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ELECTRODIALYTIC PROCESS OF NANOFILTRATION CONCENTRATES – PHOSPHORUS RECOVERY AND MICROCYSTINS REMOVAL

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ABSTRACT

Toxic cyanobacteria blooms are associated with nutrient enrichment of surface waters. Nanofiltration (NF) is a pressure-driven process that can be used in water treatment plants, to effectively remove particulate matter and organic contaminants, including cyanobacteria toxins, and nutrients. NF produces a nutrient and toxin-enriched stream, e.g. with microcystin-LR (MC-LR), that has to be safely disposed of.

The suitability of the electrodialytic (ED) process for phosphorus recovery and decrease of MC-LR concentrations from NF waste stream was assessed. In ED experiments running between 5 and 12 h, phosphorus electromigrated towards the anode compartment promoting an isolated clean phosphorus product. The maximum obtained phosphorus recovery was 84%, varying with the NF waste stream (membrane concentrate) characteristics, cell design and treatment time. After the application of the ED process the concentration of MC-LR was also reduced. These results encourage further tests, aiming the inclusion of this hybrid technology (NF followed by ED) in water treatment plants, contributing not only for the phosphorus recovery, but also for the decrease in the toxicity of the NF concentrate, lowering the costs and promoting safe disposal.

1. INTRODUCTION

The increase fluxes of nutrients arriving to water bodies, namely phosphorus and nitrogen, due to agricultural runoff/sewage treatment plants/other anthropogenic sources is one of the main factors to promote the existence of cyanobacterial blooms [1].

Microcystins are hepatotoxic cyclic peptide toxins (Fig. 1) released by freshwater cyanobacteria. Microcystin-LR (MC-LR) is the most common and toxic variant [2]. The contamination in freshwater sources may have severe health effects, leading the World Health Organization (WHO) to recommend a guideline value of 1 μg/L for MC-LR in drinking water [3].

The review of Corbel et al. [1] states the high concentrations of MC-LR in countries worldwide. It was also reported [1] that cyanobacterial blooms are used as organic fertilizer in some countries which, together with spray irrigation with contaminated water, can add more sources of health hazard as toxins, like MC-LR, may enter in the food chain. The removal of MC-LR from water may be carried out by oxidation using chlorine, ozone and permanganate as oxidants [2,5]. However, some undesired by-products may be formed, e.g. chlorine may react with certain types of naturally occurring organic compounds in water forming trihalomethanes and haloacetic acids [2]. Photolysis and advance oxidation processes (AOPs) such as UV/H_2O_2 process, Fenton reagent, sulfate radical based AOPs, radiolysis, ultrasonic degradation, TiO_2 photocatalysis, ferrate (VI) have also been used [2,6,7]. Physical treatment processes such as membranes are effective in the removal of toxins [8–11] guaranteeing safe levels in waters. In the membrane concentrate stream, toxins as well as other compounds will be present representing an environmental risk if not adequately treated or disposed.

Electrokinetic and electrodialytic (ED) processes had been used aiming to recover resources, like phosphorus, from matrices such as sewage sludge [12], sewage sludge ashes [13,14] and membrane concentrate [15]. The ED process consists in the application of an electric field to a matrix, causing the movement of its species towards one of the electrode compartments, from where they can

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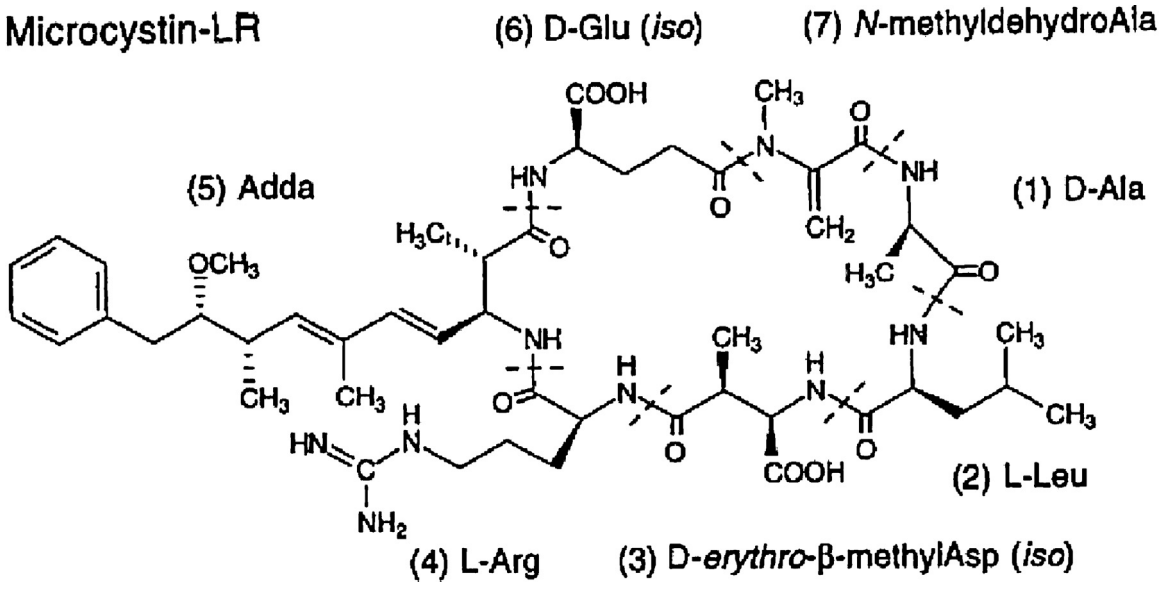

Fig. 1. Structure of MC-LR [4].

be removed. The main mechanisms responsible for the movement are electromigration, electroosmosis and electrophoresis and, in the specific case of the ED process, also electrodialysis.

This work goes forward on phosphorus recovery. It aims to integrate two water treatment processes and recover phosphorus from nanofiltration (NF) concentrates [16]. The ED process was applied to membrane concentrates in order to evaluate the recovery of phosphorus as well as to decrease MC-LR levels.

2. MATERIALS AND METHODS

2.1. Production of membrane concentrates

The production of membrane concentrate was carried out using a plate-and-frame unit (Lab-unit M20) described in detail elsewhere [10]. A thin film composite NF membrane with an hydraulic permeability of 82.2 kg/(h.m^2.bar) at 21 °C and a membrane molecular weight cut-off of *ca.* 114 Da, NF90 (DowFilmtec), was used. The experiments consisted of concentration runs, mimetizing industrial NF operation at different water recovery rates (defined between permeate and initial feed volumes).

The concentrate stream resulting from NF (membrane concentrate) contains cyanotoxins (MC-LR) and phosphorus, as well as natural organic matter. This slurry was used in ED experiments. The NF feed water was a surface water from two Portuguese Dam reservoirs: Amoreiras (101.2 km^2 and 11 hm^3, Alentejo) and Funcho (200 km^2 and 42.8 hm^3, Algarve). Since no occurrence of cyanobacterial blooms was reported in both reservoirs during the experimental period, 2.2 mg/L of KH_2PO_4 and 10 μg/L of microcystins, extracted from cultures of *Microcystis aeruginosa* grown in laboratory (supplied by Pasteur Culture Collection), were added to the surface water. Table 1 presents the characteristics of the produced membrane concentrates.

2.2. Electrodialytic laboratory cells

Two cell designs were used for the ED experiments (Fig. 2a and b). The design in Fig. 2a, described in detail elsewhere [17], is divided into three compartments, consisting of two electrode compartments (each one with an electrode) and a central one, in which the membrane concentrate was placed. The three compartments were separated by ion exchange membranes (cation exchange membrane IC1-61CZL386, and anion exchange membrane, IA1-204SXZL386, both from Ionics Inc. Massachusetts, USA). The design in Fig. 2b, adapted from [18], is divided in two (electrode) compartments, separated by an anion exchange membrane (similar to the previous one). Membrane concentrate was placed in the cathode compartment.

The electrodes were platinized titanium bars, with a 3 mm diameter and a 5 cm length (Bergsøe Anti Corrosion A/S, Denmark). A power supply (Hewlett Packard E3612A) was used to maintain a constant direct current and the voltage was monitored by a multimeter (Kiotto KT1000H). The electrolyte was a 10^{-2} M $NaNO_3$ with pH 7 being circulated using a multichannel peristaltic pump (Watson-Marlow 503 U/R, UK) in a closed circulation system.

Table 2 presents the experimental conditions used with the membrane concentrates. Summing-up, the table is divided in control experiments (C1 to C3), experiments to study phosphorus migration (A to H) and experiments to study phosphorus migration

Table 1
Characteristics of the membrane concentrates used in the experiments.

Memb Conc.	Dam	Cond (μS/cm)	pH	Turbidity (NTU)	DOC (mg C/L)	UV254nm (1/cm)	P (μg/L)	MC-LR (μg/L)
1		1635	8.5	33.0	28.8	0.25	876.2	16.5
2	Amoreiras	2980	8.3	281	42.8	0.51	1442	21.1
3		3000	8.4	300	54.1	0.48	1250	–
4		1476	8.3	188	32.0	0.36	1495	–
5	Funcho	1276	8.3	146	26.2	0.31	1245	42.9
6		804	8.2	80.7	31.0	0.20	900.5	36.7