CHAPTER 10

CONCLUSIONS AND FUTURE WORK

10.1 CONCLUSIONS

This thesis addressed the study of PAC/UF hybrid process for removing cyanobacteria and associated toxins from drinking water, focusing on the main questions involving each technology and the singularities of the cyanotoxins issues.

PAC adsorption and ultrafiltration were studied separately and, afterwards, the two technologies were integrated into the PAC/UF hybrid process. This study was performed with a commercial fine-grade mesoporous PAC (PAC Norit SA-UF), and a lab-scale UF *apparatus* especially designed and assembled for the present study and including a cellulose acetate hollow-fibre UF membrane with a MWCO of 100 kDa (from Aquasource). Laboratory cultured cells of *Microcystis aeruginosa* and the associated microcystins were studied. *M. aeruginosa* is one of the most commonly occurring cyanobacteria. The cyclic peptides microcystins produced by this cyanobacterium are very relevant for drinking water supply, as they are chemically stable, have both acute and chronic effects (hepatototoxic and tumour-promoting) and are the most widely spread cyanotoxins in freshwaters.

The most important objectives of this thesis were the investigation of: i) the microcystins adsorption (rate and capacity) onto PAC; ii) the impact of water background matrix (the combined effect of NOM and ionic strength) on microcystins adsorption onto PAC and also on UF performance; iii) the cyanobacterial cells removal and lysis by UF; iv) the PAC contribution to the NOM fouling control in PAC/UF; v) the microcystins removal by PAC/UF and the key-operating conditions of this process; vi) the microcystins removal by PAC/UF from natural waters and its comparison with the PAC application to conventional clarification (PAC+C/F/S). NOM surrogates (humic acids, AHA; tannic acid, TA; salicylic acid, SA), algogenic organic matter (AOM) and natural surface waters were studied.

Detailed conclusions relative to PAC adsorption, UF and PAC/UF were drawn in chapters 3 to 9 and this chapter summarises and integrates the most relevant findings. The main conclusions were:

▪ High capacity (K = 17.2 (μg/mg)/(L/μg)$^{1/n}$, 1/n = 0.3) and fast kinetics were observed for the adsorption of four microcystin variants (MC-LR, -LY, -LW, -LF) onto PAC Norit SA-UF in ultrapure water due to the very fine PAC particles (6 μm) and its adequate porosity for these target compounds (40% of mesoporous and 22% of secondary microporous volumes). Regarding NOM surrogates adsorption, the faster kinetics and the best adsorption capacity were found for TA, and were similar to microcystins data, which evidenced a shared range of adsorption sites. AHA and SA presented slow kinetics and poor adsorption from ultrapure water, explained by the large AHA size and the SA hydrophilicity;

▪ Microcystins and NOM surrogates adsorption were both affected by the water ionic strength (IS). IS impact depended on the cation charge ($Ca^{2+} > K^{+}$), adsorbate molar mass (high molar mass > low molar mass) and adsorbate surface concentration (IS had a positive effect for high surface concentrations and a negative effect for low surface concentrations). Potassium only slightly improved the adsorption of the highest molar mass compound (AHA), whereas calcium gradually enhanced adsorption as follows: AHA > TA > MC-LY ≈ MC-LF ≈ MC-LW > MC-LR > SA. A probable explanation was a molecular shrinkage especially relevant for larger and more negatively charged molecules in the presence of calcium, enabling their access to additional PAC pores. For the MC-LR surface concentration studied (5.3-18.7 mg/g), the enhanced adsorption regimen prevailed, *i.e.*, ionic strength improved the microcystin adsorption;

▪ Microcystins-NOM competition depended upon the NOM size, and the presence of ionic strength played an important role. Microcystins adsorption was mostly affected by NOM of closer size (TA), and a slight improvement in the adsorption capacity was observed with IS addition. Pore constriction seemed to lead the TA competition mechanism, and direct competition for microcystins adsorption sites only governed at high carbon loadings. Ionic strength induced the competition of the high molar mass AHA (not observed in IS absence), by reducing AHA size and causing pore blockage. Small hydrophilic compounds (SA) almost did not disturb microcystins adsorption as they adsorb on different pores;

▪ PAC adsorption capacity for microcystins was strongly affected by a moderately hard clarified water with hydrophilic small organics (Tavira's WTP water), although kinetic data predicted no significant negative effect of these NOM competing molecules. This feature revealed that direct-site competition would rule the microcystins-NOM competitive adsorption if a PAC/UF system is applied after the clarification step at Tavira's WTP;

▪ In competition conditions (*i.e.*, in the presence of background NOM), the adsorption capacity for microcystins decreased as its concentration (C_0) declined. However, over the C_0 range tested (67 - 221 μg/L MC-LR_{eq}), microcystins residuals (C/C_0) were not affected by the initial microcystins concentration (as found with other micropollutants), except when in the presence of the strong competitor TA. To overcome TA competition and achieve negligible residuals, PAC should be increased 50% in the presence of IS and doubled in IS absence;

▪ UF application to model and natural waters ensured an absolute removal of *M. aeruginosa* single cells and an excellent overall control of particles. Chl-a was never detected in the permeate, intracellular microcystins content was always below the

quantification limit (> 96% rejection), and turbidity below 0.1 NTU (> 98% rejection), even with feed chlorophyll-a values as high as 60 μg/L. UF results of cell retention were comparable and usually better than the removal achieved by a conventional treatment train, including C/F/S or C/F/DAF and filtration. These data obtained with single cells further confirm the UF excellent disinfection ability for cyanobacteria and protozoa. *M. aeruginosa* single cells are used as surrogate to assess the removal efficiency of particles of problematic size range (3-10 μm), like *Giardia* cysts and *Cryptosporidium* oocysts, and they better represent the size of cyanobacteria and algae that is more prone to escape from a conventional clarification process;

- UF caused *M. aeruginosa* cell lysis at all cell growth phases, but with greater damage on older cultures. However, cell lysis had not a direct reflex in permeate degradation (which was only sporadically observed), since an enhancement of microcystins rejection by the UF membrane was observed with ageing. Indeed, the cellulose acetate UF membrane presented low adsorption and low rejection of microcystins in ultrapure water, but the segregated AOM (mucopolysaccharides) and/or the protein lysed AOM enhanced the microcystins rejection;

- The same concern with the cell ageing effect on cell lysis must be considered in all water treatment processes, an issue often ignored. Another aspect to take into account in water treatment studies is the existence of AOM-driven microcystins adsorption, which may underestimate the cell lysis when its evaluation is based only on the time evolution of dissolved microcystins concentration in the feed and in the permeate;

- The type rather than the overall concentration of salts and organics ruled the membrane fouling. The worst impairment on flux and the poorest rejection were associated to

interactions between polysaccharide-rich AOM and scaling multivalent ions, which seemed to result in dense fouling layers. As found by others, TOC and UV_{254nm} were not adequate to assess membrane fouling potential by algal organic matter;

- Compared to UF, PAC/UF did not affect the permeate flux nor the reversible membrane fouling, either in the absence or in the presence of NOM, and regardless of the NOM characteristics (hydrophobicity and protein content) and water inorganics. In addition, PAC improved the irreversible membrane fouling, minimising the chemical cleaning frequency, enhanced AHA and TA rejections, increased the overall removal of AOM and notably improved the dissolved microcystins and UV_{254nm} rejections. PAC was nevertheless apparently ineffective for the highly hydrophilic EOM compounds;

- PAC/UF operated under cross-flow mode presented hydrodynamic limitations. The cross-flow velocities studied (0.5 m/s and 1 m/s) were not able to avoid the deposition of a loose and highly porous PAC cake on the membrane surface and, in addition, the PAC/UF performance (1 h-cycle) was poorer than the PAC adsorption kinetics (1 h contact time). Recent studies also showed no advantage in using cross-flow mode over dead-end mode of PAC/UF operation for treating clear waters, both in terms of PAC distribution and permeate quality;

- In pure solutions, single-pulse PAC dosing at the beginning of the UF-cycle resulted in slightly better permeate quality, compared to the multi-pulse addition of the PAC throughout the cycle, while no differences were found between these two dosing procedures in terms of transmembrane pressure. Hydraulic retention times in the recycling tank (HRT) of 34 and 55 minutes resulted in similar permeate quality;

▪ In pure solutions, PAC/UF achieved 93-98% microcystins removal and a 1 h cycle-averaged concentration of microcystins in the permeate below the WHO guideline value (1 μg/L MC-LR) using 10 mg/L PAC and for a feed concentration up to 20 μg/L MC-LR_{eq};

▪ PAC dose required was mostly affected by NOM type and concentration, and by microcystins concentration. Surface waters showed a small impact onto microcystins removal, with greater effect of some algogenic compounds, but especially of high concentrations of humic and tannic-like compounds. PAC doses of 10-15 mg/L effectively controlled *ca.* 5 μg/L MC-LR_{eq} of dissolved microcystins in model waters with 2.5-5 mg(AHA+TA)/L or with *M. aeruginosa* culture (cells and AOM) and in a clarified surface water with *M. aeruginosa* culture. High efficiency removals (86-94%) and average permeate concentrations of < 0.1-0.8 μg/L MC-LR_{eq} were obtained. However, a PAC dose of 15 mg/L was not able to attain the WHO quality from a water containing high concentrations of microcystins (*ca.* 20 μg/L MC-LR_{eq}) and NOM surrogates (5 mg/L);

▪ Compared to conventional PAC application (PAC+C/F/S), PAC/UF favoured the adsorption kinetics since it allowed longer PAC effective contact time, smaller PAC particles and PAC was not incorporated into the flocs. Chlorophyll-a was completely removed by both processes, but 10 mg/L of PAC in PAC/UF process ensured a remarkable improvement in turbidity (99% removal by PAC/UF *vs.* 84% by PAC+C/F/S) and particularly in total microcystins (90% *vs.* 36% microcystins removal and 0.72 *vs.* 5.4 μg/L MC-LR_{eq} in the treated water, respectively for PAC/UF *vs.* PAC+C/F/S). PAC+C/F/S achieved higher UV_{254nm} removal (66% *vs.* 39%), due to the preferential coagulation of large compounds and the UF cell damaging, but PAC doses above (twice or more) 15 mg/L would be necessary to effectively control the microcystins.

Summing-up, this thesis contributed to the understanding of the ability and fundamentals of PAC/UF application for controlling cyanobacteria and associated toxins, a subject of increasing concern for water industry and scientific community although barely approached.

The main achievements in PAC adsorption were the highlighting of the important contribution of the water ionic strength to the microcystins-NOM competition and the demonstration that preferential competition between similar size compounds is not indubitably related with a direct-site competition mechanism. For UF, the main accomplishments were the demonstration of cell lysis occurrence, emphasizing the need for UF integration with a process able to control the dissolved microcystins, *e.g.* PAC, for which a positive effect on irreversible membrane fouling was verified. As for PAC/UF, the main attainment was the confirmation of its high potential for microcystins removal, especially when compared with PAC conventional applications, and the assessment of the application conditions.

Indeed, this work pointed out some of the advantages and limitations of PAC/UF application for cyanobacteria and cyanotoxins control.

PAC/UF has an excellent overall performance on *M. aeruginosa* cells removal and is an efficient process for the control of the usual concentration range of dissolved microcystins in natural waters, provided the correct PAC dose and contact time are used. PAC/UF is able to achieve the WHO guideline value for drinking water with relatively low PAC doses of 10-15 mg/L, and therefore presents much better performance than the conventional PAC application. PAC/UF operational flexibility (PAC type and dose, semi dead-end UF operation, which allows dead-end or cross-flow operation mode depending on the particles content in the

feed stream) are considered important technical and economical advantages as cyanobacterial blooms are usually a seasonal problem.

Due to cell lysis occurrence, UF with no PAC addition is considered inadequate to treat cyanobacterial-rich waters. PAC addition presents benefits for UF, since it overcomes sporadic permeate degradation and improves the UF performance, *i.e.* it increases the permeate quality and decreases the membrane irreversible fouling.

A good characterisation of the water to be treated is very important to evaluate and minimise NOM competition and membrane fouling. Usual characterisation of NOM based on TOC and UV_{254nm} is not sufficient and specific analytical techniques should be applied to characterise NOM by size and functional groups. Compounds with similar size or slightly higher that microcystins, and competing through pore blocking, are expected to be the most problematic for microcystins adsorption onto PAC. As for UF, the most hydrophilic compounds present in algogenic organic matter (*e.g.* polysaccharide-type compounds) are not significantly removed by PAC and are determinant for membrane fouling, especially when interacting with multivalent scaling ions. The fouling behaviour of AOM and the cell lysis occurrence during UF, with subsequent release of dissolved microcystins and AOM to water, emphasise the importance of a roughing clarification step prior to PAC/UF.

Besides pre-treatment, PAC/UF optimisation strategies include increasing PAC doses (by 50%, 100%, or higher) and/or PAC contact time, adjusting PAC porous structure and/or decreasing the size of the PAC particles (there are some good results with submicrometre PAC recently presented by Matsui and team) and/or applying more efficient adsorbents for polysaccharide-type compounds, such as magnetic ion exchange resins (MIEX).

10.2 Future Work

The development and the findings of the present thesis allowed identifying the following issues as interesting future work:

- the combined effect of polysaccharide-type compounds with different salts (Fe, Mn, Ca) on membrane fouling;
- the PAC dosing procedure effect on the permeate quality, both in the absence and in the presence of NOM;
- the assessment of PAC/UF long-term fouling by performing several filtration cycles, simulating full-scale operation;
- the potential regeneration of PAC from PAC/UF waste stream (for instance, through wet-air oxidation);
- the combined use of PAC+MIEX/UF for the enhanced removal of NOM, especially the most hydrophilic compounds;
- the PAC/UF ability for removing other cyanotoxins of increasing concern, namely, MC-LA, cylindrospermopsin, anatoxin-a and saxitoxins;
- PAC/UF comparison with alternative membrane-based technologies, *e.g.* PAC/MF and NF, focusing on aspects like permeate quality, operational flexibility, membrane fouling and cleaning, and capital and operational costs.