Nanofiltration Performance to Remove Microcystins from Water for Human Consumption at a Pilot Scale

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INTRODUCTION

The presence of microcystins (MC) in drinking water reservoirs, even at low concentrations, is a problem for all involved in management and water treatment. This cyclic peptide hepatotoxin, produced by several species of toxic cyanobacteria as secondary metabolites, cause liver damage and is considered tumor promoter (Matsushima *et al*., 1992), representing a potential hazard to human health (Carmichael, 1994). Therefore, it is necessary to ensure their removal in water treatment plants (WTP) by innovative and effective treatments. In recent years, nanofiltration (NF) has become an attractive alternative technology to conventional water treatment due to the capacity to remove inorganic and organic compounds (disinfection by-products (DBP) precursors) with low molecular weight cut-offs and low operating pressures (Her *et al*., 2000; Costa and Pinho, 2006). However, the application of NF to drinking water treatment is affected by natural organic matter (NOM) fouling (Hong and Elimelech, 1997). Membrane fouling refers to plugging and external pore blocking (Gwon *et al*., 2003) which causes low performance and reduction of membrane time life, because of flux decline and/or transmembrane pressure increase (Her *et al*., 2000). In addition, good results were obtained with NF to remove cyanotoxins present in water for human consumption. According to some authors (Ribau Teixeira and Rosa, 2005; Gijsbertsen-Abrahamse *et al*., 2006; Ribau Teixeira and Rosa, 2006), NF removed cyanobacterial toxins from water, with removal rates greater than 99% at laboratory scale. However, pilot scale experiments in real context are missing. The aim of this work is to study NF performance to remove microcystins from natural water, at a pilot scale in a real context of WTP.

METHODS

NF experiments were performed in a commercial pilot-scale unit M20 (maximum pressure 80 bar; maximum flow 18 L/min and constant temperature maintained by a heat exchanger) using a spiral wound element (M20-2.5") and a polypiperazine amide membrane (1.1 m^2, 153 g/mol of molecular cut-off). This unit was installed at Alcantarilha Water Treatment Plant (WTP), in Algarve, Portugal, in a parallel line after preoxidation, coagulation/flocculation and sedimentation processes as presented in Figure 1. Alcantarilha WTP supplies water to *ca.* half million people in southern Portugal and was designed to treat up to 3 m^3/s since 2000, with surface water from Funcho Dam reservoir (2 km^2 and 43.4 hm^3) and after 2005, mixing with ground-water from Qurença- Silves aquifer.

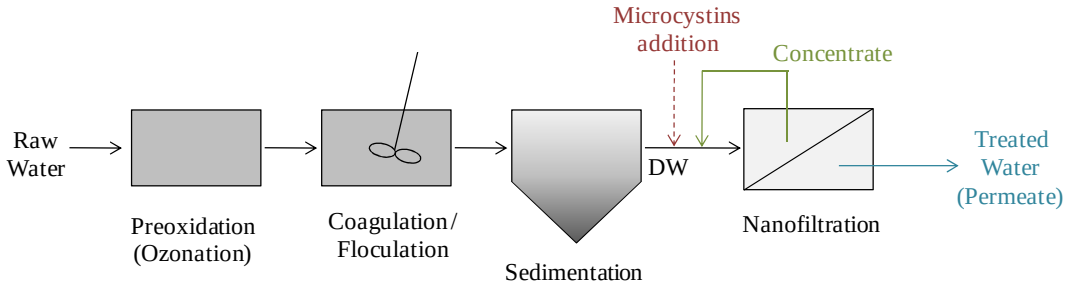

Figure 1. Experimental water treatment sequence in Alcantarilha WTP (DW - Decanted Water).

Long time operation experiments (*ca.* 120 h) were made at 10 bar, 21ºC, at a stipulated concentration and during the normal operation of the WTP. Experimental procedure consisted of a first step of permeating deionised water until achieving the steady permeate flux and then the permeation of the natural water started in recirculation mode, during *ca.* 100 h. Since no bloom of cyanobacteria occurred during experiments, microcystins were periodically added to DW. Permeate flux was continuously measured, as well as pH and conductivity. Feed and permeate samples were periodically collected to determine dissolved organic carbon (DOC), UV absorbance at 254 nm (UV) and microcystin concentration. Removal efficiencies were calculated based on feed and permeate concentrations.

Analyses were performed on a TOC-5000 analyser (Shimadzu) for DOC, a Beckman DU 640B spectrophotometer for UV, a HACH HQ30D conductimeter for conductivity and a WTW pH340 for pH. Specific UV (SUVA) was determined (defined as the ratio UV/DOC), since it represents an index of NOM aromaticity. Microcystins were extracted from a culture of *Microcystis aeruginosa* supplied by Pasteur Culture Collection (PCC7820) and maintained in laboratory. After one and an half months of growth (corresponding approximately to the maximum of *M. aeruginosa* growth obtained in the laboratory), stock solutions of microcystins were prepared as already presented elsewhere (Ribau Teixeira and Rosa, 2005). Microcystins were analysed by liquid chromatography with photodiode-array detection (HPLC-PDA). The standard operation procedures developed by Meriluoto and Spoof (2005a, b) for the concentration of microcystins in water samples and microcystins analysis were used with the adaptations described in Ribau Teixeira and Rosa (2006). A HPLC-PDA Dionex Summit system was used with a C18 column (Merck Purospher STAR RP-18 endcapped, 3 μm particles, LiChroCART 55x4 mm).

RESULTS AND DISCUSSION

Figure 2 presents the variation of permeate flux, MC concentration, DOC and UV during operation time. MC concentration in the feed varied over the experiment, because of feed concentration with operation time. This concentration increased MC in the feed (Figure $2b_1$ first 5 h) to values higher than the natural occurring in surface waters (Rosa *et al.*, 2004). To avoid this, MC were added periodically to DW and, as a result, a decrease (due to dilution) in the feed MC concentrations over time is observed. These variations are also reflected in the other studied parameters.

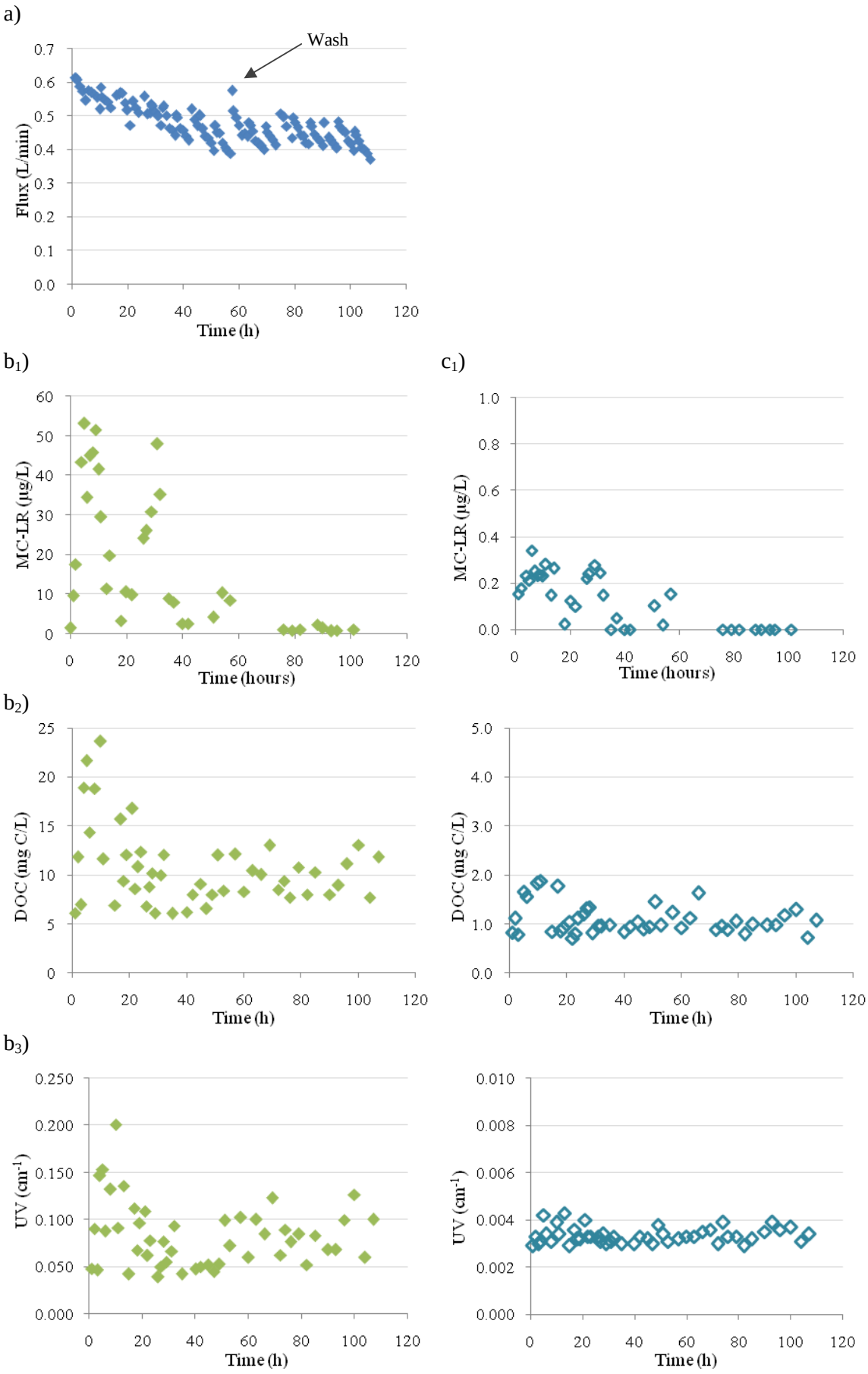

Figure 2 - a) Permeate flux, and MC, DOC and UV variation: b) feed, c) permeate quality.

The permeate flux (Figure 2a) decreases during the experiment due to an accumulation of MC and NOM near the membrane surface. The microcystin variant studied, MC-LR, is hydrophobic, weekly negatively charged (Maagd *et al.*, 1999) and with a molecular weight much higher than the membrane cut-off (991 *vs.* 153 g/mol). As already reported by some authors (Nilson and DiGiano, 1996; Jucker and Clark, 1994) hydrophobic compounds adsorb onto membrane surface, therefore the flux decrease may be due to the fouling or adsorption of the MC onto membrane surface (Ribau Teixeira and Rosa, 2005). In addition, NOM is one of the main membrane foulants (Hong and Elimelech, 1997). In this water, NOM is hydrophilic (based on SUVA values) with low molecular weight and DOC largely composed of non-humic substances (Edzwald and Benschoten, 1990), which should have little influence on the permeate flux according to Nilson and DiGiano (1996). However, other researches reported recently that hydrophilic NOM (non-humics) might also be an important foulant of the membranes (Fan *et al.*, 2001; Lee *et al.*, 2004). These findings are reflected in the results obtained for flux with this organic matter (Figure 2a). The major decrease in permeate flux was observed in the initial hours of experiment corresponding to the highest concentration of MC in feed. When the MC concentration decrease in feed, the permeate flux continues to decrease but in a less pronounced way. This decrease is due to the effect of NOM in the membrane surface.

The results present in Figure $2b_1$ show that NF at pilot-scale has ability to remove MC regardless its concentration in feed and during more than 100 h of operation. The removal rates were always higher than 98% and MC concentration in permeate (Figure $2c_1$) below 1 µg/L (WHO drinking water guideline value). These high MC removals are due size exclusion effects, since MC present a higher molecular size than membrane pore and are negatively charged (Ribau Teixeira and Rosa, 2005).

Removals of NOM are high, 94-98% for UV and 82-94% for DOC, and good permeate quality was obtained (Figure $2c_2$ and $2c_3$). Removals of DOC are lower than UV since the UV absorbance at 254 nm is mainly due to the adsorption by aromatic/hydrophobic compounds, whereas DOC measures the dissolved concentration of carbon containing molecules (Schafer and Fane, 2000). During the 120 h of operation, no significant variation is observed in permeate quality and the highest concentrations are obtained in the first 10 h of operation due to the highest influent concentrations. One of the main result from this study is that the permeate quality for DOC, UV and SUVA show low values ($\leq$2mg C/L, $\leq$0.004 cm^{-1} and 0.38 L/(m mg), Figure $2c_2$ and $2c_3$), despite the time of operation.

As far as conductivity removals are concerned (Figure 3a), the variations observed with time are related with the addition of MC, as already mentioned. As the membrane is slight negatively charge at this pH (Figure 3b), the anions are rejected and with them the cations, as referred by Ribau Teixeira and Rosa (2005).

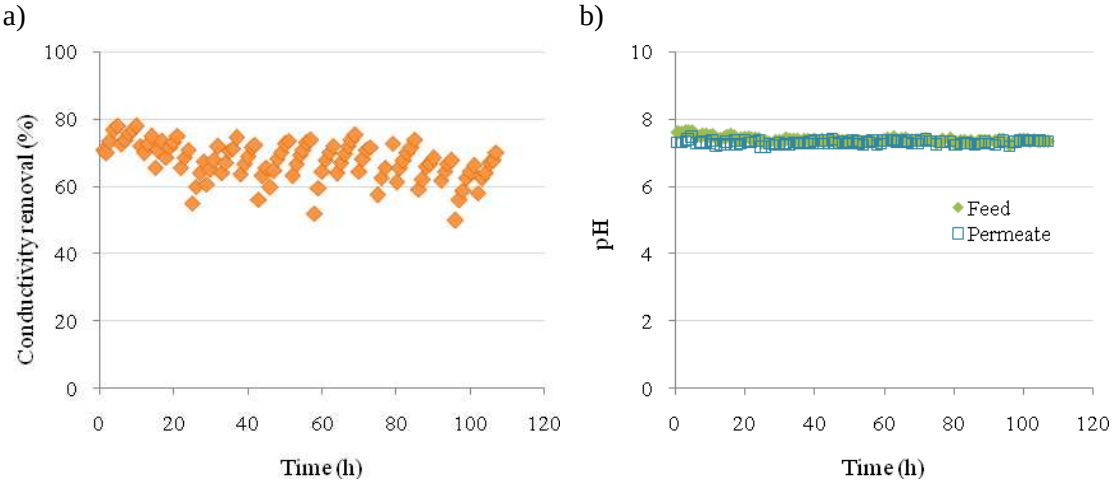

Figure 3 - a) Conductivity removal and b) pH variation.

CONCLUSIONS

This study shows that NF membranes are effective in MC removal in drinking water treatment during *ca.* 120 h of operation at a pilot-scale. NF has demonstrated its ability to remove MC regardless of the concentration variations in the feed without loss of efficiency (always higher than 98%). The decrease observed in the permeate flux during the experiment was due to the fouling or adsorption of the MC onto membrane surface, as well as the NOM hydrophilic character. The main conclusion from this work is good permeate quality is obtained in the treatment of natural hydrophilic waters with microcystins using NF membranes and during at least 120 h of operation.

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