH value raised to 9, the flocculation fractal dimension reached the highest value, and the relatively dense flocs were formed at this time. Meanwhile, ferrite solution also achieved the highest removal efficiency on turbidity, ammonia nitrogen and HA. When the pH was further increased, the fractal dimension of flocs decreased slightly, and the turbidity, ammonia nitrogen and HA removal rate also declined. It can be seen from figure 4 that the morphological structure of flocs underwent a process that started loose and then gradually compacted, finally loosened again with the change of raw water pH value. As a consequence, the optimum pH of raw water was 9, and the corresponding fractal dimension of flocs was 1.7608. At this time, the removal percentage on ferrate solution of turbidity was 92.4%, ammonia nitrogen was 59.4%, and HA was 70.8%.

![Fractal dimension vs pH](image)

**Figure 4.** Relationship between different pH value of raw water and the fractal dimension of flocs.

5. Conclusion

(1) The coagulation experiment in which the dosage of ferrate solution was single change factor and the initial concentration of ferrate solution prepared by in situ electrolysis was 0.027 mol/L. When ferrate was applied in the government of simulated surface micro-polluted water, the turbidity removal rate was improved with the ferrate dosage increasing. When the dosage was 1.5mL/L, the turbidity removal rate reached up to 92.8%, and the corresponding flocs fractal dimension was 1.7824. The
removal rate of ammonia nitrogen also enhanced with the increase of ferrate dosage, which ranged from 23.6% to 60.4%. The removal percentages of HA improved rapidly with the increase of ferrate dosage, reaching a maximum of 70.6% then followed by a slight decrease. From the relationship between the dosage of ferrate solution and the fractal dimension of flocs, it can be seen that the morphology of flocs had undergone a process of change from initial compaction to subsequent loosen. From this, it was confirmed that the optimum dosage of ferrate solution was 1.5 mL/L in the government of simulated surface micro-polluted water.

(2) In the coagulation experiment with the pH value of raw water as a single change factor, the removal rates of turbidity, ammonia nitrogen and HA changed with the pH value based on the optimal dosage of ferrate solution. It went through the process of first increasing gradually, reaching the maximum value and then decreasing slightly. The fractal dimension of flocs changed with the pH value of raw water, and maintaining a high correlation with the changes of turbidity, ammonia nitrogen and HA removal rate. Therefore, the optimum pH value of raw water was determined to be 9 and the corresponding flocculation fractal dimension was 1.7608. At this time, the removal rate of turbidity, ammonia nitrogen and HA on ferrate solution were 92.4%, 59.4% and 70.8% respectively.

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