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Effect of pretreatment by permanganate/chlorine on algae fouling control for ultrafiltration (UF) membrane system

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Abstract

The use of ultrafiltration (UF) is receiving more attention for drinking water treatment, but its fouling remains a problem. Reservoir water was selected as raw water during pilot study. Worldwide drinking water reservoirs may contain algae, which pose a threat to drinking water treatment. UF membrane has been recognized that it can remove algae for its nominal pore sizes. The algal cells cumulate on membrane surface, and the secretion released by them would cause transmembrane pressure increases or flux decreases. Also, conventional backwashing could not satisfy with the need of flux recovery. Frequent chemical cleaning may shorten the membrane unit's service life. The best available technology for UF membrane system during algae bloom should be inactivating algae and removing them before they are fed into UF membrane. The objective of this study was to investigate the effect of pretreatment by permanganate/chlorine on UF membrane operation for controlling algae fouling. It was found that combined use of permanganate and chlorine could reduce the rate of UF membrane fouling. Permanganate and chlorine could be in synergistic action in inactivating algal cell. The intermediate of permanganate, hydrous manganese dioxide (MnO_2) could adsorb on algal cells depending on its strong specific surface area. In addition to permeate water quality, specific flux (at constant TMP) and TMP (at constant flux) of UF membrane also demonstrated that pretreatment could improve UF membrane system.

Keywords: Ultrafiltration (UF); Pretreatment; Permanganate; Chlorine; Algae fouling

1. Introduction

Recently, ultrafiltration (UF) technology has been in progress as an alternative to conventional drinking water treatment [1]. UF has been known effective for the removal of turbidity, particulates and pathogens to meet more stringent regulations [2]. However, UF membrane fouling problems have become an impediment to wide application [3]. Especially for the algae-rich feed water, algae

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secrete an extracellular, mucilaginous slime material, which could cement particulates on the membrane surface and increase the resistance to filtration [4].

Several studies have developed potential pretreatment options for UF membrane fouling control [5–9]. Pretreatment has greatly expanded the use of UF membrane system beyond turbidity and pathogen removal. Preoxidation was often adopted in chemical pretreatment, and the preoxidants were investigated widely. Numerous literatures have reported that preoxidants such as ozone, chlorine, or permanganate can improve algae removal by coagulation and filtration process. These preoxidants served as both algaecide and flocculant aid [10–13].

Traditionally, prechlorination has been found to be an effective method to aid the coagulation of waters with a high organic content or algae blooms. Sukenik et al. found that chlorine had distinct effect on algal cell surface architecture, which resulted in the release of cellular organic compounds [14]. However, the use of chlorine is subjected to cause the formation of trihalomethanes (THMs) and haloacetic acids (HAAs), which are harmful by-products and this limits its use in many countries [15]. Plummer et al. reported that ozone caused the release of extracellular organic matter (EOM), which made coagulation easier and caused the increase of THM precursors [12,13]. Petrusevski et al. showed that permanganate inactivated motile micro-organisms and induced in situ production of natural, algae-derived coagulant aid [11]. Chen et al. studied the mechanism of potassium permanganate on algae removal. They reported that permanganate could promote the aggregation of algal cells [10]. However, for the disadvantages of inactivation efficiencies and color, permanganate pretreatment needs to be enhanced. The pretreatment step improved or deteriorated the coagulation and disinfection process by changing the nature of the water.

Synergistic effects of the chemicals have received more and more attention recently [16–19]. Combined use of permanganate and chlorine has been proved to be in synergistic action and the application of permanganate/chlorine controlled the production of THMs [20]. For reservoir water, permanganate and chlorine have been applied and the synergistic effects were also testified. It was indicated that combined use of permanganate and chlorine in pretreatment ensured the microbial and chemical safety for water treatment [21]. Based on the synergistic effect, permanganate and chlorine have been applied in combination to inactivate algal cells and remove them by enhancing coagulation [22].

In this study, therefore, the effect of reservoir water pretreatment by permanganate/chlorine on algae fouling control for UF was investigated.

2. Experimental

2.1. Raw water characteristics

Algae-rich reservoir water was selected in this study. A summary of the raw water quality is shown in Table 1.

Table 1
Feed water characteristics

Turbidity (NTU)	4.62–8.91
pH	7.92–8.00
COD_{Mn} (mg/L)	2.2–2.8
Algae count (×10^4 cell/L)	690–1230
Temperature (°C)	25.1–28.5

2.2. Jar tests

To optimize the dosing of coagulants and preoxidants, jar tests were conducted with a six-unit stirrer apparatus. Pretreatment by permanganate/chlorine followed by aluminum chloride (alum) coagulation-sedimentation was investigated. Different amounts of permanganate or/and chlorine were mixed at 200 rpm with water samples in each beaker for 1 min. Then all of the water samples were subjected to coagulation with the addition of a specific volume of alum solution at 120 rpm for 1 min. Thereafter, the samples were slowly stirred for 18 min at 30 rpm, and then settled for 30 min. The supernatant was extracted by siphonage from 1 cm below the water surface. The residual turbidity and COD_{Mn} were measured to evaluate the effects of pretreatment by permanganate/chlorine on the treated water quality.

2.3. Ultrafiltration experiments

The UF membrane used in this study was made of polyvinyl chloride (PVC) hollow fiber with a molecular weight cut-off (MWCO) of 80,000 Dalton and an effective surface area 48 m^2. Pilot-scale cross-flow UF experiments were performed with an inside-out type.

An explanatory sketch of the UF facility is shown in Fig. 1. Potassium permanganate and sodium hypochlorite (NaClO) were applied as preoxidants simultaneously before the mixer. Alum was used as coagulant. And the regulating tank (retention time 20 min) played the important roles in flocculation and solid–liquid separation process. The dosages of the chemicals used in the experiments were based on the result of jar tests.

The transmembrane pressure (TMP) reflects resistance of the membrane fouling, including pore narrowing and cake layer. The TMP would be expected to increase in the course of filtration due to the fouling.

Specific flux was also used to provide comparisons between pretreatment conditions, which is the ratio of permeate flux at 20°C to TMP (120 kPa).

$$J_{sp} = \frac{J_{20}}{\text{TMP}} \tag{1}$$

where J_{sp} is the specific flux (L m^{-2} h^{-1} kPa^{-1}), J_{20} is the permeate flux corrected for 20°C (L m^{-2} h^{-1}). Permeate flux was corrected for temperature effects using the following equation [1,23].

$$J_{20} = \frac{Q_p e^{-0.0239(T-20)}}{S} \tag{2}$$

where Q_p is the permeate flow (L/h), T is the feed water temperature (°C), and S is the membrane effective surface area (m^2).

3. Results and discussion

3.1. Preliminary study on chemicals' dosage optimization

Jar tests were carried out to optimize the chemicals' dosage. And the alum doses varied from 1 to 10 mg/L as aluminum chloride. Results showed that the best effect was obtained at alum 5.0 mg/L.

And prechlorination was conducted at 0.5–2.0 mg/L dosage range with alum 5.0 mg/L, chlorine 2.0 mg/L was the better selection. Although the higher chlorine dosage could get better results, the risk of disinfection by-products

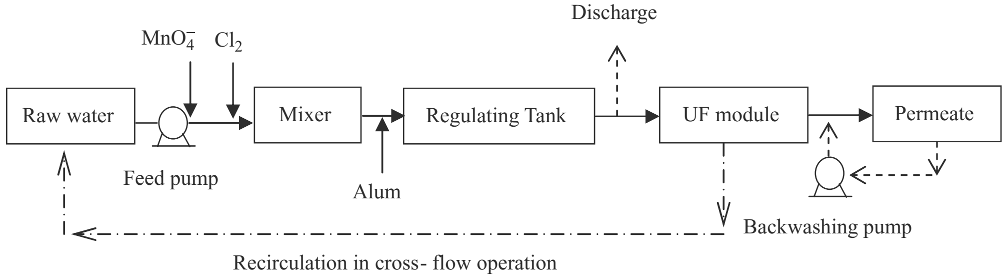

Fig. 1. Schematic diagram of the experiment.

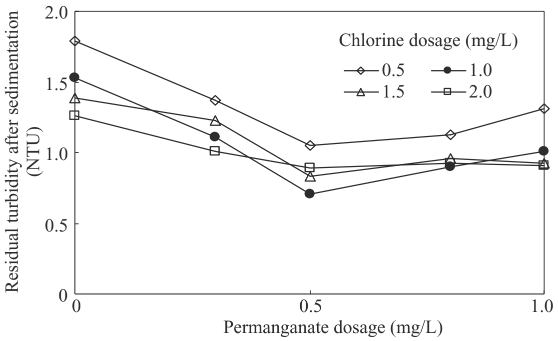

Fig. 2. Effect of the permanganate/chlorine ratios on the residual turbidity after sedimentation (Alum 5.0 mg/L).

(DBPs) limited its use. Also the permanganate pretreatment was optimized and permanganate 0.8 mg/L was observed as the best dosage.

Based on the optimization dosage of coagulant, the best dosage of permanganate/chlorine was determined as permanganate 0.5 mg/L and chlorine 1.0 mg/L, in which the best reduction efficiencies of turbidity and COD_{Mn} were obtained.

3.2. Effect of pretreatment by permanganate/chlorine on UF membrane fouling

The dosing strategy for permanganate/chlorine pretreatment was chosen based on jar tests results.

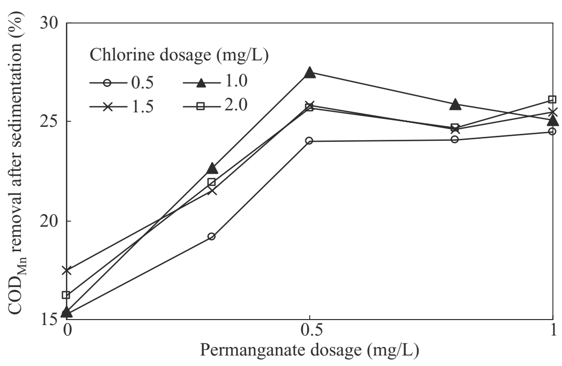

Fig. 3. Effect of the permanganate/chlorine ratios on the COD_{Mn} removal after sedimentation (Alum 5.0 mg/L).

And the effect of pretreatment by permanganate/chlorine on UF membrane fouling was evaluated at this stage of the study. Comparative experiments were performed between different pretreatment conditions.

Fig. 4 shows that the direct UF resulted in higher rate of membrane fouling. Prechlorination and permanganate pretreatment showed relatively better effects than direct UF. However, it is noteworthy that permanganate pretreatment could increase faster than prechlorination during the latter end of filtration time. And it should be that permanganate dosage was over-dose for UF operation though suitable for residual turbidity and organic matters removal. It is hypothesized that excess permanganate could form hydrous manganese dioxide (MnO_2) at an excessive amount, which made the cake layer on the membrane surface thicker by bridging the colloids on the surface [1].

Fig. 4 also shows that the best TMP performance was observed for combined pretreatment by permanganate and chlorine, which implies that it could reduce the rate and extent of membrane fouling. And the phenomenon could be explained by that permanganate/chlorine pretreatment could

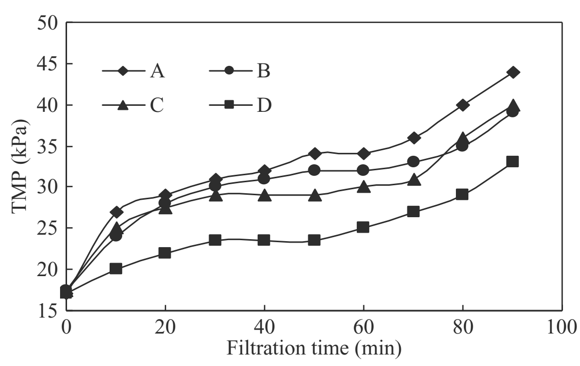

Fig. 4. Variations in TMP as a function of pretreatment conditions for UF membrane (Alum 5.0 mg/L, at constant flux 80 L $m^{-2}h^{-1}$) (A: Direct UF without pretreatment; B: Chlorine 2.0 mg/L pretreatment; C: Permanganate 0.8 mg/L pretreatment; D: Permanganate 0.5 mg/L + Chlorine 1.0 mg/L pretreatment).

produce a cake layer that showed less resistance, which was based on the efficient algae removal. Permanganate and chlorine could remove algae in synergistic action, and permanganate could enhance organic matters removal by oxidation and adsorption (by intermediate MnO_2). Natural organic matters (NOM) and algae were the main foulants in reservoir water treatment by UF [4].

By means of permanganate/chlorine pretreatment, specific flux decline was improved. Fig. 5 shows the specific flux profiles for different pretreatment conditions corrected to 20°C (at constant TMP120 kPa). As is demonstrated in Fig. 5, combined pretreatment by permanganate/chlorine shows a high and stable specific flux. The rapid loss of permeability of direct UF was due to the live algal cells adhering on the surface of membrane and the polymeric substances released by live algal cells blocking the pores. Similar results were shown for prechlorination and permanganate pretreatment, and these two pretreatment conditions could only inactivate algal cells incompletely and remove them inefficiently for UF membrane.

Therefore, applying permanganate/chlorine pretreatment process before UF membrane filtration was found to be very effective in fouling reduction.

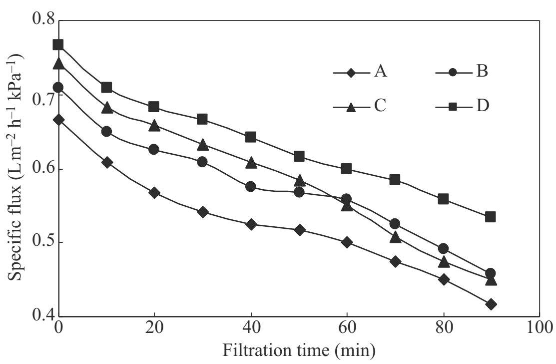

Fig. 5. Variations in specific flux (corrected to 20°C) as a function of pretreatment conditions for UF membrane (Alum 5.0 mg/L, at constant TMP120 kPa) (A: Direct UF without pretreatment; B: Chlorine 2.0 mg/L pretreatment; C: Permanganate 0.8 mg/L pretreatment; D: Permanganate 0.5 mg/L + Chlorine 1.0 mg/L pretreatment).

3.3. Performance evaluation of permanganate/chlorine pretreatment followed by UF

The effect of pretreatment conditions on permeate water quality is shown in Fig. 6. Combined pretreatment by permanganate/chorine was more effective in removing particles and NOM. The removal of COD_{Mn} represented organic matters in natural reservoir water, which was only about 8% with direct UF, whereas it was increased by 30% with combined pretreatment. A possible explanation of the difference between permanganate/chlorine and other pretreatment conditions is that permanganate and chlorine could remove NOM and particles in multiple effects.

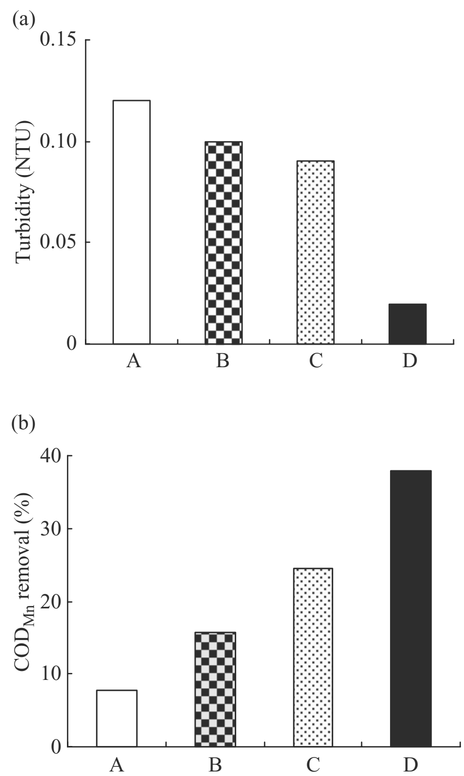

Fig. 6. Effect of pretreatment conditions on permeate water quality: (a) residual turbidity; (b) COD_{Mn} removal (Alum 5.0 mg/L, at constant TMP120 kPa) (A: Direct UF without pretreatment; B: Chlorine 2.0 mg/L pretreatment; C: Permanganate 0.8 mg/L pretreatment; D: Permanganate 0.5 mg/L + Chlorine 1.0 mg/L pretreatment).

3.4. Mechanisms in permanganate/chlorine pretreatment

The synergistic effect of combined pretreatment is likely caused by the activity of the various pre-oxidants reacting with specific chemical groups of the algal cell wall, which is described "target attacking". And it could be hypothesized that chlorine is allowed to permeate through partially oxidized cell wall layers by permanganate at a faster rate. Each oxidant has its own specific reactivity toward algal cell structure materials, so that the combined use of preoxidants means that different mechanisms are brought to explain the efficiencies of algae removal. Injury due to exposure to permanganate may be the result of oxidation of thiol groups. This may lead to structural changes in the algal cell membrane which may allow chlorine to pass through. The intermediate MnO_2 may bind to nucleic acids, resulting in cross-linking, or adsorbing on algae debris and EOM. And MnO_2 could be incorporated into algae floc, which increased its specific gravity and settling velocity [10,11]. And combined pretreatment could also enhance coagulation for NOM and particles removal. The pretreatment could remove and inactivate algal cells effectively, and the release of EOM could help coagulation for particles removal. On the other hand, the intermediate MnO_2 can remove NOM by adsorption. Combined pretreatment is suitable for UF membrane fouling control should be based on the mechanisms of synergistic inactivating effect and the intermediate MnO_2 as for its strong adsorptive capacity.

The significance of using permanganate/chlorine as UF membrane pretreatment for algae fouling control has several implications: Firstly, it reduces the dosage of chlorine, which is meaningful for DBPs reduction and protecting membrane materials in the long run. Secondly, it reduces the dosage of permanganate, which is meaningful for avoiding the problems of color and Mn^{2+} concentration. Thirdly, it shows the synergistic effect of permanganate and chlorine for inactivating algal cells, although the mechanisms should be further studied. Fourth, the intermediate MnO_2 is more effective in the combined pretreatment than in the permanganate pretreatment, for the synergistic effect may improve the inactivation of algal cells and facilitate their binding to MnO_2. Finally, the combined pretreatment is easy to operate at a lower cost when needed.

4. Conclusions

The prevention of algae fouling of UF membrane was investigated by pretreating the feed water with permanganate/chlorine prior to UF. It was found that combined use of permanganate and chlorine could reduce the rate of UF membrane fouling. Permanganate and chlorine applied in experiments could be in synergistic action in inactivating algal cell. The intermediate of permanganate, hydrous manganese dioxide (MnO_2) could adsorb on algal cells to increase the specific gravity and settling velocity. In addition to permeate water quality, specific flux and TMP of UF membrane also demonstrated that the combined pretreatment could improve UF membrane system.

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