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# Enhanced coagulation for treating slightly polluted algae-containing raw water of the Pearl River combining ozone pre-oxidation with polyaluminum chloride (PAC)

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ABSTRACT

The feasibility of using $O_3$ pre-oxidation and polyaluminum chloride (PAC)-enhanced coagulation for treating slightly polluted algae-containing raw water of the Pearl River was investigated. Results demonstrated that $O_3$ pre-oxidation and PAC-enhanced coagulation have greatly increased the removal of algae, turbidity, and natural organic material compared with PAC coagulation only. Specifically, the greatest removal of chlorophyll-*a* (chl-*a*) and TOC attained 97.67% and 32.29%, respectively, at the $O_3$ concentration of 1.0 mg/L and a PAC dose of 6.0 mg/L. 1.0 mg/L $O_3$ pre-oxidation reduces the 60% PAC dose when the residual turbidities reached 0.99 NTU. 2.0 mg/L $O_3$ pre-oxidation increased the $UV_{254}$ removal from 16.97 to 57.28% at a PAC dose of 6.0 mg/L.

*Keywords:* Pre-oxidation; Coagulation; Algae; Turbidity; Natural organic material

## 1. Introduction

The discharge of excessive nitrogen-containing and phosphate-containing nutrients into the natural water environment has lead to increased algal blooms in water worldwide, since 1950 [1]. Cyanobacterial blooms continue to be one of the most serious global issues facing water supply and the maintenance of healthy water ways [2]. Alga and its metabolites have a significant impact on water quality, such as the production of unpleasant tastes and odors, formation of disinfection by-products (DBPs) and toxins [3]. Furthermore, alga is known to interrupt the drinking water treatment process, causing short filter runs, increases in coagulant demand, and microbial regrowth in distribution systems [4–7]. Consequently, cyanobacterial blooms pose a great challenge for drinking water [8,9]. It is required that algae are removed from drinking water, preferably to ensure minimal impact on subsequent processes during the initial stages [10].

The coagulation and subsequently chlorination is the most common method for the treatment of drinking water [11–14]. Pre-chlorination has been widely

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applied to enhance the removal of algae and dissolved organic matter [15]. However, the reaction between chlorine and natural organic material (NOM) forms DBPs [16–18]. Therefore, to find a safe and efficient oxidant to replace chlorine for removing algae and other contaminants from raw water has an important significance. $O_3$, which has high oxidation and disinfection potential, has recently received much attention in water treatment technology [19]. $O_3$ pre-oxidation can deactivate algae cells and change the zeta potential and surface characteristic of algae and suspended particulate matter to promote their aggregation [20,21]. Consequently, $O_3$ is widely used in the drinking water pretreatment. Ozonation pretreatment can not only improve the efficiency of coagulation but also remove part of organic matters and algae. However, research reports of raw water treatment using $O_3$ pre-oxidation with polyaluminum chloride (PAC)-enhanced coagulation are still less. So, it is necessary to further study.

This study aimed to investigate the feasibility of $O_3$ oxidation and PAC-enhanced coagulation for treating slightly polluted algae-containing raw water of the Pearl River, which is one of China's seven major rivers and the most important river in south China, and to explore removal of chl-*a*, NOM (TOC and $UV_{254}$), and turbidity.

## 2. Materials and methods

### 2.1. Materials

Anabaena flos-aquae (A.F.), a kind of cyanobacterial, were purchased from Institute of Hydrobiology Freshwater Algae Species Pool, Chinese Academy of Sciences. It was cultivated in axenic BG-11 medium at 25 ± 1 ℃ under fluorescent light (2,000 l×, 12 h light/12 h dark). The BG-11 medium was composed of 15.0 g/L $NaNO_3$, 4.0 g/L $K_2HPO_4{\cdot}3H_2O$, 7.5 g/L $MgSO_4{\cdot}7H_2O$, 3.6 g/L $CaCl_2{\cdot}2H_2O$, 2.0 g/L $Na_2CO_3$, 0.6 g/L citric acid, 0.6 g/L ferric ammonium citrate, and 0.1 g/L EDTA-$Na_2$. It was controlled to pH 7.1 before autoclaving by adding either 0.1 mol/L HCl or 0.1 mol/L NaOH solutions. Cultures were harvested at the late exponential phase growth. All the model water experiments were carried out with cells in the exponential growth stage.

The raw water samples were collected from the Pearl River (Guangzhou section). The culture medium of A.F. was dispersed into test water samples, diluted to a concentration of chl-*a* required for the experiment, and adjusted with sodium hydroxide and hydrochloric acid to a certain pH. Test water quality parameters: *T*, 20 ± 2 ℃; pH, 7.56–7.80; turbidity, 25.4–39.4 NTU; TOC, 2.1–4.2 mg/L; chl-*a*, 150 ± 5 μg/L; and $UV_{254}$, 0.056–0.070 $cm^{-1}$.

PAC product was provided by a local factory containing 29% of $Al_2O_3$, stock solution with 1,200 mg/L $Al_2O_3$.

Ozone generated by the HF-3-type ozone generator (ZA-XF-5G), Zhengao Technology Co., Ltd, Guangzhou, China.

### 2.2. Analysis

Samples were analyzed for zeta potential, chl-*a*, turbidity, TOC, and $UV_{254}$. The zeta potential measurements utilized a zeta meter (Zetasizer Nano ZS90, Malvern Instruments, UK), which measures the zeta potential using a combination of the measurement techniques: electrophoresis and laser doppler velocimetry. Samples with adequate cell concentrations were injected slowly into the zeta meter and all zeta potential results were obtained in triplicate to calculate an average value. The zeta potential was initially measured at the end of the rapid mix section. For chl-*a* analysis, samples were filtered through 0.45 μm filter and the chlorophylls were extracted using 10 mL acetone (90%). The optical densities of the extracts were measured at 665 and 750 nm using a UNIC 2100 spectrophotometer (USA) and chl-*a* concentration was computed from Lorenzen equation [22]. Turbidity was measured in a 2100Q turbidimeter (HACH Company, US). The samples were filtered through 0.45 μm filter, and then TOC was measured by a TOC analyzer. $UV_{254}$ was measured using a spectrophotometer (UV-5800) at a wavelength of 254 nm with a 1 cm quartz cell. The samples need to filter through 0.45 μm filter to remove dissolved impurities. The determination method of ozone concentration was according to the literature [23].

### 2.3. Methods

The main device of experiment consisted of an ozone generator, a reaction column, and an ozone destructor. $O_3$ generated by the $O_3$ generator was passed into deionized water to produce $O_3$ water till $O_3$ in the water reaches some constant concentration. The concentration of $O_3$ was controlled by changing the gas flow. To make $O_3$ dissolve quickly, a sand core aerator was installed at the bottom of the reactor inlet. The water is fast mixed by magnetism blender at the same time. Reactor has a sampling connection, and the tail gas was discharged into the air after absorbing by 2% of KI solution. For ozonation pretreatment, the $O_3$ water was added quickly into the algae

suspension. After $O_3$ concentration was not detected, coagulation experiment was performed in a six-paddle stirrer (ZR4-6, CHN). Take a certain amount of water samples by a cylinder into a 1 L-glass and add PAC by a pipette. Mixing experiment generally divided into 2 ~ 3 phases. Water samples were slow mixed for 2 min at 50 rpm, then rapidly mixed for 2 min at 200 rpm, followed by a slow mixing for 10 min at 50 rpm. After a quite settling of 30 min, the supernatant was measured for the chl-*a* concentration, turbidity, TOC, and $UV_{254}$.

## 3. Results and discussion

### 3.1. The zeta potential of A.F. solution

Surface charge is an important parameter in coagulation experiments, and zeta potential gives a measurement of the apparent surface charge [24]. The zeta potential of A.F. solution was continuously measured during a growth (22 d) (Fig. 1). The zeta potential is negative in the growth, so it can be said that the surface of A.F. is negative charge. In addition, the zeta potential is changed only a little around −15.3 mV with the passage of time. Prior research has shown that algae are negatively charged bioparticles that contribute to the coagulant demand of water supplies [25]. These properties determine that A.F. cells and colloids have a certain similarity. So, it can be removed by coagulation method.

### 3.2. Algae removal

The effect of $O_3$ pre-oxidation and PAC-enhanced coagulation on the chl-*a* removal was investigated. It can be seen from Fig. 2 that under all of experimental

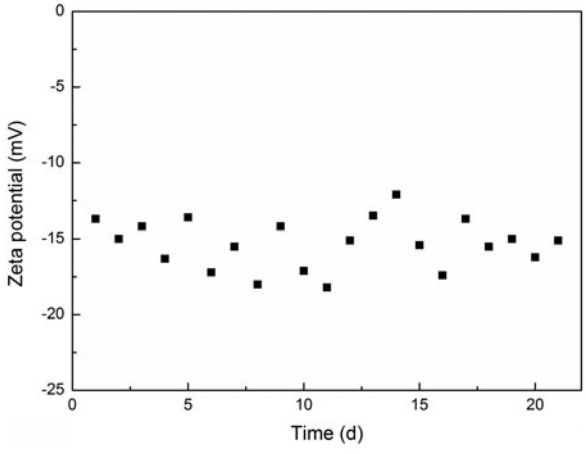


Fig. 1. Zeta potential of A.F. solution.

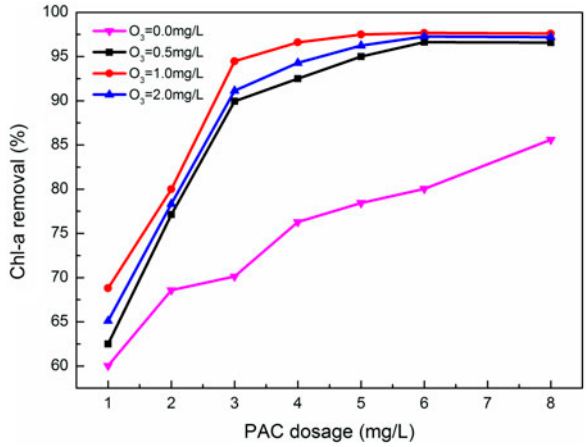


Fig. 2. Effect of $O_3$ pre-oxidation and PAC-enhanced coagulation on chl-*a* removal.

concentration of $O_3$, the removal of chl-*a* increased with increasing the PAC dosage. Meanwhile, under the same dose of PAC, the chl-*a* removal increased when the concentration of $O_3$ ranges from 0.5 to 1.0 mg/L. The promoting effect of ozone on chl-*a* removal is very significant. Although the chl-*a* removal decreased as the concentration of $O_3$ increased from 1.0 to 2.0 mg/L, the coagulation effect with $O_3$ is still better than that without $O_3$. However, when the concentration of $O_3$ is 1.0 mg/L, the removal efficiency is the best, and the greatest removal attained 97.67% at a PAC dose of 6.0 mg/L. The chl-*a* removal showed a slight reduction tendency when the PAC dosage was more than 6 mg/L in the presence of $O_3$. Subsequent experiments confirm that a PAC dose of 30 mg/L was demanded to attain the chl-*a* removal 97.17% if $O_3$ was not added. This suggests that $O_3$ pre-oxidation and PAC-enhanced coagulation have improved algae removal compared with PAC only.

### 3.3. The activity of ozone pre-oxidation on A.F.

In order to further research the action of $O_3$ pre-oxidation to remove algae, alga cells were observed under the microscope (×400) before and after $O_3$ pre-oxidation. Two treatment conditions of A.F. solution: (a) untreated; (b) 1.0 mg/L $O_3$ pre-oxidation for 5 min. Fig. 3(a) shows that the cells of A.F. are complete, oval or spherical, dark green filaments, and moving slowly. However, Fig. 3(b) shows that some of algal cells are cracked, light color, unmoving, and the part of their chain structure is destroyed. It indicates that a certain concentration of $O_3$ pre-oxidation has inhibitory effect on A.F. cells.

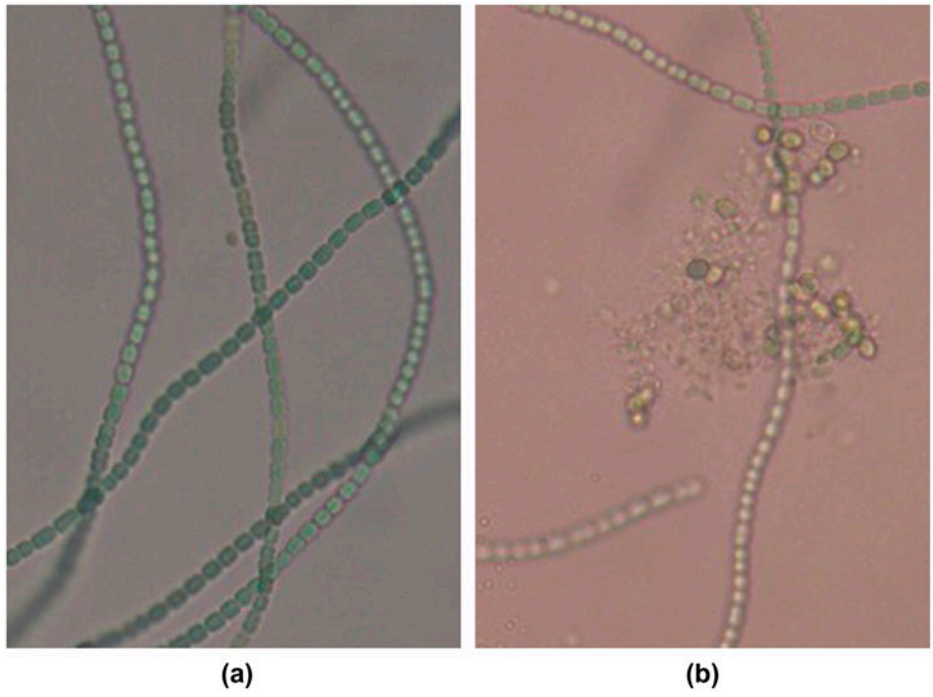


Fig. 3. Micrographs of A.F. under two treatment conditions: (a) untreated; (b) 1.0 mg/L $O_3$ pre-oxidation for 5 min.

### 3.4. Turbidity removal

Fig. 4 shows that $O_3$ has a certain promoting role for the removal of turbidity. Under all of the experimental concentrations of $O_3$, the residual turbidities decreased with the PAC dosage increasing. However, the decreasing effect is more obvious under $O_3$ pre-oxidation than without $O_3$. It is clear that the residual turbidities decreased under the same dose of PAC when the concentration of $O_3$ ranges from 0.5 to 1.0 mg/L, but it increased when the concentration of $O_3$ ranges from 1.0 to 2.0 mg/L. Moreover, the concentrations of $O_3$ were 0.0, 0.5, 1.0, and 2.0 mg/L, the residual turbidities were 2.47 NTU, 1.33 NTU, 0.99 NTU, and 1.21 NTU, respectively, when the dose of PAC was 6.0 mg/L. Subsequent experiments confirm that the residual turbidities reached 0.99 NTU at a PAC dose of 15 mg/L without $O_3$. This suggests that the presence of $O_3$ would reduce the 60% PAC dose.

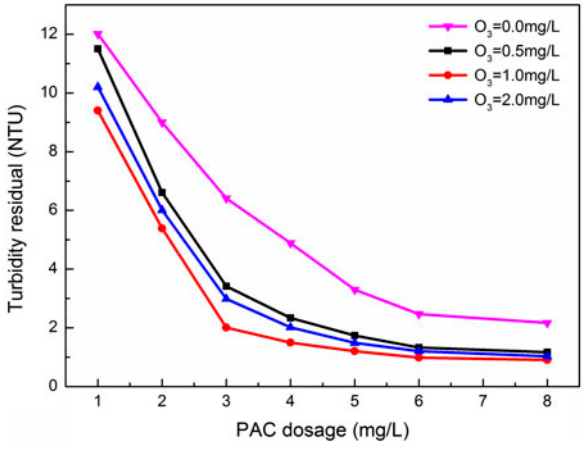


Fig. 4. Effect of $O_3$ pre-oxidation and PAC-enhanced coagulation on the turbidity removal.

### 3.5. NOM removal

The changes of TOC and $UV_{254}$ against $O_3$ concentration and PAC dose in the water sample during coagulation with PAC only and enhanced coagulation combining $O_3$ pre-oxidation and PAC are shown in Fig. 5. It can be seen from Fig. 5(a) that the presence of $O_3$ significantly improved the removal of TOC and $UV_{254}$ in the solution, and that the removal of $UV_{254}$ is especially obvious. Under all of the experimental concentrations of $O_3$, the removal of TOC increased with the PAC dose increase, and this tendency is more obvious in the presence of $O_3$ than with PAC coagulation only. When the concentration of $O_3$ ranges from 0.5 to 1.0 mg/L, the removal of TOC increased at the same dose of PAC, but the removal decreased in the range of $O_3$ concentration 1.0–2.0 mg/L. What's more, the removal of TOC is higher under the conditions of

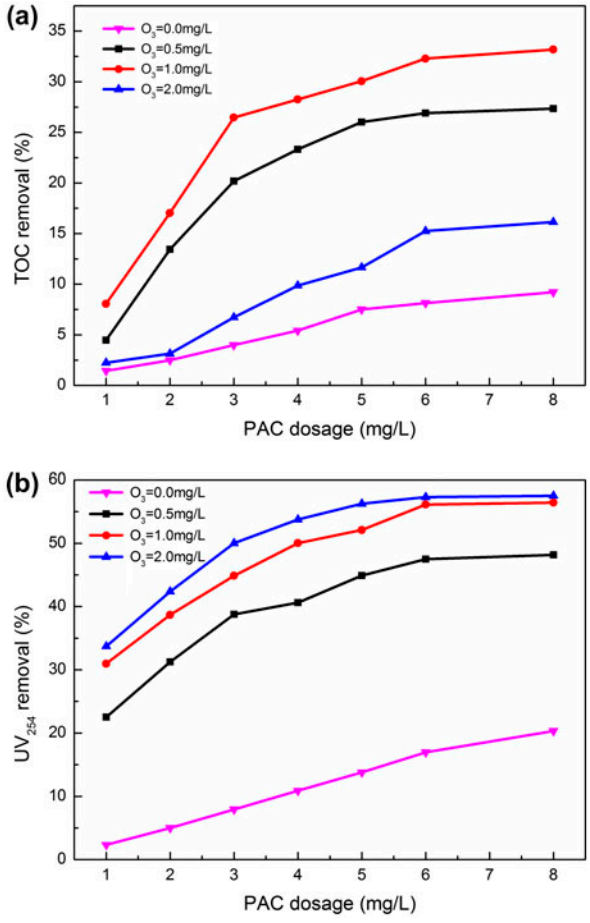


Fig. 5. Effect of $O_3$ pre-oxidation and PAC-enhanced coagulation on the NOM (TOC and $UV_{254}$) removal.

$O_3$ pre-oxidation than without $O_3$, and 1.0 mg/L $O_3$ and 6.0 mg/L PAC dose resulted in 32.29% TOC removal. It can be seen from Fig. 5(b) that $O_3$ pre-oxidation has a significant promoting role for removing $UV_{254}$. At the same dose of PAC, the removal of $UV_{254}$ increased with increasing concentration (0–2.0 mg/L) of $O_3$ in the water sample. At the same concentration of $O_3$, the removal of $UV_{254}$ increased with increasing dose (0–8.0 mg/L) of PAC. Enhanced coagulation using 2.0 mg/L $O_3$ and 6.0 mg/L PAC produced 57.28% removal of $UV_{254}$. The growth of $UV_{254}$ removal is very slow at the PAC dosage of more than 6.0 mg/L. In a word, it will greatly improve the removal of NOM after a certain concentration of $O_3$ pre-oxidation.

## 4. Conclusion

Based on the experiments reported here, the following are the conclusions arrived from this study.

The surface of A.F. is negative charge and A.F. can be removed by enhanced coagulation method. $O_3$ pre-oxidation has a certain promoting role for removal of algae, turbidity, and NOM. The greatest removal of chl-*a* and TOC attained 97.67% and 32.29%, respectively, at $O_3$ concentration of 1.0 mg/L and a PAC dose of 6.0 mg/L. 1.0 mg/L $O_3$ pre-oxidation reduces 60% of PAC adding dose with the residual turbidities 0.99 NTU. 2.0 mg/L $O_3$ pre-oxidation increases the $UV_{254}$ removal from 16.97 to 57.28% at a PAC dose of 6.0 mg/L.

Overall, the combination of $O_3$ and PAC is more effective and feasible than coagulation with PAC only for treatment of slightly polluted algae-containing surface water.

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