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Removal of cyanobacterial metabolites by nanofiltration from two treated waters

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ABSTRACT

Cyanobacterial metabolites, both toxic and non-toxic, are a major problem for the water industry. Nanofiltration (NF) may be an effective treatment option for removing organic micropollutants, such as cyanobacterial metabolites, from drinking water due to its size exclusion properties. A rapid bench scale membrane test (RBSMT) unit was utilised to trial four NF membranes to remove the cyanobacterial metabolites, microcystin, cylindrospermopsin (CYN), 2-methylisoborneol (MIB) and geosmin (GSM) in two treated waters sourced from the Palmer and Myponga water treatment plants. Membrane fouling was observed for both treated waters; however, only minor differences were observed between feed waters of differing natural organic matter (NOM) concentration. Low molecular weight cut-off (MWCO), or 'tight' NF, membranes afforded average removals above 90% for CYN, while removal by higher MWCO, or 'loose' NF membranes was lower. MIB and GSM were removed effectively (above 75%) by tight NF but less effectively by loose NF. Microcystin variants (MCRR, MCYR, MCLR, MCLA) were removed to above 90% by tight NF membranes; however, removal using loose NF membranes depended on the hydrophobicity and charge of the variant. Different NOM concentration in the treated waters had no effect on the removal of cyanobacterial metabolites.

1. Introduction

Cyanobacteria (blue–green algae) are a major problem for the water industry as they can produce substances toxic to humans in addition to taste and odour (T&O) compounds that make drinking water aesthetically displeasing [1–4]. It is likely that this problem will be intensified by the effects of climate change as water temperatures are predicted to rise which could result in an increase in the frequency and intensity of cyanobacterial blooms in water supplies [5–7]. Furthermore, cyanobacterial species such as *Cylindrospermopsis raciborskii*, formerly considered a tropical or sub-tropical species, are becoming more prevalent in temperate climates [8]. Therefore, the effective removal of cyanobacterial metabolites is an increasingly important research topic for the worldwide water industry.

In extracellular form these cyanobacterial metabolites are poorly removed by conventional water treatment processes [9,10]. Methods such as oxidation [11] and activated carbon adsorption [12–14] are routinely employed for the removal of these cyanobacterial toxins and T&O; however, they may also be removed by nanofiltration (NF) membrane processes, as compounds larger than the pore size of NF membranes should theoretically be removed by size exclusion [15]. Such processes are becoming widespread in the water industry and consequently the demand for expertise in the application of membranes for cyanobacterial toxin and T&O removal is warranted. Factors which may affect cyanobacterial metabolite removal by NF include molecular weight (MW), size, charge and hydrophobicity of the solute and molecular weight cut-off (MWCO), charge, hydrophobicity, flux, recovery and degree of fouling of the membrane surface [16]. Studies have shown that a fouling layer on the membrane surface alters the membrane surface properties [17]. As a result the removal of organic micropollutants may change due to a difference in membrane/solute interaction. Several studies have investigated the influence of natural organic matter (NOM) on membrane fouling during removal of specific organic micropollutants [17–20].

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Table 1
Membranes used in the NF trials.

Membrane	MWCO	Material	Hydrophobicity
NF90	100	Polyamide	Hydrophobic
NF270	300	Polyamide	Hydrophilic
NTR7450	600–800	Sulfonated polyethersulfone	Hydrophobic
DK	100	Polyamide/polysulfone	Hydrophilic

Limited detailed information is currently available that documents the removal of cyanobacterial metabolites using NF membranes and the effect of fouling by substances such as NOM. Such information may be useful in membrane selection of NF for cyanobacterial metabolite removal in order to maintain a high flux in the presence of differing foulant concentrations. Teixeira and Rosa [21] evaluated the NF performance for microcystin removal from natural water spiked with different types of NOM. In that study, NF removed all the microcystin variants present in water (MCLR, MCLY and MCLF) regardless of the variations in feed water quality. However, that study was limited as only a single NF membrane was tested. Likewise Gijsbertsen-Abrahamse et al. [22] investigated the removal of the microcystin variants MCRR, MCYR, MCLR and MCLA, in natural water using only a single NF membrane. Mody [23] studied the use of several membranes of differing MWCO for the removal of cyanobacterial metabolites MCLR, 2-methylisoborneol (MIB) and geosmin (GSM); however, that study focused on the effect of flux and recovery and did not detail the effects of fouling on removal.

No studies to date have evaluated the removal of cylindrospermopsin (CYN) using NF membranes. This is particularly relevant due to the propagation of *C. raciborskii* into more temperate climates [8]. A comparison of the removal of microcystin variants using different membranes and the effect of fouling substances is novel and relevant as a wide range of cyanobacterial metabolites are now being detected simultaneously in water sources [24] and so evaluation of membranes to remove a wide range of metabolites is warranted. A study of several NF membranes of differing MWCO, charge and hydrophobicity, as well as several cyanobacterial metabolites of differing MW, charge and hydrophobicity is warranted for a more in depth understanding of fouling during removal of cyanobacterial metabolites.

The aim of this study was to investigate the effect of differing feed waters on the removal of the cyanobacterial metabolites microcystin (MW = ~1000 Da), CYN (MW = 415 Da), MIB (MW = 168 Da) and GSM (MW = 182 Da) (Fig. 1) using a range of NF membranes. Particular emphasis was placed on the fouling mechanism of the NF membranes by the NOM in the feedwaters during cyanobacterial metabolite removal.

2. Materials and methods

2.1. NF membranes

Four commercially available membranes were used for the NF trials, two from Dow Filmtec (NF90 and NF270), one from Hydranautics (NTR7450) and one from GE Osmonics (Desal 5 DK). Some characteristics of these membranes are given in Table 1.

Removal of cyanobacterial metabolites was calculated according to the equation below:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

where R is the rejection (%), and C_f and C_p are the solute concentrations in feedwater and permeate, respectively.

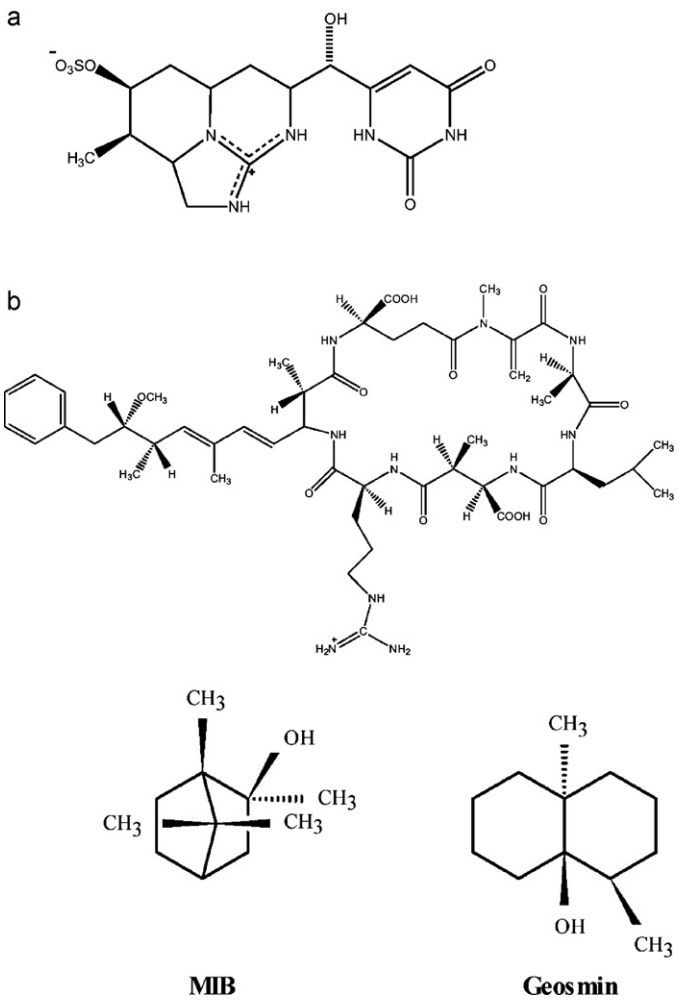

Fig. 1. Chemical structures of the cyanobacterial metabolites (a) CYN (MW = 415 Da), (b) microcystin-LR (MW = 995 Da), (c) MIB (MW = 168 Da) and (d) GSM (MW = 182 Da).

2.2. Waters

Two treated waters were used as the feedwaters for this study. Palmer water (sampled after aluminium chlorohydrate coagulation and ultrafiltration (UF)) was used to simulate a UF–NF integrated membrane system (IMS) and Myponga water (sampled after treatment by alum flocculation, dissolved air flotation and sand filtration) to simulate a conventional treatment-NF IMS. Both waters were sourced prior to chlorination to avoid oxidation of the toxins that were spiked into the test waters. Palmer water was selected as a low NOM source while Myponga water was selected as a high NOM source. Water quality data is presented in Table 2. Tests were run for 70 h with three trials undertaken for each water. The first trial was dosed with CYN (16 μg/L), the second with MIB and GSM (100 ng/L each) and the third with microcystin variants MCLR, MCLA, MCYR and MCRR (10 μg/L

Table 2
Water quality data from treated water sources for NF trial.

Treated water	Palmer	Myponga	Units
DOC	3.1	5.3	mg/L
Turbidity	0.1	0.1	NTU
Conductivity	500	700	μS/cm
Colour (456 nm)	1	6	HU
UV_{254}	0.05	0.090	cm^{-1}

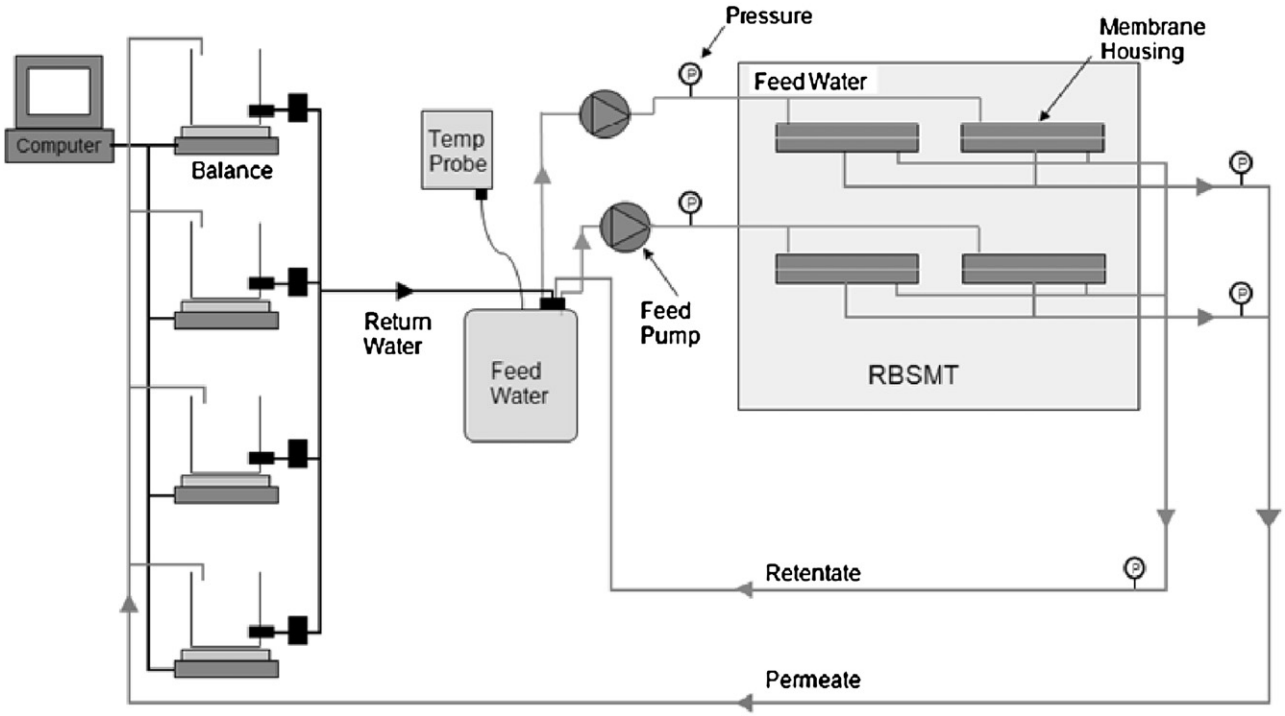

Fig. 2. Schematic of the rapid bench scale membrane test unit (RBSMT).

each). Duplicate tests were carried out for each metabolite in each water.

Palmer water used in this study had a DOC of 3.1 mg/L and a UV absorbance at 254 nm (UV_{254}) of 0.05 cm^{-1}. After 70 h of the NF trial, the feedwater had concentrated to a DOC of between 7.7 and 11.1 mg/L and a UV_{254} of between 0.15 and 0.21 cm^{-1}. Myponga water had an initial DOC of 5.3 mg/L and a UV_{254} of 0.090 cm^{-1}. After 70 h of running the NF trial, the feedwater had concentrated to a DOC of 12.7–14.7 mg/L and a UV_{254} of 0.29–0.44 cm^{-1}.

2.3. Toxin stock solutions

Experiments were conducted using purified CYN (95% pure) which was isolated from a laboratory culture of *C. raciborskii* (Palm Island, Queensland, CYP020). The toxin was dissolved in ultrapure water (Millipore Pty Ltd., USA) and stored at −20 °C prior to use. Aliquots were taken from the dissolved CYN stock solution and dosed into experiments at specified concentrations. Full details of the isolation and purification of CYN can be found in [25]. Microcystin variants (MCLR, MCLA, MCRR and MCYR) were purchased from a commercial supplier (Alexis Biochemicals, USA) as was MIB and GSM (Sigma–Aldrich, Australia)

2.4. Cylindrospermopsin analysis

Prior to high performance liquid chromatographic (HPLC) analysis, CYN was concentrated from sampled waters by solid phase extraction using methods described previously [25]. An Agilent 1100 series HPLC system consisting of a quaternary pump (G1311A), degasser (G1379A), autosampler (G1313A), column compartment (G1316A) and photodiode array detector (G1315B) driven by ChemStation software (Agilent, USA) was used for CYN analysis. Sample volumes of 50 μL were injected into a 150 mm × 4.6 mm Apollo C8 column116 (Alltech, Australia) at a flow rate of 0.6 mL/min. Concentrations of CYN were determined by calibration of the peak areas (at 262 nm) with that of a certified reference standard (Institute of Marine Biosciences, National Research Council, Canada). The method has a detection limit of 1 μg/L.

2.5. Microcystin analysis

Prior to HPLC analysis, microcystin variants (MCRR, MCLR, MCYR and MCLA) were concentrated from sample waters by solid phase extraction similar to the methods described in ref. [26]. An Agilent 1100 series HPLC system consisting of a quaternary pump (G1311A), degasser (G1379A), autosampler (G1313A), column compartment (G1316A) and photodiode array detector (G1315B) driven by ChemStation software (Agilent, USA) was used for microcystin analysis. A 150 mm × 4.6 mm Luna C18 column (Phenomenex, Australia) with a pore size of 5 μm was used. The detection limit for MCLR was 0.1 μg/L. Full details of this analysis can be found in ref. [11].

2.6. 2-Methylisoborneol and geosmin analyses

MIB and GSM samples were analyzed based on the method of Graham and Hayes [27]. Samples were concentrated using a solid phase microextraction polydimethylsiloxane–divinylbenzene syringe fibre (Supelco, Australia) and analyzed on an Agilent 7890 gas chromatograph with Agilent 5975 mass selective detector (Agilent Technologies, Australia) against quantified labeled internal standards (Ultrafine Chemicals, UK).

2.7. Dissolved organic carbon and UV_{254} absorbance analyses

Samples for DOC and UV_{254} were filtered through 0.45 μm pre-rinsed membranes. UV_{254} was measured at 254 nm through a 1 cm quartz cell using a Evolution 60 UV–vis spectrophotometer (Thermo Scientific, USA). DOC was measured using a Sievers 900 Total Organic Carbon Analyser (GE Analytical Instruments, USA).

2.8. Molecular weight distribution analyses

High performance size exclusion chromatography (HPSEC) was used for MW distribution determination of NOM. The analysis was undertaken using an Alliance 2690 separations module and 996 photodiode array detector at 260 nm (Waters Corporation, USA). Phosphate buffer (0.1 M) with 1.0 M NaCl was passed through a Shodex KW802.5 packed silica column (Showa Denko, Japan) at a flow rate of 1.0 mL/min. This column provides an effective separation range from approximately 100 Da to an exclusion limit of 50,000 Da. Apparent MW was derived by calibration with polystyrene sulfonate MW standards of 35, 18, 8 and 4.6 kDa.

2.9. Laboratory scale nanofiltration experiments

To simulate the performance of full-scale spiral wound NF elements, a rapid bench scale membrane test (RBSMT) was utilised (Fig. 2). A four membrane cell test unit was custom made for this study. Each membrane cell required a membrane sheet with surface area of 154 cm^2 and was operated with feed spacer and permeate carrier to make the test hydraulically similar to full-scale operation. A recycle loop allowed for representative recoveries and cross-flow velocities of a full-scale system. Permeate was returned to the feedwater every 3 h. Analytical balances were used to measure the permeate flow rate indirectly based on weight increase. The unit was used to compare removal of cyanobacterial metabolites by different NF membranes and the flux parameters associated with these membranes.

Four new membrane sheets of different material were cut from a larger sheet and soaked overnight in ultrapure water to wet the membranes and remove preservative chemicals. An integrity test was performed on each membrane using NaCl (0.01 M) solution. Four clean 10 L vessels were placed on each balance and the balances controlled by customised Labview software (National Instruments, USA). A volume of 40 L of treated water from either Palmer WTP or Myponga WTP was used for the trials. The prescribed amount of cyanobacterial metabolites was dosed to the feedwater. A temperature probe was used to collect data from the feedwater. The feedwater was covered with parafilm to prevent evaporation and loss of metabolites through volatilisation. After each trial the system was flushed with ultrapure water for 15 min and a pure water flux (PWF) test was carried out at 4.1, 4.8, 6.2, 7.6 and 8.2 bar using ultrapure water. A flux was calculated after temperature compensation and then normalised for pressure and the area of the membrane to give the PWF in L/h/m^2/bar at 25 °C.

3. Results and discussion

3.1. Flux decline

Specific flux (flux, J, divided by initial flux, J_0) for each membrane was calculated and plotted as a function of time in both feedwaters (Fig. 3). Exponential decay curves were fitted to the data set associated with each membrane. The DK membrane showed no flux decline, the NF270 showed some reduction in flux with time, while the NTR7450 and NF90 membranes showed a similar performance displaying the largest flux decline during the experiment. There was little difference between the two waters suggesting that the higher NOM concentration of Myponga water had little impact on the flux decline of the NF membranes.

Fig. 4 shows the MW profile of the NOM in each feedwater. The intensity of the peaks at 850 and 1050 Da for Myponga water are greater than Palmer water. However, the shoulder at 1070 Da that is seen in Palmer water is not defined in Myponga water, indicating that the only difference in the character of the NOM

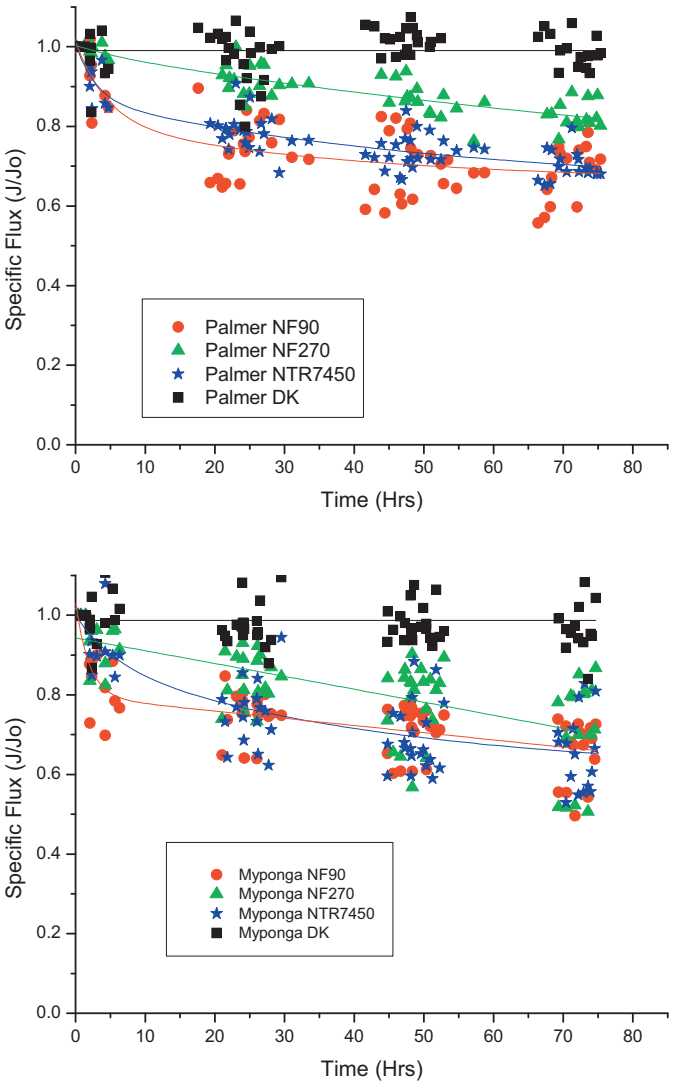

Fig. 3. Specific flux (J/J_o) for each membrane in Palmer (top) and Myponga (bottom) feedwaters.

in the two waters is a higher concentration of the higher molecular weight compounds in Palmer water. Despite this difference in NOM character and a higher DOC concentration in Myponga water, no difference in membrane fouling between the two feedwaters, as measured by the flux decline, was observed. Removal of UV_{254} was similar for each membrane with a permeate absorbance of 0.02 cm^{-1} or below for both feedwaters. DOC concentration in

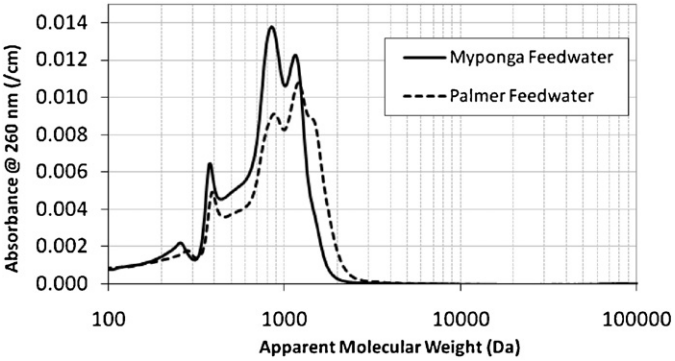

Fig. 4. Molecular weight (MW) profile of Palmer and Myponga feedwaters used for the NF trials.

Table 3
PWF values for fouled and cleaned membranes (L/h/m^2/bar) and the percent PWF recovery.

	Fouled PWF	Cleaned PWF	% Recovered
NF90	7.5	11.2	33
NF270	13.6	15.2	11
NTR7450	7.9	7.2	0
DK	3.7	8.7	57

the permeate was below 1.5 mg/L for the DK, NF90 and NF270 and below 3.0 mg/L for the NTR7450 in each feedwater. Comerton et al. [20] showed that NOM caused a statistically significant reduction in effective MWCO and a reduction in flux. In this study three of the four membranes showed a decrease in flux with fouling; however, in our study the concentration of NOM may be less important for flux reduction.

A cleaning effectiveness test was carried out after one trial to establish the amount of surface fouling on the four membranes. The membrane surface was wiped with a soft cloth and the NF experiment was repeated. Results are given in Table 3. No PWF flux was recovered by the 'loose' NF (NTR7450) due to this cleaning process but the flux recovery for the DK was 57%.

An analysis of the MWCO of fouled and virgin membranes was undertaken to establish if the MWCO of the NTR7450 membrane was reduced by NOM pore blockage. Polyethylene glycol (PEG) standards of 300, 400, 600, 1000, 1500 and 2000 Da were dosed separately to the fouled and virgin membranes at 20 mg/L for periods of 20 min. Two fouled NTR7450 membranes were compared with two virgin NTR7450 membranes (Fig. 5). While the six PEGs were removed to less than 10% using the virgin membranes, the fouled membranes showed PEG removal of up to 90%. This suggests that the virgin NTR7450 membrane had an effective MWCO of above 2000 Da compared with the MWCO of 600–800 Da spec-

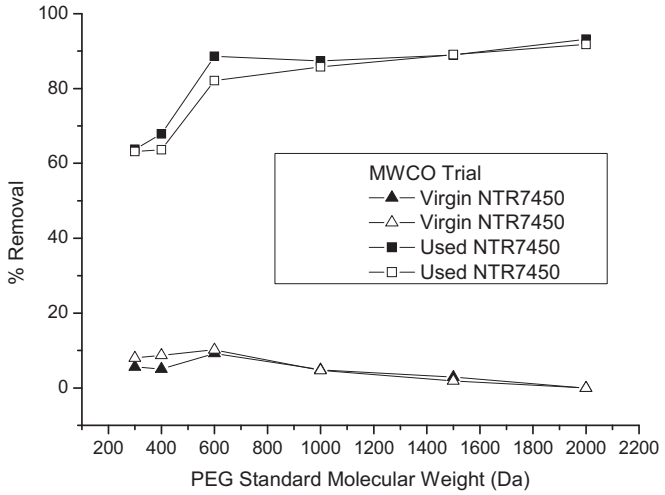

Fig. 5. MWCO trials conducted on fouled (used) and virgin NTR7450 surfaces using PEG standards of 300, 400, 600, 1000, 1500 and 2000.

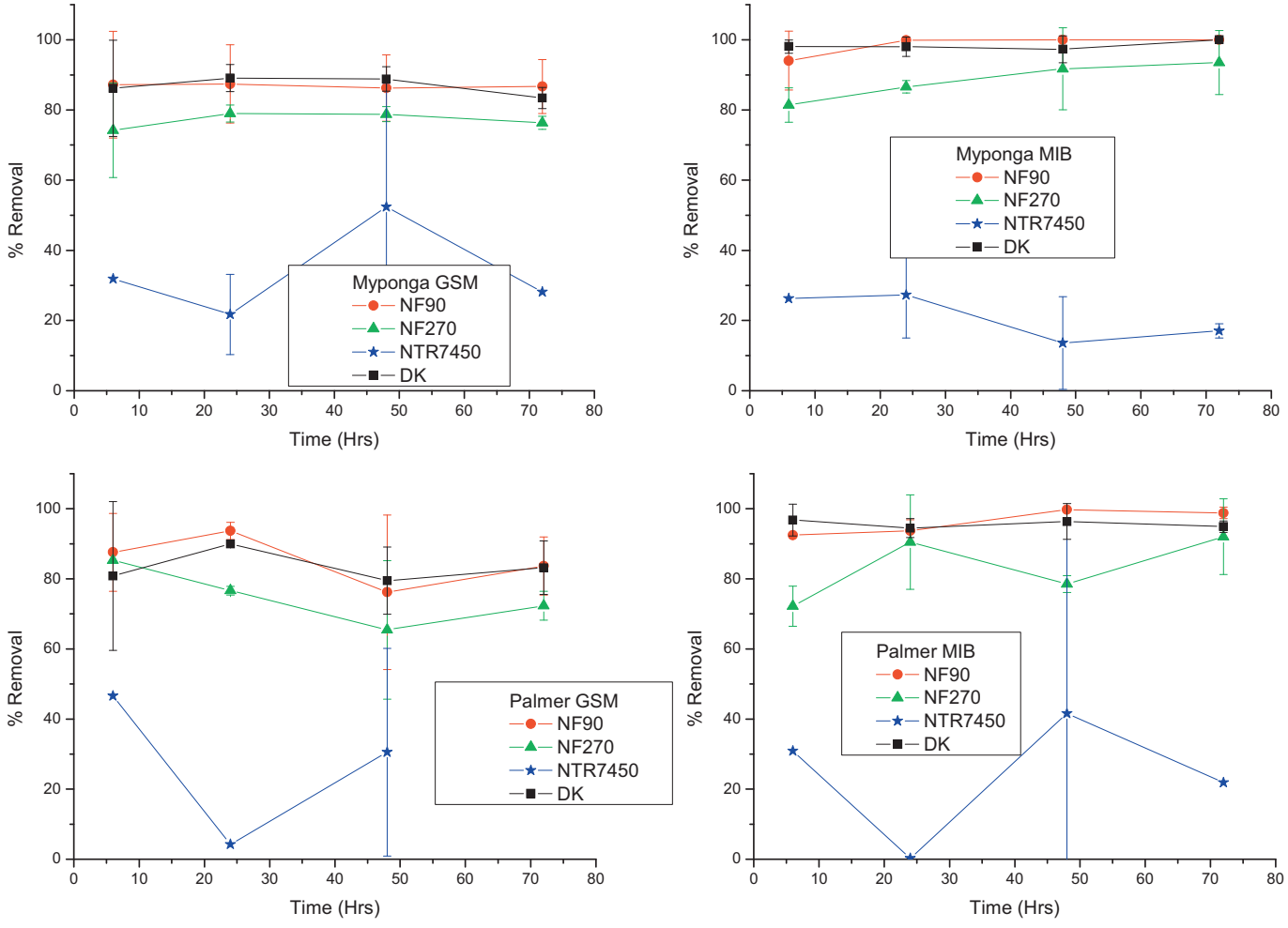

Fig. 6. Percent MIB and GSM removal over time for the Palmer and Myponga water trials. Error bars represent standard deviation from quadruplicate independent experiments.

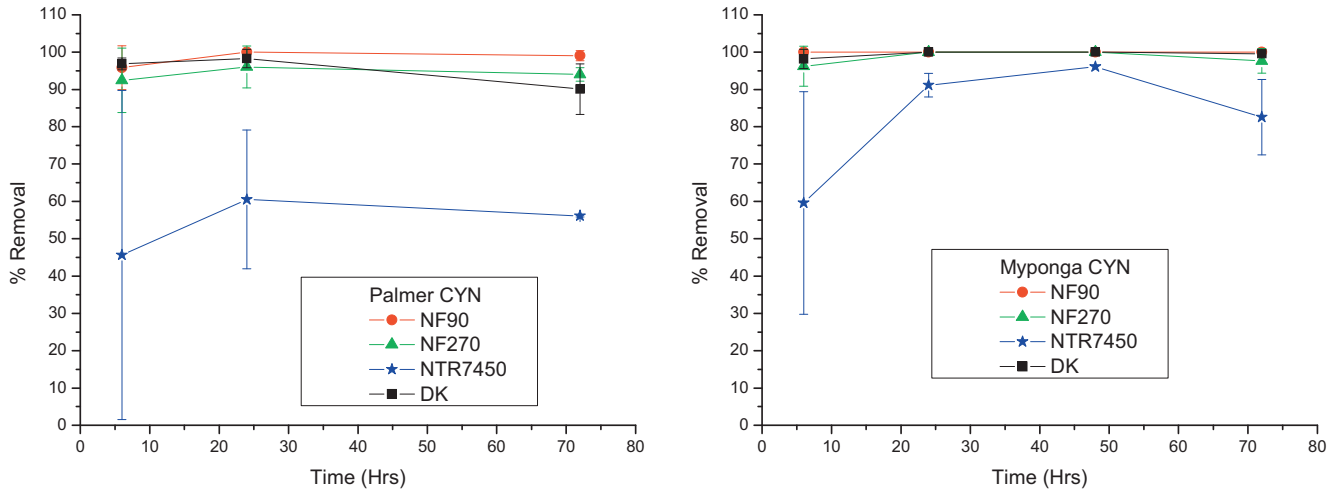

Fig. 7. Percent CYN removal over time for the Palmer and Myponga water trials. Error bars represent standard deviation from quadruplicate independent experiments.

ified by the manufacturer, while the MWCO after several hours of filtering was closer to the manufacturer's specification. This may be due to a combination of fouling of the membrane by NOM, and membrane pore compaction after several hours of pressure filtration. Van der Bruggen et al. [28] reported membrane compaction as a major drawback to NF operation with compaction values of up to 170%. Compaction is a very complex mechanism and may be significantly influenced by pressure [29–32].

3.2. MIB and geosmin removal

The removal of MIB and GSM by NF in the two waters is shown in Fig. 6. The order of membrane effectiveness followed the MWCO trend, NF90 ≥ DK > NF270 > NTR7450. Results were similar for both T&O compounds in both waters, suggesting minimal effect of water quality. The results for NTR7450 show a large variability and may be a result of the lack of pre-compaction as discussed above. Despite compaction and NOM fouling, the removal of MIB and GSM did not increase with time in these waters. In contrast, some increase in GSM and MIB removal with time was observed in ultrapure water by [33]. These results are similar to those of Alt et al. [34] who tested seven NF membranes for MIB and GSM removal using treated water. In that study the membranes were tested at 80% recovery, as this condition provided the highest membrane feed concentration. Most of the membranes had MIB and GSM rejections above 85%. As with our study, the loose NF in ref. [34] displayed lower rejections as the MW of MIB and GSM is lower than the MWCO of the loose NF membranes, which allows the compounds to pass through the pores of the membrane.

3.3. Cylindrospermopsin removal

Removal of CYN by NF in Palmer and Myponga waters was between 90 and 100% for the NF90, NF270 and DK membranes (Fig. 7). CYN removal by NTR7450 was lower in both waters with higher average removals for Myponga water. Removal of CYN (MW of 415 Da) followed an expected trend with the MWCO of the membranes similar to removal of MIB and GSM suggesting that size exclusion was the dominant removal mechanism. Contrary to a study by Bellona et al. [35] which found that organic matter could lower rejection of certain organic micropollutants, the effect of the organic fouling in this study was negligible for the removal of CYN. The removal of CYN by NF has not been reported outside our studies. High variance in removals for the cyanobacterial metabolites may not have been as pronounced for the 6 h sample if the NTR7450 was pre-compacted effectively.

3.4. Microcystin removal

The removal of the microcystin variants by the NF membranes in Palmer and Myponga waters is presented in Fig. 8. The NF90, NF270 and DK membranes removed the four microcystin variants similarly in both waters. NTR7450 afforded lower removals of MCRR, MCYR and MCLR than predicted by the MWCO (600–800 Da) of the NTR7450 but performed as well as the lower MWCO membranes for MCLA removal. This is surprising as MCLA has the lowest MW of the four variants tested. Differences in removal mechanisms for these variants may have been due to differing charge, hydrophobicity, molecular size as detailed for other organic micropollutants [16], for example the molecular size, as determined by the surface diffusion coefficient, of MCLA is larger than MCLR [36] and this may partially account for the greater rejection of MCLA by NTR7450. The trend for hydrophobicity and charge is MCLA > MCYR–MCLR > MCRR [37] which may also partially account for the trend of removal seen for NTR7450; however, a firm conclusion regarding this trend cannot be made due to the compaction issues discussed above.

The DK membrane showed no reduction in MCLR removal with time as suggested in our previous study [33]. The average removals of MCLR by NF270 and DK were higher in the treated water trial compared with similar membranes in our previous study. This may be due to the fouling layer caused by NOM, similar to the effects seen by Ngheim and Hawkes [19] who observed that the influence of membrane fouling on the retention of organic micropollutants was largely dependent upon membrane pore size. The results of our study were similar to ref. [23] which used four commercially available NF membranes at different recoveries and fluxes to investigate the removal of MCLR from conventionally treated surface water. NF membranes used were NF90, NF270, LFC1 (composite polyamide; MWCO 100–300) and NTR7450. Three NF membranes achieved excellent rejection for MCLR. These NF membranes reduced the permeate concentration of MCLR from an initial concentration of 10 μg/L to less than the World Health Organization (WHO) guideline of 1 μg/L, for all the recoveries tested. The NTR7450 showed a maximum removal of MCLR of 40% due to its lower MWCO. Our study has shown that microcystin variants were removed differently by the NTR7450, which is important in assessing removals for water

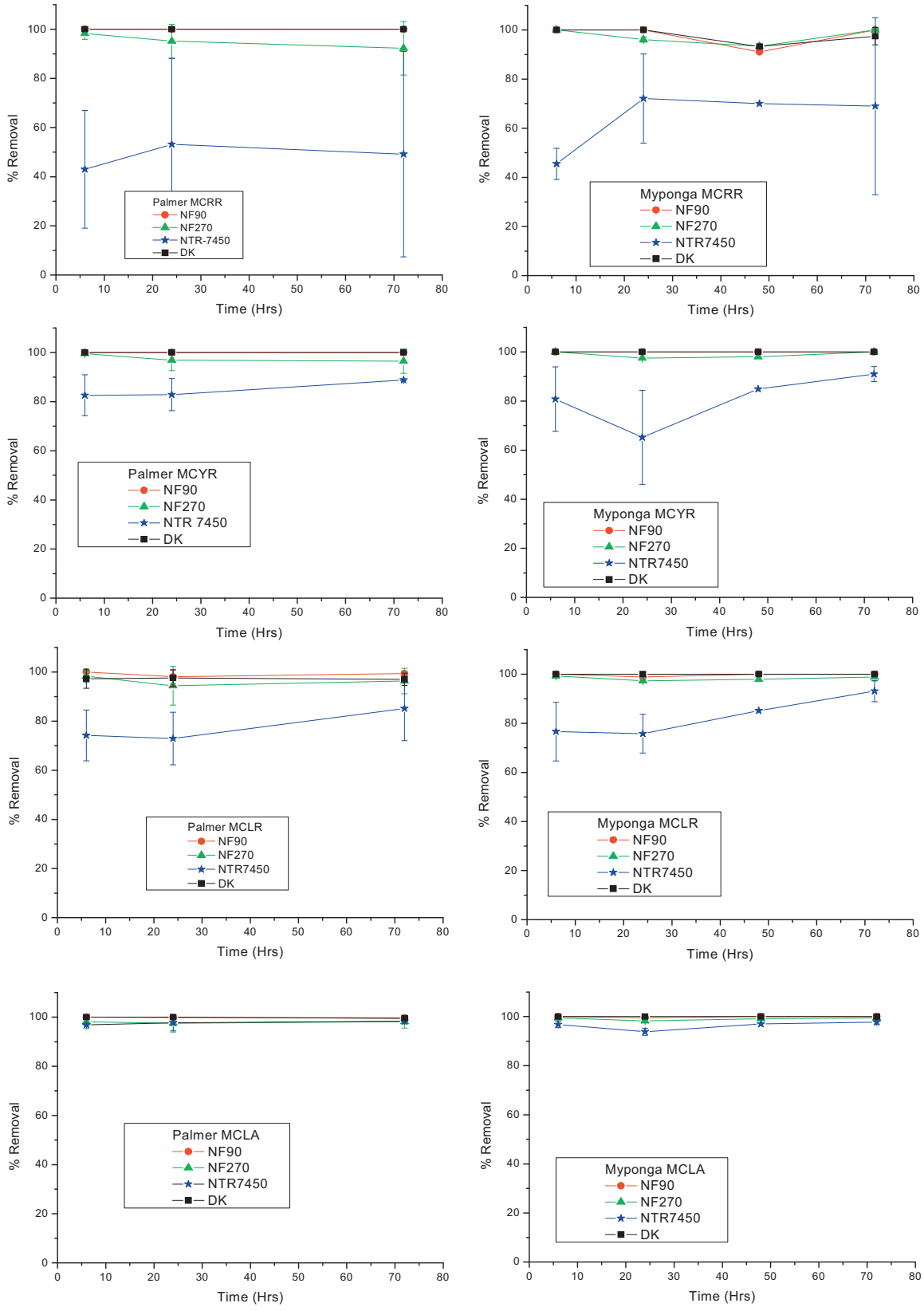

Fig. 8. Percent MCRR, MCYR, MCLR and MCLA removal over time for the Palmer and Myponga water trials. Error bars represent standard deviation from quadruplicate independent experiments.

treatment plants that are at risk from several microcystin variants.

4. Summary and conclusions

To date the effect of fouling by treated waters on NF membranes and its impact on removal of cyanobacterial metabolites had not been investigated. As climate change may increase the frequency and intensity of cyanobacterial blooms in water supplies and as membrane technology becomes more commonly used, research into this area was warranted. In our study a RBSMT unit was utilised to test four NF membranes for their ability to remove four microcystins (MCRR, MCYR, MCLR, MCLA), CYN, MIB and GSM in two treated waters of differing NOM concentration.

In the treated waters membrane filtration of the cyanobacterial metabolites was effective using the NF90, NF270 and DK. The NTR7450 membrane showed lower removal. Different concentrations and character of NOM in the two feedwaters had negligible effect on the flux or removal of the cyanobacterial metabolites. While the MWCO of the NTR7450 was lower than the MW of the microcystins, complete removal was not achieved for MCRR, MCYR and MCLR. The removal of MCLA was higher than the other variants for the NTR7450 membrane. Different physical characteristics such as hydrophobicity and net charge could have influenced the higher rejection of this compound.

Acknowledgements

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