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Membrane Fouling Alleviation by Chemically Enhanced Backwashing in Treating Algae-Containing Surface Water: From Bench-Scale to Full-Scale Application

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ABSTRACT

Ultrafiltration (UF) has been increasingly implemented in drinking water treatment plants; however, algae and their secretions can cause severe membrane fouling and pose great challenges to UF in practice. In this study, a simple and practical chemically enhanced backwashing (CEB) process was developed to address such issues using various cleaning reagents, including sodium hypochlorite (NaClO), sodium chloride (NaCl), sodium hydroxide (NaOH), sodium citrate, and their combinations. The results indicate that the type of chemical played a fundamental role in alleviating the hydraulically irreversible membrane fouling (HIMF), with NaClO as the best-performing reagent, followed by NaCl. Furthermore, a CEB process using a combination of NaClO with NaCl, NaOH, or sodium citrate delivered little improvement in the alleviation of membrane fouling compared with NaClO alone. The optimized dosage and dosing frequency of NaClO were 10 $mg\cdot L^{-1}$ two times per day. Long-term pilot-scale and full-scale experiments further verified the feasibility of the CEB process in relieving algae-derived membrane fouling. Compared with the conventional hydraulic backwashing without chemical involvement, the CEB process can effectively remove the organic foulants including biopolymers, humic substances, and protein-like substances by means of oxidization, thereby weakening the cohesive forces between the organic foulants and the membrane surface. Therefore, the CEB process can efficiently alleviate the algae-related membrane fouling with lower chemical consumption, and is proposed as an alternative to control membrane fouling in treating the algae-containing surface water.

1. Introduction

Algae contamination has been regularly reported in reservoirs and lakes due to specific hydrological conditions and eutrophication [1]. However, conventional drinking water treatment processes (i.e., coagulation, sedimentation, filtration, and disinfection) cannot efficiently remove algae, which thus present great challenges for drinking water safety [2–4]. Ultrafiltration (UF), with its inherent capabilities for microorganism rejection and advantages of modular design, automated operation, and a small footprint, has been regarded as an appealing alternative for treating algae-containing surface water [5]. Nevertheless, algal cells and algae-related intracellular organic matter (IOM) and extracellular organic matter (EOM) can accumulate on the membrane surface and deposit within the membrane pores, causing severe membrane fouling and flux reduction. Conventional hydraulic cleaning strategies (e.g., backwashing and air scouring) cannot prevent the ongoing increase of transmembrane pressure (TMP) [6–9], which presents practical challenges in the extensive application of the UF process.

Interestingly, a chemically enhanced backwashing (CEB) process with a low dosage of chemical reagents (e.g., NaCl and NaClO) was found to confer supplementary effects between hydraulic backwashing and chemical cleaning, and can efficiently mitigate the severe membrane fouling caused by organic foulants, espe-

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cially the hydraulically irreversible membrane fouling (HIMF) [8,10,11]. In the CEB process, the types, combinations, dosages, and dosing frequency of chemical reagents played a vital role in membrane fouling control [12]. NaCl, as a simple, cheap, and green agent, can reduce the intermolecular adhesive foulant–foulant forces, resulting in the disassociation of cross-linked gel layer structures; thus, its addition to backwash water can effectively benefit to alleviating the HIMF caused by humic substances, sodium alginate, and biopolymers [8,13]. Furthermore, NaCl addition (0.1 $mol{\cdot}L^{-1}$) has been found to effectively abate the UF membrane fouling derived from the hydrophilic organic matter, and its flux recovery was higher than those of either NaOH- or citric acid-involved backwashing [10,14,15]. Furthermore, CEB using NaClO has been found to significantly alleviate HIMF and prolong the filtration duration due to its enhanced removal of foulants from the membrane surface and membrane pores, as well as its inhibition of microorganism growth [16–18]. Certain other reagents (e.g., NaOH, HCl, and citric acid) can also enhance HIMF alleviation, and their combination (e.g., NaOH + NaClO) exhibits a greater cleaning efficiency than their individual use. Further studies have even indicated that chemical cleaning using NaClO and NaOH can change the adhesive forces between extracellular polymeric substances (EPSs) and the membrane surface due to the oxidation, hydrolysis, and solubilization, resulting in higher flux recovery [19,20].

Studies reporting on the CEB process have mainly used the synthetic water in a lab; however, the feasibility of this process in alleviating the membrane fouling in treating natural water—especially the algae-containing surface water, required further investigation. Furthermore, due to the scale difference, bench-scale experimental results may not prove to be of practical relevance to the process application and needed to be validated further. Thus, a systematic investigation of CEB process from bench scale to pilot scale and full scale was urgently required. Furthermore, most CEB facilities and its operational parameters (e.g., chemical species, dosages, and dosing frequency) have generally been implemented based on rules of thumb. To the best of our knowledge, there is a lack of systematic investigation of the key operational parameters of CEB in alleviating the algae-related membrane fouling (especially the hydraulically irreversible fouling), particularly under the conditions of treating real algae-containing surface water. In addition, the mechanisms of the CEB process in alleviating membrane fouling required further evaluation.

Therefore, the objective of this study was to investigate the effects of CEB parameters, including reagent types and their combinations, dosages, and dosing frequency, on the alleviation of HIMF in treating natural algae-containing surface water from bench-scale to full-scale perspectives. The concentrations and compositions of the foulants that accumulate in the cake layer on the membrane surface and exist in the backwash wastewater were determined in order to further probe the mechanisms of membrane fouling control by CEB operation. The mechanisms of the CEB process in alleviating membrane fouling were further revealed.

2. Materials and methods

2.1. Characteristics of raw water

The experimental setups were located in a UF-based drinking water treatment plant (DWTP), and reservoir water was employed as the raw water. During the period from July to October, algae blooms in the reservoir water. The algae concentration in the raw water was found to be approximately 3×10^6–1×10^7 $cells{\cdot}L^{-1}$, which was much higher than the concentration in other months (less than 3×10^5 $cells{\cdot}L^{-1}$, even not detected). The details of algae cell quantification can be found in Appendix A. Section S3. The algal cells, IOM, and EOM would go through the upstream process and then flow into the membrane tank, where they were rejected by the UF membrane, resulting in severe membrane fouling. In order to simulate real-life DWTP scenarios, effluent from a sand filter was adopted as the feed water in the bench-scale and pilot-scale UF experiments (Appendix A. Fig. S1). During the experimental period, the feed water was characterized by means of its turbidity, total organic carbon (TOC), dissolved organic carbon (DOC), algae, pH, and temperature, with values in the range of 0.6–1.5 NTU, 2.5–3.6 $mg{\cdot}L^{-1}$, 2.1–2.8 $mg{\cdot}L^{-1}$, 5.8×10^5–1×10^6 $cells{\cdot}L^{-1}$, 6.9–7.8, and 25–31 °C, respectively.

2.2. Experimental setups

2.2.1. Bench-scale experiment

To address algae-derived HIMF, bench-scale, pilot-scale, and full-scale experiments were carried out on treating the algae-containing surface water. As shown in Fig. 1, the bench-scale experimental setup consisted of a feed water tank, a membrane tank, a permeate tank, an automatic control system, pumps, an air blower, flowmeters, and a backwashing system. The feed water from the DWTP V-type sand filter flowed by means of gravity into the feed water tank, where a float valve was used to keep the water level constant. Subsequently, the water flowed into the membrane tank, where a polyvinylidene fluoride (PVDF) hollow-fiber membrane (100 kDa) module with an effective filtration area of 0.025 m^2 was positioned. The membrane module was immersed under a water level of 20 cm. After membrane filtration, the effluent flowed directly into the permeate tank, and an overflow was used to maintain an effective water volume for routine hydraulic backwashing. During filtration, the operations of the pump, air blower, and valves, as well as the TMP data collection, were controlled by an auto-control system.

The membrane filtration mode in each cycle was based on a time sequence of 87 min of filtration at a constant flux of 30 $L{\cdot}m^{-2}{\cdot}h^{-1}$, followed by 3 min of backwashing at a given flux of 60 $L{\cdot}m^{-2}{\cdot}h^{-1}$ and an aeration intensity of 15 $m^3{\cdot}h^{-1}{\cdot}m^{-2}$. This study used the CEB process to further alleviate HIMF. During the CEB process, pumps 1 and 2 were operated simultaneously, and the solution synthesized by the membrane permeate and chemical reagents (e.g., NaClO and NaCl) from the CEB tank was added into the backwashing water at a given concentration. The chemical solution was updated daily in order to sustain an effective chlorine concentration. As a control line, pump 1 was operated with no chemical addition in order to perform routine physical backwashing. After backwashing, the bulk solution in the membrane tank was discharged immediately; the tank was then refilled with feed water and another filtration cycle was started.

2.2.2. Pilot- and full-scale experiments

A schematic diagram of the full-scale DWTP is provided in Fig. S1, and the pilot-scale experimental setup was very similar. In the pilot-scale experimental setup, the PVDF hollow-fiber membrane that was used in the bench-scale experiment was adopted, with an effective membrane filtration area of 15 m^2. The operation conditions, including the filtration flux, backwashing flux, operation cycle, and feed water characteristics, were exactly the same as those in the bench-scale experiment. In addition, full-scale experiments with the same PVDF membrane (12 500 m^2) were carried out to further verify the feasibility of the CEB process in treating the algae-containing surface water; in these experiments, the same operation conditions as those in the bench-scale experiment were adopted. The details of the CEB operation are described in Section 2.3.

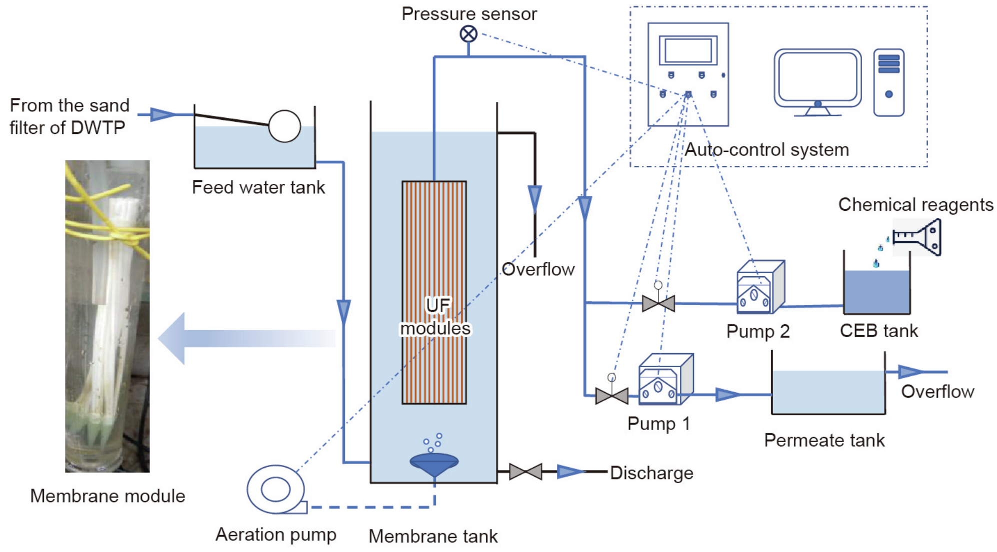

Fig. 1. Schematic diagram of the bench-scale UF process with the CEB operation.

2.3. Experimental protocols

In order to systematically investigate the effects of the parameters of the CEB process (e.g., chemical types, their combinations, dosage and dosing frequency) on the alleviation of membrane fouling in treating the algae-containing surface water, a series of bench-scale, pilot-scale, and full-scale experiments were carried out. Detailed experimental protocols are shown in Table 1.

In Stage 1 of this research, bench-scale experiments were carried out to evaluate the influence of different chemical reagents in CEB operation on the control of membrane fouling, with a continuous filtration period of ~20 d. Based on the experimental results of Stage 1, we attempted to optimize the dosages of NaClO and NaCl while ensuring that the chemical cleaning frequency was not increased. During Stage 2, bench-scale experiments were conducted for ~20 d. In Stage 3, a pilot-scale experiment was conducted to optimize the CEB operational frequency, with a running time of ~16 d. Finally, in Stage 4, a full-scale experiment was carried out to validate the feasibility of CEB operation under the optimized conditions for alleviating HIMF in a real UF-based DWTP.

2.4. Analytical methods

2.4.1. TOC and DOC

The water samples were collected into a 20 mL carbon-free vial, and then fully homogenized, transferred into a 10 mL carbon-free vial, and placed in a fridge at 4 °C prior to detection. For the DOC analysis, the sample preparation procedure was similar to that for TOC, but all the samples were pre-filtered using 0.45 μm hydrophilic filters before the measurements. A TOC analyzer (multi N/C 2100S, Analytic Jena GmbH, Germany) was utilized to determine the concentrations of DOC and TOC, and all the samples were detected in triplicate.

2.4.2. 3D excitation-emission matrix

A three-dimensional excitation-emission matrix (3D EEM) was obtained as follows: at the end of the experiment, the cake layer on the membrane surface was collected into a 50 mL carbon-free vial and then extracted using ultrasonic- and heating-based methods [21,22]. The samples were first fully homogenized using a vortex mixer for 10 min; next, they were ultrasonically treated for 2 min based on a time sequence of 30 s on and 10 s off, in an

Table 1
Experimental protocols of CEB operation in this study.

Stage	Factors	Protocols	Types	Operation time (d)
1	Chemical types	Setup 1: control system without the addition of any chemicals; Setup 2: NaClO (10 mg·L^{-1}); Setup 3: NaCl (300 mg·L^{-1}); Setup 4: NaClO (10 mg·L^{-1}) and NaCl (300 mg·L^{-1}); Setup 5: NaClO (10 mg·L^{-1}) and NaOH (pH 11); Setup 6: NaClO (10 mg·L^{-1}) and sodium citrate (0.5 wt%);	Bench-scale	~20
2	Chemical dosages	Setup 7: NaCl: 100, 300, and 500 mg·L^{-1}; Setup 8: NaClO: 5, 10, and 20 mg·L^{-1};	Bench-scale	~20
3	CEB frequency	NaClO dosage: 10 mg·L^{-1}; CEB frequency: continuous addition, 2 and 4 times per day, respectively.	Pilot-scale	~16
4	CEB feasibility validation	NaClO dosage: 10 mg·L^{-1}; CEB frequency: 2 and 4 times per day.	Full-scale	~16

The control system was operated under the same conditions as shown in Table 1 without any chemical additions. The stock solutions were synthesized by adding the reagents (e.g., NaClO and NaCl) into Mili-Q water in the bench-scale experiments and into the membrane permeate in the pilot-scale and full-scale experiments, respectively. All synthesized solutions were stirred (300 r·min^{-1}, 5 min) and fully mixed prior to dosing.

ice-water bath. The samples were then heated for 30 min in a water bath (80 °C) and centrifuged at $1 \times 10^4 g$ (4 °C) for 10 min. Finally, the supernatant was collected for further analysis. After extraction, the fluorescent foulants in the extracted solution were determined using a three-dimensional (3D) fluorescence spectrophotometer (F7000, Hitachi Ltd., Japan), with excitation spectrum scanning that ranged from 220 to 450 nm in 5 nm increments, and emission spectrum scanning that ranged from 250 to 550 nm in 1 nm increment.

2.4.3. LC-UV analysis

Liquid chromatography–ultraviolet (LC–UV) analysis was performed as follows: the water samples were pre-filtered using a 0.45 μm hydrophilic filter. Next, a high-performance liquid chromatograph (HPLC; Agilent 1200, Agilent Technologies, Inc., USA) coupled with a silica gel column (TSK-gel G4000PWXL) and an ultraviolet (UV) detector at 254 nm was used to determine the apparent molecular weight (MW) distributions. NaCl (0.1 $\text{mol}\cdot\text{L}^{-1}$), KH_2PO_4 (0.002 $\text{mol}\cdot\text{L}^{-1}$), and K_2HPO_4 (0.002 $\text{mol}\cdot\text{L}^{-1}$) were employed to synthesize the mobile phase, and the flow rate was set as 0.6 $\text{mL}\cdot\text{min}^{-1}$. Polystyrene sulfonates with MWs of 3, 4, 7, 15, and 30 kDa were used as the standard substance, and a calibration curve was obtained based on the relationship between retention time and MW.

2.4.4. Hydraulically irreversible fouling index

For the UF process with a periodic sequence of filtration and backwashing, the hydraulically irreversible fouling index (HIFI) was employed to evaluate the membrane fouling that cannot solely be controlled by hydraulic cleaning. The HIFI value can be calculated using the following equations [12,23].

$$1/J' = 1 + \text{HIFI}V_s \tag{1}$$

$$J' = (J/\text{TMP}_i)/(J/\text{TMP}_0) \tag{2}$$

where TMP_0 (kPa) represents the TMP of the pristine membrane, and TMP_i (kPa) is the incipient TMP after each hydraulic backwashing. V_s ($\text{L}\cdot\text{m}^{-2}$) is calculated by dividing the permeate volume by the effective membrane area.

3. Results and discussion

3.1. Effects of chemical types on membrane fouling alleviation

The TMP development over time during the treatment of the algae-containing reservoir water is shown in Fig. 2, and the experimental protocols are provided in Table 1 (Stage 1). As illustrated in Fig. 2(a), although the TMP decreased during each hydraulic backwashing process in the control system, measurable HIMF occurred during long-term filtration. After a 13-day filtration period, the HIMF-derived TMP increased to approximately 36 kPa, for an average growth rate of 2.53 $\text{kPa}\cdot\text{d}^{-1}$, while the total TMP increased to 47 kPa due to the severe membrane fouling. To address this situation, routine chemical backwash cleaning was introduced using NaClO at a dosage of 500 $\text{mg}\cdot\text{L}^{-1}$ and a duration of 5 min; this was expected to alleviate the severe membrane fouling and restore the membrane permeability. However, the TMP was only slightly restored after chemical cleaning, which indicated that the algae-derived HIMF could not be relieved using a short-time one-off chemical backwash cleaning strategy. Based on the practical experience with the DWTP, the membrane modules should first be soaked in concentrated NaClO solution (1000 $\text{mg}\cdot\text{L}^{-1}$) for around 5–12 h with air bubble scrubbing (15 $\text{m}^3\cdot\text{h}^{-1}\cdot\text{m}^{-2}$) for 5 min every 1–2 h. After further backwashing for 5 min, the TMP can be nearly restored to the original value. However, this chemical cleaning approach requires the membrane modules to stop working for quite a long time, which negatively impacts water production; furthermore, the high chemical concentration negatively affects the membrane integrity.

Promisingly, in comparison with the control system, the membrane fouling—especially the HIMF—was significantly alleviated under CEB operation (Figs. 2(b)–(f)). Furthermore, different chemical reagents and their combinations were found to have appreciably different influences on the remission of HIMF. NaClO, a routine and cost-effective chemical cleaning reagent with strong oxidizability, can oxidize organic substances, increase their hydrophilicity, and reduce their MW to weaken their cohesive forces with the membrane surface and destroy the EPS gel layer [24,25]. As displayed in Fig. 2(b), even though the TMP increased significantly due to the foulants rejection on the membrane surface in each cycle, the NaClO-assisted CEB reduced the TMP significantly, bringing it close to its initial value in this study. The growth rate of HIMF-derived TMP was 0.185 $\text{kPa}\cdot\text{d}^{-1}$ and was reduced by 92.7% compared with the control system (Fig. 2(a)). During the experimental period (~20 d), the HIMF-derived TMP increase was nearly negligible, with an extremely low HIFI of 0.043 m^{-1} (Fig. 2(h)), which indicated that the NaClO-assisted CEB process could efficiently control HIMF formation. A previous study has demonstrated that NaClO cleaning can effectively diminish the accumulation of most major foulants (e.g., protein- and carbohydrate-like substances) on the membrane surface and can reduce irreversible membrane fouling resistance (> 88%) [26]. Another study has indicated that NaClO can readily destroy biomacromolecules (e.g., biopolymers and humic substances) to alleviate membrane fouling [27].

Previous studies have elucidated that Na^+ exchanged the Ca^{2+} in the bonds of the "foulants–Ca–membrane" and "foulants–Ca–foulants" combinations, resulting in the breakup of the cross-linked structures of the organic foulants layer [12,13]. Thus, organic foulants can be easily washed away from the membrane surface under Na^+-assisted CEB operation, significantly alleviating the HIMF caused by humic substances and sodium alginate. Consequently, the present study utilized NaCl with a dosage of 300 $\text{mg}\cdot\text{L}^{-1}$ with the aim of controlling algae-related HIMF (Fig. 2(c)). Compared with the control system, the TMP in the NaCl-assisted CEB process increased much more slowly; finally, the HIMF-related TMP increased to about 18 kPa, with a reduction in the HIMF-related TMP growth rate of 47.3% (Fig. 2(g)). Similarly, another study has indicated that NaCl addition (0.1 $\text{mol}\cdot\text{L}^{-1}$) can reduce the intermolecular foulant–foulant adhesive forces and thus break up the cake layer on the membrane surface; it even demonstrated a higher cleaning efficiency than the typical chemical cleaning reagents (e.g., NaOH and citric acid) [15].

As such, both the NaClO- and the NaCl-assisted CEB process efficiently mitigated the algae-related HIMF, although NaClO outperformed NaCl. In order to further improve the HIMF alleviation, combinations of different reagents (i.e., NaClO + NaCl, NaClO + NaOH, and NaClO + sodium citrate) were evaluated. As shown in Fig. 2(d), compared with the control system (Fig. 2(a)), HIMF was effectively reduced under CEB operation using combinations of NaClO + NaCl. Unexpectedly, although either NaCl or NaClO could significantly improve the cleaning efficiency and alleviate the membrane fouling, combinations of NaCl + NaClO did not show any significant improvements in HIMF alleviation in comparison with CEB operation using NaClO alone. In contrast, the HIMF-derived TMP slightly increased over time under CEB operation using the combinations of either NaClO + NaOH or NaClO + sodium citrate, with the growth rate of HIMF-derived TMP increasing by 185% and 307% relative to the CEB operation assisted by NaClO alone (Fig. 2(g)), in addition to a significant increase in HIFI (Fig. 2(f)). These results demonstrated that the

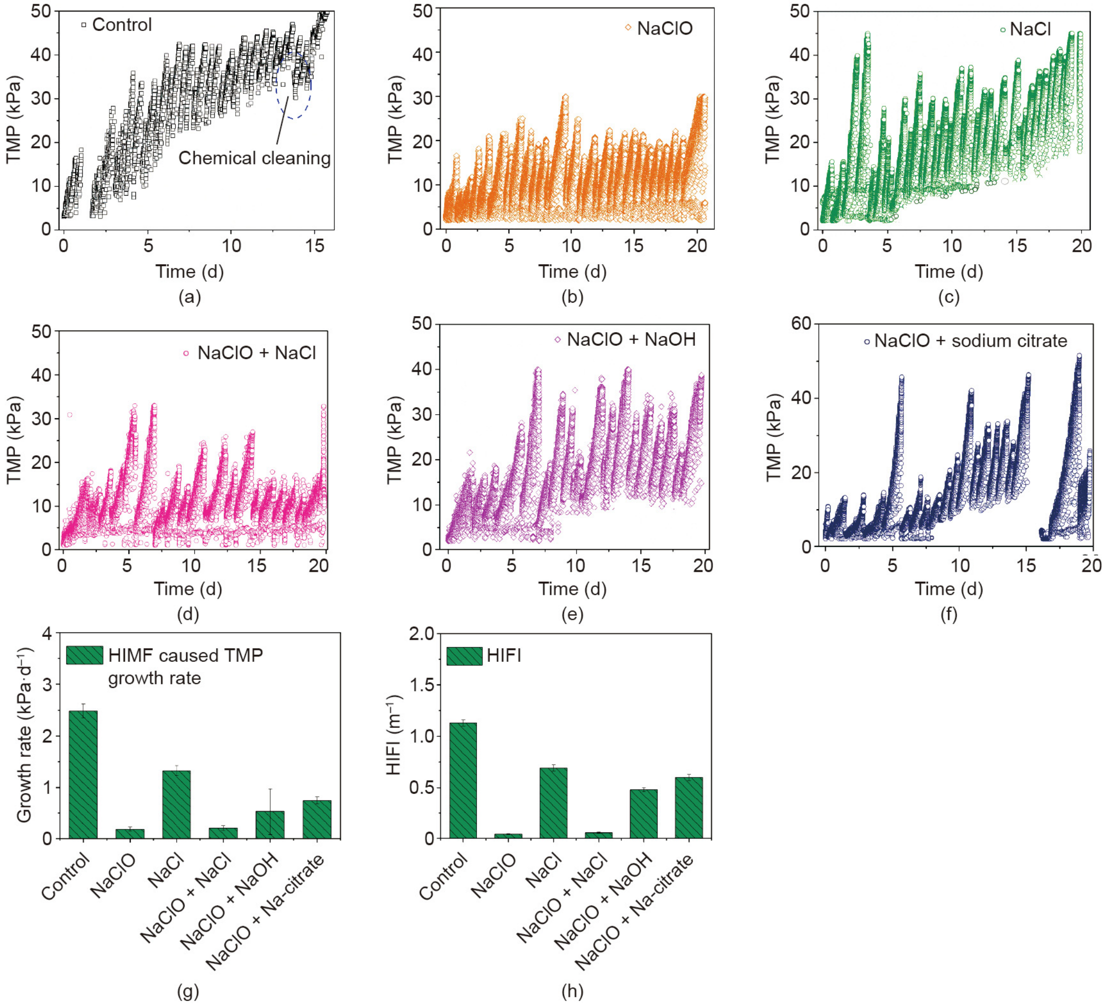

Fig. 2. TMP development during treatments of algae-containing surface water under CEB operation using different chemical reagents. (a) Control; (b) NaClO; (c) NaCl; (d) NaClO + NaCl; (e) NaClO + NaOH; (f) NaClO + sodium citrate; (g) HIMF-caused TMP growth rate; and (h) HIFI. The experimental protocols are provided in Table 1 (Stage 1). The CEB process was performed every 12 h.

addition of either NaOH or sodium citrate to the NaClO had a negative influence on the membrane fouling control, probably because combinations of oxidants and alkali increased the molecular size of protein-like substances (e.g., bovine serum albumin) due to the cross-linkage of protein molecules, which would reduce the cleaning efficiency [27]. Another potential explanation is that the oxidation potential of chlorine significantly decreased as the pH increased, resulting in a decline of cleaning efficiency. Moreover, the pH conditions of the chlorinated water played a fundamental role in damaging the membrane integrity, due to the chlorine oxidation. Thus, specific attention should be paid to the pH conditions during the CEB operation.

3.2. Effects of chemical dosages on membrane fouling alleviation

As summarized in Section 3.1, NaClO and NaCl were both determined to be the optimal reagents to alleviate the algae-related HIMF. Thus, the impacts of NaCl and NaClO dosages on the TMP development were evaluated, the results of which are shown in Fig. 3. On the whole, the cleaning efficiency of HIMF improved with an increase in the dosages of both NaClO and NaCl. In the NaCl-assisted CEB process, a low dosage of NaCl (100 mg·L^{-1}) had little effect on the alleviation of HIMF relative to the control system (Fig. 2(a)); consequently, the TMP increased after each physical backwashing. Due to the rapid formation of HIMF, with the TMP increasing up to 50 kPa, chemical cleaning had to be employed after 5 d of filtration. In line with this result, another UF experiment using NaCl-assisted backwashing also reported that a low-concentration NaCl solution did not show any significant influence on membrane fouling control during the filtration of river water without algae [12].

Interestingly, with the increase of the NaCl dosage from 100 to 300 mg·L^{-1}, the HIMF was significantly alleviated, and the TMP was nearly recovered to its initial value during each backwashing cycle. Compared with the control system, the NaCl-assisted CEB operation at a concentration of 300 mg·L^{-1} efficiently relieved the algae-related membrane fouling and resulted in significant reductions in the HIMF-caused TMP growth rate. Similarly, some previous studies have also indicated that a NaCl-assisted cleaning approach efficiently relieved the membrane fouling caused by hydrophilic organic foulants and gel fouling [14,15]. A further study has indicated that ion exchange and gel layer swelling involved the main mechanisms of membrane fouling remission in the NaCl-assisted CEB operation [12]. However, adding NaCl at a concentration of 300 mg·L^{-1} could not completely eliminate the formation of HIMF. With an increase in the NaCl dosage from 300 to 500 mg·L^{-1}, the HIMF-derived TMP increase rate was further reduced and the chemical cleaning interval could be prolonged by 4–5 times, relative to the control system (Fig. 3(c)). However, HIMF still inevitably occurred, with an average TMP

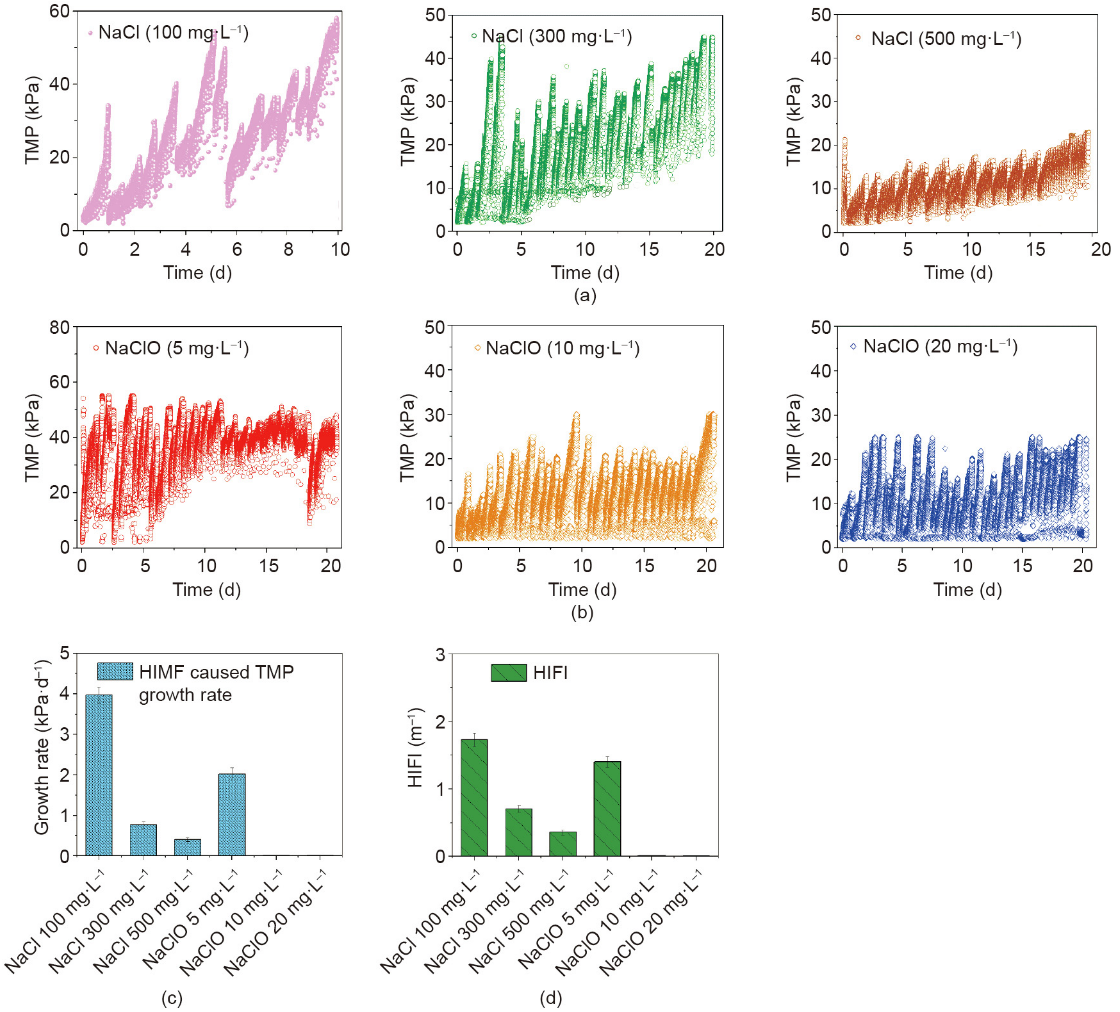

Fig. 3. The effects of different dosages of NaClO and NaCl in CEB operation on TMP development when treating the algae-containing reservoir water. (a) NaCl; (b) NaClO; (c) HIMF-caused TMP growth rate; and (d) HIFI. The experimental protocols are given in Table 1 (Stage 2). The CEB process was performed every 12 h.

growth rate of 0.55 kPa·d^{-1}. A previous study has indicated that high concentrations of NaCl solution (6–12 mmol·L^{-1}) would result in charge screening effects and confer little improvement in the HIMF alleviation [28]. Therefore, optimizing the dosage of NaCl was an acceptable approach to improve the cleaning efficiency and cost efficiency of the CEB process for the membrane fouling control during the treatment of algae-containing surface water.

As shown in Fig. 3(b), the HIMF was significantly diminished during the first 5 d of filtration with the assistance of the CEB process at a NaClO dosage of 5 mg·L^{-1}, compared with the control system (Fig. 2(a)). However, the TMP caused by HIMF increased rapidly during days 5–10 and then remained constant until the end of the experiment. This result indicated that the CEB process with a low dosage of NaClO could not achieve a steady and long-term alleviation of HIMF during the treatment of algae-containing surface water. When the dosage of NaClO was increased from 5 to 10 mg·L^{-1}, it was found that the HIMF was almost suppressed completely and the TMP was nearly restored to its initial point in each backwashing cycle. During a 20-day filtration period, algae-derived HIMF was scarcely observed, there was a negligible HIFI (Fig. 3(d)), and the TMP remained constant. One explanation might be that the structures and MW of the major foulants (e.g., biopolymers) were damaged with the increase of NaClO dosage, as for example, oxidative cleavage of long molecule chains occurred, which contributed to a higher flux recovery or TMP reduction [27]. Furthermore, when the dosage of NaClO was elevated from 10 to 20 mg·L^{-1}, only a limited difference was observed in the HIMF-caused TMP growth rate, which demonstrated that the optimized dosage of NaClO for CEB operation was 10 mg·L^{-1}. In addition, compared with NaCl-assisted CEB operation, the NaClO-assisted CEB process exhibited a better performance in eliminating HIMF, and was determined to be the preferable strategy for the alleviation of membrane fouling in treating the algae-containing surface water.

3.3. Effects of CEB frequency on membrane fouling in pilot-scale operation

As stated above, NaClO was found to be the most effective reagent for controlling the HIMF during the treatment of algae-containing surface water. In order to further verify the feasibility of CEB and reduce its daily chemical consumption, a pilot-scale experiment was carried out to evaluate the effects of CEB frequency on membrane fouling control. An optimal dosage of NaClO at 10 mg·L^{-1} was employed, as determined in Section 3.2. In comparison with the bench-scale scenarios, the pilot-scale UF process demonstrated a better anti-fouling capability in treating algae-containing surface water, with relatively lower and more stable changes of TMP in each filtration cycle, as shown in Fig. 4. As shown in Fig. 4(d), the HIMF was effectively retarded relative to

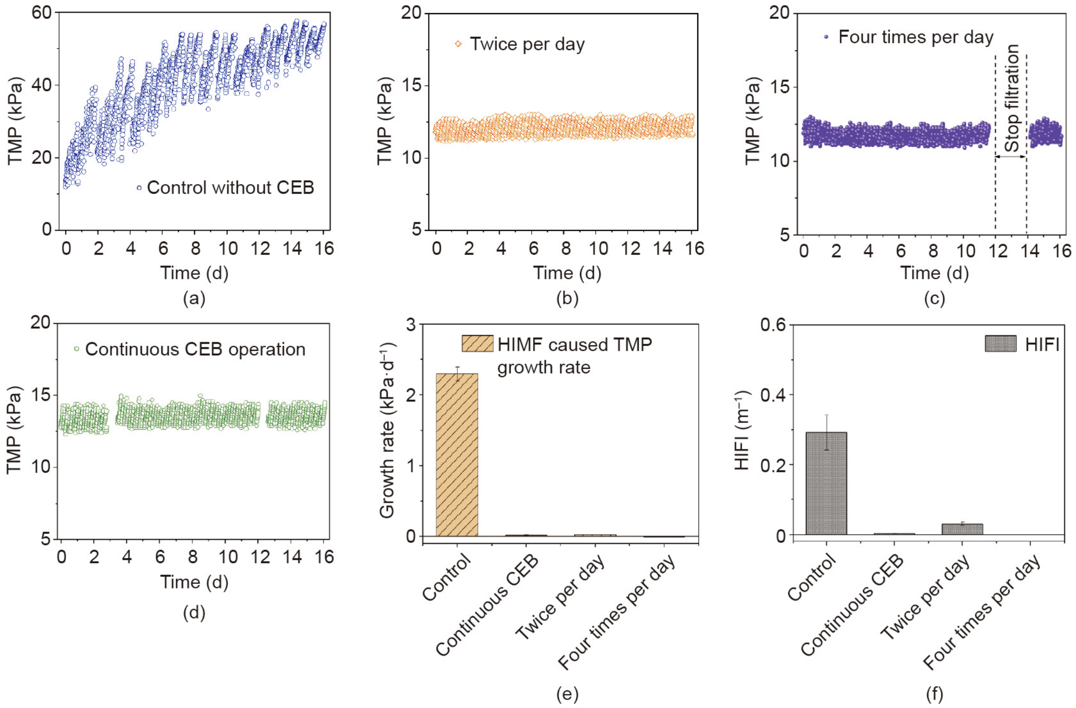

Fig. 4. The effects of CEB frequency using NaClO (10 mg·L^{-1}) on TMP development in the pilot-scale experiments. (a) Control system; (b) CEB operation twice per day; (c) CEB operation four times per day; (d) continuous CEB operation with NaClO in each backwashing;(e) the HIMF-caused growth rate; and (f) HIFI.

the control system (Fig. 4(a)), and the TMP remained constant during long-term filtration under continuous CEB operation. However, continuous CEB operation meant that NaClO was added at each backwashing, resulting in a high chemical consumption, despite the effectiveness of this process in the alleviation of membrane fouling. In order to diminish the consumption of NaClO, intermittent CEB operation was employed, with dosing frequencies of two or four times per day, and the effect on TMP development and HIMF control was investigated.

As illustrated in Fig. 4(b), compared with the scenario with continuous CEB operation, even when CEB operation was performed twice per day, the HIMF was still effectively regulated, and the total increase in HIMF-related TMP was ~0.3 kPa during ~16 d of filtration, for a growth rate of 0.019 kPa·d^{-1}. Typically, given that chemical cleaning should be adopted when the TMP caused by HIMF increased to 40–50 kPa, there were no extra requirements for chemical cleaning for the UF process under a CEB operation of two times per day from July to October. When the frequency of CEB operation increased from two to four times per day, more effective control of membrane fouling (e.g., HIMF) was achieved (Fig. 4(c)), and the HIMF-caused TMP growth rate and HIFI value were close to 0 (Figs. 4(e)–(f)). The overall TMP remained constant, and even declined slightly during long-term filtration.

Interestingly, the UF system stopped for 2 d due to problems with the feed water system. It was then restarted, and a slight decrease of TMP was observed (Fig. 4(c)), probably due to the relaxation of the cake layer and back diffusion of foulants from the membrane surface to the bulk solution during the standby period [29]. Consequently, it can be stated that the optimized frequency of CEB operation was two times per day during the treatment of algae-containing surface water.

3.4. CEB operation in a full-scale experiment

The aforementioned bench-scale and pilot-scale trials demonstrated that the CEB process with the addition of NaClO can effectively allay the algae-derived membrane fouling. However, experience has shown that, due to the influence of experimental scale, the results that have been obtained based on bench-scale and even pilot-scale experiments may not be suitable for a full-scale DWTP. Consequently, full-scale experiments with CEB operation two and four times per day, respectively, with a NaClO dosage of 10 mg·L^{-1} were carried out in the present study.

In the full-scale DWTP, the HIMF-related TMP continuously increased from 13–16 up to 40–50 kPa after 10–14 d of filtration when treating algae-containing surface water without CEB operation (not shown); chemical cleaning was subsequently required in order to restore the membrane permeability. As expected, with the CEB operation occurring twice per day, the HIMF was effectively reduced and the TMP was almost restored to the initial values in each CEB cycle. During a 16-day period of filtration, the total increase in HIMF-related TMP was 2.4 kPa, which was equivalent to a growth rate of 0.15 kPa·d^{-1} (Fig. 5(c)). This TMP increase was higher than those in the bench-scale and pilot-scale scenarios, probably due to the difference in experimental scales. When the frequency of CEB operation increased to four times per day, the TMP maintained a steady state (Fig. 5(c)) and even slightly declined during a 16-day filtration period (Fig. 5(c)). Interestingly, the CEB process was not adopted for ~2 d due to the problems with the reagent-dosing pumps; consequently, the TMP significantly increased. After that, CEB operation was restarted (at a NaClO dosage of 20 mg·L^{-1} on the first day and then decreased to the typical dosage of 10 mg·L^{-1}) and it was found that the TMP was almost restored, which further verified the feasibility of the CEB process in the alleviation of membrane fouling in treating the algae-containing surface water.

3.5. Effects of the CEB process on the membrane foulants removal

In order to further probe the mechanisms of the CEB process in the alleviation of membrane fouling, the concentrations and compositions of the foulants in the backwash wastewater and those

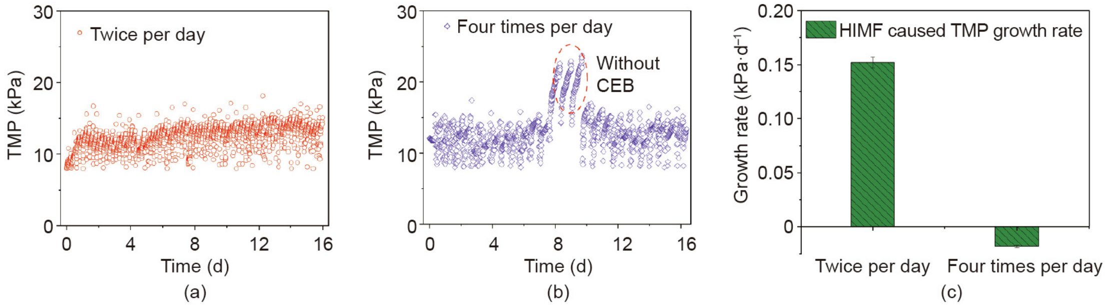

Fig. 5. The effects of CEB operation using NaClO (10 mg·L^{-1}) on TMP development in full-scale experiments during the treatment of algae-containing surface water. (a) Twice per day; (b) four times per day; and (c) the HIMF-caused growth rate.

that had accumulated on the membrane surface were evaluated; the results are presented in Figs. 6 and 7.

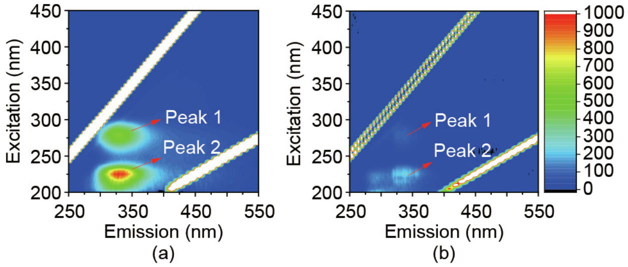

Fig. 7. Florescent foulants of cake layer accumulated on the membrane surface in the pilot-scale experiment. (a) Conventional backwashing; (b) CEB using NaClO (10 mg·L^{-1}) with a frequency of twice per day.

3.5.1. Organic foulants in the backwash wastewater

The concentrations of organic foulants in the backwash wastewater with and without the CEB process were determined. As shown in Fig. 6(a), the concentrations of TOC and DOC in the backwash wastewater under CEB operation were higher than those under a conventional backwashing process, amounting to average increases of 35.4% ± 1.93% and 27.5% ± 1.89% for TOC and DOC, respectively. The higher concentrations of organic foulants in the backwash wastewater demonstrated that the CEB operation efficiently reduced the accumulation of organic foulants on the membrane surface and in the membrane pores, thereby alleviating the membrane fouling. This finding corresponded well with the lower growth rate of TMP in the CEB-assisted filtration, as presented in Fig. 4. In line with this observation, some studies have elucidated that a NaClO-involved cleaning process can significantly rinse off organic foulants (e.g., NOM and algae-derived organic substances) from the membrane surface and provided significant benefits for flux recovery [24,26]. The higher levels of organics in the backwash wastewater may be related to the improvement in the removal of algae cells and their debris from the membrane surface due to CEB operation.

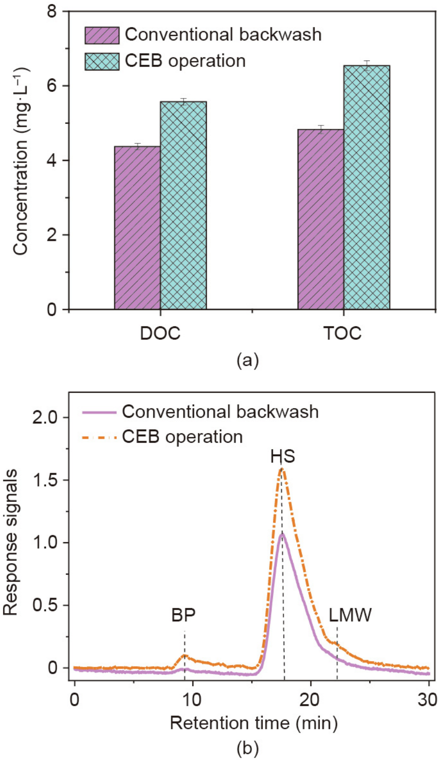

Fig. 6. Concentrations of (a) TOC and DOC, as well as (b) the apparent MW distribution of dissolved organic foulants in the backwash wastewater under conventional backwashing and CEB operation using NaClO (10 mg·L^{-1}, twice per day) in the pilot-scale experiment. BP: biopolymers, HS: humic substances, LMW: low-MW compounds.

Furthermore, LC-UV was employed to evaluate the compositions of the organic foulants in the backwash wastewater. As shown in Fig. 6(b), the LC-UV results indicated that typical organic foulants, including biopolymers, humic substances, and low-MW compounds, were present in the backwash wastewater. The concentrations of organic foulants under CEB operation were significantly higher than those in the case of conventional backwashing. These results indicated that more of the biopolymers and humic substances accumulated on the membrane surface and deposited within the membrane pores had been washed out under the CEB operation. Both biopolymers and humic substances are regarded as the major foulants in membrane fouling [13,30]. In the control system, insufficient removal of biopolymers and humic substances meant that more foulants still adhered on the membrane surface or deposited in the membrane pores, resulting in the increasing accumulation of membrane foulant and an ongoing increase in TMP. As a comparison, in the NaClO-assisted CEB process, NaClO oxidation altered the physicochemical properties (i.e., gelling properties, adhesivity, and MW) of the biopolymers and induced changes in their functional or structural makeup (i.e., carboxylic groups) [27]. As a result, the biopolymers could be washed away from the membrane surface and membrane pores more easily, which contributed to the significant alleviation of membrane fouling. The limited changes of TMP in the CEB-assisted UF system further verified this hypothesis.

3.5.2. Fluorescent foulants in the cake layer

At the end of the experiment, the cake layer adhered on the membrane surface was collected, and the EPS was extracted and determined through 3D EMM analysis. As illustrated in Fig. 7, two main peaks (Peak 1 and Peak 2) were found, which were identified as tryptophan protein-like substances and simple aromatic proteins such as tyrosine, both of which were related to biopolymers [31,32]. Under conventional backwashing operation, both Peak 1 and Peak 2 were observed in the extracted solution of the cake layer from the membrane surface, and their intensities were quite high; this finding indicated that there was significant accumulation of organic foulants on the membrane surface. It was noticeable that the intensities of Peak 1 and Peak 2 were significantly reduced due to the application of the CEB process (Fig. 7(b)); Peak 1 even disappeared completely, which indicated that much less EPS accumulated on the membrane surface relative to the cases of the conventional backwashing-assisted UF process. The concentration of EPS accumulated in the cake layer was positively correlated to the TMP development (Fig. 4). In line with this observation, another study has indicated that a cleaning approach incorporating NaClO can effectively dissociate the gel structures formed by the EPS, bacteria, algae, and their debris, contributing to more than 80% flux recovery [24]. A previous study has also indicated that oxidation would break down the structures of peptide and 1,4-b-glycoside bonds and make the EPS (e.g., proteins and polysaccharides) more hydrolysable to be washed out [33]. It has even been reported that NaClO cleaning would destroy protein structures and reduce the fluorescent intensities, significantly facilitating the membrane flux recovery [25].

3.6. Advantages and future perspectives

Recently, algae contamination in surface water (mainly lake or reservoir water) has been a common phenomenon due to the increasing eutrophication. UF technology has been increasingly employed in DWTPs to produce microbiologically safe water; thus, algae-related severe membrane fouling has attracted widespread concern. Routine chemical cleaning has negative impacts on the membrane integrity and promotes the formation of halogenated byproducts, which are of great concern, so it should be adopted carefully [34]. Promisingly, the present study found that the CEB process assisted with NaClO at a low concentration can efficiently suppress HIMF during treatments of algae-containing surface water in order to maintain the clean water production and steady operation of the UF system. Comparisons among hydraulic backwashing, chemical cleaning, and CEB operation in the membrane fouling control, chemical consumption, operation and maintenance, and the formation of halogenated byproducts are summarized in Table 2. Compared with chemical cleaning, the CEB process significantly reduced the production of halogenated byproducts due to the much lower concentration of NaClO solution (10 mg·L^{-1}) and shorter reaction time (< 3 min); it also reduced the production of backwash wastewater containing a high concentration of NaClO. The lower dosage of NaClO and the shorter reaction time in CEB operation further contributed to maintaining the integrity of the UF membrane and reducing the potential corrosion of tubes and other auxiliary equipment. Moreover, the CEB process has a small footprint and is easily automated and integrated, so it has the advantages of simple operation and low maintenance. Overall, the NaClO-assisted CEB process was found to be an environmentally friendly, cost-efficient, and membrane-friendly strategy for the alleviation of membrane fouling in the treatment of algae-containing surface water.

4. Conclusions

In this study, a PVDF membrane was used to investigate the use of CEB for alleviating the membrane fouling (especially hydraulically irreversible fouling) in treating the algae-containing surface water. Experiments were performed from the bench scale up to the pilot scale and full scale. The main findings are as follows:

(1) Conventional backwashing could not effectively control the membrane fouling during the treatment of algae-containing surface water, and chemical cleaning had to be adopted every 14 d.

(2) CEB operation could efficiently alleviate the algae-derived hydraulic irreversible membrane fouling and maintain the stable operation of the UF process. NaClO was found to be the optimal reagent for this purpose, and its combination with other chemicals (e.g., NaOH and sodium citrate) conferred little improvement in membrane fouling control.

(3) The HIMF-caused TMP growth rate and HIFI value decreased with the increase in NaClO dosages and dosing frequency. The optimized dosage and dosing frequency of NaClO were 10 mg·L^{-1} and two times per day, respectively.

(4) NaCl-involved CEB operation could also significantly relieve the algae-related membrane fouling, and its optimal dosage was found to be 500 mg·L^{-1}. However, under these conditions, the TMP could not be maintained at a constant level, and hydraulic irreversible membrane fouling occurred gradually during long-term filtration.

(5) Compared with conventional backwashing, the CEB process can efficiently enhance the removal of organic foulants (e.g., biopolymers, humic substances, and protein-like substances) from the membrane surface (> 27.5%), leaving fewer foulants behind and thereby contributing to the recovery of membrane permeability.

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Table 2
Comparisons of hydraulic backwashing, routine chemical cleaning, and CEB during UF in treating algae-containing surface water.

Characteristics	Hydraulic backwashing	Chemical cleaning	CEB (NaClO)	CEB (NaCl)
Membrane fouling control	++	++++	++++	+++
HIMF control	+	++++	++++	+++
Lasting effects on HIMF control	+	–	++++	++
Chemical consumption	–	++++	++	++
Operation and maintenance	+	++++	++	++
Formation of halogenated byproducts [34,35]	–	++++	+	–

The chemical consumption and formation of halogenated byproducts were considered only for the cleaning operation during the UF process. The symbol – represent no effect; the symbols +, ++, +++, ++++, and +++++ represent weak to strong effects.

Compliance with ethics guidelines

Xiaobin Tang, Tiecheng Guo, Haiqing Chang, Xiao Yue, Jinlong Wang, Haikuan Yu, Binghan Xie, Xuewu Zhu, Guibai Li, and Heng Liang declare that they have no conflict of interest or financial conflicts to disclose.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eng.2021.01.013.

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