CHAPTER 7

ASSESSING THE PAC CONTRIBUTION TO THE NOM FOULING CONTROL IN PAC/UF SYSTEMS

ABSTRACT

This paper investigates the powdered activated carbon (PAC) contribution to the fouling control by natural organic matter (NOM) in PAC/UF hybrid process, as well as the foulant behaviour of the PAC itself. Solutions of NOM surrogates (humic acids (AHA) and tannic acid (TA)) and AOM/EOM (algogenic organic matter/extracellular organic matter) fractions from a *Microcystis aeruginosa* culture were permeated through a UF hollow-fibre cellulose acetate membrane (100 kDa cut-off). The worst impairment on flux and the poorest rejection were associated to polysaccharide-like EOM substances combined with mono- and multivalent ions. PAC, either in the absence or in the presence of NOM, did not affect the permeate flux nor the reversible membrane fouling, regardless of the NOM characteristics (hydrophobicity and protein content) and water inorganics. However, PAC improved the irreversible membrane fouling, minimising the chemical cleaning frequency. Furthermore, PAC enhanced AHA and TA rejections and the overall removal of AOM, although it was apparently ineffective for the highly hydrophilic EOM compounds.

7.1 INTRODUCTION

Natural organic matter (NOM) negatively impacts the efficiency of several water treatment processes, is the major precursor of disinfection by-products, and is responsible for tastes, odours and bacterial re-growth in the distribution system. NOM is usually not significantly removed by ultrafiltration (UF), but is a major contributor to membrane fouling, which is one of the critical issues in membrane technologies application for water and wastewater treatment.

NOM fouling mechanisms are gel formation (an extreme case of concentration-polarisation), cake formation, pore blockage and pore constriction (Taniguchi *et al.*, 2003). Concentration-polarisation has weaker effects than pore blockage and surface deposition (Cho *et al.*, 1999; Yuan and Zydney, 2000). Of particular importance is the size distribution of the feed solution components relative to the membrane pore size. Foulants smaller than membrane pores may adsorb on the porous surface and lead to pore constriction, while larger components may block the pore entrances and contribute to cake or gel formation on the membrane surface (Taniguchi *et al.*, 2003; Costa *et al.*, 2006).

Last years' research in the membrane field has been greatly focused in the understanding of which NOM components are responsible for membrane fouling. Researchers used sophisticated separation and analytical techniques to characterise NOM during membrane runs or through membrane autopsies, focusing on NOM molecular size, hydrophilicity/ hydrophobicity and functional groups analysis. Several researchers suggested that, among the different NOM molecular size fractions, the colloidal fraction causes the most significant flux decline (Carroll *et al.*, 2000; Schäfer *et al.*, 2000; Kwon *et al.*, 2005; Costa *et al.*, 2006; Lee *et al.*, 2006). Others have demonstrated the strong foulant behaviour of the humic substances

(Combe *et al.*, 1999; Yuan and Zydney, 1999; Jones and O'Melia, 2000). Nevertheless, recent studies showed the leading role of the hydrophilic neutral NOM fraction (polysaccharides, proteins, amino sugars) on low-pressure membrane (microfiltration (MF)/UF) fouling, particularly the irreversible one (Carroll *et al.*, 2000; Cho *et al.*, 2000; Fan *et al.*, 2001; Lee *et al.*, 2004; Kennedy *et al.*, 2005; Kwon *et al.*, 2005; Kimura *et al.*, 2005, 2006; Kim *et al.*, 2006; Lee *et al.*, 2006; Park *et al.*, 2006; Yamamura *et al.*, 2007).

In addition, when treating algal rich-waters, NOM includes algogenic organic matter (AOM) whose intracellular fraction has in a previous nanofiltration study shown a fouling behaviour (Her *et al.*, 2004). Previous UF studies for cyanobacterial removal from drinking water (chapter 6) indicated the need of UF performance enhancement by a process able to simultaneously control the dissolved toxins and minimise the membrane fouling exhibited by the extracellular fraction (EOM) of AOM in the presence of background multivalent ions.

PAC in combination with UF is a promising option, particularly when seeking the safe control of cyanobacteria and associated toxins. UF is a safe barrier against cyanobacteria (chapter 6) and PAC is able to compete with the membrane for the NOM compounds and thus reduce their adsorption on the membrane surface and/or pores and is efficient for microcystins removal (chapters 3-5). However, there are contradictory results reported concerning the PAC effect on membrane fouling. Some authors reported an improvement of permeate flux, longer filtration runs or a reduced frequency of chemical washing (Laîné *et al.*, 1990; Adham *et al.*, 1991; Pirbazari *et al.*, 1992; Jacangelo *et al.*, 1995; Farahbakhsh and Smith, 2002; Konieczny and Klomfas, 2002; Meier *et al.*, 2002; Lee *et al.*, 2007). Others presented similar flux behaviour (Jack and Clark, 1998; Yiantsios and Karabelas, 2001; Tomaszewaska and Mozia, 2002; Mozia and Tomaszewaska, 2004; Matsui *et al.*, 2005, 2006) or exacerbated flux decline

(Nilson and DiGiano, 1996; Lin *et al.*, 1999; Carroll *et al.*, 2000; Zhang *et al.*, 2003; Li and Chen, 2004; Meier and Melin, 2005; Zhao *et al.*, 2005; Zularisam *et al.*, 2007).

The PAC effect on membrane fouling seems to be a function of the membrane characteristics, namely its hydrophobicity. The studies of Lin *et al.* (2001), Crozes *et al.* (1993) and Mozia *et al.* (2005) showed that PAC reduced or did not affect the flux decline of hydrophilic membranes, but it was not effective or worsened the flux of the hydrophobic membranes. Raw water diversity is also often used to explain the contradictory PAC effects on membrane fouling, although there is a lack of studies on this area.

For that matter, the main purpose of this study is to investigate the contribution of PAC to the fouling control of a UF hydrophilic membrane, including the effects of different NOM characteristics on the performance (fluxes and retention) of the PAC/UF hybrid process.

7.2 MATERIALS AND METHODS

7.2.1 NOM Solutions

Commercial humic acid (AHA, Aldrich Chemicals) and tannic acid (TA, Sigma) were chosen as NOM model compounds, representing hydrophobic high molar mass and relatively hydrophilic moderate molar mass organic compounds, respectively. Prior to use, AHA was purified to remove bound iron and decrease the ash content, through hydrochloric acid precipitation, using Hong and Elimelech (1997) method. AHA stock solution was sequentially filtered through GF-C (1.2 μm) and GF-F (0.7 μm) Whatman filters before being used to prepare the UF feed solutions. AHA and TA solutions with a TOC concentration of 2-4 mgC/L were prepared with deionised water (DI) to which a background ionic strength (IS) of 2.5 mM was adjusted by KCl (up to 1 mM IS) and $CaCl_2.2H_2O$ (1.5 mM IS) addition. The pH was corrected to *ca.* 7 with KOH and H_2SO_4.

Solutions of algal organic matter were also used, being separately studied the extracellular organic matter excreted during cyanobacterial growth (EOM) and AOM, which includes EOM and the intracellular organic matter released during cell lysis. A *Microcystis aeruginosa* culture was used (Pasteur Culture Collection, PCC 7820), which was grown in BG11 medium, at 23-24ºC under a light regimen of 12h fluorescent light, 12 h dark. Algae were harvested after one month, corresponding to the exponential growth phase (section 6.3.2). EOM and AOM preparation was adapted from Takaara *et al.* (2004). For EOM, the culture growth media (including cells) was sequentially filtered through a 1.2 µm glass filter (Whatman, GF-C), a 0.7 µm glass filter (Whatman, GF-F) and a 0.22 µm hydrophilic polypropylene membrane filter (Millipore). The final filtrate was concentrated tenfold with a rotary evaporator and stored at 4ºC until use. For AOM, harvested growth cells were destroyed with combined ultrasonic treatment (10 W, 10 min, 6x) and two freezing-thawing cycles. The residuals from cell lysis together with the culture growth media were submitted to the filtration sequence previously described for EOM (1.2 µm; 0.7 µm, 0.22 µm) and the final filtrate was also stored at 4ºC until use. Specific volumes of EOM and AOM final filtrates were used to prepare the UF feed solutions with a TOC concentration *ca.* 4 mgC/L. Given the high content of salts in EOM solutions, no further salts were added, besides the pH adjustment to around 7. In AOM solutions, the conductivity was completed to *ca.* 300 µS/cm with KCl and the pH was corrected to 7.

7.2.2 UF Membrane and PAC

UF experiments used a hollow-fibre hydrophilic cellulose acetate membrane from Aquasource (Table 7.1).

Table 7.1 – Cellulose acetate membrane specifications (manufacturer data).

Specification	Aquasource
Molecular Weight Cut-off , kDa	100
Total Surface Area, m^2	0.05
Pure Water Permeability, L/(h.m^2.bar)	250
Number of Fibres	16
Fibre Length, m	1.1
Internal Fibre Diameter, mm	0.93
Max. Applied Pressure, bar	1.5
Max. Backwash Pressure, bar	2.5

The module was mounted in a bench *apparatus* including a feed tank (FT), a positive displacement pump, two manometers (P1, P2), one flow meter (Flm), a permeate tank (PT) and the valves and tubing involved in the backwashing and in the recirculating loop (V1-V5) (Figure 7.1).

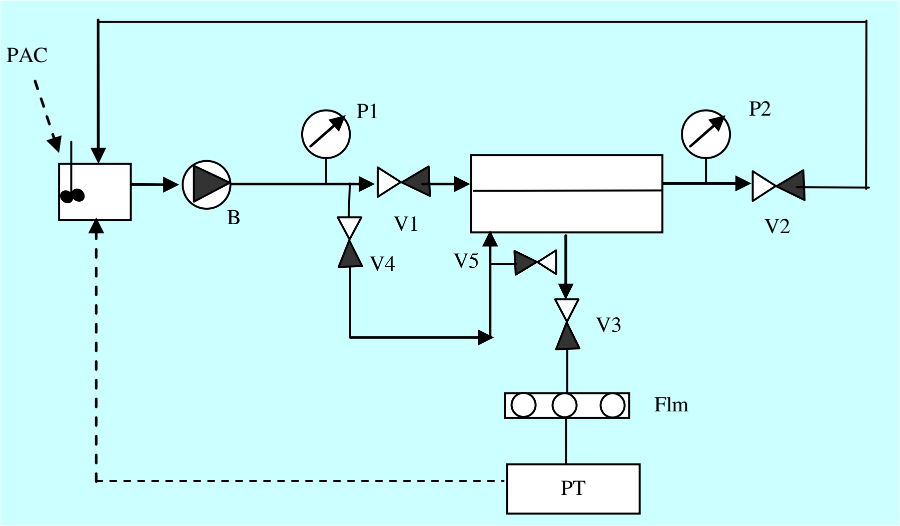

Figure 7.1 - Flow diagram of UF *apparatus* (FT - Stirred feed tank; B - Positive displacement pump; P - Manometers; Flm- Flowmeter; PT - Permeate tank; V1,V4,V5- Valves for backwashing; V2 - Concentrate valve; V3 - Permeate valve).

PAC/UF experiments used commercially available Norit SA-UF powdered activated carbon (PAC), a highly mesoporous carbon, with a low average particle diameter (6 μm) suitable for circulating within the narrow UF hollow-fibres.

7.2.3 UF Experiments

All the UF experiments were performed in a cross-flow filtration mode, and the module was operated under the inside-out configuration during the filtration cycles and membrane flushing, and under outside-in flow during backwashing. Prior to the UF experiments, the membranes were washed and compacted with DI until achieving a steady permeate flux, at the pressure and cross-flow velocity values to be used in the experiments.

Two different types of fouling runs were performed at a constant transmembrane pressure (TMP) of 0.65 bar and at a 0.5 m/s cross-flow velocity (CFV) (1 m/s was tested only once): 1) time-depending fouling runs, with the concentrate and the permeate being recycled back to the feed tank during two hours and 2) concentration-time-depending fouling runs, with the concentrate being recycled to the feed tank and the permeate being discarded until reaching a predetermined water recovery rate (WRR, defined as the ratio between the permeate and the initial feed volumes). The positive displacement pump provided the necessary pressure and recirculation, and a variable-frequency drive allowed adjusting the CFV in the hollow-fibres. Permeate flow rate and temperature were periodically measured and, whenever necessary, TMP was adjusted by manual control of the concentrate valve.

During the time-depending fouling runs, permeate samples were collected at a given time intervals (after 30 min., 1 and 2 hours of filtration). During the concentration-time-depending fouling runs, the permeate was discarded and when the predefined WRR was achieved (0%, 66% and 90%), it was recycled to the feed tank during five minutes, after which samples of the feed and the permeate were taken.

In PAC/UF experiments, PAC was directly added to the feed tank, which was continuously stirred at 150 rpm. The total mass of PAC was always added at the beginning of the filtration cycle, and was only wasted at the end of the run.

At the end of each experiment, membranes were backwashed and flushed. Backwashing lasted 1 min with a 5 mg/L (as Cl_2) sodium hypochlorite solution to inhibit the biological activity on the UF system, and flushing was performed with deionised water during 3 min.

Normalised flux, as a function of time (in time-depending fouling runs) or WRR (in concentration-time-depending fouling runs), was used as the membrane fouling indicator. Normalised fluxes were calculated as the ratio of solution flux over the pure water flux before starting the run. All flux values were corrected to a constant temperature (20ºC) using Crozes *et al.* (1997) equation, $J_{20}=J_T\ e^{-0.0239\ (T-20)}$, which is based on the variation of water viscosity with temperature, and where J_{20} is the flux (L/min.m^2) at 20ºC, T is the temperature (ºC) and J_T is the flux (L/min.m^2) at temperature T.

Mass-balance equations were applied to compute the percentage of solute adsorbed. The general equation derived to all UF runs (time-depending fouling runs, concentration-time-depending fouling runs and constant flow runs (described in chapter 6)) is:

$$\%Adsorbed = \frac{(V_0C_0 + QtC - V_fC_f - \sum_{i=1}^{4} Q_{pi}t_iC_{pi})}{(V_0C_0 + QtC - \sum_{i=1}^{4} Q_{pi}t_iC_{pi})} \times 100\% \qquad \text{(Equation 7.1)}$$

where V_0 and C_0 are the initial feed volume (L) and concentration (mg/L), respectively; Q is the feed flow (L/min) (make-up to balance the permeate flow output), t and C are the associated feed pumping time (min) and concentration (mg/L); V_f and C_f are the final volume (L) and concentration (mg/L); Q_{pi}, t_i and C_{pi} are the permeate flow (L/min), pumping time (min) and concentration (mg/L). The equation simplifies according to the experiment, *e.g.*, in the concentration-time-depending fouling runs, QtC does not apply and $\sum_{i=1}^{4} Q_{pi}t_iC_{pi}$ simplifies to $\sum_{i=1}^{3} V_{pi}C_{pi}$, where V_{pi} is the permeate volume (L).

7.2.4 Analytical Methods

Samples were analysed for pH at 20ºC (WTW 340 pH meter), electrical conductivity at 25ºC, (Crison GLP 32 conductimeter), turbidity (HACH 2100N turbidimeter of high resolution, 0.001 NTU), total and dissolved organic carbon (TOC, DOC) (measured as non purgeable organic carbon by a high temperature combustion method in a Shimadzu TOC 5000A) and/or UV absorbance (UV/VIS spectrophotometer-Beckman DU 640B) at 215 nm and 254 nm, whenever applicable depending on the objective of the experimental run. The DOC concentration and the UV absorbance were both measured on filtered samples (0.45 μm acrodisks), and TA and AHA concentrations in single solute solutions were computed from calibration curves against UV_{215nm} and UV_{254nm}, respectively. The nature of NOM was assessed through UV_{254nm} absorbance and SUVA parameter, computed by UV_{254nm}/DOC.

7.3 RESULTS AND DISCUSSION

7.3.1 UF Fouling Potential of NOM Surrogates

Concentration-time-depending fouling runs were performed with single-solute solutions of AHA and TA and with a AHA and TA mixture (with *ca.* 2.5 mg/L each) to investigate the individual and combined effects of hydrophobic high molar mass and relatively hydrophilic moderate molar mass NOM fractions on the UF membrane fouling. Data are depicted on Figure 7.2.

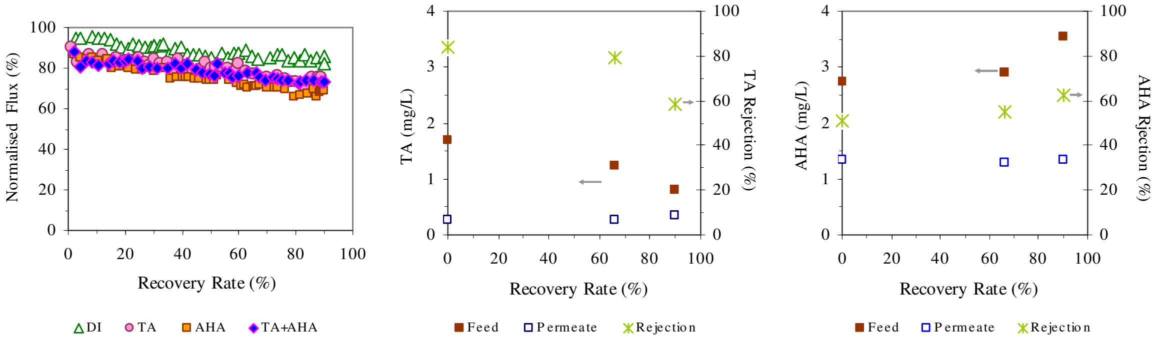

Figure 7.2 - Concentration-time-depending fouling runs with NOM model compounds: normalised flux (left), feed and permeate quality, and rejection of TA (centre) and AHA (right) (*ca.* 2.5 mg/L each NOM surrogate, 2.5 mM IS background electrolyte).

A moderate and rather similar flux decline with WRR was observed for AHA, TA and the mixture of both – the normalised flux decreased from 90% at 0% WRR to *ca.* 70% (AHA) and *ca.* 80% (TA and TA+AHA) at 90% WRR (Figure 7.2, left). However, membrane compaction effects (a limitation of the experimental *apparatus*) during the concentration runs (evidenced by the DI trend) accounted for *ca.* half of the overall flux decline exhibited by these NOM surrogates, throughout the entire range of WRR tested. Data also show that AHA and TA did not interact to produce stronger foulant behaviour.

TA rejection was quite high (*ca.* 80%) for WRR up to 66% and decreased to *ca.* 60% for 90% WRR, due to a decrease in the feed concentration and a fairly constant permeate quality (Figure 7.2, centre). Since TA is much smaller than the membrane MWCO (1.7 kDa *vs.* 100 kDa) size exclusion/steric hindrance does not apply. On the other hand, the water background ionic strength attenuates potential electrostatic repulsions within (intramolecular) or between (intermolecular) TA molecules and between TA molecules and the membrane. TA adsorption must therefore dominate rejection. Its contribution was computed by mass-balance (equation 7.1) and yielded 16 mg TA adsorbed during the concentration-time-depending fouling run, *i.e.*, 95% of the available mass. In UF runs performed at constant flow (data not depicted here) TA rejection was also high and relatively constant (78 ± 4%, duplicate runs) and the mass-balance indicated that 70% of the available mass was adsorbed during the 1 h runs. Crozes *et al.* (1993) also obtained a significant flux decline (80%) onto both hydrophobic and hydrophilic membranes caused by the adsorption of high concentration (15 mg/L) of tannic acid.

AHA was less rejected than TA for all WRR and the rejection increased from *ca.* 51% to 62% with WRR (Figure 7.2, right). During constant flow runs (data not shown) AHA rejection was kept constant (71±2%, duplicate runs).

AHA retention by the membrane may be due to sieving, steric hindrance or adsorption. Although the fouling mechanisms were not studied, the enhancement of AHA rejection with WRR is probably explained by the pore constriction caused by AHA adsorption to the porous surface and/or by the additional sieving provided by the AHA deposits onto the membrane surface, as observed by others (Yuan and Zydney, 1999, 2000; Schäfer *et al.*, 2000; García-Molina *et al.*, 2006). Moreover, the flux decline observed, especially at the higher solute concentrations, also agree with a combined effect of concentration-polarisation, pore constriction/pore blockage and cake layer formation (Schäfer *et al.*, 2000; Yuan *et al.*, 2000).

A mass-balance derived for AHA showed that actually 83% of the available mass was adsorbed during concentration-time-depending runs and 43% during constant flow runs. These results point out the importance of the adsorption phenomenon for AHA, although to a lower extension than for TA (at 90% WRR, TA feed concentration decreased 40%, whereas AHA increased 30%). Recent results from kinetic fouling models suggest that in UF membrane fouling there is a transition from internal pore adsorption to pore blocking and latter to cake development (Katsoufidou *et al.*, 2005; Costa *et al.*, 2006; Jung *et al.*, 2006).

7.3.2 UF Fouling Potential of Algal Organic Matter

Time-depending fouling runs were performed with EOM and AOM and, for comparison purposes, also with AHA and TA. Since similar initial TOC concentrations were granted, these four assayed waters allowed to studying the effect of NOM characteristics rather than the overall concentration (Table 7.2).

Table 7.2 – Characteristics of the NOM solutions

NOM solutions	pH	Conductivity (µS/cm)	TOC (mgC/L)	SUVA (L/(mgC.m))
AHA	7.2	284	3.9	6.9
TA	7.3	285	3.7	4.6
EOM	7.2	831	4.5	1.4
AOM	7.2	288	3.7	1.0

The uppermost values of SUVA belong to AHA, indicating large amounts of aromatic carbon, of high molar mass and hydrophobicity. TA solution has intermediate SUVA values and algal organic matter (EOM and AOM) have low SUVA values. These data are in agreement with Her *et al.* (2004) and Henderson *et al.* (2008) AOM characterisation: SUVA values below 1.65 L/(mgC.m), corresponding to a hydrophilic fraction of 57% (or more) and a hydrophobic fraction of 26%.

Henderson *et al.* (2008) characterised the EOM extracted from four algal species, including *Microcystis aeruginosa*, during the exponential and the stationary growth phases. They concluded that EOM was dominated by hydrophilic polysaccharides and hydrophobic proteins. During the stationary phase, the *M. aeruginosa* EOM had a bimodal distribution with 55% greater than 30 kDa (46% is even higher than 500 kDa) and 38% smaller than 1 kDa. Also, about 72% of total carbohydrates and 52% of total proteins were higher than 100 kDa, meaning that much of the high molar mass EOM was carbohydrates and proteins. The protein/carbohydrate ratio was 0.31 during the exponential phase and 0.6 during the stationary phase, demonstrating that the amount of proteins relative to carbohydrates doubled with age. Her *et al.* (2004) also found a greater portion of proteins, mainly of high molar mass (> 100 kDa) contained in the IOM (intracellular organic matter) compared to the EOM fraction. The AOM solution has the contribution of both extracellular and intracellular organic matter, so it is expected to have a composition similar to EOM during the stationary phase, but more affected by cell lysis contribution. According to the previous characterisation, the AOM solution used in the present experiments is thus probably mainly composed of two fractions: a high molar mass fraction (> 100 kDa), dominated by hydrophilic polysaccharides and hydrophobic proteins, and a low molar mass fraction (< 1 kDa). As to the EOM solution, it should have a similar composition, but with greater carbohydrates/DOC ratio and with some minor portion of hydrophobic proteins.

The normalised flux and respective TOC and UV rejections obtained in the time-depending fouling runs with TA, AHA, AOM and EOM are depicted on Figure 7.3.

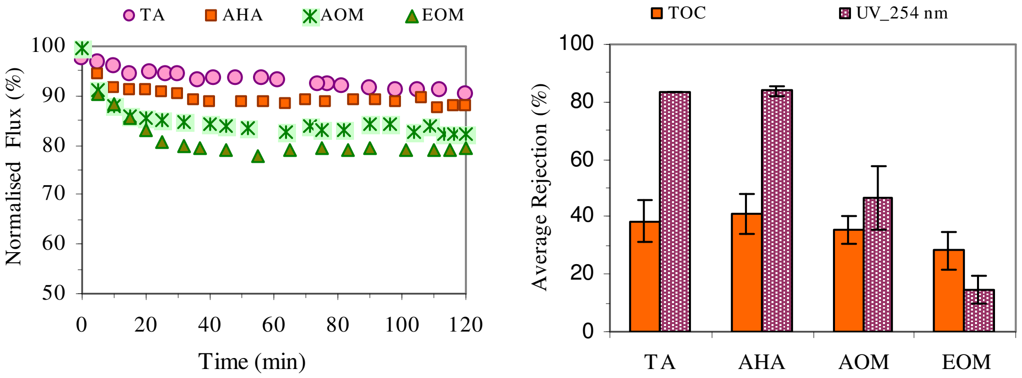

Figure 7.3 - Normalised flux (left) and average rejection of organic matter (right) during time-depending fouling runs with different NOM (error bars represents standard deviations).

The EOM was found to have the most significant impact on membrane fouling, exhibiting a flux decline of 21% after 2 h of operation, slightly higher than that of AOM (18%) and further distant from AHA (12%) and TA (10%). The higher fouling potential of hydrophilic NOM like the one prevalent on the AOM and EOM fractions studied (SUVA of 1.0 and 1.4 L/(mgC.m)), has already been referred by several authors (Fan *et al.*, 2001; Her *et al.*, 2004; Kecili *et al.*, 2006; Lee *et al.*, 2006; Zularisam *et al.*, 2007). Moreover, the EOM run showed a more severe membrane fouling effect than the AOM run, which, given the much higher salt content of EOM solution of similar TOC concentration, must not be associated only with the type of organic substances.

In fact, adsorption computed from mass-balance indicated that during the 2 h-runs, the EOM presented the lowest adsorption percentage, 17% of the available mass, compared to 22% for TA, 25% for AHA, and 27% for AOM. Regarding TOC rejections, algogenic organic matter presented lower values than NOM surrogates (Figure 7.3, right). Also, UV_{254nm} rejections were much lower for EOM and AOM (particularly for the former), which could be associated with the fact that polysaccharides have low UV absorbance and the aromatic tryptophan-like proteins have low absorbance at 254nm (Henderson *et al.*, 2008). These results show that TOC and UV_{254nm} are not good indicators of membrane fouling due to algal matter, supporting other authors conclusions (Her *et al.*, 2004; Zularisam *et al.*, 2007).

NOM aggregation, complexation and precipitation phenomena driven by multivalent ions therefore arise as the main responsible for EOM membrane fouling. The interactions between polysaccharide-type compounds and multivalent cations must produce a denser fouling layer resulting in an increased overall resistance to water permeation. Similar results were found by Jermann *et al.* (2007) and Katsoufidou *et al.* (2007) in UF studies with sodium alginate (a typical model polysaccharide for EOM) in the presence of calcium.

7.3.3 UF Fouling Potential of PAC

The impact of PAC addition on UF performance was evaluated in concentration-time-depending fouling runs. PAC was added to deionised water with a 2.5 mM background IS ($KCl+CaCl_2$) at a concentration of 5 mg/L. The runs were carried out using two CFV, 0.5 m/s (used in all previous runs) and 1.0 m/s. Normalised flux of PAC/UF runs compared to analogous UF runs (with no PAC addition) are presented in Figure 7.4, as a function of WRR.

Data (Figure 7.4, left) demonstrate that PAC alone does not affect the permeate flux of a hydrophilic UF membrane (the curves with and without PAC completely overlap), as found by Pirbazari *et al.* (1992), Lin *et al.* (1999), Yantsios and Karabelas (2001), Li and Chen (2004), Mozia *et al.* (2005) and Saravia *et al.* (2006). It seems that the PAC particles are large enough (6 µm average diameter) to avoid membrane pore blocking. PAC should deposit on the membrane surface, but must form a porous layer that allows the passage of water without an increasing resistance. The deposition of the PAC particles depends on convective flux and shear forces created by the cross-flow velocity. For the conditions tested, no advantage was observed in performing runs at higher velocities. Actually, while a similar decrease pattern was observed for both CFV values, with 1.0 m/s a lower permeate flux was found since the beginning of the run (*ca.* 90% at 1 m/s *vs.* 100% at 0.5 m/s, both for 0% WRR).

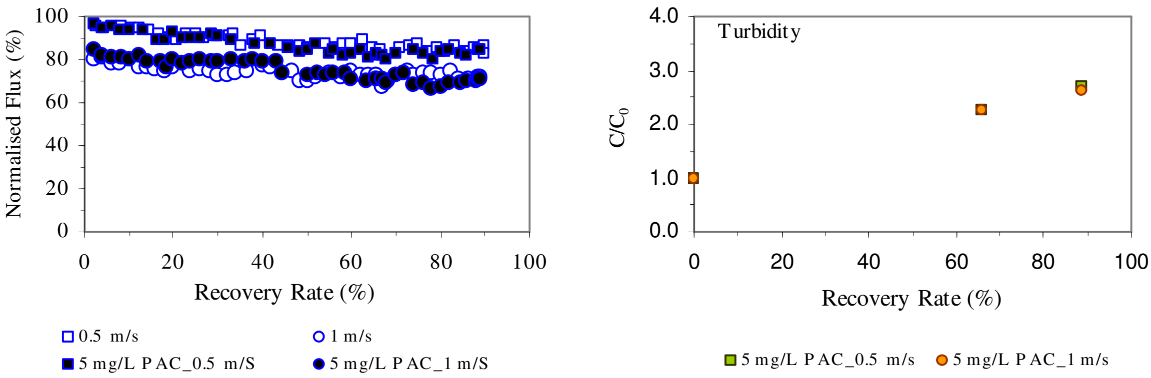

Figure 7.4 - Normalised flux (left) and normalised feed turbidity (right) during UF and PAC/UF concentration-time-depending fouling runs at two cross-flow velocities (UF: no PAC addition; PAC/UF: 5 mg/L PAC addition (2.1.-2.9 NTU), 2.5 mM IS of background electrolyte).

Figure 7.4 (right) displays the normalised turbidity of PAC/UF feed during the concentration-time-depending runs. The higher CFV did not allow a higher feed normalised turbidity, indicating a similar PAC deposition rate. The permeate turbidity never exceeded 0.1 NTU, even when the feed turbidity reached 7.5 NTU. Hence, UF membrane ensured an effective PAC retention.

Crozes *et al.* (1997) concluded that the CFV should be increased proportionally to the membrane flux. Their results revealed that at 35 L/(hm^2) the flux was CFV independent, whereas at higher flux (110 L/(h.m^2)), even a CFV of 0.9 m/s was not enough to keep the particles in suspension. On the other side, Matsui *et al.* (2001) concluded that the cross-flow velocity did not contribute much to the suspending of PAC. Even with a CFV above 1 m/s the PAC was recycled as a suspension for only a short period of time. Both velocities used in the present UF experiments (0.5 m/s and 1.0 m/s) were thus most probably able to maintain only a small fraction of PAC in suspension and for just a short time period. Therefore, the most cost-effective CFV of 0.5 m/s was used in the following experiments.

7.3.4 NOM Fouling Potential in PAC/UF System

PAC is expected to act competitively with the UF membrane for the adsorption of NOM compounds which otherwise would adsorb on the membrane, causing its fouling. However, some authors have referred that although PAC itself does not impose significant membrane fouling, when in the presence of NOM it increases fouling resistance (Lin *et al.*, 1999; Zhang *et al.*, 2003; Li and Chen, 2004). NOM is pointed to act as glue that binds the PAC particles to one another and to the membrane surface, enhancing fouling. To investigate the combined effect of PAC with different NOM compounds on the membrane fouling, the time-depending fouling runs presented on section 7.3.2 were repeated as PAC/UF, *i.e.*, this time adding 10 mg/L PAC in the beginning of filtration. The normalised flux and respective TOC and UV_{254nm} rejections are presented on Figures 7.5 and 7.6, respectively. For direct comparison purposes, data from analogous UF runs (section 7.3.2) are also shown.

Figure 7.5 shows no differences at all of the normalised flux with and without the PAC addition, which indicates that PAC did not promote nor controlled the membrane reversible fouling. This same trend has already been obtained by other authors (Jacangelo *et al.*, 1995; Jack and Clark, 1998; Tomaszewska and Mozia, 2002; Mozia and Tomaszewska, 2004;

Matsui *et al.*, 2005, 2006; Mozia *et al.*, 2005). Moreover, the different characteristics of the NOM used in the experiments, like the hydrophobic or the hydrophilic character, higher or lower protein content or even the higher content of salts (in EOM solutions) did not seem to change the PAC impact on the membrane reversible fouling. Zhao *et al.* (2005) also concluded that NOM plays a quite limited role on PAC cake formation, while a more relevant effect is due to the combination of metal ions, colloids (especially ferric colloids) and PAC. Further experiments onto this combined effect are necessary.

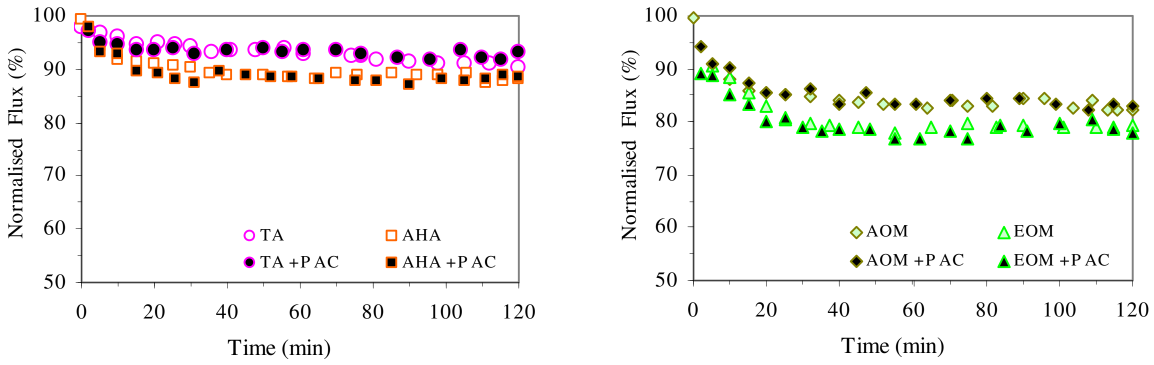

Figure 7.5 - Normalised flux during PAC/UF (10 mg/L PAC) and UF time-depending fouling runs with NOM surrogates (left) and algogenic organic fractions (right).

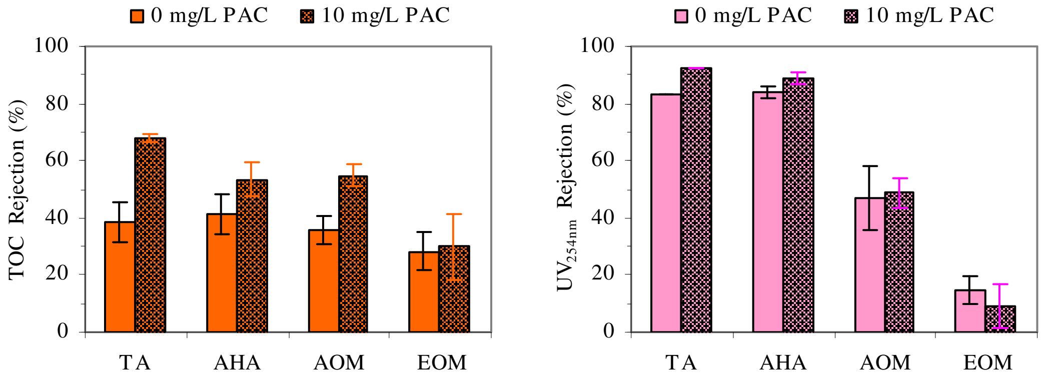

Figure 7.6 - TOC (left) and UV_{254nm} (right) rejections of NOM surrogates and algogenic organic fractions during PAC/UF (10 mg/L PAC) and UF fouling runs (error bars represents standard deviations).

Results of NOM rejection obtained with and without PAC addition (Figure 7.6) indicate a PAC-driven retention enhancement of AHA, and especially TA: 41% (AHA) and 38% (TA) average TOC retention without PAC addition *vs.* 54% (AHA) and 68% (TA) with 10 mg/L PAC; 83% average $UV_{254\ nm}$ rejection of both AHA and TA without PAC *vs.* 89% (AHA) and 92% (TA) with PAC. For AHA and TA, UV_{254nm} rejections far exceeded the TOC rejections, revealing that the UV_{254nm} absorbing compounds are preferentially removed.

Concerning the algal organic matter, PAC had an apparently different impact onto AOM and EOM fractions, with better results for the former. In fact, PAC enhanced the TOC rejection of AOM (35% *vs.* 55%) and had no significant effect on the UV_{254nm} absorbing substances of AOM nor on TOC and UV_{254nm} rejections of EOM constituents. The higher removal of AOM compared to EOM is probably associated with the presence of more hydrophobic compounds in the former fraction, which explains the PAC-driven improvement of TOC rejection. Apparently, PAC was not able to adsorb the highly hydrophilic compounds of EOM (only expressed by the overall content as TOC, since UV_{254nm} is a very poor indicator for polysaccharides and aromatic tryptophan-like proteins) and as such, did not improve the membrane reversible fouling.

7.3.5 Membrane Cleaning

Membrane fouling may be reversible, and thus be easily cancelled by membrane backwashing, or irreversible, requiring chemical cleaning of the membrane. The control of irreversible fouling is particularly important for reducing the operating costs of the membrane process. A very important aspect of this study was therefore to find if PAC has any effect onto membrane irreversible fouling.

The recovery of the membrane permeability to pure water was computed as J_1/J_0, where J_1 is the pure water flux after backwashing and J_0 is the initial pure water flux. Figure 7.7 shows J_1/J_0 values after the time-depending fouling experiments with AHA, TA, EOM and AOM with and without PAC addition.

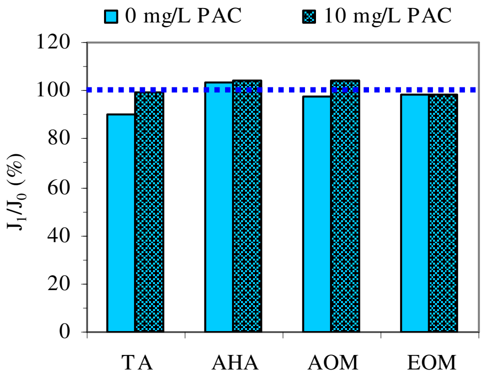

Figure 7.7 - Recovery of membrane pure water permeability after time-depending fouling runs with different NOM and with/without PAC addition (J_1- pure water flux after backwashing; J_0- initial pure water flux).

Results show that without PAC, the membrane fouling by AHA, AOM and EOM was completely reversible but for TA, there was a fraction (10%) of permeability not recovered by backwashing (irreversible fouling). Reversible EOM fouling was also reported by Katsoufidou *et al.* (2007) in UF studies with sodium alginate in the presence of calcium. TA irreversible fouling coincides with the overall flux decline caused by this solute and indicates its strong adsorption to membrane pores. With PAC addition, the fouling observed was completely reversible for all solutes, including TA, which is explained by the high adsorption capacity of PAC Norit SA-UF for that compound.

Figure 7.8 shows the J_1/J_0 values achieved by different cleaning procedures, after the UF concentration-time-depending fouling runs with TA.

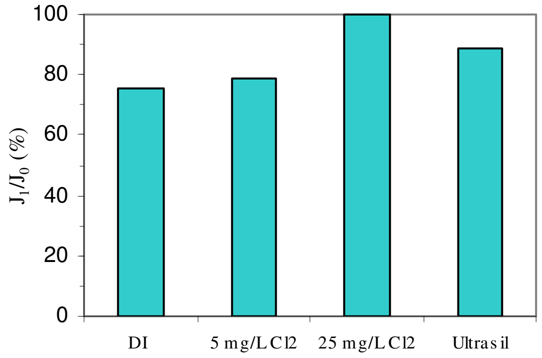

Figure 7.8 - Recovery of membrane pure water permeability, after the concentration-time-depending fouling runs with TA, using different cleaning procedures (J_1- pure water flux after membrane cleaning; J_0- initial pure water flux).

After the simplest cleaning with deionised water (DI), a permeability lost of 25% was observed and the usual chemical cleaning with a low dose of sodium hypochlorite (5 mg/L as Cl_2) was able to recover only 4% of the membrane permeability to pure water. This means an irreversible fouling of *ca.* 21% in TA concentration experiments. The use of a 0.02% (w/w) solution of an alkaline detergent (Ultrasil) attenuated half (52%) of the TA irreversible fouling and the use of high doses of sodium hypochlorite (minimum of 25 mg/L as Cl_2) cancelled all the irreversible fouling. With PAC addition (10 mg/L), irreversible fouling of the UF membrane during the TA concentration runs decreased to 14%. Furthermore, since the starting of the PAC/UF experiments minimal irreversible fouling was observed and the regular use of 25 mg/L as Cl_2 was no longer required, being almost always obtained the full recovery of the membrane water permeability, after a backwash with a 5 mg/L Cl_2 solution and a final flushing with DI. This feature may be explained by the NOM adsorption capacity of PAC and by the relatively loose structure and high porosity of the PAC cake deposited on the membrane, which is therefore easily backwashed. In fact, the membrane backwashing easily removed the PAC cake layer (that looked like skin straws) from the hollow-fibres, and the implementation of a quick flush after backwashing further increased the removal of the deposited PAC, as reported by Adham *et al.* (1991).

7.4 CONCLUSIONS

This study investigated the PAC contribution to the NOM fouling control in PAC/UF systems, as well as the foulant behaviour of the PAC itself on the reversible and irreversible fouling of a hydrophilic UF membrane. Humic acids (AHA), tannic acid (TA) and AOM/EOM (algogenic organic matter/extracellular organic matter) were studied.

Data from UF time-depending fouling runs indicated that the EOM had the most significant impact on membrane fouling followed by AOM, AHA and TA. The higher fouling potential of EOM seemed to be mainly associated with polysaccharide-like substances interaction with multivalent ions, resulting in dense fouling layers. Results also showed that TOC and UV_{254nm} are not adequate to assess membrane fouling potential by algal organic matter.

UF concentration-time-depending runs with 5 mg/L PAC Norit SA-UF at 0.5 m/s and 1 m/s cross-flow velocity showed that PAC alone did not affect the permeate flux of the hydrophilic membrane. Moreover, both velocities studied were not able to avoid the deposition of a loose and highly porous PAC cake on the membrane surface, and therefore there is no advantage in using the least cost-effective (1 m/s) velocity.

PAC (10 mg/L) combined with different NOM did not improve nor exacerbate the flux decline, during the UF time-depending fouling runs with each of the NOM solutions tested. The different hydrophobic/hydrophilic character, protein and salts content of the NOM solutions did not change the PAC impact on the membrane reversible fouling. PAC increased

AHA, TA and AOM rejections, but was apparently ineffective for adsorbing the highly hydrophilic EOM, and as such, did not improve the EOM-driven membrane reversible fouling.

Furthermore, while no PAC effect was found on the membrane reversible fouling by AHA, AOM and EOM, PAC was able to control the irreversible fouling caused by tannic acid (a solute able to penetrate and adsorb within the membrane pores but to which the studied PAC has a high adsorption capacity), avoiding the need for severe membrane cleaning (with > 25 mg Cl_2/L) after the UF runs. In addition, PAC enhanced the UF rejection of AHA, TA and hydrophobic AOM (with subsequent benefits in disinfection by-products control), whereas the UF membrane effectively retained the fine PAC particles.

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