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Recycled desalination membranes as a support material for biofilm development: A new approach for microcystin removal during water treatment

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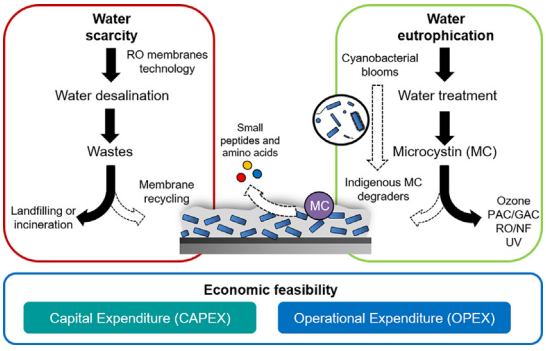
HIGHLIGHTS

- Discarded RO membranes could be used as a support material for bacterial attachment.
- The characteristics of discarded RO membranes promoted the biofilm development.
- MC-degrading biofilm on discarded RO membranes removed 2 mg·L^{-1} of MC in 24 h.
- The hereby developed R-MBfR proof-of-concept proved its economic feasibility.

GRAPHICAL ABSTRACT



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ABSTRACT

Increased harmful cyanobacterial blooms and drought are some negative impacts of global warming. To deal with cyanotoxin release during water treatment, and to manage the massive quantities of end-of-life membrane waste generated by desalination processes, we propose an innovative biological system developed from recycled reverse osmosis (RO) membranes to remove microcystins (MC). Our system, named the Recycled-Membrane Biofilm Reactor (R-MBfR), effectively removes microcystins, while reducing the pollution impact of RO membrane waste by prolonging their life span at the same time. This multidisciplinary work showed that the inherent flaw of RO membranes, i.e., fouling, can be considered an advantageous characteristic for biofilm attachment. Factors such as roughness, hydrophilic surfaces, and the role of calcium in cell-cell and cell-surface interactions, encouraged bacterial growth on discarded membranes. Biofilm development was stimulated by using a laboratory-scale membrane module simulator cell. The R-MBfR proved versatile and was capable of degrading 2 mg·L^{-1} of MC in 24 h. The economic feasibility of the scaling-up of the hypothetical R-MBfR was also validated. Therefore, this membrane recycling could be a future green cost-effective alternative technology for MC removal.

1. Introduction

Cyanobacterial mass proliferation as a harmful algal bloom (cyanoHABs) is an increasing phenomenon in eutrophic water bodies worldwide, due mainly to climate change (e.g. global warming and persistent drought) and eutrophication. To date, several types of toxins

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produced by cyanobacteria have been identified. Microcystins (hereafter MC) are among the most abundant and widely spread cyanotoxins worldwide. MC comprise a structurally diverse group of potent hepatotoxins with a cyclic heptapeptide structure that are produced by cyanobacteria as intracellular metabolites, released mainly by cell lysis. Under natural conditions, MC are relatively stable compounds when exposed to sunlight and a wide range of temperatures and pH (Wörmer et al., 2010). The half-life of MC-LR by photosensitized degradation in natural systems was estimated to be approximately 90–120 days per meter of water (Welker and Steinberg, 2000).

As MC persist for long periods in the natural environment, developing mechanisms to avoid toxins reaching water supplies is mandatory. Nevertheless, most drinking water utilities still rely on conventional treatment processes that lack adequate optimized MC removal processes. To achieve drinking water quality standards, drinking water treatment plants (hereafter DWTPs) usually eliminate MC by a variety of physicochemical methods (Merel et al., 2010). However, these processes are costly and may produce harmful by-products. Biological filtration has also been used in drinking water treatment to remove cyanotoxins. Nonetheless, biological MC degradation is considered a slow process compared to chemical treatments and its cost-effectiveness greatly depends on the type of support used (sand, activated carbon, anthracite, etc.) (Eleuterio and Batista, 2010; Ho et al., 2012a).

Desalination of sea and brackish water by reverse osmosis (hereafter RO) membrane technology is broadly implemented worldwide given its low cost and easy handling. However, >840,000 end-of-life (hereafter EoL) membranes modules (>14,000 Tn/year) are discarded every year worldwide (Landaburu-Aguirre et al., 2016). There is global concern about managing these wastes because current management options for EoL-RO membrane modules are, unfortunately, landfilling and incineration, which pose relevant environmental risks. In general, EoL-RO membrane modules are formed by different polymers, such as epoxy resin, polypropylene, polyester, polyamide, polysulfone, etc. All these polymers are high-performance materials excellent high mechanical and chemical durability. Therefore, when these modules are disposed in landfills, they persist for prolonged periods of time, which aggravates the environmental problem. Of the different membrane types, polyamide thin film composite (PA-TFC) membranes currently account for over 95% of existing RO desalination plants (Geise et al., 2010). For this reason, PA-TFC RO membranes were studied herein. These membranes are formed by three layers: a non-woven polyester support, an asymmetric porous polysulfone (PSF) interlayer and a polyamide (PA) ultra-thin layer.

Emerging membrane technologies, such as the membrane biofilm reactor (MBfR), have received attention in the last 20 years (Nerenberg, 2016). Unlike conventional filtration membranes, MBfRs do not separate solids from liquids. Instead biofilms form on the outer membrane surface and are able to remove pollutants, among several other reactions (Kinh et al., 2017; Martin and Nerenberg, 2012). The aim of the present research is to provide a new concept for biological MC removal during drinking water treatment. To this end, we reused the EoL RO membranes discarded by desalination plants as supports for biofilm immobilization that is capable of selectively removing MC. This approach is based on the most innovative biofilm reactor developments, and we provide the new development of reactors made from recycled materials (Halan et al., 2012). We call this pioneering concept the Recycled-Membrane Biofilm Reactor (hereafter R-MBfR) (Fig. 1). We studied the characteristics of two different membrane models and the influence of their previous fouling for bacterial association as an active biofilm. These biologically-active membranes were tested to remove MC by passing MC-polluted water. Finally, this hypothetical system was also economically detailed and analyzed in relation to current physico-chemical methods to provide a first understanding of its feasibility.

2. Materials and methods

2.1. MC-degrading bacteria

The MC-degrading bacterium selected for this study was *Sphingopyxis* sp. strain IM-1, which possesses a specific cluster of genes for MC degradation (Lezcano et al., 2016).

2.2. Membranes

Discarded RO membranes were used as the support material to grow MC-degrading strain IM-1. The membrane samples (coupons) studied herein came from EoL (PA-TCF) RO membranes (spirally wound modules) after treating; a) brackish water (hereafter BW discarded or BWd), TM720-400 (*Toray*), and b) seawater (hereafter SW discarded or SWd), HSWC3 (*Hydranautics*). In addition, new commercial membranes were used as a control: TM720-400 (*Toray*) for the BW type (hereafter BWc) and SW30HRLE-440i (*DowFilmtec*) for the SW type (hereafter SWc). It is noteworthy that we used the SW30HRLE-440i model as a control because the HSWC3 model is currently unlisted. Despite the different brands and models, according to the manufacturer's information both membranes have identical properties. All the membranes were conserved in Milli-Q water prior to use.

2.3. Extraction of microcystins

MC were extracted from fresh cyanobacterial scum using methanol 100%, followed by a 15-minute sonication in an ultrasonication bath (P-Selecta Ultrasons), and were stored at 4 °C for 1 h to extract MC. The extract was then centrifuged (Heraeus Megafuge 16) at 4000 ×*g* for 15 min, and the supernatant was stored at −20 °C. When the pellet lost most of its chlorophyll (after repeating the above step 3 times), the extract was vacuum-dried at 40 °C in a rotavapor (Rotavapor-R, Büchi, Switzerland), resuspended in 10% methanol and bonded to 5 g C18 cartridges (Extrabond C18, 5 g, 20 mL, Sharlab) for partial MC purification. First, the cartridge was activated with 100% methanol, followed by Milli-Q water and subsequent conditioning with 10% methanol. Afterward samples were added and washed with Milli-Q water and 30% methanol. MC were eluted in 20 mL of 90% methanol and dried in a SpeedVac concentrator (Savant, SPD131DDA) at 45 °C and 0.2 Torr for 2 h. Finally, MC were resuspended in Milli-Q water, passed through a sterile syringe with 0.22 μm filters (25 mm, Pall Corporation) for sterilization and stored at −20 °C. The MC solution was composed of 84.5% MC-LR, 9.86% MC-RR and 5.64% MC-YR.

2.4. Initial fouling characterization

To determine the percentage of organic and inorganic fouling, a thermogravimetric analysis (TGA) of membrane fouling from the RO discarded membranes was carried out. The membrane fouling TGA data were recorded in a TGA Q500 analyzer in an oxidative (air) atmosphere at a heating rate of 5 °C/min from 45 °C to 800 °C. To complement this analysis, SEM images were taken in the discarded membranes, according to Section 2.9.

2.5. Membrane surfaces characterization

2.5.1. Zeta potential measurements

The surface Zeta potential was measured via electrophoretic light scattering in a Zetasizer Nano ZS (Zen 1020). Measurements were taken at 25 °C in 10 mM KCl and pH 7.0 using an aqueous solution with of 0.5% (w/w) poly (acrylic acid) (450 kDa) as a tracer. pH was adjusted using 1 M KOH and 1 M HCl (Santiago-Morales et al., 2016).