Desalination 315 (2013) 149–155

Contents lists available at SciVerse ScienceDirect

Desalination

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

# Fouling of nanofiltration membrane: Effects of NOM molecular weight and microcystins

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ARTICLE INFO

*Article history:*
Received 25 January 2012
Received in revised form 15 March 2012
Accepted 16 March 2012
Available online 16 April 2012

*Keywords:*
Natural organic matter (NOM)
Low molecular weight
HPSEC
Microcystins
Adsorption
Water treatment

ABSTRACT

Toxic cyanotoxins such as microcystins represent a human health risk in water bodies. Nanofiltration is an effective technology to remove these micro-contaminants from drinking water. However, long-term operational sustainability is necessary because of decreases in membrane fluxes over time and increasing operation costs. The rejection of natural organic matter (NOM) is a key issue regarding membrane fouling and flux decline, and is also of great importance in the water industry due to its relationship with public health. Therefore, this study aimed to analyse the effect of microcystins and NOM properties on membrane fouling and to understand the fouling mechanisms, using a series of experiments with different water types. Results showed that nanofiltration was capable of reducing low molecular weight NOM fractions from water and that these fractions were responsible for flux decline and membrane fouling. The adsorption of NOM onto the membrane surface was reduced in the presence of microcystins due to the hydrophobic character of microcystins, which are the first to be adsorbed on the membrane surface. Microcystins contributed to the rejection of smaller natural organic fractions by blocking the membrane pores and reducing NOM adsorption onto the membrane pores.



## 1. Introduction

The presence of toxic cyanobacteria and cyanotoxins in a water body represents a potential risk for human health because cyanotoxins are responsible for hepatic and neuromuscular lesions and tumours. Cyanobacteria release into the water not only cyanotoxins but also other compounds that may cause changes to odour and taste, decreasing the water's organoleptic and chemical quality. Microcystins, the most commonly occurring cyanotoxins in surface water reservoirs used for water supply, are cyclic heptapeptides. They are relatively hydrophobic compounds, neutral or slightly negative at pH 6–9, and have molar masses varying between 900 and 1100 Da [30,53].

Microcystins (MCs) may occur within the cells (cell-bound or intracellular) or be released into water (extracellular or dissolved) due to cell ageing and/or induced cell lysis. In their dissolved form, microcystins are not effectively removed by conventional water treatment processes. However, treatment processes such as activated carbon adsorption [14,24], oxidation [1,47,49] and nanofiltration (NF) [13,19,43,45] have proved to be effective in removing these compounds.

Natural organic matter (NOM) has also become an important issue in the water industry due to its relationship to public health [27,33]. NOM reacts with disinfectants to produce disinfection by-products (DBPs); it also acts as a substrate for microbial growth in distribution systems, and additionally reduces water quality in terms of colour, taste, and odour. Various water treatment processes can either directly or indirectly remove NOM from water, depending on their operational conditions and the specific characteristics of the NOM such as its molecular weight (MW) distribution, carboxylic acidity, and humic substances content [12,40]. However, recent studies have shown that low MW NOM compounds are considered the most difficult to remove by conventional coagulation [16,52]; they compete with other compounds for adsorption sites in activated carbon [35], and are also considered as DBPs [4,50]. In addition, some investigations have found that hydrophilic NOM (non-humics) might also be a significant membrane foulant [17,29].

In this context, membrane technology, namely nanofiltration, can be used by the water industry to remove both organic contaminates (cyanotoxins and NOM), resulting in a significant impact on the environment since it is a process with high selectivity and rejection. This process reduces or sometimes avoids the production of waste by recovering and recycling components (production-integrated process) [41], and guarantees the quality of the treated water. The rejection characteristic of NF membranes is a combination of size exclusion, electrostatic repulsion mechanisms and adsorption [11,25,44]. NF can remove more than 80% of NOM, with high recovery rates (85–90%) [20,44], as well as multivalent ions [9,46] and small hazardous compounds such as pesticides and toxins [7,8,45]. However, NOM is the major component responsible for flux decline and the fouling of NF [38], due to the accumulation of materials near the membrane surface (concentration polarisation, adsorption, and cake/gel formation), and pore blocking. A decline in membrane performance causes problems and is costly for

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doi:10.1016/j.desal.2012.03.012

water managers, and there is an established link between imposed flux and fouling [18].

Detailed information is limited concerning the rejection of cyanotoxins by NF membranes and NOM fouling [13]. Existing studies [13,19,34,43,45] have not analysed the characteristics of the NOM with respect to the rejection of microcystins. In addition, the effect of the MCs on NOM rejection, which could influence the membrane fouling, was not addressed. Therefore, the current study investigates the effect of MCs and NOM molecular weight on membrane fouling.

## 2. Materials and methods

### 2.1. Water samples

Two treated water samples were studied as feed waters. These waters were collected from the Alcantarilha Water Treatment Plant, in Algarve, southern Portugal. At the plant, water treatment consists of pre-ozonation, coagulation/flocculation/sedimentation (C/F/S), rapid sand filtration and chlorination. Ozonated water (OW) was collected after pre-ozonation, and decanted water (DW) after C/F/S, in two periods, the autumn of 2008 and spring of 2009. These waters were chosen because they are natural waters with low NOM contents (Table 1) and they represent two NF pre-treatments, namely ozonation and ozonation/C/F/S, before the NF step.

Microcystins-LR at a concentration of 10 μg/L [13,34,43,45] were added to spring waters. Microcystins were extracted from a culture of *Microcystis aeruginosa* supplied by Pasteur Culture Collection (PCC7820) and maintained in laboratory, according to the enclosed instructions, *i.e.* BG11 medium at 23–24 °C under a light regimen of 12 h light, 12 h dark (~5 μM photon $m^{-2}$ $s^{-1}$). Cultures were harvested at the late exponential phase of growth. Stock solutions of microcystins were prepared as already described elsewhere [43]. This strain of *M. aeruginosa* produces four microcystin variants (MC-LR, -LY, -LW, -LF), however due to the low feed concentration tested (around 10 μg/L) only MC-LR (the dominant variant) was identified and quantified. Microcystin-LR (MC-LR) is a cyclic heptapeptide that shares a general structure containing five fixed amino acids and two variable L-amino acids, namely leucine in position X and arginine in position Z [32].

### 2.2. Membrane test units

Laboratory NF experiments were performed in a commercial bench-scale plate and frame unit (M20 unit from Danish Separation Systems, with: a membrane area of 0.0360 $m^2$ up to 0.720 $m^2$; maximum pressure 80 bar; maximum flow 18 L/min; and constant temperature maintained by an heat exchanger), using four NFT50 polypiperazine amide membranes (Alfa Laval) with a membrane area of 0.0720 $m^2$. Experiments were performed at a constant pressure of 10 bar, a neutral pH and a temperature of 21 °C. The membrane pure water permeability was 7.64 kg/(h.$m^2$.bar) at 21 °C ($r^2 = 0.997$), and the membrane molecular weight cut-off was approximately 150 Da (using the method proposed by [48]). This membrane is negatively charged at neutral pH [46].

Initial permeate flux was established using deionised water, after compaction of the membrane and achievement of a steady flux. Natural waters were placed in the feed reservoir and permeation started. At the beginning of the experiments the solutions were given time to equilibrate, after which a flux measurement and samples from both the feed and the permeate were taken. Experiments continued for approximately 100 h in recirculation mode (permeate was recycled to the feed reservoir). The recirculation of the permeate to the feed reservoir is a fouling protocol according to several authors [2,21,25,54]. Permeate flux was continuously measured during the experiments and samples from both the feed and the permeate were taken periodically. Samples were analysed by High-Performance Size-Exclusion Chromatography (HPSEC) to determine the MW of NOM compounds present in waters, as well as the relative distribution of the compounds. Rejections were calculated based on feed and permeate concentrations.

**Table 1**
Characterisation of the waters used.

| Water sample | | pH (20 °C) | DOC (mg/L) | $UV_{254}$ (1/cm) | SUVA (L/(m.mg)) | Turbidity (NTU) | Conductivity (μS/cm) |
|---|---|---|---|---|---|---|---|
| *Without MCs* | | | | | | | |
| Autumn | RW | 7.52 | 1.80 | 0.013 | 0.99 | – | 587 |
| | OW | 7.45 | 1.24 | 0.008 | 0.65 | 2.01 | 614 |
| | DW | 7.61 | 1.66 | 0.011 | 0.66 | 0.29 | 500 |
| *With MCs* | | | | | | | |
| Spring | RW | 7.35 | 1.92 | 0.035 | 1.82 | – | 578 |
| | OW +MC | 7.63 | 1.25 | 0.009 | 0.73 | 2.40 | 615 |
| | DW +MC | 7.80 | 1.35 | 0.012 | 0.91 | 1.45 | 600 |

RW: raw water; OW: ozonated water; DW: decanted water; MC: microcystin-LR; DOC: dissolved organic carbon; $UV_{254}$: ultraviolet absorbance ate 254 nm; SUVA: $UVA_{254}$/DOC.

### 2.3. Analytical methods

All samples were analysed based on procedures described in Standard Methods [3], namely DOC (TOC-5000, Shimadzu), $UVA_{254}$ (Beckman DU 640B, wavelength between 90 and 1100 nm), turbidity (HACH 2100N), conductivity (Crison GLP 32) and pH (Crison Basic 20+). Triplicate samples of all nanofiltration streams were taken to minimise statistical variance of the results. All analyses were made within 24 h, and blank samples were used as control.

HPSEC was used to determine the molecular weight distribution of NOM. The HPSEC system includes an HPLC (Dionex system) with a photodiode-array detector at 254 nm. The column was a TSK-G3000SWxl column (7.5 mm ID × 300 mm) protected by a TSK-SWxl guard column (6.0 mm ID × 40 mm) (Tosoh Biosciences, GmbH). Details on the experimental procedure were already presented elsewhere [57].

The number-averaged ($M_n$) and weight-averaged ($M_w$) molecular weights were determined using equations proposed by [55] (Eq. (1)). The polydispersivity ratio ($M_w/M_n$) was also calculated and is a measure of sample heterogeneity [42].

$$M_n = \frac{\sum_{i=1}^{n} h_i}{\sum_{i=1}^{n} \frac{h_i}{M_i}} \quad M_w = \frac{\sum_{i=1}^{n} h_i M_i}{\sum_{i=1}^{n} h_i} \tag{1}$$

where $h_i$ is the height of the curve eluted at the $i$th retention time ($Rt_i$) (mAu) and $M_i$ is the molecular weight of some solute at the $i$th retention time ($Rt_i$).

## 3. Results and discussion

### 3.1. Water characterisation

Table 1 describes the characteristics of the source waters used in the experiments (OW and DW), as well as raw water (RW, before any water treatment). The waters used were very similar in terms of NOM parameters, they presented low values of both dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm ($UV_{254}$), and also low values of aromaticity as expressed by specific UV (SUVA, defined as the ratio $UVA_{254}$/DOC, representing an index of NOM aromaticity). However, autumn samples (without MCs) presented slightly lower aromaticity. Regardless of the season, OW always presented higher turbidity than DW but lower $UV_{254}$ values. These waters were hydrophilic according to the classification of [15].

RW quality (Table 1) and its molecular weight distribution (Fig. 1) are shown for comparison purposes, since these waters were not used