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LABORATORY AND FULL-SCALE PLANT STUDIES OF PERMANGANATE OXIDATION AS AN AID IN COAGULATION

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ABSTRACT

Standard jar tests and full-scale plant studies were conducted to evaluate the effectiveness of permanganate preoxidation as an aid to coagulation-flocculation of surface waters. The results of the jar tests demonstrated that permanganate preoxidation obviously enhanced the coagulation-flocculation of the studied surface waters. Through full-scale plant studies, the positive effects of permanganate assistance in coagulation-flocculation of surface waters were confirmed by the turbidity reduction of about 4～11 FTU at permanganate dosages of 1～2 mg／L. It was observed that the size of flocs in the reaction tank became bigger if the water was preoxidized with permanganate, lowering the polyaluminium chloride (PAC) consumption by about 36% . In addition, the effectiveness of prechlorination and permanganate preoxidation on assisting in coagulation-flocculation were compared through full-scale studies at a water treatment plant using a shallow lake as its water source, showing that permanganate preoxidation was a more effective means to aid coagulation-flocculation.

KEYWORDS

Permanganate; surface water; flocculation; preoxidation; coagulation.

INTRODUCTION

Surface waters which are characterized by relatively high content of natural organic materials have been the main sources of drinking water. Recent investigations (Jekel, 1986 a, 1986 b; Grasso and Weber, 1988) revealed that the presence of natural organic materials stabilized the inorganic colloids in water. It was reported (Gibbs, 1983) that the stabilization of inorganic colloids by natural organic materials was due to the formation of organic coating on the surface of inorganic particles, causing the repulsive action and steric hindrance between the particles.

According to the investigation by Narkis and Rebhun (1975) it was demonstrated that in the presence of natural organic materials flocculants react first with the free natural organic acids in the solution, but only after the flocculant dosage was high enough to neutralize the electric charge of natural organic materials in the solution or on the solid particles could the flocculant take part in the bridging process. Yao and Yan (1989) observed that to coagulate the clay suspensions containing natural organic materials the required flocculant dosages were much higher than when natural organic materials were absent, for example , when the spiked fulvic acid concentration in the clay suspension increased by 3 mg/L (as TOC), the alum dosage would be raised 5.3 times to destabilize the suspension; and if the increase of fulvic concentration was 7 mg/L (as TOC), the alum dosage elevation had to be 10.2 times to cause the destabilization. Consequently, for surface waters , especially when the natural organic material concentrations are relatively high, to achieve satisfactory coagulation-flocculation results the flocculant dosage had to be raised, resulting in the increment of water cost.

Preoxidation has been the means for solving the above problem. Traditionally, chlorine and ozone were the two main oxidants used as an aid to coagulation-flocculation of surface water. Prechlorination has been practised quite early due to the cheapness of chlorine. But high yields of chlorination by-products which are harmful to human health have aroused more and more attention (Yong and Singer, 1979, Singer and Chang, 1989). In recent years, much work has been focused on the study of ozone preoxidation to aid coagulation-flocculation. Generally, many investigators (Saunier et al.,1983; Farvardin and Collins, 1989) agreed that at an optimium ozone dosage for a specific surface water, preozonation had a positive effect on the coagulation-flocculation process. However, even though ozone has been used extensively in developed countries it is still little used in developing countries due to a lack of funds. Thus, it is necessary that an economical pretreatment method without harmful side-effects be considered.

In this article, the authors proposed the preoxidation with permanganate as an aid to coagulation-flocculation based on the consideration of its cheapness, flexibility, and low cost in capital investment, as well as its convenience of application.

EXPERIMENTAL PROCEDURE

Jar Test

Standard jar tests were conducted in a mixer equipped with multiple stirring apparatus. A carefully calculated amount of permanganate solution was injected into beakers before the addition of flocculant. Agitation was at 300 rpm for 0.5 min followed by agitation at 35 rpm for 5 min. Afterwards, the water was allowed to stand quiescently for 15 min. Then the supernatant was siphoned 2cm below the water surface, and the residual turbidity was determined with a turbidimeter using formazin as the standard for calibration.When necessary the supernatant of each jar was further filtered through a filter paper in order to evaluate the impact of preoxidation of permanganate on the quality of filtered water.

Full-Scale Plant Study

The Da Qing Reservoir Water Treatment Plant was used as the site for our full-scale studies. The water in Da Qing reservoir is introduced from the Nen river through a canal. The typical water quality parameters are listed in table 1. Conventional water treatment processes are applied in this plant using liquid polyaluminium chloride (PAC) as the flocculant. There are two parallel conventional treatment systems in this plant having the same design parameters and inflow rates, as shown in figure 1, and this fact facilitated a comparison study to evaluate the effectiveness of preoxidation of permanganate as an aid to coagulation-flocculation.

TABLE 1 Characterization of Raw Water in Da Qing Reservoir

Parameters	Total Hardness mg $CaCO_3$/L	Carbonate Hardness mg $CaCO_3$/L	Total Alkalinity mg $CaCO_3$/L	TOC mg/L	BOD_5 mg/L	Colour mg Pt/L	COD_{Mn} mg/L	pH
Concentration	100.0	100.0	157.6	8.0	1.5	10.0	10.5	7.8

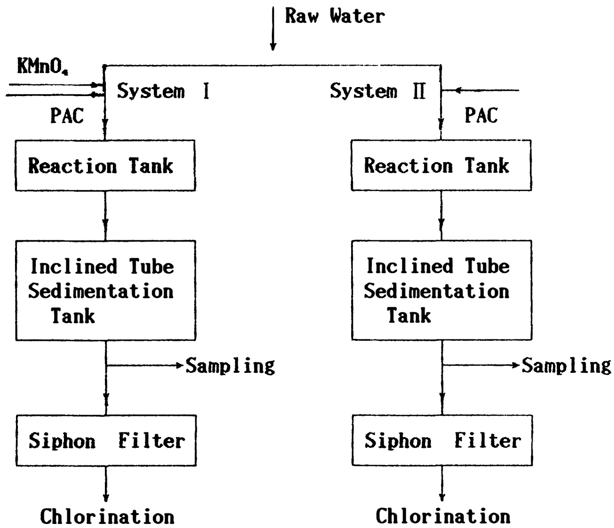

Fig.1. Diagram of water treatment process used in the full-scale study

In addition, comparison of the effect of prechlorination and permanganate preoxidation on assisting in coagulation-flocculation was made through field studies at the Ba Bai-shang water treatment plant which uses a shallow lake as its water source.

RESULTS AND DISCUSSION

Laboratory Study

Figure 2 shows the effect of preoxidation with permanganate on the Coagulation of Songhua river water. The experiment was conducted during the Spring season with COD_{Mn} of the raw water ranging from 9 to 13 mg/L and colour at about 20 mg Pt/L. The figure shows that permanganate preoxidation has an obvious effect on the coagulation of Songhua river water. At any flocculant dosages the residual turbidity of the settled water is lowered several FTU more than is the case without permanganate treatment. Even if permanganate dosage is only 0.5 mg/L, an obvious effect can be observed. The figure also shows that when permanganate is applied there is little variation of optimum alum dosage. The curves of residual turbidity move downward as permanganate dosage increases. If the water is pretreated with permanganate the optimum flocculation range becomes slightly wider. It is worth noting that the effect of permanganate preoxidation on improving the water quality becomes more obvious if the water is further filtered, as shown in figure 3. Even though the permanganate dosage is only 0.5 mg/L, the turbidity of filtered water is much decreased. With the continuing increase of permanganate dosage, the residual turbidity decreases further.

With regard to the increase in stability of colloids as the natural organics content increases (Yao and Yan, 1989), 5mg/l of humic acid was spiked in Songhua river raw water to simulate the condition of high organic content, and the effect of preoxidation with permanganate on the coagulation-flocculation under such conditions was studied. The variation of residual turbidity of settled and filtered water with and without permanganate pretreatment is shown in figure 4. The results illustrate that the addition of humic acid greatly stabilizes the colloids with little reduction of residual turbidity if the water is flocculated with alum alone. But when the water is pretreated with permanganate the residual turbidity of settled water decreases as the dosage of permanganate increases. It is demonstrated that permanganate preoxidation is more effective in improving the quality of the filtered water , for example, when permanganate dosage is only 0.5 mg/L, the residual

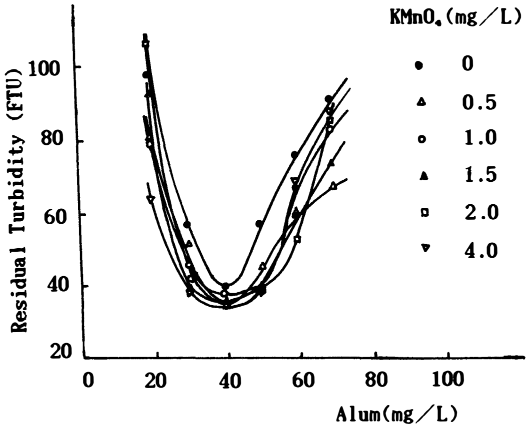

Fig.2. Effect of permanganate oxidation on the residual turbidity of settled water

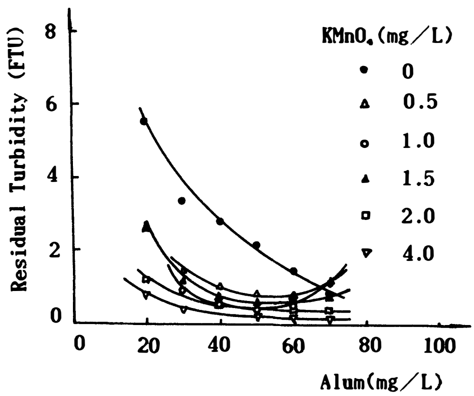

Fig.3. Effect of permanganate oxidation on the residual turbidity of filtered water

turbidity of the filtered water is about 50% lower than that with alum coagulation alone, and if permanganate dosage is 4 mg/L,the subsidence of residual turbidities of the filtered water is about 70% . The results of the above experiment indicate that permanganate preoxidation is more effective in assisting in coagulation when the organic content of the water is high.

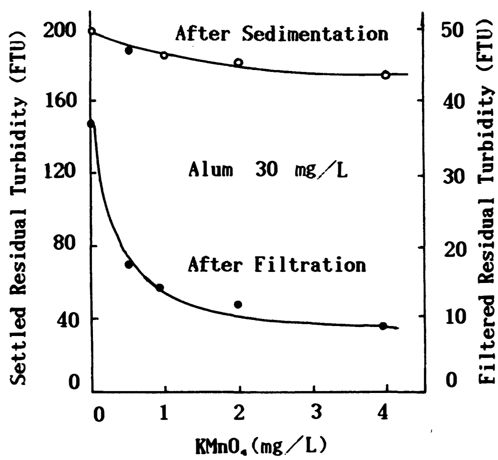

Fig.4. Effectiveness of preoxidation on coagulation of the water with high organic content

Table 2 shows the effect of permanganate preoxidation on the coagulation of BaBai-shang shallow lake water, which is characterized by high colour (30~50 mg Pt/L) and low turbidity (about 40 FTU), and is rather difficult to treat. The results of jar tests show that permanganate preoxidation is very effective in reducing the turbidity of this shallow lake water. When polyaluminium chloride dosages are 50 mg/L and 100 mg/L, a permanganate preteatment dosage of 1.5 mg/L results in the reduction of settled water of 17.2 and 10. 6 FTU respectively compared with the samples not subjected to permanganate preoxidation. This result further confirms that permanganate preoxidation is more effective under conditions of high organic content.

TABLE 2 Effect of Permanganate Preoxidation on the Settled Residual Turbidity of BaBai-shang Lake Water

PAC mg/L	Permanganate mg/L 0	1.0	1.5	2.0
500	4.9	2.5		0
100	35.2	29.5	24.6	
50	54.9		37.7	

Permanganate dosage is one of the key parameters in the process of permanganate preoxidation. In order to investigate the influence of permanganate dosage on the effectiveness of coagulation assistance and residual permanganate concentration, the following experiment was conducted: 5 mg/L of humic acid was spiked in Songhua river raw water to raise the organic content in the water. Different permanganate dosages were used and the alum dosages were controlled at 90 mg/L. Having contacted with permanganate for 20 min, the water was flocculated with alum, then the light absorbances of the supernatant of settled water were measured with a spectrophotometer at the wavelength of 420, 530,and 680 nm. The results are shown in figure 5. The wavelength of 530nm is the characteristic wavelength of permanganate at which the variation of absorbances reflects the change of residual permanganate concentration,while absorbance at 420 and 680 nm may indicate the relative changes of humic acid concentration and the residual turbidity in the water. It is shown in figure 5 that when permanganate dosage is at 2 mg/L,the absorbance at the wavelength of 530 nm is higher than in the samples without permanganate preoxidation, demonstrating the presence of trace surplus permanganate in the water . But, as permanganate dosages further increase, the absorbances at this wavelength decrease gradually and are even lower than without permanganate preoxidation, showing the absence of permanganate in the water. After permanganate dosage is increased above 8 mg/L, the absorbance at 530nm begins to increase, indicating the existence of surplus permanganate in the water. The above phenomena

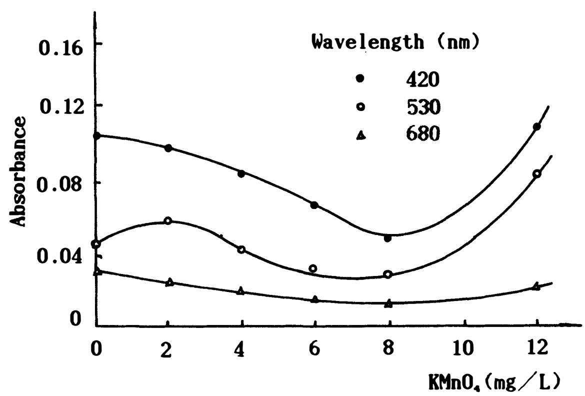

Fig.5. Influence of permanganate dosage on the effectiveness of coagulation assistance and residual permanganate concentration

demonstrate that at lower permanganate dosage the reaction between permanganate and humic matters may be slow , leaving trace surplus permanganate in the solution , while if permanganate dosages are further increased the initially produced hydrous manganese dioxide may act as a catalyst between permanganate and humic acid, thus exhausting the permanganate. From the variation of the absorbance at the wavelength of 420 and 680 nm , the effectiveness of permanganate assistance in coagulation increases with the increasing of permanganate dosages, but if permanganate dosage is beyond 8 mg/L,the residual permanganate concentration begins to increase and the effectiveness declines. The results of the above experiments suggest that for a specific surface water there exists an optimum permanganate dosage.

Full-Scale Plant Study

Figure 6 shows the results of a full-scale field study carried out from 22 June to 25 June 1991 , at the Da Qing Reservoir Water Treatment Plant. The two parallel conventional treatment systems used in this experiment had the same hydraulic load (1512 m^3/h), and polyaluminium chloride (PAC) dosages were controlled at 34.7 mg/L. Before the addition of permanganate the residual turbidity of the settled water in the two parallel systems were almost the same , and the two curves of the residual turbidity nearly overlapped with each other. But upon addition of permanganate in system I (0.96 mg/L), obvious differences in the residual turbidity of the settled water between the two systems was observed. The residual turbidity of system I which was subjected to permanganate oxidation was 4.0~11.0 FTU lower than the case without permanganate oxidation (system II). It was also discovered that the size of flocs was obviously increased after the additon of permanganate.

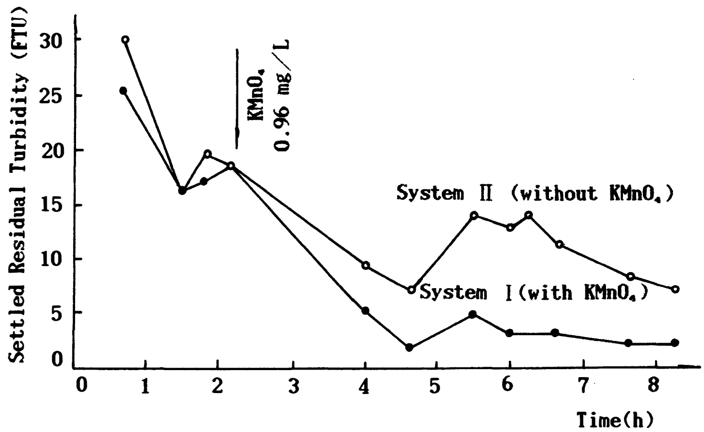

Fig.6. Results of full-scale study conducted at Da Qing Reservoir Water Treatment Plant in Summer

Figure 7 shows the results of a full-scale field study carried out from 31 August to 2 September 1991 . As with the previous example, the PAC dosages of the two parallel conventional treatment systems were controlled at 34.7 mg/L. When the two systems reached steady state, the residual turbidities of the settled water in both systems were identical Afterwards, permanganate was added in system I (1.9 mg/L). After 8h of stabilization, the residual turbidities of the settled water in both systems were monitored continously. The results shown in figure 7 indicate that after the addition of permanganate in system I the residual turbidity of the settled water reduced 4.0~8.0 FTU compared with system II, which was not subjected to permanganate treatment. This shows the obvious effectiveness of permanganate oxidation as an aid in the flocculation of this reservoir water.

In order to evaluate how much PAC could be reduced when permanganate oxidation was used as an aid in the coagulation of the water, the experiment was further developed as follows: The flocculant (PAC) and permanganate dosage in system I were kept constant. Then the PAC dosage of system II was elevated step by step. At the same time, the residual turbidity of the settled water in both systems was monitored continuously. The residual turbidity of the settled water in system II decreased with the increase of PAC dosage, as shown in figure 7. It is worth noting that the lower the residual turbidity the more difficult it is to

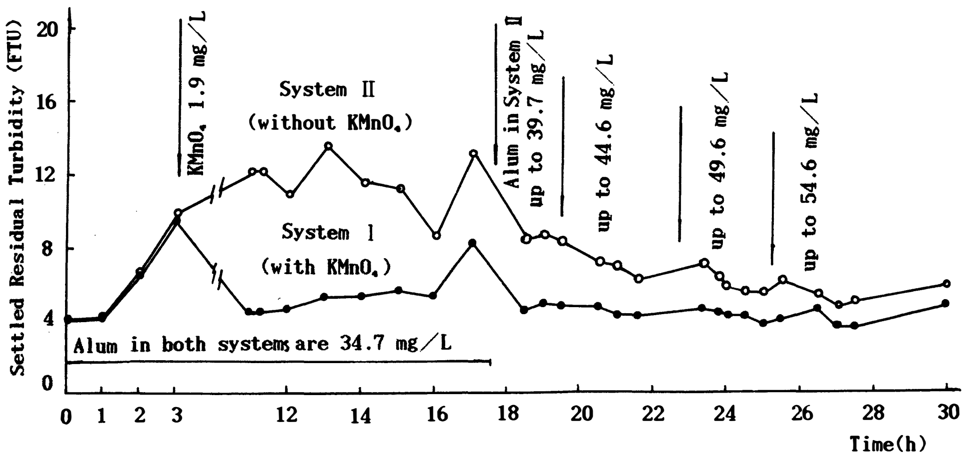

Fig.7. Results of full-scale study conducted at Da Qing Reservoir Water Treatment Plant in Autumn

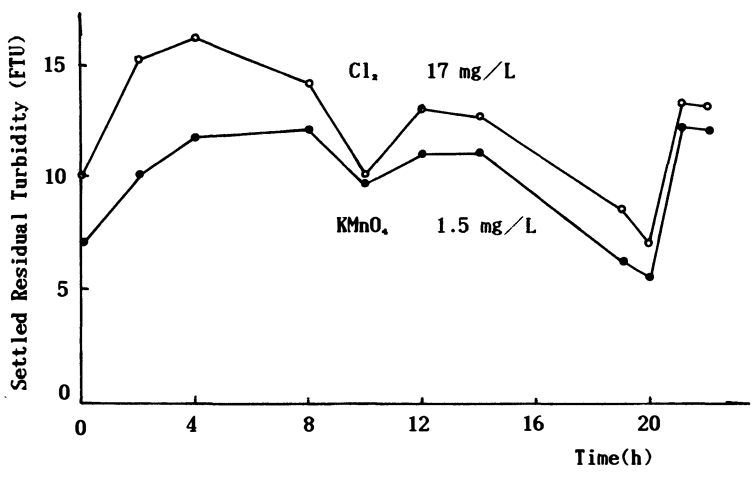

Fig.8. Results of comparison study of prechlorination and preoxidation with permanganate on aiding the coagulation of BaBai-shang lake water

further decrease the residual turbidity of the settled water. When the PAC dosage in system II was raised to 54.6 mg/L.the residual turbidities of the two systems were nearly identical

But the residual turbidity of system I, which was subjected to permanganate treatment, was still about 1 FTU lower than that of system II, in which permanganate was not applied. Thus, at least 20 mg/L less PAC was used when the system was subjected to permanganate oxidation; i.e., at least 36% of PAC was saved.

If the cost of permanganate consumption was taken into consideration, the net reduction of PAC was at least 14% when permanganate preoxidation was used.

Furthermore, comparison of prechlorination and permanganate oxidation was investigated at Ba Bai-shang Water Treatment Plant through a full-scale field study using two parallel conventional water treatment systems. The results shown in Figure 8 demonstrate that 1.5 mg/L permanganate oxidation was more effective than 17 mg/L chlorine oxidation in aiding the coagulation of this water.

CONCLUSION

Both laboratory and full-scale plant studies demonstrate the obvious positive effect of permanganate preoxidation of surface water as an aid to its coagulation. resulting in either reduction of turbidity or decrease of the cost of water. Under conditions of higher organic content permanganate preoxidation is likely more effective in the assistance of its coagulation . Moreover , there may exist an optimum permanganate dosage in aiding the coagulation of surface water.

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