Journal of Hazardous Materials 186 (2011) 1415–1424

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

# Effect of PAC addition on immersed ultrafiltration for the treatment of algal-rich water

Yan Zhang*, Jiayu Tian, Jun Nan, ShanShan Gao, Heng Liang, Meilian Wang, Guibai Li

*State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, 73 Huanghe Road, Nangang District, Harbin 150090, China*

ARTICLE INFO

*Article history:*
Received 1 April 2010
Received in revised form 30 August 2010
Accepted 6 December 2010
Available online 14 December 2010

*Keywords:*
*Microcystis aeruginosa*
PAC
Ultrafiltration (UF)
Algogenic organic matter
Cyanotoxins

ABSTRACT

The aim of this study was to evaluate the effect of powdered activated carbon (PAC) addition on the treatment of algal-rich water by immersed ultrafiltration (UF), in terms of permeate quality and membrane fouling. Experiments were performed with a hollow-fiber polyvinyl chloride ultrafiltration membrane at a laboratory scale, 20–25 °C and 10 L/(m$^2$ h) constant permeate flux. UF could achieve an absolute removal of *Microcystis aeruginosa* cells, but a poor removal of algogenic organic matter (AOM) released into water, contaminants responsible for severe membrane fouling. The addition of 4 g/L PAC to the immersed UF reactor significantly alleviated the development of trans-membrane pressure and enhanced the removal of dissovled organic carbon (by 10.9 ± 1.7%), $UV_{254}$ (by 27.1 ± 1.7%), and microcystins (expressed as MC-$LR_{eq}$, by 40.8 ± 4.2%). However, PAC had little effect on the rejection of hydrophilic high molecular weight AOM such as carbohydrates and proteins. It was also identified that PAC reduced the concentrations of carbohydrates and proteins in the reactor due to decreased light intensity, as well as the MC-$LR_{eq}$ concentration by PAC adsorption.



## 1. Introduction

The occurrence of cyanobacteria blooms has become one of the major concerns for drinking water production. The cyanobacterial cells themselves, as well as their extracellular products in water adversely affect the conventional drinking water treatment processes from many aspects, such as causing taste and odor, increasing coagulant demand, clogging filter media and leading to the formation of disinfection by-products. The algogenic organic matter (AOM) includes proteins, neutral and charged polysaccharides, nucleic acids, lipids and small organic molecules [1]. It is estimated that extracellular organic matter (EOM), especially carbohydrates and carbonyl compounds, usually accounts for 60–80% of the total released AOM [2]. Cyanotoxins as the secondary metabolites of cyanobacteria are seriously harmful to human health by promoting liver tumors. Microcystins are the most frequently occurring class of cyanotoxins in natural waters, of which microcystin-LR (MC-LR) is the most toxic and frequently detected species [3]. A guideline value of 1.0 μg/L for microcystins in drinking water has been proposed by the World Health Organization [4].

In drinking water treatment, conventional treatment processes are still the main treatment processes for algae removal. However, it has been proved that coagulation, flocculation and filtration are effective for the rejection of cyanobacterial cells, but not for the dissolved toxins [5,6]. Furthermore, although pre-oxidation by chlorine, ozone, potassium permanganate and potassium ferrate has been shown to be effective for inactivating algal cells [7–9], the high dosage required may induce cell lysis, thus resulting in the release of undesirable compounds and the formation of harmful by-products [9,10,5,6].

Membrane filtration technology is a promising alternative to conventional water treatment processes for the removal of algae, since it offers an absolute removal of the algal cells and is less affected by raw water quality changes [11,12]. However, membrane fouling is still a major obstacle for the wider application of the membrane filtration technology. Campinas and Rosa [12] showed that although UF ensured a complete cell removal without degradation of permeate quality, the membrane fouling caused by cell damage hindered the applicability of UF for treating algal-rich water. Nanofiltration membrane fouling phenomenon was observed during filtration of AOM extracted from B-G algae [13]. It was proved that alginate could cause greater NF flux decline than humic acid under the same conditions [14]. Kwon et al. [15] found that the combination of microcystis and natural organic matter (NOM) could induce more serious UF membrane fouling as compared with single microcystis or NOM. Castaing et al. [16] showed that cake formation was the main fouling mechanism of immersed MF and UF membranes used for removing micro-algae (*Alexandrium* sp.) from seawater. To enhance the MF performance

* Corresponding author. Tel.: +86 451 86840238; fax: +86 451 86283088.
*E-mail address:* zhang.yan113@163.com (Y. Zhang).

0304-3894/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2010.12.015

**Table 1**
PAC characteristics.

| Characteristics | Value |
|---|---|
| BET surface area ($m^2$/g) | 1114.7 ± 10.9 |
| Ash content (%) | 5.31 ± 0.21 |
| Moisture (%) | 5.6 ± 0.7 |
| Methylene blue number (mg/g) | 295 ± 3.7 |
| Iodine number (mg/g) | 1005 ± 9.5 |
| pHpzc | 9.11 |
| Primary micropore (<8 Å) volume ($cm^3$/g) | 0.361 |
| Secondary micropore (8–20 Å) volume ($cm^3$/g) | 0.217 |
| Mesopore (20–500 Å) volume ($cm^3$/g) | 0.523 |
| Carbon (%) | 87% |

Values represent average ± standard deviation for three replicates.

for algae removal, pre-ozonation was investigated by Hung and Liu [17], but the results indicated that the dissolved polysaccharide released during pre-ozonation even exacerbated the membrane fouling.

The combination of PAC and membrane filtration is a promising process for drinking water treatment. It has been proved that PAC can compete with membrane to adsorb organic matter, thus effectively mitigating the membrane fouling [18–20]. Some investigations [21,22] have also been conducted with regard to the application of PAC/UF process for the rejection of microcystins, with the results showing that more than 95% of removal could be achieved. However, few studies have been focused on the removal of algae, especially the AOM by PAC/UF process. To deal with that matter, the effectiveness of PAC/immersed UF process is assessed for algal-rich water treatment, and the influence of PAC on the concentration of AOM in the reactor is also discussed.

## 2. Materials and methods

### 2.1. Cyanobacterial culture

The target algae used in the experiments was *Microcystis aeruginosa* (*M. aeruginosa*) which is one of the dominant cyanobacteria in most eutrophic rivers and lakes in China. *M. aeruginosa* was supplied by Wuhan Institute of Hydrobiology of Chinese Academy of Sciences, and was cultivated in the laboratory in modified BG11 medium at 23–24 °C, under a light regimen of 12 h fluorescent light/12 h dark [12]. The *M. aeruginosa* was at the stationary growth phase after being incubated for 10 days. The testing water used in the study was prepared by diluting the culture suspension of *M. aeruginosa* with 5 mg/l ammonia-N in distilled water ($NH_4Cl$, analytical grade). The ammonia added in the testing water was also used to evaluate the bacteria development in the reactors. The algal cell concentration in the raw water was controlled at $1.0 \times 10^8$ to $1.5 \times 10^8$ cells/L obtained from a particle counter (model WGC-267, Met One, Oregon, USA).

Cyanotoxins are very diverse in their chemical structure and toxicity. There were MC-LR, MC-RR and MC-YR detected in the lab culture and the overall concentration was quantified in MC-LR equivalent concentration (μg/L MC-$LR_{eq}$), since it was the most toxic and typically produced by *M. aeruginosa*.

### 2.2. PAC

The properties of the PAC (coconut shell, China) used in the experiments are listed in Table 1. The PAC sample exhibited an alkaline pHpzc which was determined by acid–base titration [23]. The PAC was also characterized by a high specific surface area and corresponding high adsorption capacity expressed by the methylene blue and iodine numbers which were determined by Chinese standard examination methods (GB/T12496.2-1990 and GB/T12496.7-1990). The pore structure characteristics of the PAC were determined by an automatic Micromeritics ASAP-2010 volumetric sorption analyzer. It was found that PAC was mostly mesoporous.

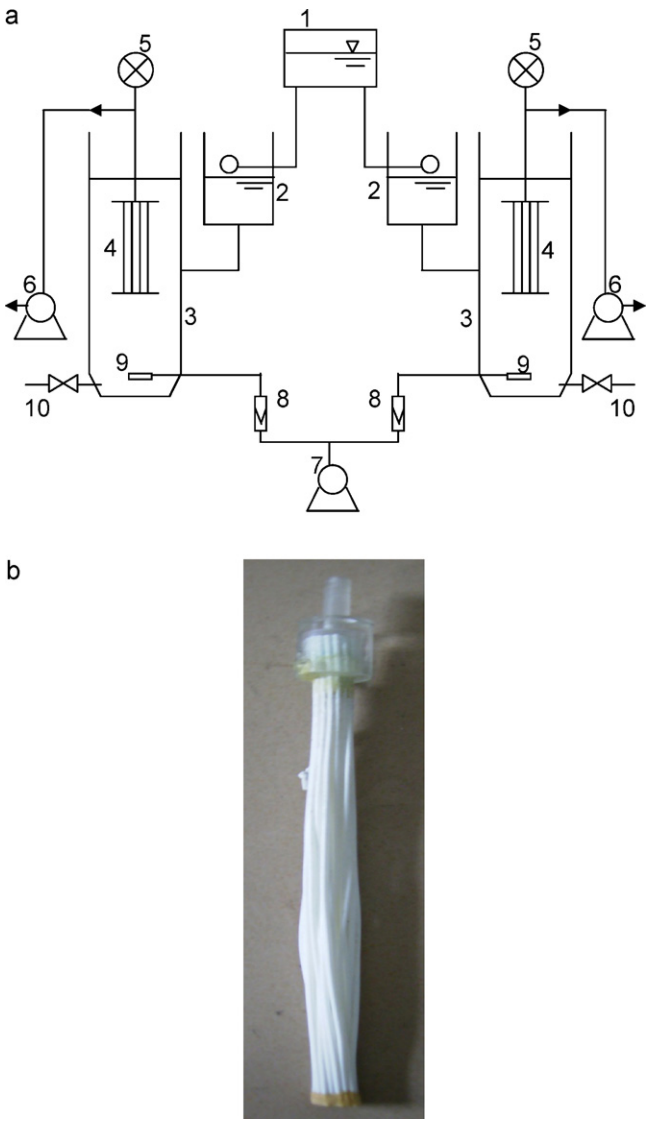


**Fig. 1.** (a) Schematic diagram of the experimental set-up (1-raw water tank; 2-constant level water tank; 3-reactor; 4-ultrafiltration membrane module; 5-manometer; 6-suction pump; 7-air blower; 8-air flowmeter; 9-air diffuser; 10-discharge valve). (b) Immersed hollow-fiber UF membrane module.

### 2.3. Experimental set-up

The two parallel laboratory-scale immersed membrane reactors (schematically shown in Fig. 1a) were constructed and employed in this study. Two hollow-fiber modules of polyvinyl chloride (PVC) UF membrane (Litree, China) with 0.025 $m^2$ membrane area (12.6 cm length, 14 fibers) and a nominal pore size of 0.01 μm were used (Fig. 1b). The reactors (effective volume of 320 mL) were fed with raw water through constant level tanks and the effluents were drawn directly from the membrane modules by using suction pumps. Pressure transducers were set between the membrane modules and the suction pumps to monitor the trans-membrane pressure (TMP) during UF process, for following the changes in the permeation resistance due to fouling phenomena. There was no discharge from the reactors during the experiment. Continuous

aeration was provided at the bottom of each reactor to bring strong turbulence for PAC mixing, membrane cleaning and to provide oxygen for the aerobic bacterial growth.

### 2.4. Operating conditions

Both the reactors with and without PAC were operated under the same experimental conditions as follows: UF membrane flux was set at 10 L/($m^2$ h), corresponding to an 80-min hydraulic retention time (HRT), and the temperature was maintained at 20–25 °C. Air to influent ratio was kept at 12:1, and the duration of filtration was 15 days.

To determine the optimum dose of PAC in the reactor, the influence of PAC dose (0 g/L, 2 g/L, 4 g/L, 8 g/L, calculated based on reactor volume) on the TMP increase was pre-examined in the UF membrane system, with the same experimental conditions as those described. It was found that when the dose of PAC was 4 g/L, the TMP increased slowest during the tested doses.

Therefore, the predetermined dose of PAC (4 g/L) was added to one reactor at the beginning of operation. There was no PAC addition or discharge during the subsequent experimental period. So it could be calculated that during the 15 days of operation, the PAC consumed by the raw water corresponded to 13 mg/L on average.

Prior to use, each membrane was washed, flushed and compacted with deionized water under the same condition as that used in the subsequent experiments, until a steady pure water permeate flux was obtained.

### 2.5. Analytical methods

#### 2.5.1. DOC, $UV_{254}$ and SUVA analysis

Dissolved organic carbon (DOC, prefiltration through 0.45 μm membrane) was measured by a total organic carbon analyzer (TOC-VCPH, SHIMADZU, JAPAN) using the high-temperature combustion method. UV254 absorbance was determined by using a spectrometer (UV754, CANY, CHINA). The value of specific UV absorbance (SUVA) was determined as the UV absorbance at 254 nm divided by the DOC concentration.

#### 2.5.2. Carbohydrate and protein analysis

The carbohydrate content was determined by the phenol–sulfuric acid method, using glucose as standard [24]. Protein was analyzed using the BCA protein assay (Pierce BCA Protein Assay Reagent Kit No. 23225). Carbohydrate and protein measurements were performed on triplicate basis, and the average values were reported in the paper.

#### 2.5.3. Chlorophyll-a analysis

The chlorophyll-*a* was determined by spectrophotometric method. Water sample (100 mL) was first filtered through a GF/F filter (Whatman), then the chlorophyll was extracted with 14 mL of ethanol. The absorbance of the extracts at 664 nm and 750 nm was determined by a spectrometer (UV754, CANY, CHINA) with 5 cm cuvette [25]. The measurements were carried out in triplicate and the average values were shown.

#### 2.5.4. Microcystin analysis

Microcystin extraction and analysis was conducted according to the procedures used by Zhao [26] and Zhang et al. [27] with some adaptations. The sample was first passed through a Whatman GF/C glass microfibre, and was then concentrated by solid-phase extraction in a C18 cartridge (Agilent). The cartridge was conditioned before use by rinsing with 10 mL of 100% methanol, followed by 10 mL of pure water (Milli-Q, Millipore). After that, 300 mL of the filtered water sample was passed through the cartridge under vacuum at the flow rate of 4 mL/min. The cartridge was then washed by 10 mL of 20%, 10 mL of 30%, 5 mL of 40% methanol and 5 mL of 75% methanol in sequence. Finally, the mixed elute solution was concentrated to 1 mL under water bath. HPLC analysis was performed with an Agilent 1200 series (USA) to determine the three microcystin variants which were all quantified as μg/L MC-LR (MC-$LR_{eq}$) using a pure MC-LR standard. The mobile phase was composed of methanol and 0.1% trifluoracetic acid with the volume ratio of 60:40. HPLC analyses were conducted at 238 nm with VWD detector (G1314B) and the Zorbox Eclipse XDB-C18 column (150 × 4.6 mm, 5 μm) at a flow rate of 1 mL/min.

#### 2.5.5. Molecular weight fractionation

The apparent MW distributions of algogenic organic matter in the raw water was analyzed using Millipore membranes with different pore sizes, and expressed in terms of DOC. Five fractions of the EOM were obtained, i.e. >30, 30–10, 10–3, 3–1 and <1 kDa. The analysis was conducted in triplicate [28].

#### 2.5.6. EOM fractionation

The XAD-8 and XAD-4 resins were used in series to separate the EOM in the raw water into hydrophobic (HPO), hydrophilic (HPI) and transphilic (TPI) fractions. The sample was filtered with 0.45 μm membranes and adjusted to pH 2 before being filtered through the XAD-8 and XAD-4 resins. The concentration of each fraction of the EOM was determined in terms of DOC [29]. Measurements of samples were carried out in triplicate.

#### 2.5.7. Ammonia-N and nitrite-N analysis

Ammonia-N and nitrite-N were determined by the colorimetric methods using a spectrometer (UV754, CANY, China) [30].

### 2.6. Microscopic observations

At the end of the experiments, scanning electronic microscopy (SEM) was used to analyze the change of UF membrane surface. A piece of membrane fiber was cut from the inside and bottom of each membrane module operated under different conditions. These membrane samples together with a clean sample of the same membrane were rinsed with 0.1 M phosphate buffer and fixed with 3.0% glutaraldehyde in 0.1 M phosphate buffer (pH 7.2) for 3 h. This was followed by dehydration in a graded ethanol series (50, 70, 80, 90, and 100, 100, 100%; each for 15 min). Finally, the samples were gold-coated by a sputter and observed under the SEM (HITACHI S4800 HSD, Japan) [30].

## 3. Results and discussion

### 3.1. Improvement of UF effectiveness by PAC addition

#### 3.1.1. Algal cells removal

In this study, chlorophyll-*a* was used to assess the removal efficiency of algal cells. Fig. 2 shows the concentrations of chlorophyll-*a* before and after UF and PAC/UF treatments. It can be seen that although during the filtration experiments the influent chlorophyll-*a* content was as high as 34.2 ± 3.5 μg/L, the chlorophyll-*a* was almost completely removed and could not be detected in UF permeate whether PAC was added or not. The UF ability for the absolute removal of *M. aeruginosa* cells was thus confirmed, which is consistent with the results obtained by others [12,31]. This could be explained by the bigger size of *M. aeruginosa* cells (3–7 μm) as compared with the membrane MW cut-off of 100 kDa (approximately 0.01 μm) [12].

#### 3.1.2. DOC and $UV_{254}$ removal

While algal cells are particulate matter and may therefore be easily and completely rejected by the membrane, the algogenic

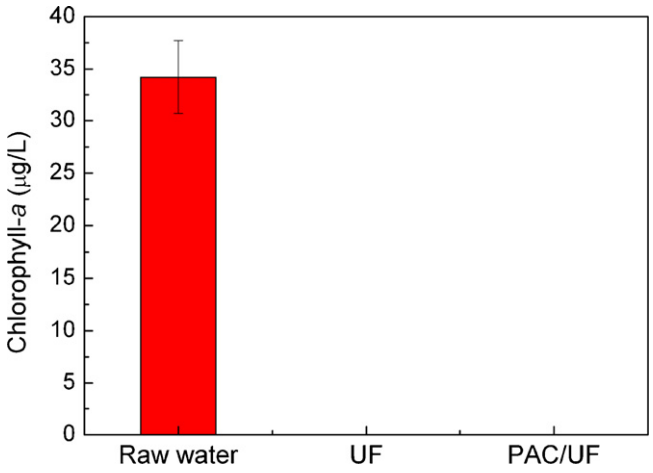


**Fig. 2.** Comparison of chlorophyll-*a* before and after UF and PAC/UF treatment (values represent average ± standard deviation for three replicates).

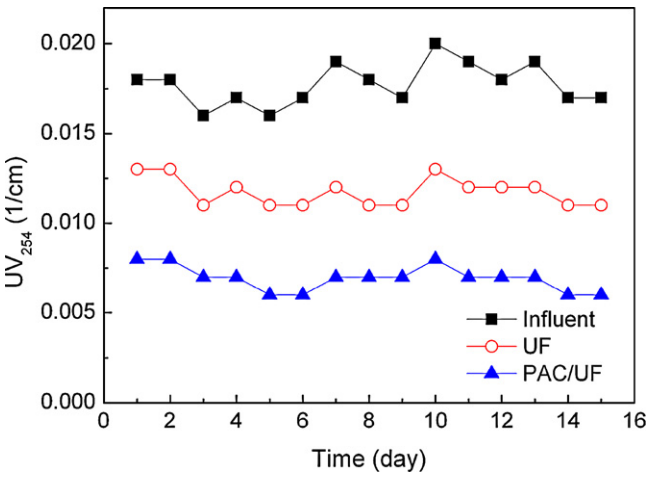


**Fig. 4.** Comparison of $UV_{254}$ before and after UF and PAC/UF treatment.

organic compounds released into water through metabolism activity are difficult to be removed and may cause severe membrane fouling. DOC is widely employed to represent the total content of released AOM. As illustrated in Fig. 3 the average DOC removal efficiency by the UF membrane alone was 53.7 ± 7.1%, while a moderate increase of 10.9 ± 1.7% was obtained when PAC was added to the membrane system. It could be seen that PAC improved the efficiency of DOC removal. The value of $UV_{254}$ indicates the concentration of aromatic organic compounds in water. The effect of PAC on UF performance for $UV_{254}$ removal is shown in Fig. 4. As could be seen, the $UV_{254}$ in the raw water could be reduced by 61.1 ± 2.3% with the PAC/UF process, and by 34.0 ± 3.2% with UF alone. It was obvious that the PAC should be responsible for the remarkable increase (by 27.1 ± 1.7%) in $UV_{254}$ removal.

SUVA values in the raw water were between 0.8 and 1.6 L/(m mg) (Fig. 5). The low SUVA means that less organochlorinated compounds could be formed during the algal-rich water disinfection by chlorine, resulting in less trihalomethanes (THMs) and other disinfection byproducts (DBPs) formation [32]. Furthermore, SUVA is also an indicator of the hydrophobicity and/or aromatic nature of the organic matter. The low SUVA is a result of the relatively low aromaticity and of the hydrophilicity associated with AOM, which would be further proved in the following section.

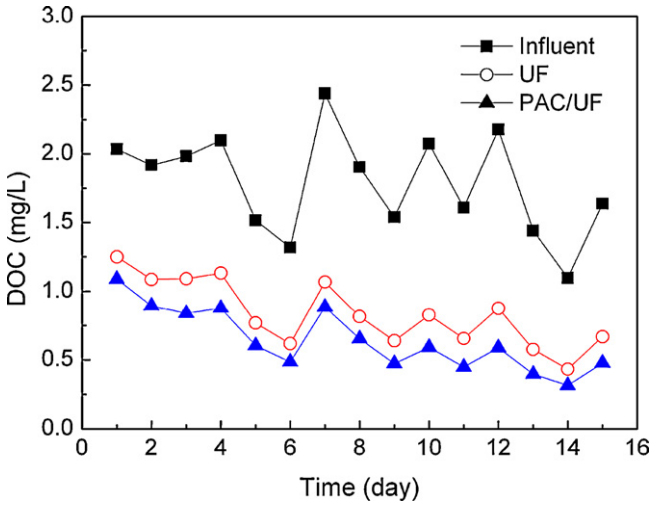


**Fig. 3.** Comparison of DOC before and after UF and PAC/UF treatment.

From Fig. 6a, it can be seen that the *M. aeruginosa* AOM had a MW distribution of 57.3 ± 2.0% greater than 30 kDa and 26.5 ± 0.5% smaller than 1 kDa. Thus, it could be inferred that the UF membrane rejected a part of the high MW AOM through sieving mechanism, and PAC could enhance the removal of organic matter below 1 kDa. Fig. 6b displays the data from AOM fractionation by XAD 8/4 resins. The hydrophilic fraction reached up to 62.6 ± 1.92%, which was consistent with the results obtained by Her et al. [13], who identified the HPI and HPO as 57% and 26% in algae solution, respectively. Henderson et al. [33] characterized the AOM extracted from four algal species in the exponential and the stationary growth phases. According to them, carbohydrate accounted for 69% of the HPI fraction in the stationary phase for *M. aeruginosa* AOM, which was predominantly hydrophilic or transphilic. As to the EOM fraction, it should have a similar composition [33]. Carbohydrates have low UV absorbance but high proportion in the AOM, which might explain why the PAC significantly enhanced the removal of $UV_{254}$, but only a moderate increase of DOC removal was obtained.

### 3.1.3. Carbohydrate removal

Due to the importance of carbohydrates in algal-rich water, the removal of carbohydrates by UF with and without PAC was also investigated (Fig. 7). For the 15 days of operation, similar removal efficiencies of carbohydrates were observed for the PAC/UF process and UF membrane alone (by 51.5 ± 11.2% vs. 49.8 ± 11.1%). The results indicated that the PAC was not effective for removing the highly hydrophilic carbohydrates through adsorption, which was in accordance with the observations made by Campinas and Rosa

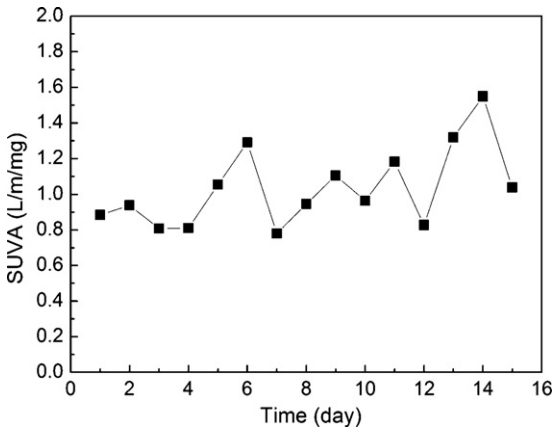


**Fig. 5.** SUVA values of AOM released into the water by cultured *M. aeruginosa*.

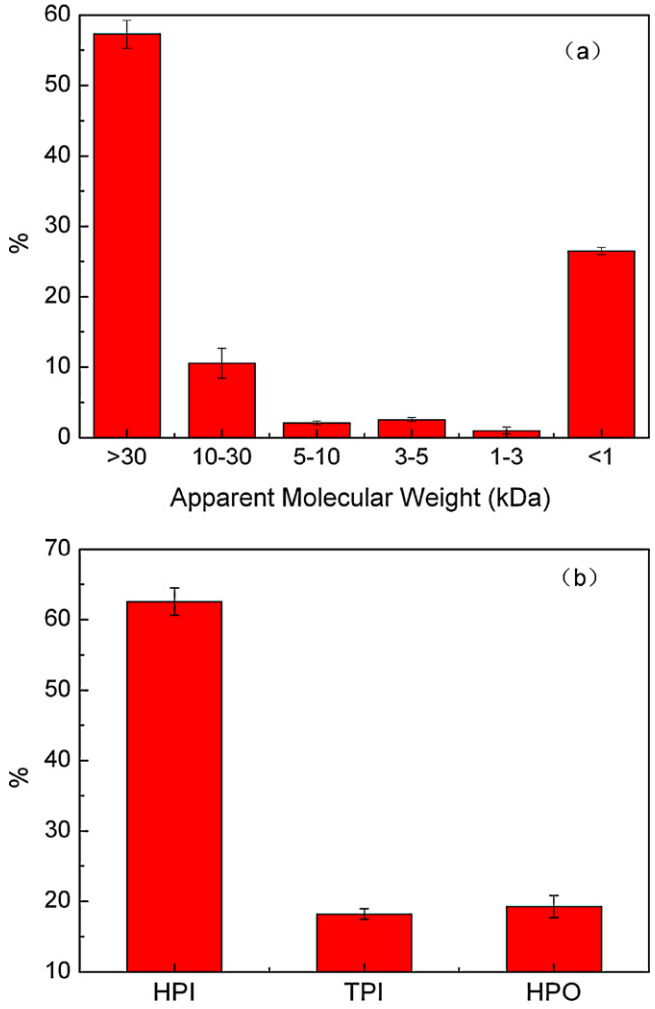


**Fig. 6.** MW distribution (a) and XAD-8/4 fractionation (b) of AOM released into the water by cultured *M. aeruginosa* in the raw water (values represent average ± standard deviation for three replicates).

[34]. Because of the particle size distribution of carbohydrates in feed suspension and the molecular weight cut off (MWCO) of the membrane, the removal mechanisms of carbohydrates in the algal water by UF membrane seemed to have changed during the filtration cycle [35,14,36]. In the initial stage of filtration, adsorption and sieving might have been the dominant mechanisms for the removal of carbohydrates. Then, the carbohydrates in the reactors appeared to aggregate by intermolecular adhesion, becoming large enough to be rejected by the membrane and forming the nuclei for further deposition of carbohydrate. Furthermore, since there was no liquid discharged from the reactors during experimental period, aerobic bacteria could grow in the reactors making use of the released AOM and oxygen in the reactors, which would improve the carbohydrate reduction due to biodegradation. These might explain why the carbohydrate removal by PAC/immersed UF process gradually increased from an initial value of 20.4% to 55.4% after 7 days of operation, and then became stable.

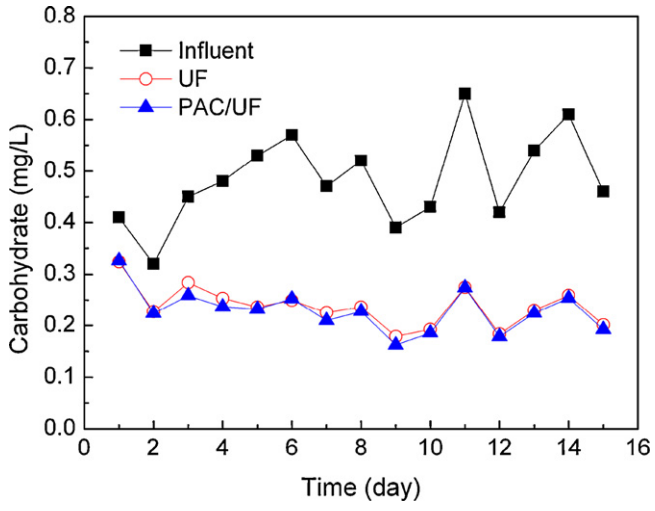


**Fig. 7.** Comparison of carbohydrate before and after UF and PAC/UF treatment.

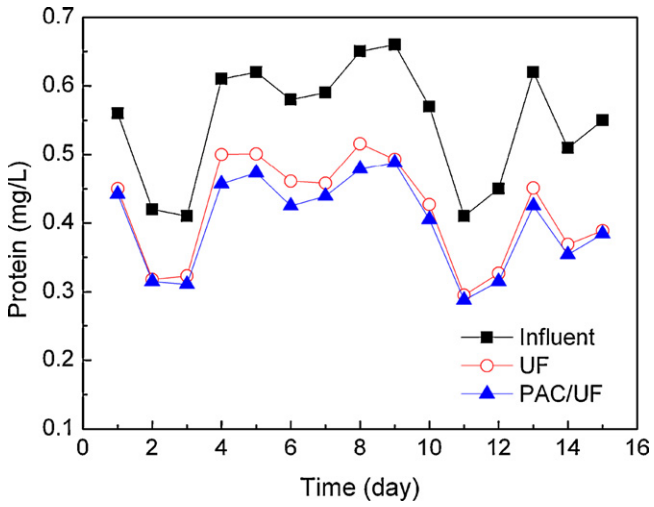


**Fig. 8.** Comparison of protein before and after UF and PAC/UF treatment.

### 3.1.4. Protein removal

During the experiments, the average protein removal rates by UF alone and PAC/UF process were 23.7 ± 3.6% and 27.0 ± 2.9%, respectively (Fig. 8). The minimal increase in protein removal suggested that PAC could not effectively remove the protein released by algae. Due to the wide MW range of proteins, the UF membrane was able to retain a part of them. With the adsorption of some protein onto the membrane pore walls, the pore size decreased correspondingly, which would result in an increased removal rate of the proteins during the filtration cycle and in a significant increase of the TMP [37]. Furthermore, the polysaccharides rejected by the UF membrane would also adsorb the proteins and retain them in the reactor [38]. There may be intermolecular binding (ionic bonds, or multiple hydrogen bonds) between polysaccharides and proteins to form a network structure, thus causing synergistic membrane fouling effects [39,40].

Fig. 9a displays the influent and effluent concentrations of ammonia-N in UF and PAC/UF process during the filtration period. It showed that little removal of ammonia-N was observed in PAC and PAC/UF processes in the first 4 days. On the other hand, the reduction of ammonia concentration in UF and PAC/UF process increased gradually to 45.6% and 57.7% in the 7th day. It has been proved that ammonia cannot be removed by adsorption to PAC nor by rejection through UF membrane. It implies that ammonia-N is oxidized biologically in the reactors. In Fig. 9b, it can be seen that nitrite-N was first detected on the 4th day, then gradually increased and finally reached 2.3 mg/L in the UF effluent and 3.7 mg/L in the PAC/UF effluent, respectively. The result demonstrates that the ammonia-N was converted into nitrite-N from the 4th day by ammonia oxidation bacteria. It can be inferred that some kinds of aerobic bacteria could develop in the reactor in a comparatively short operating period,

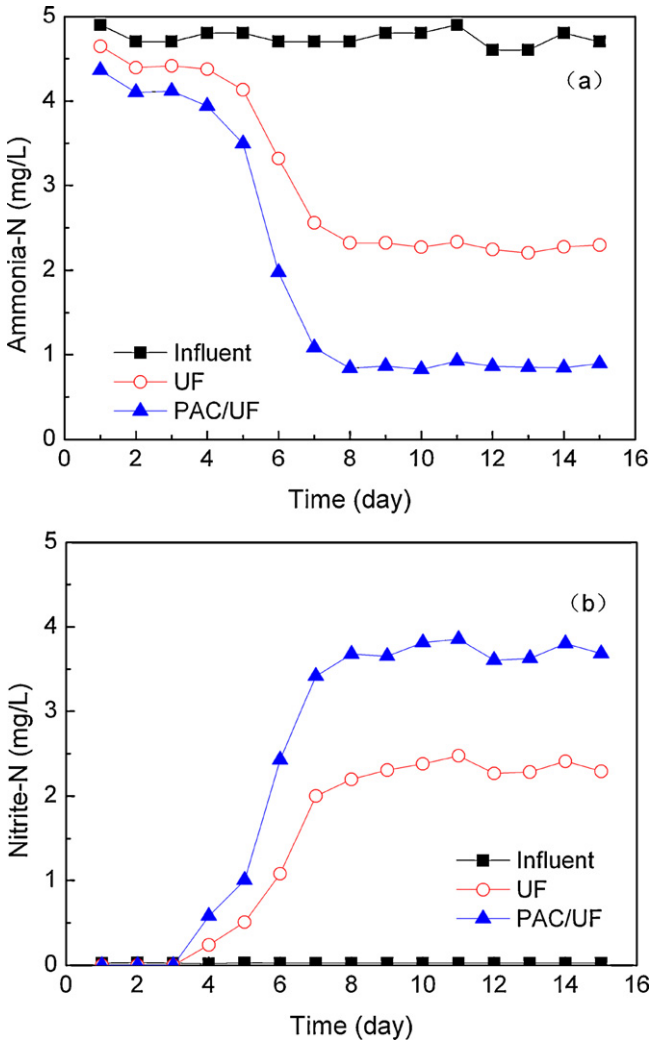


**Fig. 9.** Comparison of ammonia-N (a) and nitrite-N (b) before and after UF and PAC/UF treatment.

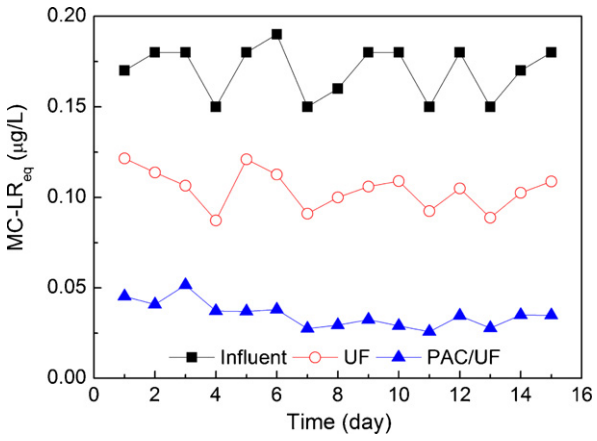


**Fig. 10.** Comparison of MC-LR$_{eq}$ before and after UF and PAC/UF treatment.

which might be partly responsible for the increasing removal of DOC, carbohydrates and proteins. It is known that ammonia is oxidized to nitrite by ammonia oxidation bacteria and further to nitrate by nitrification bacteria. However, there is no nitrate-N detected in the influent and effluent, may be due to the fact that a longer operating period is required for the nitrification bacteria to develop in the reactors.

In the PAC/UF system, the final reduction of ammonia can reach up to 61.1%, which was 10.0% higher than that in UF system. It means that the high concentration PAC has a positive effect on ammonia oxidation bacteria as a supporting medium.

### 3.1.5. MC-LR$_{eq}$ removal

Cyanotoxins would be produced during all stages of cyanobacterial growth, and cell aging or cell lysis would cause them to be released to the surrounding water. Fig. 10 illustrates that the PAC/UF process could achieve 79.4 ± 3.5% removal of MC-LR$_{eq}$ on average, which was 40.8 ± 4.2% higher than the parallel UF process. The MC-LR exhibits relatively hydrophobic characteristic with a molecular weight of 900–1100 Da [41,42], which is much smaller than the cut-off of the UF membrane (100 kDa in this study). Therefore, the MC-LR removal by UF was mainly due to adsorption onto the membrane [43]. However, the MC-LR's diameter of 12–26 Å [44] was consistent with the micro- and mesopore size of the PAC used in the experiments. Thus, the removal of MC-LR$_{eq}$ could have been significantly increased through the PAC addition in the PAC/UF process. It should be noted that the polysaccharides in the reactors might also benefit the removal of MC-LR$_{eq}$.

The result showed that the UF process achieved 35.1 ± 6.6% of MC-LR$_{eq}$ removal, resulting in an average permeate concentration below the WHO drinking water guideline value (1 μg/L) when the influent concentration of MC-LR$_{eq}$ was just 0.17 ± 0.02 μg/L. On the other hand, Campinas and Rosa found that with no PAC addition, the removal rate of microcystins was just 4% by the cellulose acetate UF membrane when the feed concentration of MC-LR was 12 μg/L [22]. According to Lee and Walker, the MC-LR removal depended on the specific conditions, such as MC-LR feed concentration, the membrane characteristics and operating conditions [43]. For an economic viability consideration for the MC-LR$_{eq}$ removal in the test condition, the UF process without PAC was prioritized.

## 3.2. Effect of PAC on the AOM release to the reactor

The algal cells retained in the reactors by the UF membrane would release AOM into the water. There are many factors influencing the photosynthesis, growth and morphogenesis of algae, such as hydrodynamics and light intensity [45–47]. According to Chen et al. [48], the biomass of *M. aeruginosa* could be reduced by more than 65% at a residence time of 5 days, when treated with aeration under light-shading. Unfortunately, there are no conclusive results regarding the light intensity effect on AOM releasing production from the published studies. Individual reports are not readily comparable due to the different algal strain, culturing methods and analytical methods employed in the different studies. In this investigation, it was inferred that apart from adsorption function, PAC would also influence the algal metabolism through the decreased light intensity and changed micro-environment for algae living.

To identify the PAC effect on the release of AOM in the reactor, another parallel UF system covered with cloth was employed to simulate the light intensity of that with PAC addition, and operated under the same experimental conditions as described in Section 2.4.

### 3.2.1. Carbohydrate and protein contents in the reactor

During the experimental period, the carbohydrate concentration in the reactor with PAC and in the reactor shaded by cloth were quite similar (3.5 ± 0.8 and 3.6 ± 0.7 mg/L, respectively), whereas the concentration in the reactor without PAC was 4.1 ± 0.6 mg/L (Fig. 11). It was thus inferred that the release of carbohydrates declined with the decrease of light intensity due to the inhibition of photosynthesis, which weakened the metabolism activity of algal cells.

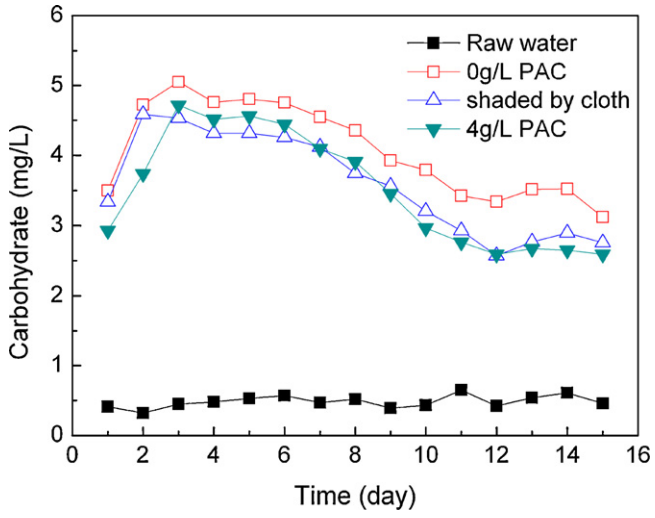


**Fig. 11.** Effect of PAC on carbohydrate content in the reactors.

As Fig. 12 illustrates, the average concentration of proteins in raw water was only $0.55 \pm 0.08$ mg/L, while the concentration increased to $3.0 \pm 1.2$ mg/L in the UF reactor without PAC. As for the reactor with PAC addition and that shaded by cloth, the protein contents were both much lower than those without PAC (by $37.6 \pm 13.3\%$ and $32.2 \pm 11.9\%$, respectively). It was deemed that low light intensity had negative effect on the release of proteins from algae cells. It had been demonstrated that the PAC had little capacity for adsorbing carbohydrates and proteins in Sections 3.1.3 and 3.1.4 (as shown in Figs. 7 and 8), this could explain why there was no significant difference between the reactor with PAC and that shaded with cloth in terms of carbohydrate and protein contents.

Figs. 11 and 12 also show that from the 1st day to the 4th day of the operation, the carbohydrate and protein concentrations in the reactors increased gradually both in UF and PAC/UF process. The reason might be the metabolism of algal cells accumulating in the reactors and the sieving by the UF membrane. However, 4 days later, the contents of carbohydrates and proteins decrease and then kept relatively stable concentrations in UF and PAC/UF process, which could be due to concentration polarization and the aerobic bacteria growth which might decompose a part of carbohydrates and proteins.

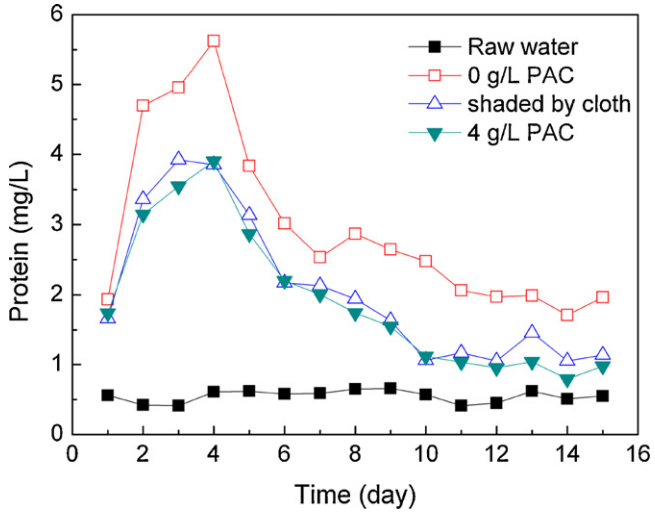


**Fig. 12.** Effect of PAC on protein content in the reactors.

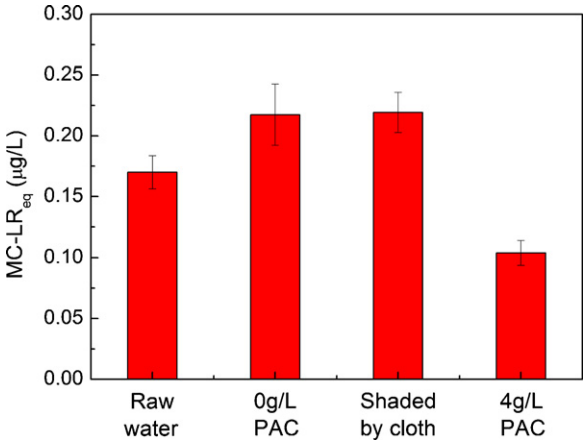


**Fig. 13.** Effect of PAC on MC-$LR_{eq}$ content in the reactors.

### 3.2.2. *MC-$LR_{eq}$ content in the reactor*

As illustrated in Fig. 13, quite similar MC-$LR_{eq}$ content was observed in the reactor without PAC addition and that covered with cloth, with the concentrations of $0.22 \pm 0.03$ μg/L and $0.22 \pm 0.02$ μg/L, respectively. A reasonable explanation is that light illumination had little or insignificant effect on MC-$LR_{eq}$ synthesis. This explanation is consistent with some published studies [46,47], but in conflict with the reports that photosynthetically active radiation could promote the synthesis of microcystin [49,50]. Fig. 13 also showed that the MC-$LR_{eq}$ concentration was reduced to $0.10 \pm 0.01$ μg/L when 4 g/L of PAC was added to the reactor, which was even lower than that in the influent (by $38.7 \pm 4.4\%$). The low content of MC-$LR_{eq}$ in the reactor with 4 g/L of PAC is consistent with its adsorption by PAC, discussed in Section 3.1.5.

### 3.3. *Comparison of TMP developments with and without PAC addition*

The influence of PAC addition on membrane fouling during UF of the algal-rich water is depicted in Fig. 14. The results show that the TMP generally increased with the operating time from the initial 7 kPa in both reactors. At the end of this investigation, the final TMP increased to 46.3 kPa in the UF process versus the 29.5 kPa obtained in the PAC/UF process. It was thus obvious that PAC addition was an efficient strategy to mitigate membrane fouling, though it was ineffective for removing the hydrophilic high MW AOM.

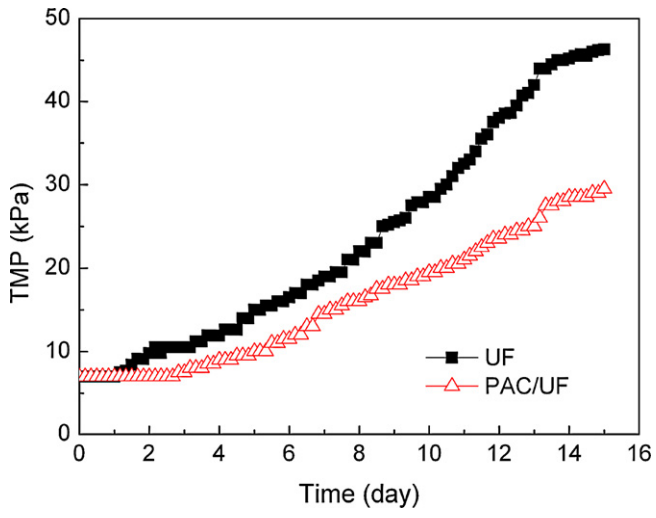


**Fig. 14.** Comparison of TMP development with and without PAC.

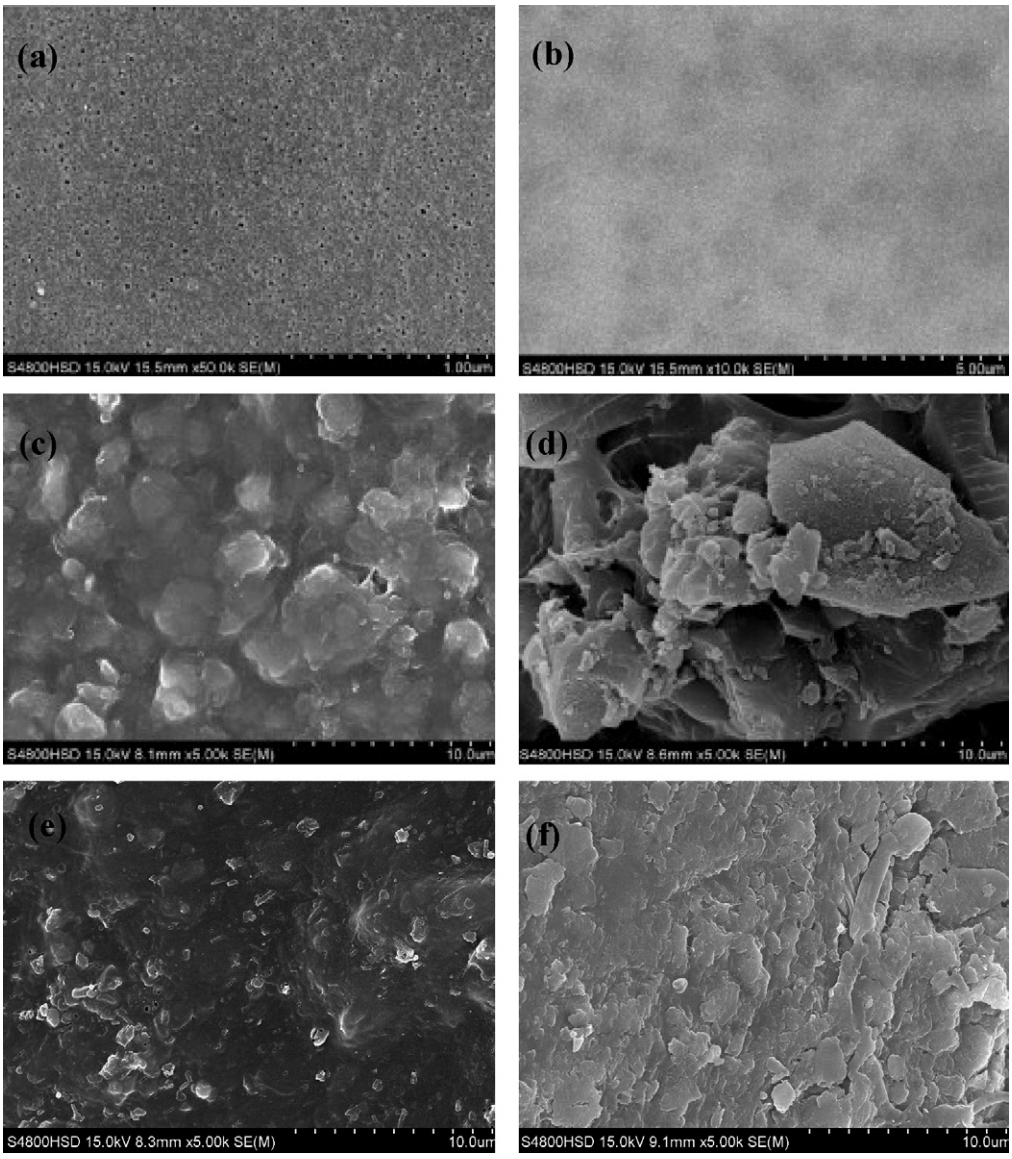


**Fig. 15.** SEM images of clean membrane surface (a, b), on the layer of membrane surface before physical cleaning in (c) UF process and (d) PAC/UF process, as well as after physical cleaning in (e) UF process and (f) PAC/UF process.

According to literature [51–53], PAC alone does not affect the permeate flux of a hydrophilic UF membrane. However, when PAC added to the reactor, the PAC particles adhered to the membrane surface and partially replaced the algal cells layer. Since most of the PAC particles had a diameter 100 times larger than the membrane pore size (0.01 μm), the PAC layer on the membrane was relatively loose with greater porosity, which would have a positive effect on the membrane permeability. This would be further discussed by SEM analysis in Section 3.4.

The membranes used in the UF and in the PAC/UF processes were taken out and thoroughly flushed and backwashed with distilled water. Meanwhile, all the solution in each reactor was discharged. After that, the membranes were re-installed into the reactors and the normal running was restored. It was found that the TMP in UF process and PAC/UF process reduced to 20.1 kPa and 13.8 kPa, respectively. Therefore, it could be approximately calculated that, in UF process the reversible fouling resistance contributed to 26.2 kPa (56.6%) of TMP increase; while the contribution of irreversible resistance was 13.1 kPa (28.3%). On the other hand, the contributions of reversible and irreversible fouling resistances to the increase of TMP in PAC/UF process were 15.7 kPa (53.2%) and 6.8 kPa (23.1%). The results indicated that PAC could not efficiently decrease the proportion of irreversible resistance in the total fouling resistance due to the low adsorption capacity of carbohydrates and proteins. Nevertheless, PAC decreased both reversible and irreversible UF fouling. Campinas and Rosa [34] found that PAC had no effect on the UF membrane reversible fouling, but it controlled the irreversible fouling minimizing the chemical cleaning frequency. The differences in these two studies might be due to the influence of the PAC and membrane materials on the reversible fouling resistance.

It may be then concluded that compared with the UF process, the economic viability of the PAC/UF process for the algal-rich water treatment is a great improvement due to more effective fouling control and removal of the released AOM (such as MC-$LR_{eq}$) with modest input of PAC.

### 3.4. SEM observations of the membrane surface

At the end of the investigation, the membranes in the PAC/UF and UF processes as well as a clean one were observed under SEM to identify the surface characteristics after each treatment process.

It should be noted that the sample preparation procedures might have taken away most of the cake layer and even part of the gel layer on the membrane surface because of their loose attachment to the membrane. As shown in Fig. 15, in comparison with the flat and smooth surface of the clean membrane (Fig. 15a and b), the surface of the membranes in both PAC/UF and UF processes were covered with a fouling layer, which seemed rather rough. The membrane surface in UF process was found to be mainly covered by algal cells and AOM (Fig. 15c), which appeared to be more dense and nonporous than that in PAC/UF process (Fig. 15d). This should account for the more rapid development of TMP in the UF process as compared with that in the PAC/UF process. After physical cleaning, some fouling materials were removed from the membrane while others remained attached in both the UF process and PAC/UF process (Fig. 15e and f). This indicates that the observed fouling was not completely reversible (in agreement with the results in Section 3.3) and that further chemical cleaning was necessary for removing the irreversible fouling.

## 4. Conclusions

Based on the evaluation of the effectiveness of PAC/immersed UF process for algal-rich water treatment and on its comparison with immersed UF alone, the major conclusions follows:

(1) Complete algae removal in terms of chlorophyll-*a* was achieved by both PAC/UF and UF processes in the experiments, due to UF sieving.
(2) Due to PAC addition, higher organic matter removal could be obtained by the PAC/UF process in terms of DOC, $UV_{254}$ and MC-$LR_{eq}$ than by UF alone. However, PAC had little adsorption capacity for carbohydrates and proteins released by cyanobacterial cells, indicating that PAC could not efficiently adsorb the hydrophilic, high MW AOM of algogenic organic matter.
(3) The PAC could effectively mitigate UF membrane fouling by algal-rich water, as demonstrated by the slower development of TMP in the PAC/UF process as compared with that in UF alone.
(4) PAC addition reduced the production of carbohydrates and proteins in the reactor due to the reduction of light intensity. On the other hand, MC-$LR_{eq}$ concentration in the reactor with PAC was significantly decreased due to adsorption.
(5) Through SEM examination, a layer of algal cells combined with AOM was observed on the membrane surface in UF process; whereas the membrane fouling layer in PAC/UF process appeared to be much more porous and loose, which is consistent with the PAC ability for alleviating the UF membrane fouling.

## Acknowledgements

This research is financially supported by the Important Special Program of Science and Technology for the Control and Treatment of Water Pollution in China (Grant No. 2008ZX07422-005), the State Key Laboratory of Urban Water Resource and Environment (HIT, Grant No. 2010DX01), and the National Postdoctoral Science Foundation of China (No. 20100471074). We would like to give our sincere thanks to Litree Company in China, and their kindly free provision of UF membrane modules in this study is highly appreciated.

## References

[1] R.G. Wetzel, Limnology, W.B. Saunders Company, Philadelphia, 1975.
[2] S. Aaronson, T. Berner, Z. Dubinsky, Microalgae as a source of chemical and natural products, in: G. Shelef, C.J. Soeder (Eds.), Algae Biomass: Production and Use, Elsevier-North Holland Biomedical Press, New York, 1980, pp. 20–105.
[3] N. Gupta, S.C. Pant, R. Vijayarghavan, P.V.L. Rao, Comparative toxicity evaluation of cyanobacterial cyclic peptide toxin microcystin variants (LR, RR, YR) in mice, Toxicology 188 (2003) 285–296.
[4] WHO, Cyanobacterial Toxins, Microcystin-LR Guidelines for Drinking-Water Quality, World Health Organization, Geneva, 1998.
[5] L.A. Lawton, P.K.J. Robertson, Physico-chemical treatment methods for the removal of microcystins (cyanobacterial hepatotoxins) from potable waters, Chem. Soc. Rev. 28 (1999) 217–224.
[6] K. Himberg, A.M. Keijola, H. Pyysalo, K. Sivonen, The effect of water treatment processes on the removal of hepatotoxins from Microcystis and Oscillatoria cyanobacteria: a laboratory study, Water Res. 23 (1989) 979–984.
[7] A. Montiel, B. Welté, Preozonation coupled with flotation filtration: successful removal of algae, Water Sci. Technol. 37 (1998) 65–73.
[8] J. Ma, W. Liu, Effectiveness and mechanism of potassium ferrate (VI) preoxidation for algae removal by coagulation, Water Res. 36 (2002) 871–878.
[9] J.J. Chen, H.H. Yeh, The mechanisms of potassium permanganate on algae removal, Water Res. 39 (2005) 4420–4428.
[10] N.J.D. Graham, V.E. Wardlaw, R. Perry, J. Jiang, The significance of algae as trihalomethane precursors, Water Sci. Technol. 37 (1998) 83–89.
[11] J.H. Kweon, H.W. Hur, G.T. Seo, T.R. Jang, J.H. Park, K.Y. Choi, H.S. Kim, Evaluation of coagulation and PAC adsorption pretreatments on membrane filtration for a surface water in Korea: a pilot study, Desalination 249 (2009) 212–216.
[12] M. Campinas, M.J. Rosa, Evaluation of cyanobacterial cells removal and lysis by ultrafiltration, Sep. Purif. Technol. 70 (2010) 345–353.
[13] N. Her, G. Amy, H.R. Park, M. Song, Characterizing algogenic organic matter (AOM) and evaluating associated NF membrane fouling, Water Res. 38 (2004) 1427–1438.
[14] M.A. Zazouli, S. Nasseri, M. Ulbricht, Fouling effects of humic and alginic acids in nanofiltration and influence of solution composition, Desalination 250 (2010) 688–692.
[15] B. Kwon, N. Park, J. Cho, Effect of algae on fouling and efficiency of UF membranes, Desalination 179 (2005) 203–214.
[16] J.B. Castaing, A. Massé, M. Pontié, V. Séchet, J. Haure, P. Jaouen, Investigating submerged ultrafiltration (UF) and microfiltration (MF) membranes for seawater pre-treatment dedicated to total removal of undesirable micro-algae, Desalination 253 (2010) 71–77.
[17] M.T. Hung, J.C. Liu, Microfiltration for separation of green algae from water, Colloids Surf., B 51 (2006) 157–164.
[18] M. Tomaszewska, S. Mozia, Removal of organic matter from water by PAC/UF system, Water Res. 36 (2002) 4137–4143.
[19] S.J. Xia, Y.N. Liu, X. Li, J.J. Yao, Drinking water production by ultrafiltration of Songhuajiang River with PAC adsorption, J. Environ. Sci. 19 (2007) 536–539.
[20] I.I. Tumbas, R. Hobby, B. Küchle, S. Panglisch, R. Gimbel, p-Nitrophenol removal by combination of powdered activated carbon adsorption and ultrafiltration-comparison of different operational modes, Water Res. 42 (2008) 4117–4124.
[21] J. Lee, H.W. Walker, Effect of process variables and natural organic matter on removal of microcystin-LR by PAC-UF, Environ. Sci. Technol. 40 (2006) 7336–7342.
[22] M. Campinas, M.J. Rosa, Removal of microcystins by PAC/UF, Sep. Purif. Technol. 71 (2010) 114–120.
[23] N. Wibowo, L. Setyadhi, D. Wibowo, J. Setiawan, S. Ismadji, Adsorption of benzene and toluene from aqueous solutions onto activated carbon and its acid and heat treated forms: Influence of surface chemistry on adsorption, J. Hazard. Mater. 146 (2007) 237–242.
[24] X. Zhang, P.L. Bishop, B.K. Kinkle, Comparison of extraction methods for quantifying extracellular polymers in biofilms, Water Sci. Technol. 39 (1999) 211–218.
[25] W.J. Huang, C.H. Lai, Y.L. Cheng, Evaluation of extracellular products and mutagenicity in cyanobacteria cultures separated from a eutrophic reservoir, Sci. Total Environ. 377 (2007) 214–223.
[26] J.W. Zhao, Studies on analytical and removal method and oxidative degradation mechanism of microcystins in eutrophic water, PhD Thesis, Xi'An University of Architecture and Technology, China, 2006.
[27] L.F. Zhang, X.F. Ping, Z.G. Yang, Determination of microcystin-LR in surface water using high performance liquid chromatography tandem electro spray ionization mass detector, Talanta 62 (2004) 191–198.
[28] I. Sentana, M.A. De La Rubia, M. Rodríguez, E. Sentana, D. Prats, Removal of natural organic matter by cationic and anionic polyacrylonitrile membranes. The effect of pressure, ionic strength and pH, Sep. Purif. Technol. 68 (2009) 305–311.
[29] S. Yiantsios, A. Karabelas, An experimental study of humic acid and powdered activated carbon deposition on UF membranes and their removal by backwashing, Desalination 140 (2001) 195–209.
[30] J.Y. Tian, H. Liang, Y.L. Yang, S. Tian, G.B. Li, Membrane adsorption bioreactor (MABR) for treating slightly polluted surface water supplies: as compared to membrane bioreactor (MBR), J. Membr. Sci. 325 (2008) 262–270.
[31] J. Ottoson, A. Hansen, B. Björlenius, H. Norder, T. Stenström, Removal of viruses, parasitic protozoa and microbial indicators in conventional and membrane processes in a wastewater pilot plant, Water Res. 40 (2006) 1449–1457.
[32] P.C. Singer, Humic substances as precursors for potentially harmful disinfection by-products, Water Sci. Technol. 40 (1999) 25–30.
[33] R.K. Henderson, A. Baker, S.A. Parsons, B. Jefferson, Characterisation of algogenic organic matter extracted from cyanobacteria, green algae and diatoms, Water Res. 42 (2008) 3435–3445.
[34] M. Campinas, M.J. Rosa, Assessing PAC contribution to the NOM fouling control in PAC/UF systems, Water Res. 44 (2010) 1636–1644.

[35] S. Nataraj, R. Schomäcker, M. Kraume, I.M. Mishra, A. Drews, Analyses of polysaccharide fouling mechanisms during crossflow membrane filtration, J. Membr. Sci. 308 (2008) 152–161.
[36] K. Listiarini, W. Chun, D.D. Sun, J.O. Leckie, Fouling mechanism and resistance analyses of systems containing sodium alginate, calcium, alum and their combination in dead-end fouling of nanofiltration membranes, J. Membr. Sci. 344 (2009) 244–251.
[37] K.J. Hwang, P.Y. Sz, Filtration characteristics and membrane fouling in crossflow microfiltration of BSA/dextran binary suspension, J. Membr. Sci. 347 (2010) 75–82.
[38] N.M. Velings, M.M. Mestdagh, Protein adsorption in calcium alginate gel beads, J. Bioact. Compat. Polym. 9 (1994) 133.
[39] H. Susanto, H. Arafat, E.M.L. Janssen, M. Ulbricht, Ultrafiltration of polysaccharide-protein mixtures: elucidation of fouling mechanisms and fouling control by membrane surface modification, Sep. Purif. Technol. 63 (2008) 558–565.
[40] W.S. Ang, M. Elimelech, Protein (BSA) fouling of reverse osmosis membranes: implications for wastewater reclamation, J. Membr. Sci. 296 (2007) 83–92.
[41] M.G. Antoniou, A.A. de la Cruz, D.D. Dionysiou, Cyanotoxins: new generation of water contaminants, J. Environ. Sci. Eng. 131 (2005) 1239–1243.
[42] P.S.M. Vesterkvist, J.A.O. Meriluoto, Interaction between microcystins of different hydrophobicities and lipid monolayers, Toxicon 41 (2003) 349–355.
[43] J. Lee, H.W. Walker, Mechanisms and factors influencing the removal of microcystin-LR by ultrafiltration membranes, J. Membr. Sci. 320 (2008) 240–247.
[44] C. Donati, M. Drikas, R. Hayes, G. Newcombe, Microcystin-LR adsorption by powdered activated carbon, Water Res. 28 (1994) 1735–1742.
[45] F. Pustizzi, H. MacIntyre, M.E. Warner, D.A. Hutchins, Interaction of nitrogen source and light intensity on the growth and photosynthesis of the brown tide alga *Aureococcus anophagefferens*, Harmful Algae 3 (2004) 343–360.
[46] G. Böttcher, I. Chorus, S. Ewald, T. Hintze, N. Walz, Light limited growth and microcystin content of *Planktothrix agardhii* and *Microcystis aeruginosa* in turbidostats, in: I. Chorus (Ed.), Cyanotoxins-Occurrence, Causes, Consequences, Springer, Berlin, 2001, pp. 115–133.
[47] K. Hesse, J.G. Kohl, Effects of light and nutrient supply on growth and microcystin content of different strains of *Microcystis aeruginosa*, in: I. Chorus (Ed.), Cyanotoxins-Occurrence, Causes, Consequences, Springer, Berlin, 2001, pp. 104–115.
[48] X.C. Chen, S.B. He, Y.Y. Huang, H.N. Kong, Y. Lin, C.J. Li, G.Q. Zeng, Laboratory investigation of reducing two algae from eutrophic water treated with light-shading plus aeration, Chemosphere 76 (2009) 1303–1307.
[49] M. Kaebernick, B.A. Neilan, Ecological and molecular investigations of cyanotoxin production, FEMS Microbiol. Ecol. 35 (2001) 1–9.
[50] C. Wiedner, P.M. Visser, J. Fastner, J.S. Metcalf, G.A. Codd, L.R. Mur, Effects of light on the microcystin content of Microcystis strain PCC 7806, Appl. Environ. Microbiol. 69 (2003) 1475–1481.
[51] C.F. Lin, Y.J. Huang, O.J. Hao, Ultrafiltration processes for removing humic substances: effect of molecular weight fractions and PAC treatment, Water Res. 33 (1999) 1252–1264.
[52] C.W. Li, Y.S. Chen, Fouling of UF membrane by humic substances: effects of molecular weight and powder-activated carbon (PAC) pre-treatment, Desalination 170 (2004) 59–67.
[53] S. Mozia, M. Tomaszewska, A.W. Morawski, Studies on the effect of humic acids and phenol on adsorption-ultrafiltration process performance, Water Res. 39 (2005) 501–509.