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Effect of chemical preoxidation coupled with in-line coagulation as a pretreatment to ultrafiltration for algae fouling control

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ABSTRACT

Algae fouling can cause a transmembrane pressure (TMP) increase or flux decrease during ultrafiltration of surface waters. In this study, chemical preoxidation coupled with in-line coagulation was investigated as a pretreatment step for algae fouling control. The coupled strategy was able to control the flux decline. Also, the treated water quality could be improved. Chemical preoxidation by potassium permanganate composites (PPC) and chlorine (Cl_2) removed algae cells by both cell death and adsorption, which could also alleviate the load on the ultrafiltration unit. During the coupled treatment, the electrostatic forces between algae cells and the flocs weaken. The cells could be packed by *in situ* formed hydrous manganese dioxide and flocs. The flocs would be trapped on the cake layer and the algae fouling for ultrafitlration could be controlled.

Keywords: Chemical preoxidation; In-line coagulation; Ultrafiltration; Algae; Fouling

1. Introduction

Ultrafiltration (UF) is a promising advanced treatment technology for drinking water purification [1]. However, the onset of membrane fouling has become an impediment to its wide application [2–3]. To control fouling and improve water quality, pretreatment technology can be applied before UF [4]. Chemical preoxidation is often used to satisfy the needs of improving water quality. Common preoxidants include ozone (O_3), chlorine dioxide (ClO_2), potassium permanganate ($KMnO_4$) and chlorine (Cl_2). O_3 upstream of UF system was investigated coupled with conventional water treatment processes, and it was reported that 6–12mg/L O_3 could improve the turbidity removal efficiency [5]. The application of O_3 in water treatment has attracted the researchers' attention, although its wide use in developing countries still needs time because of the high cost. Conversely, $KMnO_4$ preoxidation has been widely applied for a number of years. Ellis et al. applied $KMnO_4$ for controlling microfiltration (MF) membrane fouling[6]. $KMnO_4$ was also used in reducing inorganic fouling for immersed UF membranes [7]. The application of $KMnO_4$ is suitable for emergent treatment for its ease and flexibility, although its strong color is still an important limitation for its application. Other options such as prechlorination could also reduce UF membrane fouling. Prechlorination coupled with adsorption/UF was investigated for natural organic matter removal, and the flux decline was alleviated by changing the particle size [8]. However, the chlorinated disinfection by-products (DBPs) created also limited its use. Finally, little research has been reported about ClO_2 oxidation as a pretreatment for membrane operations because of difficulties in preparation and instability.

In recent years, the combined use of coagulation and UF has attracted more and more attention. Coagulation causes dissolved organic matter to aggregate and adsorb on metal oxides to form flocs. These flocs can deposit on the membrane surface and reduce the pollutant concentration here. Jung et al. reported that coagulation could

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alleviate the fouling and increase the critical flux for the membrane [9]. Farahbakhsh et al. compared different low pressure membrane water treatment processes. Coagulation was proved to be efficient for removing DBP precursors and controlling the fouling rate [10]. "In-line coagulation" means coagulant is continuously dosed, and the flocculated water is directly fed to the UF module without any barriers for removing flocs. Guigui et al. found that in-line coagulation could control UF fouling and improve the treated water quality[11]. Qin et al. applied an in-line coagulation/UF system for reservoir water treatment, and the results showed that the system could run at lower transmembrane pressure (TMP) while maintaining higher flux [12].

Algae and its by-products have become important pollutants for drinking water production. As to its nominal pore size, UF membrane can remove algae cells. However, the trapped cells may release extracellular matter that can block the module outlet and lead to severe flux decline or TMP increase.

This study was conduced in Hainan Province (China) and the objective of the study was to provide a new way to improve UF membrane performance in algae-rich water treatment. Based on these published results, chemical preoxidation coupled with in-line coagulation as the pretreatment for UF was investigated in this study for algae-rich water treatment.

2. Materials and methods

2.1. Raw water characteristics

Algae-rich reservoir water served as the source of surface water in this study. A summary of the source water characteristics is shown in Table 1.

Table 1
Source water characteristics.

Turbidity, NTU	3.1–11.5
pH	7.61–8.05
COD_{Mn}, mg/L	3.2–3.7
Algae count, 10^4cell/L	930–1260
Temperature, °C	21.2–24.3

2.2. Experimental set-up

Based on published results on algal removal during water treatment, potassium permanganate composites (PPC, made from 75% potassium permanganate, 15% ferric chloride and 10% lime, produced by Beijing Single-factor Co. Ltd., China) and chlorine (chlorine gas was injected into the feed water and chlorinated water formed with 0.5g/L available chlorine) were applied as preoxidants [13]. The coagulant used in the study was alkaline aluminium chloride(alum, produced by Henan Gongyi Chemicals Co.Ltd., China). The coagulant and preoxidants were dosed simultaneously before the mixer. The addition of these chemicals did not change the pH of the water significantly (the pH of the resulting solution varied in the range of 7.59~7.98). All of the chemicals used were dosed by electronic metering pumps (LMI, Milton Roy, Acton MA01720, USA). The in-line mixing time was 1min, and the pipes used in the pilot device were all made of UPVC (Fig. 1).

Table 2
Physical characteristics of the UF membrane module.

Parameter	Membrane
Material	PVC
Type	Hollow fiber
Length of fibers (mm)	1,200
Total membrane area (m^2)	48
Recommended working pressure (MPa)	0.05~0.20
MWCO(Dalton)	80,000

A pilot scale hollow fiber UF membrane module (Hainan Litree Membrane Separation Company, China) was employed in the study. The related parameters of the module are shown in Table 2. The UF module was operated at a pressure of 0.10MPa in a crossflow mode. The feed water supplied to the lumen side with the initial flux set at 83L/m^2·h. The concentrate discharge ratio was 5%. The backwashing cycle was 2h, with backwashing for 120s at a pressure of 0.20MPa.

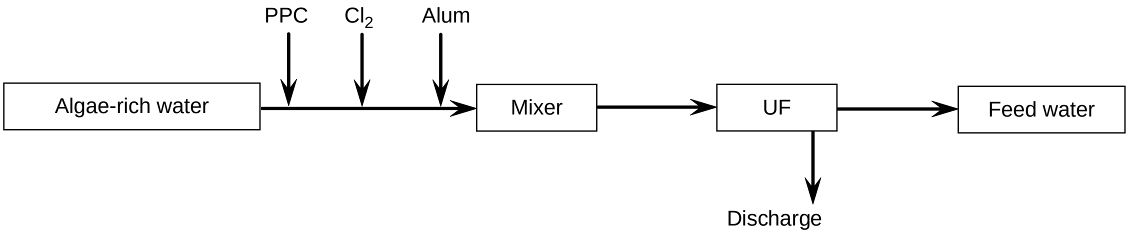

Fig. 1. Pilot-scale UF process.

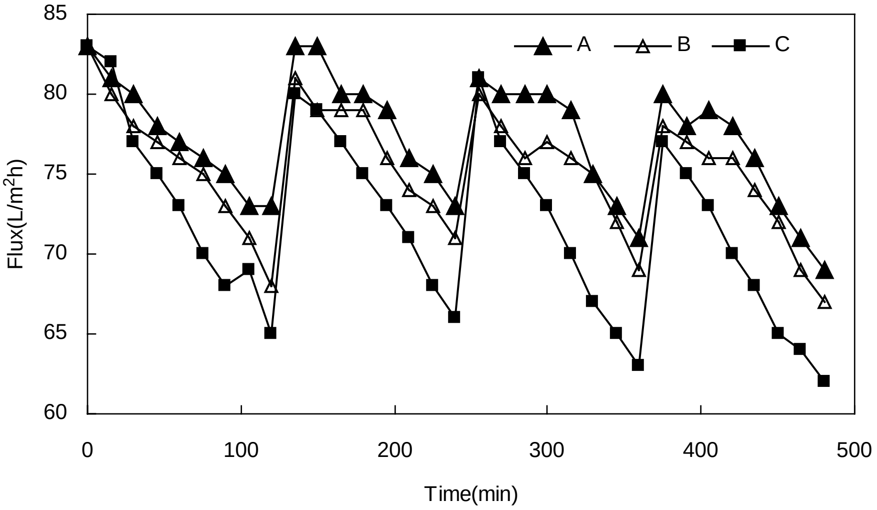

Fig. 2. Effect of preoxidatant dosage on the flux variations during UF.

2.3. *Analytical methods*

The turbidity was determined using a turbidimeter (Hach 2100N). A UV spectrophotometer (Shimadzu UV-2201) was used to measure UV_{254}. COD_{Mn} was analysed by acid permanganate oxidation.

3. Results

The optimal coagulant dosage was 12.5 mg/L alum based on previously published results [13]. The dosages of preoxidants were varied as follows:

A. PPC 0.3mg/L, Cl_2 0.3mg/L;
B. PPC 0.5mg/L, Cl_2 0.5mg/L;
C. PPC 0.7mg/L, Cl_2 0.7mg/L;

3.1. *Effect of preoxidatants' dosages on flux variations during UF*

Process A (PPC 0.3mg/L, Cl_2 0.3mg/L) maintained the lowest rate of flux decline compared with other two processes. Increasing the oxidant dosage beyond this level had no evident effect on maintaining flux. This phenomenon can be explained by the *in situ* production of hydrous manganese dioxide (the reaction byproduct of the PPC) acting to nucleate flocs. Liu et al. reported that hydrous manganese dioxide shows plentiful reactive surface sites and exhibits excellent interfacial characteristics for adsorbing pollutants from solution. Hydrous manganese dioxide thus enhances the heterogeneous coagulation process and facilitates larger floc formation [14]. However, the larger flocs may affect filtration and increase the cake layer resistance. During the application of combined preoxidation by PPC and Cl_2, this double effect should be taken into account. PPC and chlorine could oxidize most of the algae cells, which could reduce the number of live algae cells entering the UF module. On the other hand, as the reaction by-product of PPC, hydrous manganese dioxide may make flocs denser and increase the mass transfer resistance during UF filtration. The ability to optimize the dosage of preoxidants according to raw water quality is thus very important for application in algae-rich water treatment.

3.2. *Effect of preoxidatant dosage on treated water quality during UF*

The treated water quality resulting from the three pretreatment dosage levels was investigated. It was found that the effluent from Dosage level A achieved the best water quality (Figure 3). Thus it can be inferred that algae cell death is the dominant action at the lower dosages, which acts to reduce the fouling rate for UF. In-line coagulation results in loose flocs, which can trap organic matter and protect the UF from organic fouling. This loose cake layer may also trap more suspended particles and improve treated water quality.

4. Discussion

As shown in Fig.4a in the absence of any pretreatment, algae cells and organic matter can easily enter the UF module. Organic matter can penetrate within the membrane pore and cause evident flux decline. Live algae cells can also deposit on the surface of membrane and release extracellular material during filtration. The released polysaccharides can bond with other organic species and increase the resistance for filtration. For this reason, a direct UF system is not suitable for algae-rich water treatment.

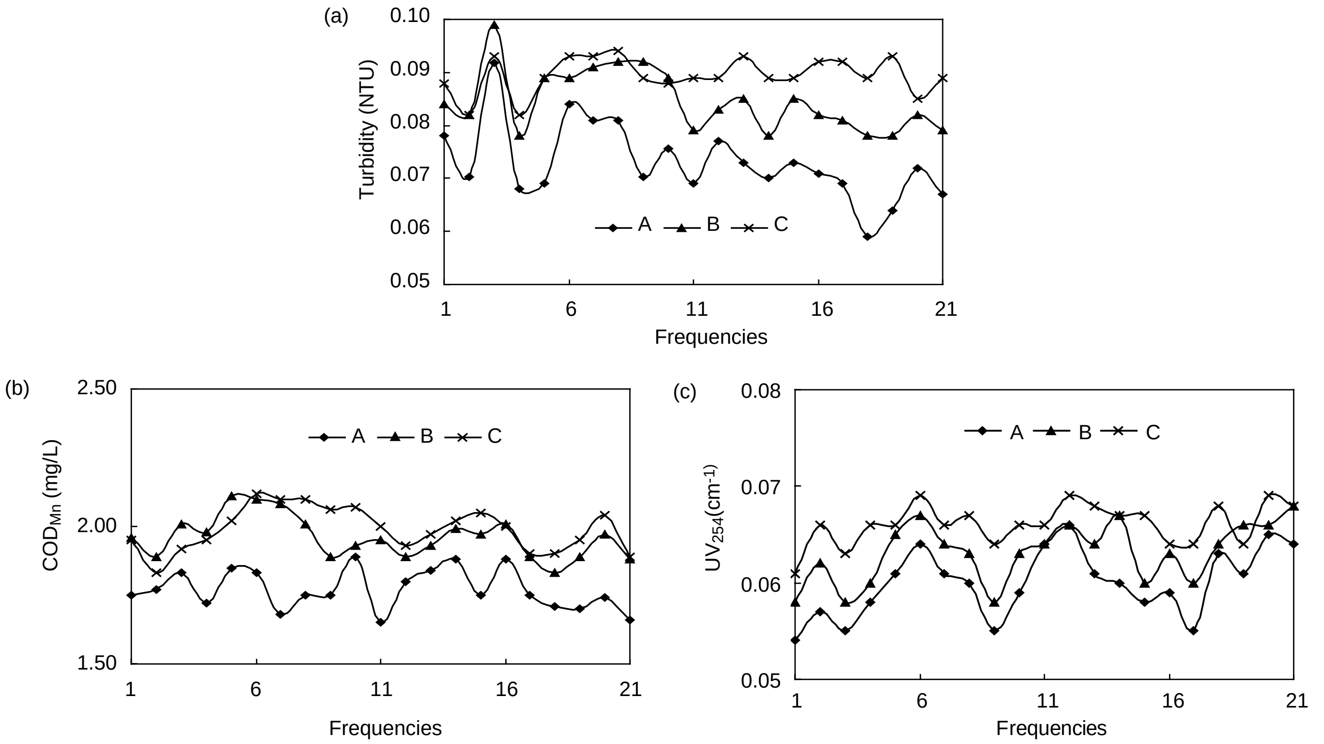

Fig. 3. Effect of preoxidation on the treated water quality during UF (3a: Turbidity variations during UF; 3b: COD_{Mn} variations during UF; 3c: UV_{254} variations during UF).

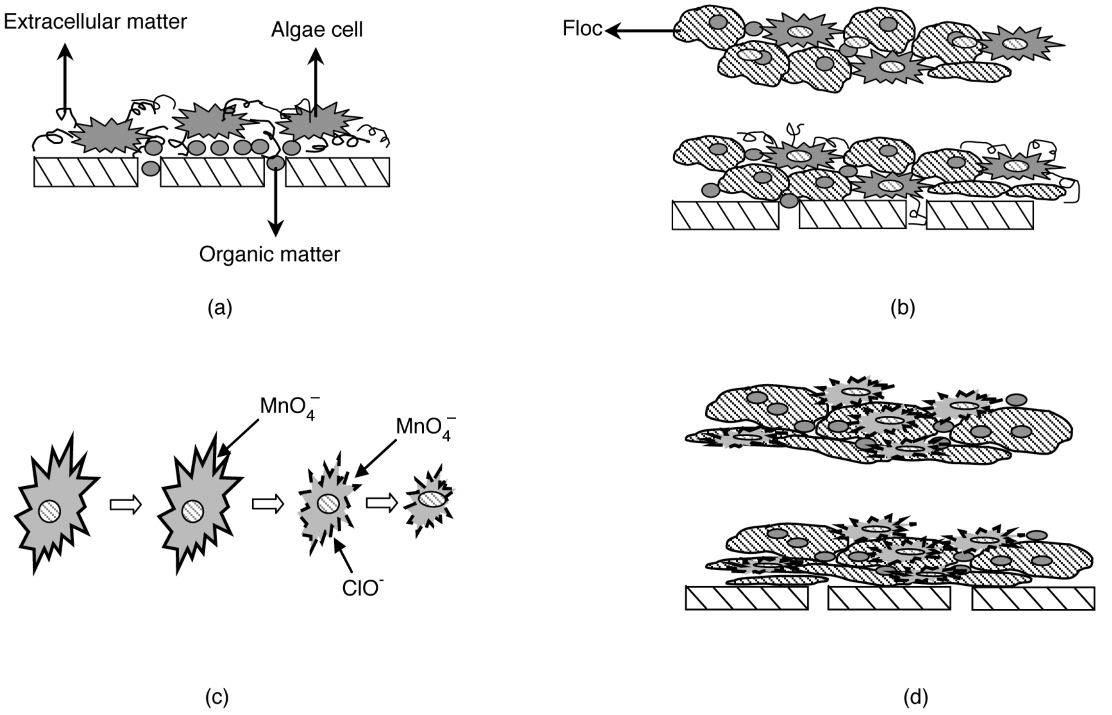

Fig. 4. Mechanisms of chemical preoxidation coupled with in-line coagulation as a pretreatment for UF during algae-rich water treatment (4a: Mechanisms of direct UF; 4b: Mechanisms of in-line coagulation as pretreatment for UF; 4c: Mechanisms of synergistic effect for algae by PPC and Cl_2; 4d: Mechanism of chemical preoxidation coupled with in-line coagulation as the pretreatment for UF.).

Coagulation pretreatment can improve UF by flocculating the material depositing on the membrane surface, which can then form a loose cake layer. The low molecular organic matters can be trapped within this the layer and the fouling is reduced (Fig.4b). During the algae-rich water treatment, coagulation can only adsorb and flocculate the algae cells, while it can not make them inactive. Algae cells can still release extracellular matter and affect filtration. Coagulation pretreatment alone can thus not satisfy the needs of UF application in algae-rich water treatment.

Literature has reported that combined preoxidation by PPC and Cl_2 is optimal for removing algae [15]. Based on the difference in their oxidizing abilities, PPC and Cl_2 can selectively kill algae cells. Also, manganate (MnO_4^-) as the main ingredient in PPC may attack the algae cell wall, which can provide a channel for available chlorine to penetrate. With the death of the algal cells, the release of extracellular matter is prevented. (Fig.4c)

However, the hydrous manganese dioxide produced *in situ* by PPC has a strongly adsorbing surface which can flocculate the algae cells (including dead cells and residual live cells). The flocs will be trapped on the cake layer and the algae fouling for UF can be controlled (Fig. 4d). It should be pointed out that at higher dosages of PPC, the flocs become more dense and the cake layer resistance increases. The more dense cake may also lead to difficulty in cleaning the cake layer from the membrane. The dosing strategy should be optimised according to the concentration of algae cells and the concentration of organic matter.

5. Conclusions

The effect of chemical preoxidation coupled with in-line coagulation on UF for algae fouling control was investigated. The optimal dosing strategy was PPC 0.3mg/L, Cl_2 0.3mg/L and alum 12.5mg/L. The mechanisms involved in the use of such a combined approach as pretreatment for UF was discussed. Combined preoxidation by PPC and Cl_2 plays an important role in killing algae cells before they enter the UF module. The operation mode for UF systems in algae-rich water treatment should be further studied.

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