CHAPTER 1

INTRODUCTION

1.1 SCOPE OF THE THESIS

Cyanobacterial blooms seasonally challenge drinking water treatment, increasing turbidity, causing poor settling and filter clogging, producing tastes and odours and increasing the production of disinfection-by-products. Nevertheless, the main concern with cyanobacterial blooms arises from the health risk associated with the ability of many species and strains to produce cyanotoxins as secondary metabolites, including the cyclic peptide hepatoxins (*e.g.*, microcystins, MC) and/or the alkaloid neurotoxins (*e.g.*, anatoxin-a). The focus of this thesis was on microcystins, for these are the most frequently occurring cyanotoxins, are chemically stable and may cause both acute and chronic effects (liver damage; tumour promoting). Furthermore, microcystins are the only ones for which the World Health Organization (WHO) derived a drinking water provisional guideline value (1 μg/L for daily exposure to the microcystin-LR), very recently adopted as a national standard for drinking water quality (DL 306/2007, dating 27 August).

An optimal water treatment requires the removal of intact cyanobacterial cells (particulate matter), given that cyanotoxins are largely cell-bound, as well as the removal of soluble compounds, since there is always a fraction of cyanotoxins that is dissolved in the water (by natural or induced release from cells). Conventional treatment is considered ineffective for the removal of dissolved cyanotoxins, making the study and implementation of alternative technologies crucial to minimise or eliminate their negative impact.

Membrane technologies are considered attractive as they act as physical barriers and do not form by-products, but only the tighter and higher pressure membrane processes, like nanofiltration and reverse osmosis, are able to remove dissolved organic matter to a significant degree. Promising low-pressure hybrid membrane processes were recently developed, such as PAC/UF (powdered activated carbon adsorption/ultrafiltration), which combines the ability of PAC to adsorb organics with the particle removal aptitude of the UF membranes. UF membranes are expected to remove cyanobacterial cells, with its intracellular microcystins, and PAC is expected to adsorb dissolved microcystins. Some of the advantages of PAC/UF are its operational flexibility, easy cleaning, high disinfection capacity and improved efficiency for PAC usage (faster kinetics, higher effective contact time, better separation and sludge minimisation). Even though PAC/UF presents a high potential for cyanotoxins removal, it has been applied and studied for other purposes (pesticides, tastes and odours, and disinfection-by-products control), and there is a lack of information in this application.

This context prompted the development of this thesis, addressing the removal of both cyanobacteria and cyanotoxins from drinking water by PAC/UF, focusing on the main questions involving each technology and the singularities of the cyanotoxins issues.

PAC adsorption performance depends on the contaminant and carbon properties and on the raw water characteristics (inorganic and organic background matrices). Several studies have demonstrated the adverse impact of water natural organic matter (NOM) on the adsorption kinetics and/or adsorption capacity for micropollutants, which adsorb in pores that NOM cannot access. However, microcystins (molar mass ranging from 900 to 1100 Da) are relatively higher than most of the synthetic compounds studied (*e.g.* pesticides, geosmin, MIB) and closer to the NOM fraction of intermediate molar mass, which may change the competition mechanisms and the overall impact of NOM. Hence, the competing mechanisms between microcystins and different types of NOM were explored in this thesis. Furthermore, inorganic species coexist with NOM in natural waters and may interfere with its adsorption as well as with microcystins adsorption, so this work also addressed the impact of water ionic strength on microcystins-NOM competitive adsorption, an approach usually not considered in the literature.

The limited number of existing studies on UF for cyanobacterial control has demonstrated very high cyanobacterial cells removal by UF, with a small proportion of cells damage. Further studies are therefore necessary, especially to test the cell sensitivity to shear-stresses and subsequent toxin release at operating conditions close to full-scale application. In addition, cell integrity decreases and algogenic organic matter (AOM) changes (in concentration and in nature) during the growth phases. For that matter, UF performance was studied for removing cyanobacterial cells under different growth ages, with special attention to cell damaging and subsequent degradation of UF permeate (treated water). One key-issue in membrane processes is membrane fouling, and therefore it was investigated which NOM components may be determinant in the flux decline of an UF hydrophilic hollow-fibre membrane. Besides the usual NOM model compounds, NOM associated with cyanobacterial blooms, *i.e.* algogenic organic matter segregated or released during cell lysis, was also considered.

Regarding the PAC/UF process, the effect of PAC on membrane fouling is crucial, but the literature is not unanimous, reporting positive, negative and even neutral impact. Raw water diversity is frequently pointed out as one of the explanations for the contradictory PAC effects on membrane fouling, although there is a lack of studies on this area. Therefore, this thesis assessed PAC contribution to the NOM fouling control in PAC/UF systems and analysed if different NOM components interfere and change the overall PAC impact on the UF performance. Microcystins removal by PAC/UF was investigated under different feed concentrations, PAC doses, operating conditions, aqueous organic (NOM) and inorganic (mono- and divalent cations) matrices. It was also performed a comparative study between PAC application in conventional water treatment train and PAC integrated with UF, an issue not yet approached in the literature.

1.2 OBJECTIVES

This thesis addressed the study of PAC/UF hybrid process for the removal of cyanobacteria and associated toxins from drinking water. Specific objectives for each process and for the integrated PAC/UF were defined as follows:

1- To evaluate the dissolved microcystins adsorption onto PAC, namely its capacity and rate of adsorption, and to investigate:

- the effect of the water background inorganic matrix (ionic strength);
- the effect of the water background organic matrix (NOM);
- the combined effect of the water background inorganic and organic matrices (NOM and ionic strength);

2- To study the UF capacity for removing microcystins and cyanobacteria, specifically to assess:

- the cyanobacterial cell removal;
- the occurrence of cell lysis during different cell growth phases;
- the microcystins removal (dissolved and cell-bound);
- the impact of water background matrix (NOM and ionic strength) on UF performance;
- the impact of PAC addition on UF performance;

3- To investigate the PAC/UF ability for removing microcystins and cyanobacteria, focusing on:

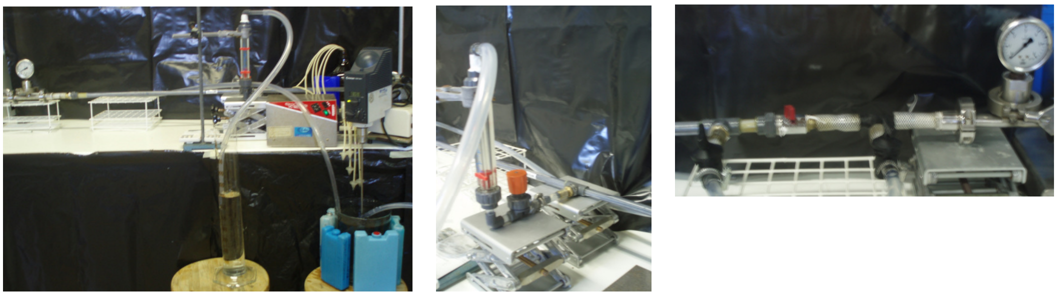
- the key-operating conditions;
- the impact of water background matrix (NOM and ionic strength) on PAC/UF performance;
- the comparison of PAC/UF performance with PAC application in conventional clarification (PAC+C/F/S).

1.3 RESEARCH STRATEGY

Given the decision of structuring the thesis in self-contained papers (detailed in section 1.4) it is important to present the research strategy defined to accomplish the objectives outlined above, including the general experimental methodology.

PAC/UF studies involved, in a first stage, the selection of the PAC and UF membrane, and also the design and assemblage of the UF bench-scale *apparatus*. PAC Norit SA-UF was chosen for it was well characterised in the literature, it had the pore size distribution adequate for microcystins adsorption and it had an extremely fine grade, especially designed for UF hollow-fibre membranes (low ratio of PAC particle to UF feed channel) and advantageous for fast adsorption kinetics. For the UF tests, an Aquasource hollow-fibre module was selected and purchased, with cellulose acetate membranes of 100 kDa molecular weight cut-off (MWCO). This arrangement was chosen since it was used in many PAC/UF full-scale applications, seemed advantageous for fouling minimisation (hydrophilic membranes) and for cleaning (it allows backwashing and it is tolerant to chlorine).

The lab UF system consisted on a feed tank, a peristaltic pump, a positive displacement pump, two manometers, one permeate tank, one permeate flow meter, valves and the tubing and recirculating tank (RT) involved in the UF recirculating loop (Figures 1.1. and 1.2). The schematic diagram is presented in chapters 6-8.



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