Reducing the effect of cyanobacteria in the microfiltration of secondary effluent

Y. T. Goh, J. L. Harris and F. A. Roddick

ABSTRACT

Cyanobacterial blooms in the lagoons of sewage treatment plants can severely impact the performance of membrane plants treating the effluent. This paper investigates the impact of *Microcystis aeruginosa* in a secondary effluent on the microfiltration filterability and cleaning of the membrane. Alum coagulation and dissolved air flotation (DAF) were investigated to remove the algae and so enhance the volume of effluent processed, and their influence on reversible and irreversible fouling. Degree of fouling due to the algal components was found to be in decreasing order of algal cells, algal organic matter and extracellular organic matter. Alum coagulation with 5 mg L^{-1} as Al^{3+} led to a substantial increase in permeate volume, an increase in dissolved organic carbon removal, and a foulant layer which protected the membrane from internal fouling but which was hydraulically removable resulting in full flux recovery. Pre-treatment by DAF or 1.5 μm filtration following alum coagulation enhanced the flux rate and permeate volume but exposed the membrane to internal irreversible fouling.

Key words | algae, coagulation, dissolved air flotation, *Microcystis aeruginosa*, microfiltration, secondary effluent

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INTRODUCTION

Cyanobacterial blooms are a serious water quality problem in reservoirs, lakes, rivers and drinking water treatment plants at certain times of the year (Teixeira & Rosa 2006; Henderson *et al.* 2008*b*; Heng *et al.* 2009). Blooms also occur in the lagoons of biological sewage treatment plants with long residence times (30 days), elevated residual nutrients, and light and temperatures conducive to growth. Such periodic large blooms of cyanobacteria (commonly known as blue-green algae) typically involve *Microcystis aeruginosa* (Vasconcelos & Pereira 2001).

The presence of *M. aeruginosa* is one of the common causes of odour problems in Australian wastewater treatment plants (Bolch & Blackburn 1996). *M. aeruginosa* forms buoyant colonies of small coccoid cells (2–8 μm diameter) embedded in a gelatinous matrix (Baker 1992) and can produce a range of potent cyclic heptapeptide hepatotoxins known as microcystins (Carmichael 1992). *M. aeruginosa* also secretes a mucilaginous slime material, or extracellular organic matter (EOM), forming a thick layered structure surrounding the cell (Kwon *et al.* 2005). The EOM can cement particles of natural organic matter (NOM) from the treated effluent on the filtration membrane surface causing an increase in resistance to filtration (Kwon *et al.* 2005). Furthermore, as the bloom collapses it releases intracellular organic matter (IOM) and toxins to the surrounding water in significant concentrations (Jones & Orr 1994).

The presence of *M. aeruginosa* can impact severely on the performance of microfiltration and ultrafiltration units upstream of reverse osmosis units used in the desalination of secondary effluent. Although ultrafiltration is able to remove microorganisms (>99.99%), Gijsbertsen-Abrahamse *et al.* (2006) reported the release of up to 2% of the cell-bound microcystins into the permeate which was

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caused by shear due to the filtration process itself. Minimisation of the impact of algae by effective pre-treatment is the initial line of defence in controlling membrane fouling and assuring successful RO operation (Kim *et al.* 2002). Alum treatment was effective in removing *M. aeruginosa* cells from reservoir water and no damage was found to algae cells (Chow *et al.* 1999). According to a recent review by Henderson *et al.* (2008*a*), DAF is efficient at treating algae and consistently achieved greater than 90% cell removal.

In this study, we investigated the impact of algae in the secondary effluent from a municipal biological sewage treatment plant on its treatment by microfiltration, and tested various pre-treatment methods (alum coagulation, DAF and 1.5 μm pre-filtration (surrogate for media filtration)) to mitigate the effect. Membrane performance was examined in terms of flux profiles, permeate volume collected, removal of algogenic and effluent organic matter, and the reduction of irreversible fouling.

MATERIALS AND METHODS

Wastewater sample

A fifty litre sample of the secondary biologically treated effluent from the Western Treatment Plant, Victoria, Australia was collected from the holding ponds referred to as Head of Road Storage (HORS) in January 2009. The effluent (Table 1) was stored at 4°C with 2 L being withdrawn and warmed to 20 ± 2°C for each test.

Table 1 | Characteristics of the secondary effluent

Parameters	Value
pH	8.2
Turbidity (NTU)	3.2
DOC ($mg\,L^{-1}$)	9.85
$UVA_{254}(cm^{-1})$	0.24
SUVA ($L\,m^{-1}\,mg^{-1}$)	2.5
Chl-a ($\mu g\,L^{-1}$)	11
Algae ($cells\,mL^{-1}$)	7.5×10^4

Cultivation of *M. aeruginosa*

M. aeruginosa (CS 566/01-A01) was obtained from CSIRO Microalgae Research Centre (Tasmania, Australia) and was grown in 5 L Schott bottles at 22°C using MLA medium under humidified aeration (0.45 μm filtered). A 16/8 h light/dark cycle using aquatic lights was employed. Growth of the algae was followed by developing a correlation between cell count and chlorophyll-a concentration (Chl-a). For the Chl-a analysis, the algal cells were harvested by filtration (1 μm, Whatman, GF/B) and the chlorophyll extracted from the cells with 20 ml acetone overnight. The optical densities of the extracts were measured at 630, 645, 663 and 750 nm using a UV/vis spectrophotometer (UV2, Unicam) and Chl-a concentration was calculated according to ESS Method 150.1 (1991). The relationship between cell count and Chl-a measurement was found to be linear ($R^2 = 0.988$) up to a cell count of 2.0×10^7:

$$\text{Cell Count}\,[\text{cells}\,mL^{-1}] = 6848 \times \text{Chl} - a[\mu g\,L^{-1}]. \quad (1)$$

For samples with cell count higher than 2.0×10^7, the samples were homogenised, diluted to fit into the linear range, and the cell count readjusted for the dilution.

Experiments involving algal matter

Experiments were conducted to isolate the effect of HORS, HORS with the addition of algal organic matter (AOM), algal cells, and the extracellular organic matter (EOM). The term AOM as used in this paper refers to the broth consisting of algal cells and extracellular matter. Aliquots (160 ml) of the *M. aeruginosa* broth was taken after 21 days of growth at which stage the Chl-a and DOC concentrations were $1750\,\mu g\,L^{-1}$ (12×10^6 cells mL^{-1}) and $16.6\,mg\,L^{-1}$, respectively.

The DOC of the AOM aliquot was adjusted by dilution with Milli-Q water (pure deionised water) to $9.85\,mg\,L^{-1}$ to match the DOC of HORS and then added to 2 L of HORS. Centrifugation (4,400 rpm for 30 mins) was employed to separate the algal cells from the EOM supernatant and the separated algal cells were resuspended back into 2 L of HORS. Chl-a concentration for algal cells and AOM were $128\,\mu g\,L^{-1}$ (8.8×10^5 cells mL^{-1}). The DOC of the EOM

supernatant was adjusted by dilution with Milli-Q water to 9.85 mg L^{-1} before adding into 2 L of HORS.

Microfiltration

An Amicon 8050 stirred cell (membrane area 13.4 cm^2) was connected to a feed reservoir and operated at a transmembrane pressure of 70 kPa regulated by nitrogen gas and stirrer speed of 430 rpm. All experiments were conducted at room temperature (20 ± 2°C). The permeate flux was determined using a top-loading electronic balance (BP6100, Sartorius, accuracy ±0.1 g) with data logging function connected to a computer. Hydrophilic polyvinylidene fluoride (PVDF) microfiltration membranes (Durapore VVPP, 0.1 μm, Millipore) were used. New membranes were soaked overnight in Milli-Q water and 500 ml of Milli-Q water was passed through each membrane prior to filtration tests. The membranes only selected for use when the measured pure water flux J_o was in the range of 1,400–1,600 L $m^{-2} h^{-1}$. The experiments with effluent were conducted till the permeate flux reached a final value of 40 L $m^{-2} h^{-1}$.

For membrane cleaning, the fouled membrane was hydraulically cleaned by surface washing and backflushed by placing the membrane upside down in the filtration cell and filtering 1 L of Milli-Q water. The membrane was returned to its original processing position and the pure water flux J_w measured. Flux recovery (J_w /J_o) was used as an indication of the extent of membrane cleaning.

Pre-treatment methods

Coagulation using aluminium sulphate (alum) and dissolved air flotation (DAF) were investigated as pre-treatment for the algae-dosed effluent. Alum stock solution (1,000 mg L^{-1} Al^{3+}) was prepared from analytical grade $Al_2(SO_4)_3 \cdot 16H_2O$ (Sigma-Aldrich) and dosed at 5 mg L^{-1} Al^{3+} in a laboratory jar tester unit (Phipps and Bird, PB-700). The solution was rapid mixed for 1 min at 200 rpm followed by slow mixing for 20 min at 30 rpm. Following coagulation, the solution was studied in three ways: direct filtration of the whole coagulated solution, DAF treatment, and pre-filtering through 1.5 μm glass-fibre membranes (Whatman, GF/A).

DAF treatment involved saturating 20% of the settled water with air in a pressure vessel (XX6700P10, Millipore) at 450 kPa, and releasing this saturated stream into the remaining 80% of the coagulated wastewater. The DAF-treated water was left intact for 3 minutes after which the top layer was siphoned off and the remaining water was used in the filtration tests.

Characterisation and analytical methods

Samples were pre-filtered through cellulose acetate 0.45 μm filter (C045A047A, Advantec) prior to dissolved organic carbon (DOC) and ultraviolet light absorbance (UVA_{254}) analysis. DOC was analysed using a Sievers 820 TOC analyser, and UVA_{254} was measured using a UV/vis spectrometer (UV2, Unicam). Specific ultraviolet light absorbance (SUVA) was determined as follows: (UVA_{254} (cm^{-1}) / DOC (mg L^{-1})) × 100. Samples were adjusted to the same DOC (9 mg L^{-1}) with Milli-Q water prior to fluorescence excitation emission matrix (EEM) analysis using a fluorescence spectrophotometer (LS 55, PerkinElmer). The foulant layer on the membrane surface was examined by scanning electron microscopy (SEM) running in environmental mode under low-vacuum conditions (Quanta 200, FEI). Using this mode of operation, the wet sample was able to be examined.

RESULTS AND DISCUSSION

Effect of algal matter

Typical curves of flux versus permeate volume for the HORS with additions of EOM, AOM, and algal cells are shown in Figure 1. HORS exhibited the highest flux, with major fouling by the algal cells and also by AOM and EOM.

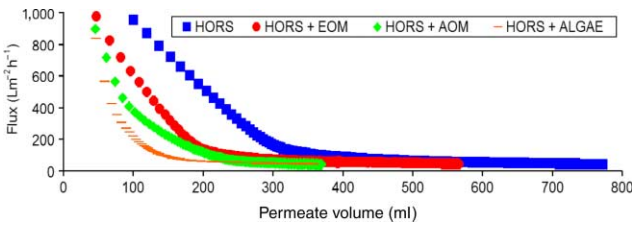

Figure 1 | Comparison of effect of algal cells, EOM and AOM on microfiltration flux rate.

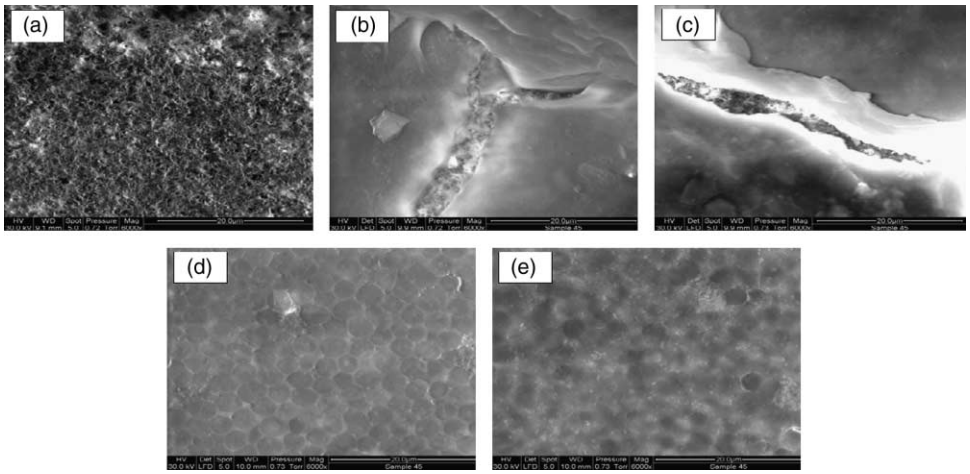

Figure 2 | SEM micrographs at 6000x for (a) Clean microfiltration membrane; (b) Membrane fouled by HORS; (c) HORS + EOM; (d) HORS + algal cells; (e) HORS + AOM. Scale bar indicates 20 μm.

Filterability was compared in terms of the volume of permeate collected at a final flux of 40 L m^{-2} h^{-1}. The permeate volume of 772 ml for HORS declined with the addition of EOM (567 ml), AOM (370 ml) and *M. aeruginosa* cells (359 ml).

SEM micrographs of the foulant layers for each of the above cases are shown in Figure 2. The SEM images in Figure 2(b, c) were taken near micro-cracks to show the thickness of the foulant layer. The addition of EOM to HORS led to a thicker foulant layer compared with HORS alone and provided more resistance to filtration resulting in the reduction in flux rate and permeate volume. The addition of algal cells to HORS produced a compacted and evenly distributed algal layer (Figure 2d) and consequently produced lower flux rate and less permeate volume. The addition of AOM resulted in a looser and unevenly distributed algal layer on the membrane surface (Figure 2e) which gave a higher flux rate and higher permeate volume compared with the algal cells alone.

Effect of pre-treatments

Flux profiles for the microfiltration of HORS, HORS with the addition of algal cells and following various pre-treatment processes are shown in Figure 3. HORS exhibited a sharp flux decline with permeate volume. The addition of algal cells led to a higher flux in the initial stages but the situation was reversed after the passage of 350 ml permeate. Compared with the base case of 606 ml for HORS, the addition of algae resulted in 491 ml permeate. After alum treatment, the permeate volume increased to 1,647 ml, almost three times that of HORS alone. Alum treatment of HORS plus algal cells produced 1,095 ml, twice that of HORS with algal cells. Sequential use of alum and DAF on HORS with algal cells achieved a permeate volume of 1,500 ml, three times that of HORS with algal cells. In testing the sequential use of alum and 1.5 μm pre-filtration on HORS with algal cells, the sample was exhausted at 78 L m^{-2} h^{-1} with a volume of 1,426 ml

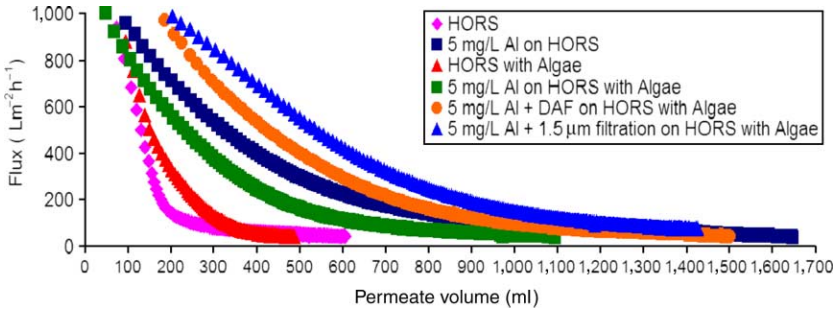

Figure 3 | Permeate flux profiles for the microfiltration of HORS, HORS with algal cell addition and pre-treated water.

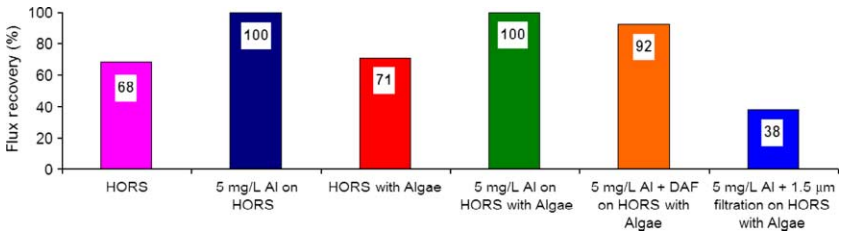

Figure 4 | Flux recovery after hydraulic cleaning with back flushing of fouled microfiltration membranes.

collected. This demonstrated that particulates larger than 1.5 μm were a definite contributor to membrane fouling. The use of alum and DAF, and alum and 1.5 μm pre-filtration, on HORS with algal cells were more effective than alum treatment alone in yielding high volumes of permeate. However, as shown later, the pre-treatments which included removal of the alum flocs exposed the membrane to irreversible fouling.

Flux recovery and membrane cleaning

The flux recovery for HORS was 68% (Figure 4). With the addition of algal cells to HORS, the flux recovery was marginally higher at 71%. This was attributed to the build-up of the algal cell layer on the membrane surface which acted as a protective layer preventing foulants from coming into direct contact with the membrane surface thus reducing membrane fouling. With alum treatment, full flux recovery was achieved for HORS and HORS with algal cell addition. When DAF or 1.5 μm pre-filtration was used to remove the alum flocs, the permeate volume increased but at the detriment of lower flux recovery of 92 and 38%, respectively.

The effectiveness of hydraulic cleaning was examined using SEM micrographs of the membrane surface (Figure 5). The membrane for HORS (Figure 5a) and HORS with algal cells (Figure 5b) revealed that some particulates and foulants remained on the membrane after hydraulic cleaning and so reduced the flux recovery. Hydraulic cleaning of the alum-treated samples was very effective for removing the membrane deposit as evidenced in Figure 5(c, d). The use of alum coagulation followed by DAF on HORS with algal cells achieved a lower flux recovery of 92%. Some of the foulant layer persisted on the membrane after back-flushing (Figure 5e). Internal fouling was evident when 1.5 μm pre-filtration was included as the flux recovery was only 38%. The absence of alum flocs meant that there was no protective layer on the membrane surface which enabled

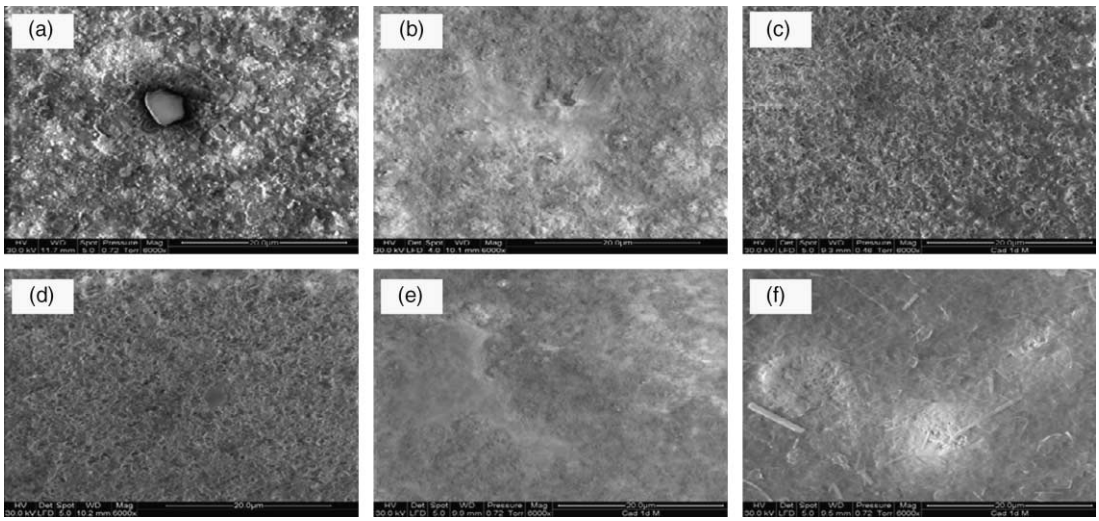

Figure 5 | SEM micrographs of hydraulically cleaned microfiltration membranes (6000x). (a) HORS; (b) HORS with algal cells; (c) Alum-treated HORS; (d) Alum-treated HORS with algal cells; (e) Alum and DAF-treated HORS with algal cells; (f) Alum-treated and 1.5 μm pre-filtered HORS with algal cells. Scale bar indicates 20 μm.

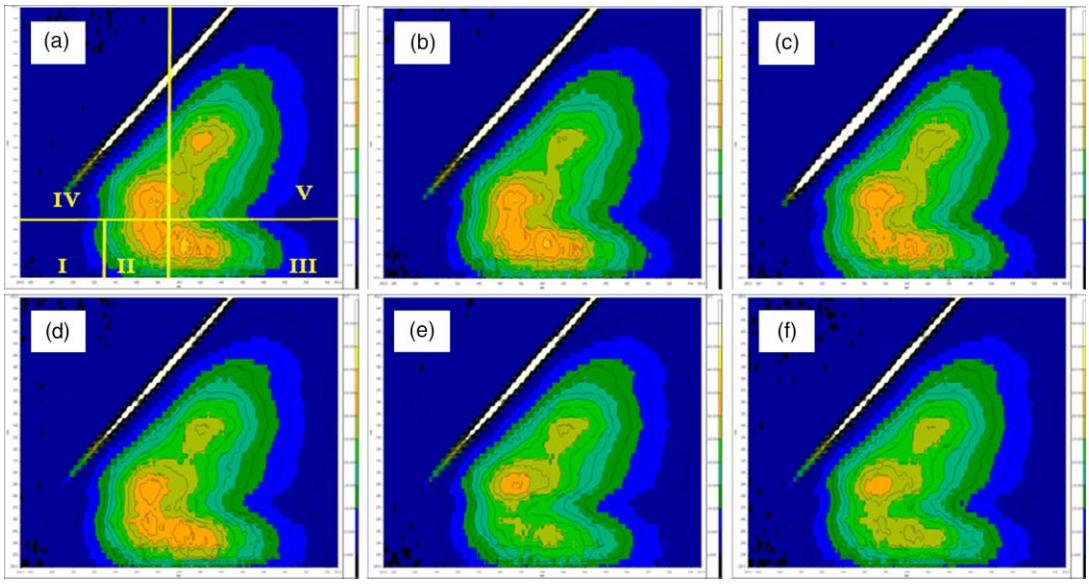

Figure 6 | EEMs for (a) HORS; (b) HORS with algae; and the permeate for (c) HORS with algae; (d) 5 mg L^{-1} Al + DAF on HORS with algae; (e) 5 mg L^{-1} Al on HORS with algae; (f) 5 mg L^{-1} Al + 1.5 μm pre-filtration on HORS with algae.

foulants smaller than 1.5 μm to deposit on the membrane surface and within the pores, resulting in pore blockage and causing the significant reduction in the flux recovery (Figure 5f) (Fan *et al.* 2008).

Water quality improvement

The reduction of DOC in the permeate for HORS and HORS with algal cells was low (6 and 3%, respectively). Alum treatment of these solutions increased the DOC removal to 13 and 7%, respectively. DOC removal for the HORS with algal cells was enhanced by the sequential use of alum and DAF to 10%, and to 18% with the inclusion of 1.5 μm pre-filtration. Microfiltration gave high removal of turbidity (96–99%), and the residual chlorophyll-a concentration was negligible for all cases.

Fluorescence Excitation Emission Matrix (EEM) Spectroscopy

Fluorescent EEMs of HORS with and without pre-treatment are shown in Figure 6. The separate regions have been designated according to Chen *et al.* (2003) as follows: region I and II = aromatic protein I and II respectively; region III = fulvic acid-like; region IV = soluble microbial by-products; region V = humic acid-like. The addition of algal cells to HORS caused a slight reduction in the humic acid-like region (Figure 6b). This was attributed to the adsorption of humic substance to the external algogenic material on the algae cells (Kwon *et al.* 2005). The intensity of all peaks in the permeate for HORS with algae (Figure 6c) was not significantly different from the feed, consistent with the DOC removal of 3% by microfiltration. For the sequential use of alum and DAF, the intensity of all peaks in the permeate were similar to the permeate of HORS with algae. This revealed that DAF was relatively ineffective for the removal of fluorescent DOC (Figure 6d) despite the higher DOC removal. However, there was a marked reduction in intensity of regions I, II, III and IV in the permeate for alum-treated HORS with algae (Figure 6e) and the sequential use of alum and 1.5 μm pre-filtration (Figure 6f) demonstrating that a significant proportion of fluorescent aromatic proteins, fulvic acid-like and soluble microbial by-products were removed.

CONCLUSION

The presence of *M. aeruginosa* in secondary effluent had a substantial effect on microfiltration performance in terms of decreased volume of permeate and only partial removal of the fouling deposit by hydraulic cleaning. Fouling of the membranes by the algal components was found to be in

decreasing order of algal cells, algal organic matter and extracellular organic matter. Microfiltration alone showed low removal of DOC for HORS (6%) and HORS plus algal cells (3%). Improvements in DOC rejection were obtained when pre-treatments were applied to HORS with algal cells. With alum coagulation the DOC of the permeate was 7%, alum coagulation treatment followed by DAF was 10%, and alum coagulation with 1.5 μm pre-filtration was 18%. Alum coagulation also improved the filterability for HORS and HORS plus algal cells. The coupling of alum coagulation with DAF or 1.5 μm pre-filtration further enhanced the flux rate and increased the filtration volume. Particulates larger than 1.5 μm were shown to contribute to membrane fouling by depositing on the membrane surface.

Alum treatment had the effect of improving the flux rate and the permeate volume collected before the final flux of $40\,L\,m^{-2}\,h^{-1}$ was reached and backwashing was required. It also formed a porous cake layer which protected the membrane from internal fouling but which was readily removed by hydraulic cleaning, leading to full flux recovery. Coupling alum coagulation with DAF or 1.5 μm pre-filtration had a negative effect on flux recovery. This was mainly due to the absence of the protective alum-organic floc layer on the membrane surface enabling freer access to the internal pores of the membrane by the smaller foulants.

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