# Comparison of ozone and permanganate as preoxidant on treating eutrophic raw water

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## Abstract

A pilot-scale study, using ozone and potassium permanganate as preoxidant, was conducted to examine their effects on algae, turbidity, and organic matter removal by coagulation. Continuous operation of two parallel treatment trains with or without the two preoidants was carried out. The results show that adding either ozone or permanganate as preoxidants could enhance algae removal by coagulation. The removal of green algae (*Chloella sp.*) was found to be lower than those of diatoms and blue-green algae. There are optimum dosages for both preoxidants. As ozone dosage exceeded optimum value, the algae and turbidity removal deteriorated significantly. However, regardless of preoxidant dosage tested, the ozone had better performance in the NPDOC, A254, and THMFP removal, as compared to permanganate.

## 1 Introduction

A continuing worldwide problem for drinking water treatment industry is the presence of algae in source water. Algae in drinking water supply can cause significant disturbances including taste and odor, production of disinfection by-product (DBP), obstruction to coagulation, clogging of filter, and assimilable organic carbon (AOC) for growth of biofilm [1-5]. Some specific algae in water source, moreover, are capable of producing toxins [6].

The major process for removing algae in conventional drinking water treatment is coagulation, sedimentation, and filtration. Algae removal by

conventional treatment is more difficult than inorganic particle, due to their low specific density, motility, morphological characteristics and negative surface charge [7-9]. Pretreatment with oxidants are commonly used in drinking water treatment to enhance algae removal. Numerous studies have showed that preoxidition can improve algae removal by coagulation [10-12]. These preoxidants such as ozone, chlorine dioxide, chlorine, or permanganate not only served as algocide to inactivate the algal cell, but also as flocculation aids to improve the removal of taste and odor, color, inorganics and natural organic matters in the purification plants [13-15].

The effect of preoxidant on drinking water treatment might be dependent on its type and dosage. Sukenik et al. [16] found various preoxidant at different dosages had distinct effect on algal cell surface architecture, in which ozone or chlorine dioxide was beneficial to coagulation, but not chlorine. Edzwald [17] also indicated that preozonation with low dosage was capable of enhancing algae removal, but high ozone dosage had adverse effect.

The objectives of this study were (1) to compare the effects of ozone and permanganate as preoxidant on treating eutrophic raw water, and (2) to evaluate the effect of the preoxidants for algae removal followed by coagulation process.

## 2 Materials and methods

### 2.1 Pilot plant

The pilot plant located in the Cheng Ching Lake Water Works (CCLWW), which is the major supplier of domestic water to about 2.5 millions people in the Greater Kaohsiung Area in Southern Taiwan. Its raw water came from the nearby eutrophic Cheng Ching Lake. The pilot experiments involved operation of two parallel treatment trains, which included preoxidation, coagulation, flocculation, sedimentation, filtration, and postchlorination. Ozone and potassium permanganate were used separately as preoxidants for each train. The dosage for ozone and permanganate were ranged from 0.9-7 mg/L, and 0.5-1.75 mg/L, respectively. Both trains used liquid alum (7.5% $Al_2O_3$) as coagulant, with a dosage about 70 mg/L. The mean velocity gradient for slow mixing was controlled at 40 $sec^{-1}$. Tube settlers were used for sedimentation with overflow rate of 69.8 $m^3/m^2$-d.

### 2.2 Raw water

Due to the inputs of domestic sewage, farming, and industrial wastewaters, the lake is eutrophic, as indicated by high algal concentration $1.3\times10^3$-$1.6\times10^5$ cells $mL^{-1}$. The algae species frequently caused various unpleasant tastes and odors. The dominant species cycled from green algae (*Chlorella*) to diatom (*Cyclotella, Synedra,* and *Melosira*) and then to blue-green algae (*Microcystis*). When water temperature was low, diatom dominated, and the prevailing odor was fishy. At higher temperature, blue-green algae dominated, and the main odor was earthy. Raw water quality parameters during the study are summarized in Table 1. The presence of nutrients in water also explains the algae bloom. Raw water quality is characterized by high hardness and moderate dissolved organic content and turbidity.

Table 1: Characteristics of raw lake water quality.

| Parameters | Range | Average |
|---|---|---|
| Temperature ( ) | 16.6-31.3 | 25.1 |
| PH | 7.9-8.7 | 8.2 |
| Turbidity (NTU) | 5.8-113 | 18.2 |
| Alkalinity (mg/L as $CaCO_3$) | 103-218 | 162 |
| Dissolved oxygen (mg/L) | 5.7-11 | 8.2 |
| Total hardness (mg/L as $CaCO_3$) | 190-273 | 238 |
| NPDOC (mg/L) | 0.5-2.09 | 1.2 |
| UV-absorbance at 254 nm ($m^{-1}$) | 1.2-4.4 | 2.5 |
| Algae counts (cells $mL^{-1}$) | 3743-16426 | 8140 |
| $NH_3$-N (mg/L) | 0.07-0.59 | 0.21 |
| $NO_2^-$-N (mg/L) | 0.02-0.23 | 0.09 |
| $NO_3^-$-N (mg/L) | 0.21-1.8 | 0.94 |
| Total phosphate (mg P/L) | 0.04-0.31 | 0.13 |

### 2.3 Water quality analyses

During the testing period of pilot study, samples of the raw water and settled water were collected twice per week. The water quality parameters analyzed included nonpurgeable dissolved organic carbon (NPDOC), UV-absorbance at 254 nm (A254), turbidity, trihalomethanes (THM) and trihalomethane formation potential (THMFP). NPDOC was measured by the combustion-infrared method using a total organic carbon analyzer (Model TOC-5000, Shimadzu, Kyoto, Japan). THM was measured by the purge and trap packed-column gas chromatographic method using a gas chromatograph (Model 3400, Varian, Walnut Creek, CA) equipped with a purge and trap module (Model LCS-2000, Tekmar, Cincinnati, OH) and an electron-capture detector (ECD). For THMFP analysis, an adequate amount of sodium hypochlorite solution was injected into the sample to insure that at least 1 mg/L free chlorine residual existed at the end of the 7-day (at 25 ) incubation period. The analysis of other water quality parameters, such as turbidity, A254, *etc.*, were followed that of the Standard Methods [18].

## 3 Results and discussion

### 3.1 Algae concentration

The settled water quality varied with the algae concentration in raw water. Figure 1 shows the relationship between the algae concentrations of raw water and the residual turbidity of the settled water during the pilot testing period from

November 1998 to August 2000. The algae concentrations of raw water ranged from 3700 to 16000 cells $mL^{-1}$. The settled water turbidity increased with algae concentration of the raw water. It is obvious that water with higher algae concentration affected coagulation processes, leading to the deterioration of settled water quality. When the algae concentration exceeded 7000 cells $mL^{-1}$, the settled water turbidity was difficult to meet the presetted 2 NTU criteria.

### 3.2 Preoxidant enhancing algae removal

To understand the effect of preoxidation on algae coagulation, ozone and permanganate were used as preoxidant in the pilot plant. Table 2 shows the effect of ozone and permanganate dosage on algae removal by coagulation process. Both preoxidants were capable of enhancing algae removal. It was observed that 79.87% algae removal by coagulation was achieved without preoxidant, while algae removal increased up to >85.4% in the presence of permanganate and >92% in ozone, respectively. However, it also can be noticed that increase ozone dosage to 7 mg/L led to drastic decrease in algae removal. Similar results were observed when permanganate dosage increased to 1.75 mg/L. Therefore, there are optimum dosages for both oxidants. When dosage exceeded the optimum valve, the algae removal deteriorated. This phenomenon was more significant for ozone than that for permanganate.

Figure 2 shows two sets of data, comparing the effect of type of peoxidants and dosage on the coagulation removal of various algae species. Figure 2A shows that when the permanganate and ozone dosages were 0.75 and 1 mg/L, respectively, the total algae removal and that for various species were comparable, except blue-green algae. However, when ozone dosage increased to 3 mg/L (Figure 2B), the algae removal rates were all lower than that of permanganate at 0.75 mg/L. It is speculated that high ozone dosage may rupture algae cell, causing the release of intracellular, organic matter. Parts of the coagulant added were used to react with these organic matters. Therefore, the amounts of coagulants available for coagulating algal cells were reduced. Figure 2 also shows that the removal rate for green algae was lower than those of diatom and blue-green algae. This probably is due to the small size and low cell density of the green algae.

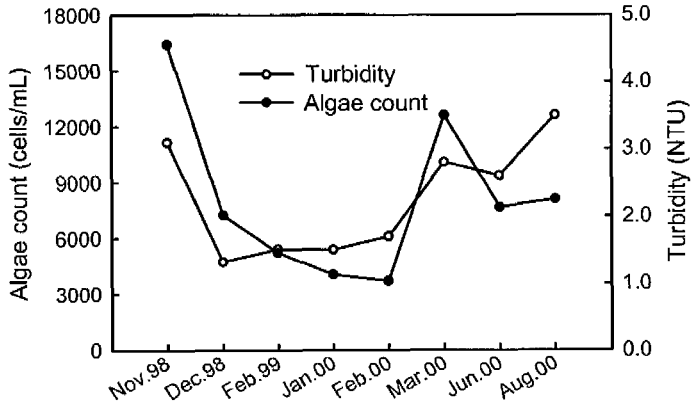


Figure 1: Changes in the raw water algae concentration and in settled water turbidity. Average raw water turbidity: 12.2 NTU, alum dosage: 75 mg/L.

Table 2: Effect of ozone and permanganate preoxidant dosage on the algae removal by coagulation

| Preoxidant | Dosage, mg/L | Removal, % |
|---|---|---|
| Without | N | 79.87 |
| $O_3$ | 1 | 92.64 |
| | 3 | 93.23 |
| | 7 | 43.46 |
| $KMnO_4$ | 0.5 | 85.40 |
| | 1 | 87.48 |
| | 1.25 | 97.39 |
| | 1.75 | 88.00 |

Alum (7.5% $Al_2O_3$): 70 mg/L

### 3.3 Particulates and dissolved organic matters removal

Figure 3 compares the effect of ozone and permanganate as preoxidants on the coagulation removal of turbidity and dissolved organic, expressed as NPDOC, A254, and THMFP, from raw water. It shows that ozonation at 1 mg/L had higher removal rate for all the parameters analyzed than permanganate at 0.75 mg/L. This may be due to the high oxidation power of ozone than that of permanganate. When ozone dosage was increased to 3 mg/L, the removal of dissolved organic, as expressed by NPDOC, A254, and THMFP, was still higher or comparable to ozone at 1 mg/L. However, turbidity removal by coagulation was significantly lower at 3 mg/L preozonation than those at 1 mg/L preozonation. This is consistent with the results of algae removal at various dosages of preoxidants, as shown in Figure 2. Figure 4 shows the relationship

between value of the preozonated raw water from Cheng Ching Lake and various ratios of ozone dosage and the NPDOC valve of the raw water. It clearly shows the increase in NPDOC valve with high ozone dosage. All these support our previous speculation that high ozone dosage may rupture algae cells, and causing the release of intracellular organics into water. Many researchers have shown that the coagulants added during water treatment process first reacted with organics, then with colloids and particulates [19]. Therefore, turbidity removal by coagulation would be inhibited if excessive organics were existed, and coagulant dosages not meet the requirement from both organics and colloid/particulates.

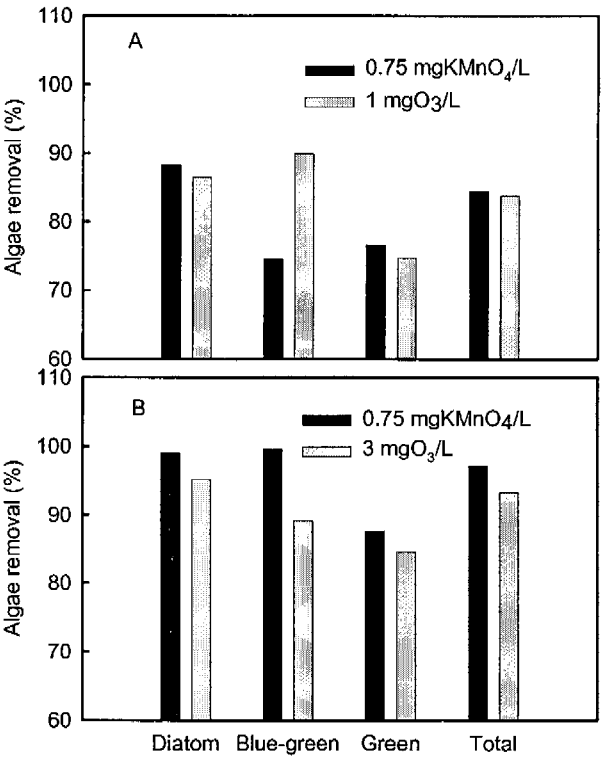


Figure 2: Comparisons of ozone and permanganate in parallel on the different algal species removal by coagulation process.

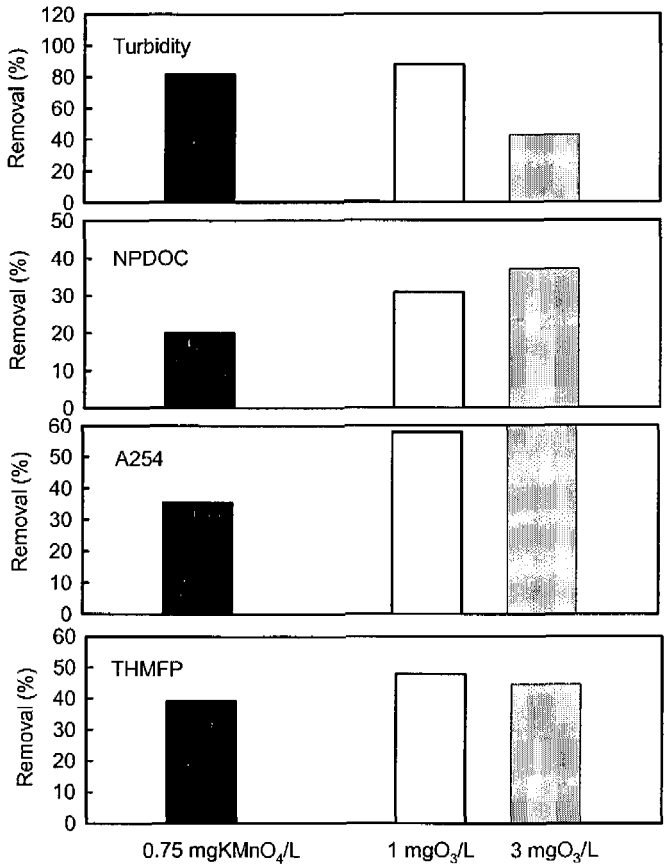


Figure 3: Comparisons of ozone and permanganate on the turbidity, NPDOC, A254, and THMFP removal after coagulation process.

## 4 Conclusions

Pilot-scale study of ozone and permanganate as preoxidant were conducted to examine the effects on algae removal by coagulation. Results show that both preoxidants were capable of enhancing the removal of algae. And there were optimum dosage for both preoxidants. As dosage exceeded optimum value, the algae removal deteriorated. This phenomenon was more significant for ozone than that for permanganate. Owing to its superior oxidation power, excessive ozone dosage may rupture algae cell, and increased organic content of the water. As a result, the colloid and particulates removal may be inhibited.

General speaking, ozonation under adequate dosage had better removal in particulates, dissolved organic matter and disinfection by-product precursor than those of permanganate.

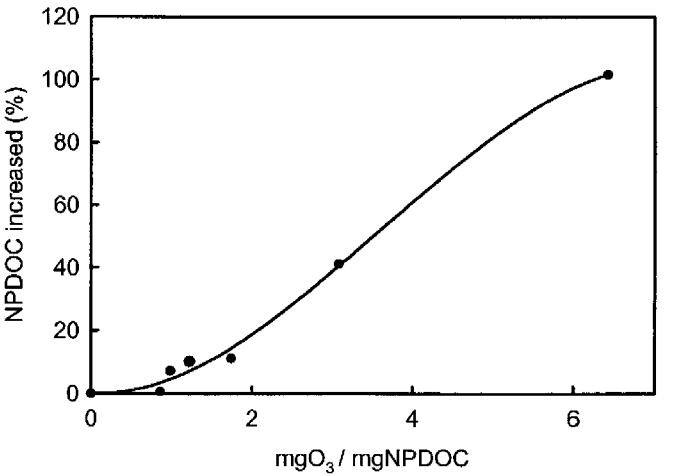


Figure 4: Effect of preozonation on NPDOC concentration in the pilot study.

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