Ceramic Ultrafiltration of Marine Algal Solutions: A Comprehensive Study

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Abstract

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Algal bloom can significantly impact reverse osmosis desalination process and reduce the drinking water production. In 2008, a major bloom event forced several UAE reverse osmosis plants to stop their production, and in this context, a better understanding of UF membrane fouling caused by algal organic matter (AOM) is needed, in order to adjust the filtration conditions during algal bloom events. Polymeric MF/UF membranes are already widely used for RO pretreatment, but ceramic UF membranes can also be an alternative for the filtration of marine algal solutions. The fouling potential of the Red Sea and the Arabian Sea, sampled at different seasons, along with four algal monocultures grown in laboratory, and one mesocosm experiment in the Red Sea was investigated. Algal solutions induce a stronger and more irreversible fouling than terrestrial humic solution, toward ceramic membrane. During algal bloom events, this fouling is enhanced and becomes even more problematic at the decline phase of the bloom, for a similar initial DOC. Three main mechanisms are involved: the formation of a cake layer at the membrane surface; the penetration of the algal organic matter (AOM) in the pore network of the membrane; the strong adhesion of AOM with the membrane surface. The last mechanism is species-specific and metal-oxide specific.

In order to understand the stronger ceramic UF fouling at the decline phase, AOM quality was analyzed every two days. During growth, AOM is getting enriched in High Molecular Weight (HMW) structures (> 200 kDa), which are mainly composed by proteins and polysaccharides, and these compounds seem to be responsible for the stronger fouling at decline phase. In order to prevent the fouling of ceramic membrane, coagulation-flocculation (CF) using ferric chloride was implemented prior to filtration. It permits a high removal of HMW compounds and greatly reduces the fouling potential of the algal solution. During brief algal bloom events, CF should be implemented prior to UF to protect the membranes. A comparison between polymeric and ceramic UF membranes showed that ceramic membrane suffers from a stronger fouling but permits a better removal of DOC and particularly HMW compounds.
Acknowledgement

This work is the result of four years of experimental research (2010-2014), carried out at the WDRC center at KAUST, Saudi Arabia. During that time I had the chance to get support and encouragement for many people and you like to express my gratitude to them.

First of all, I would like to greatly thank my advisor Jean-Philippe Croué for supervising this work, for his advices, his encouragements and his patience throughout the years. Thank you also for letting me travel the world to present my work to international audiences.

I would like to thank Don Anderson and David Kulis from the Woods Hole Oceanographic Institute for teaching me the basics of algae and Claude Courties and François Lantoine from Banuyls Oceanography Laboratory for the algal stains and their support on starting the algal cultures in the laboratory as well as for their flow-cytometer tutoring.

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<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<tr>
<td>AOC</td>
<td>Assimilable Organic Carbon</td>
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<td>AOM</td>
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<td>Algal Organic Matter released during growth</td>
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<td>Biofilm Formation Rate</td>
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<td>DAF</td>
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<td>DLVO theory</td>
<td>Derjaguin and Landau, and Verwey and Overbeek theory</td>
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<td>DMF</td>
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<tr>
<td>dp</td>
<td>pore diameter</td>
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<td>EP</td>
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<tr>
<td>FEEM</td>
<td>Fluorescence Emission Excitation Matrix</td>
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<td>FTIR</td>
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<td>1H-NMR</td>
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<td>HAB</td>
<td>Harmful Algal Bloom</td>
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<tr>
<td>HMW</td>
<td>High Molecular Weight</td>
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<td>HPOA</td>
<td>Hydrophobic Acid</td>
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<td>HS</td>
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<td>HYM</td>
<td>Hymenomonas sp.</td>
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<td>IS</td>
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<td>LC-OCD-UVD</td>
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<td>OM</td>
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<td>PAC</td>
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<tr>
<td>PES</td>
<td>polyethersulfone</td>
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<td>PHAs</td>
<td>Polyhydroxyalkanoate</td>
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<td>pH$_{zpc}$</td>
<td>pH of zero point charge</td>
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<td>PVDF</td>
<td>PolyVinylIride Fluoride</td>
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<tr>
<td>Py-GC-MS</td>
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<td>Silt Density Index</td>
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<td>SP</td>
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<td>Southern Red Sea</td>
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<td>SST</td>
<td>Sea Surface Temperature</td>
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<td>Synthetic seawater</td>
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<td>SWRO</td>
<td>SeaWater Reverse Osmosis</td>
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<td>SYN</td>
<td>Synechococcus sp.</td>
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<td>TEP</td>
<td>Transparent Exopolymer</td>
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<td>Tetraselmis sp.</td>
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Introduction

Water scarcity has become a real problem in many parts of the world. Water demand has increased due to the development of megacities, higher living standards, development of industries and intensive agriculture. Controversially, the quality of the freshwater resources has deteriorated forcing water suppliers to develop new processes, such as seawater desalination. Figure 0-1 shows the evolution of the desalination market for the different regions of the world, for the last 10 years (Fritzmann et al., 2007).

![Desalination capacity growth](image)

**Figure 0-1: Desalination capacity growth** (Fritzmann et al. 2007)

In the Middle East, and more specifically in the Gulf region, population growth is rapid and freshwater resource is very limited. Seawater desalination is a good alternative to supply the water demand and the desalination market is rapidly growing in this region.
In 2011, Saudi Arabia was the largest desalinated water producer, generating 25% of the worldwide output in its more than 2000 plants (Henthorne, 2009; Berktay, 2011).

Thermal seawater desalination was the most common technology used, few decades ago, but Reverse Osmosis (RO) is starting to lead the seawater desalination market. RO is a semi-permeable membrane process that removes colloids, dissolved organic matter and salts. Pretreatment before RO is necessary to reduce the fouling and hence increase the lifetime of the RO membranes. Chemical (coagulants, disinfectants,…) and physical (screening, Dual Media Filter, cartridges, membranes) pretreatments are used. Conventional pretreatments use a combination of chemical and physical processes, and are usually a sequence of flocculation, settling, sand filtration and cartridge filtration (Fritzmann et al. 2007). However, Microfiltration (MF) and Ultrafiltration (UF) are becoming of interest as they produce a higher stability of the permeate quality. Polymeric MF/UF membranes are widely used but ceramic MF/UF membranes can also be an alternative (Xu et al., 2010a; Matsui et al., 2012; Cui et al., 2013; Cui et al., 2011; Condom et al., 2004; Massé et al., 2011).

Episodic algal bloom events are affecting the seawater quality and can have strong consequences in the desalination plant production. In 2008, a Cochlodinium polykrikoides bloom occurred in the Arabian Gulf and Gulf of Oman, forcing the desalination plants to stop their production (Richlen et al. 2010). In this context, a better understanding of UF membrane fouling caused by algal organic matter (AOM) is needed,
in order to adjust the filtration conditions during algal bloom events. Because of the advantages that present ceramic membranes (high filtration specific flux, strong acid, base and oxidant resistances, long lifetime), ceramic UF disk was studied to filter marine algal solutions, using two different ceramic membrane (alumina membrane characterized by a nominal pore size of 80 nm – Al$_2$O$_3$-80 nm, and a titanium oxide membrane characterized by a nominal pore size of 30 nm – TiO$_2$-30 nm). This work was divided in three parts:

(1) the AOM characterization of the algal monocultures during growth. Every two days, AOM was sampled from the culture solution and different analytical measurements (pH, Fluorescence Emission Excitation Matrix, UV spectra, Dissolved Organic Carbon analysis, Liquid Chromatography analysis) were conducted, in order to monitor the change of the AOM composition during growth. At the end of the growth, the High Molecular Weight (HMW) structures (i.e., biopolymers) were harvested, freeze dried and analyzed using Elemental Analysis, Fourier Transform InfraRouge, Pyrolysis-GC-MS, $^{13}$C-NMR and $^1$H-NMR.

(2) the ceramic ultrafiltration of natural solutions sampled in the Red Sea and in the Arabian Sea, at different seasons, along with four algal monoculture solutions grown in laboratory (Skeletonema costatum, Tetraselmis sp., Hymenomonas sp., and Synechococcus sp.) and one mesocosm solution grown in the Red Sea was investigated. The fouling potential of marine solutions was compared to the fouling potential of humic substances coming from treated (i.e., clarification and ozonation) Colorado River, USA.
(3) the implementation of coagulation-flocculation (CF) prior UF experiments. In this last part, the performances of the Al₂O₃-80 nm membrane were compared to the performances of polymeric membrane (H-PVDF, 30 nm pore size). Three different CF configurations, using ferric chloride, were studied: CF followed by flotation, and CF followed by sedimentation, with and without addition of clay (bentonite). The performances of the different CF were assessed by following the turbidity, the Chlorophyll-a (Chl-a) concentration and the DOC concentration. The impact of the different CF configurations on the UF filtration was examined by feeding the UF membranes with the different clarified waters.
1. Literature Review

1.1. Algal Bloom

1.1.1. Definition

Marine algae bloom is characterized by a rapid proliferation of the microscopic planktonic algae in the ocean, such as dinoflagellates, microflagellates or diatoms. Cell concentration can reach up to a million cells/mL, and are present at the surface of the water (0-20 m) (Niven et al., 1995). This phenomenon is usually accompanied by a coloration of the water and a large release of organic matter. Some algae release toxins and the term Harmful Algal Bloom (HAB) is employed when that is the case. These blooms can have a significant negative effect, causing severe economic losses to aquaculture, fisheries, and tourism, and having major environmental, ecological and health impacts.

Algal growth often impacts surface water supplies used for drinking water by: (1) increasing the dissolved organic matter (DOM) content and turbidity (e.g., algae cells), (2) producing taste and odor compounds, and (3) contributing to precursors of disinfection by-products (DBP) upon chlorination (Nguyen et al. 2005).

1.1.2. Occurrence

In the last two decades the frequency, intensity and geographic distribution of HAB have increased significantly (Figure 1-1). This increase can result from different causes such as climate change, terrestrial contamination, and nutrient discharges due to human activities.
Algal bloom is not a new phenomena but the scientific community agrees on the higher frequency of these events for the last decades. Blooms are usually located in coastal areas, which increase their impact on human activities.

![Figure 1-1: Frequency of Algal Bloom in the world in 1970 and 2005](Anderson, 2012)

Algal bloom can be monitored by satellite by forecasting the Chlorophyll-a (Chl-a) concentration in the sea (MODIS Website). Chl-a is produced by the chloroplasts and remains stable while inside the living algal cells but is not soluble in water. During the cell lysis, the Chl-a is released to the seawater bulk, degrades and is not measurable anymore. An increase in the Chl-a concentration is then an indicator of a growth of the phytoplankton community. Figure 1-2 shows the satellite image and the calculated Chl-a concentration in the Arabian Sea in October 2004. It is clear that the Chl-a profile is following the appearing bloom. However, MODIS monitoring is only accurate for oceanic water dominated by phytoplankton. When terrestrial input is important, the variable optical signature is not dominated by phytoplankton and satellite algorithms are
unable to accurately retrieve the Chl-a concentration. In this case, the Chl-a monitoring is not accurate and usually underestimated (Allen et al. 2008).

Figure 1-2: Algal bloom in Arabian Sea, October 2004 monitored by satellite (MODIS Website)

Seasonal pattern can then be assessed. Figure 1-3 presents the Red Sea average seasonal change in Chl-a and Sea Surface Temperature (SST) for the 8 years period (2003 to 2011) (Raitos et al. 2013).
Local Area Coverage (LAC) dataset are presented for the period 2003-2011 (Raitsos et al., 2013). The seasonal behavior of the Chl-a concentration over the past 8 years permits to assess an annual algal bloom pattern, and thus predict the algal bloom events in the future. In the Red Sea, important blooms are mainly happening in the south where nutrient-rich water enters from the Gulf of Aden and Arabian Sea and mixes with the Red Sea water. However, in the other regions of the Red Sea, local blooms can also be detected by a peak in the Chl-a concentration. Figure 1-4 plots the annual evolution of the Chl-a content recorded at different regions of the Red Sea, for the past ten years (Raitsos et al., 2013).
Raistos et al. (2013) distinguished 4 provinces: Northern Red Sea - NRS, the North-Central Red Sea - NCRS, the South-Central Red Sea - SCRS, and the Southern Red Sea – SRS. The Red Sea is characterized by different Chl-a concentration depending on the time, but also on the geographic position. SRS region has an average Chl-a concentration of 5 to 10 times higher than NRS or NCRS regions, which means that phytoplankton communities are more abundant at the SRS region and that is mainly due to nutrients imput. Figure 1-4 (b) indicates for each region, the statistical algal bloom events in the Red Sea for the past 10 years. For Jeddah region (located North of SCRS region), we can observe 2 main annual algal bloom events in winter (January-February) and summer (June-July).
1.1.3. Consequences for Seawater Desalination Market in Middle East

Marine organic matter released by algal bloom is particularly sticky (Passow, 2002; Villacorte, 2013). During such events, seawater desalination plants are struggling to maintain their drinking water production, due to high and irreversible fouling. In 2008, an algal bloom caused by *Cochlodinium polykrikoides* has been reported in the Arabian Gulf, affecting more than 1200 km of coastline. The maximum cell concentration reached up to $2.1 \times 10^7$ cells/mL at Fujairah, United Arab Emirates (Berktay, 2011; Richlen et al., 2010; Sambidge, 2008). At least five plants were forced to shut down due to strong fouling in their media filter (Desalination.com 2008). The hydraulic backwash frequency, usually implemented every 24 hours, was forced to be conducted every two hours, and this increase was not sufficient to maintain a good permeate quality. The plant had to shut down before more severe irreversible fouling of the RO membranes occurred.

In the Middle East, because seawater is a major drinking water resource, a production interruption by the desalination plants can have a major impact in terms of economy and human life.

1.1.4. Algal Organic Matter Characterization

In Open Ocean, the primary source of Natural Organic Matter (NOM) comes from marine phytoplankton activity. In coastal area, organic matter is originated from terrestrial input and from marine bioactivity. The Algal Organic Matter (AOM) includes Extracellular Organic Matter (EOM) - which is excreted by the algal cell during growth, and Intracellular Organic Matter (IOM) - which is produced inside the cell, and released when the cell is lysing. AOM refers to a wide range of compounds such as
oligosaccharides, polysaccharides, proteins, peptides, amino acids, lipids and many other organic compounds.

During the growth of an algal bloom, the AOM concentration increases and is linearly correlated with the number of algal cells (i.e., Chl-a concentration) for either the dissolved AOM (filtration through 1.2 μm for Mague et al., 1980; or through 0.2 μm for Floge et al., 2007) or the AOM larger than 0.2 μm (Wells et al., 1994; Floge et al., 2007). Once the bloom declines, AOM becomes more abundant due to the lysis of the phytoplankton cells and the increase of the bacterial activity (Floge et al., 2007). However, the Chl-a concentration at a given time is not a sufficient parameter to predict the AOM concentration in the sea. Indeed, the Chl-a concentration is species-specific (Wells et al., 1994; Kepkay et al., 1997), and only the evolution of the chlorophyll-a content, at a given region, is a marker of an algal bloom event.

Liquid Chromatography coupled with Organic Carbon Detector and UV Detector at 254 nm (commonly called LC-OCD) analyses performed on the culture solution of algal monocultures are presented in Figure 1-5 (Villacorte, 2013; Sandin et al., 2013). Different fractions of AOM can be distinguished from the LC-OCD profile using one separation column: the biopolymer peak, which has a retention time between 25 and 40 minutes and does not absorb in the UV region; the aromatic fraction (including the building blocks, the humic like and the low molecular weight acids), which has a retention time comprised between 40 and 65 minutes and absorbs at 254 nm; and the low molecular weight (LMW) neutrals that are characterized by a retention time over 65 minutes. When two separative columns are used (Sandin et al., 2013), the retention time of each fraction is longer and the biopolymer fraction is detected between 25 to 55
minutes, the aromatic fraction between 55 and 90 minutes, and the LMW neutral fraction from 90 minutes.

Figure 1-5: LC-OCD-UVD profiles of AOM for the culture of (a) *Alexandrium tamarense*, (b) *Chaetoceros affinis*, (c) *Microcystis* sp. and (d) *Scenedesmus* sp. (Villacorte 2013; Sandin et al. 2013)
As expected from numerous studies (Henderson et al., 2008; Fang et al., 2010; Nguyen et al., 2005; Pivokonsky et al., 2014), AOM is characterized by a low response at 254 nm (i.e., UV@254). During growth, the biopolymer fraction increases and may become the main fraction of the AOM. At the end of the growth, the biopolymer fraction contributes to 53.4%, 59.1%, 55.8% of the Total Organic Carbon (TOC) (prefiltration through 2 μm) for *Alexandrium tamarense*, *Chaetoceros affinis* and *Microcystis sp.*, respectively; and 70.8% of the total DOC for *Scenedesmus sp.* (Villacorte, 2013; Samdin et al., 2013).

These results are in accordance with different papers highlighting the strong contribution of large molecules to the AOM pool (Myklestad, 1995; Boehme et al., 2006; Henderson et al., 2008; Benner et al., 1992). These large molecules are identified to be mainly polysaccharides, proteins (Huber et al., 2011; Villacorte, 2013; Lancelot, 1984; Myklestad, 1995; Henderson et al., 2008), as well as lipids (Lancelot, 1984). Henderson et al. (2008) discovered that 62 to 78% of the total carbohydrate and 60 to 90% of the total proteins were passing through a membrane with a nominal pore size of 0.7 μm, but retained by a membrane characterized by a nominal pore size of 30 kDa. Boehme et al. (2006) suggested that these large molecules are not the result of the aggregation of smaller ones, but are compounds excreted in situ by the cells. Henderson et al. (2008) found that AOM (filtered through 0.7 μm porosity membrane) included both “hydrophobic” proteins and “hydrophilic” polysaccharides. Hydrophilic compounds are dominating AOM for all phases of growth for either EOM or IOM (Pivokonsky et al., 2014; R. Henderson et al., 2008; Huang et al., 2012; Qu et al., 2012).
At the beginning of the growth (i.e., lag phase and exponential phase of growth), the AOM present in solution can be considered as EOM. Small molecules such as monosugars, amino acids, and organic acids are released in the solution by simple diffusion through the cell membrane. For larger molecules such as proteins and polysaccharides, a more complex and still unknown mechanism is involved (Myklestad, 1995). Once the stationary phase of growth is reached, cells lyse and release IOM to the solution. AOM becomes a mixture of EOM and IOM (Pivokonsky et al., 2006).

IOM contains more proteinaceous material than EOM, probably due to the DNA material present inside the cells (Pivokonsky et al., 2006; Fang et al., 2010) and small compounds in AOM are found to be coming from IOM pool (Mague et al., 1980; Lancelot, 1984; Nguyen et al., 2005). Myklestad (1995) describes EOM as jelly material, essentially composed of polysaccharides and/or proteoglycans. Kepkay et al. (1997) also considers EOM carbohydrates as very sticky compounds. AOM remains a very complex matrix and is species-specific, however, general observations on the AOM composition can be highlighted (Jensen, 1983; Myklestad, 1995; Henderson et al., 2008; Villacorte, 2013). In comparison with terrestrial NOM, AOM is considered to be less diverse in its compositions (Baldock et al., 2004; Jørgensen et al., 2011; Her et al., 2004; Boehme et al., 2006; Fang et al., 2010).

Fluorophore regions and Fluorescence Emission Excitation Matrices (FEEM) of different AOM are presented in Figure 1-6. Chen et al. (2003) distinguished different fluorophore regions after analyzing different fractions of NOM extracted from surface waters. Fluorophores corresponding to the protein-like (i.e., tyrosine like, tryptophan like and more complex molecules such as soluble microbial by-product like) are located at an
excitation wavelength of 200 to 270 nm and at an emission wavelength of 280 to 380 nm. Humic-like chromophores are located at excitation wavelengths comprised between 250 nm and 400 nm and emission wavelengths comprised between 380 nm and 550 nm, and fulvic-like are located at excitation wavelengths comprised between 200 nm and 250 nm and emission wavelengths comprised between 380 nm and 550 nm.

Figure 1-6: (a) Fluorophore regions and FEEM of (b) *Microcystis* sp. EOM and (c) *Microcystis* sp. IOM (Chen et al., 2003; Fang et al., 2010)
FEEM of a *Microcystis sp.* culture are characterized by two main fluorophores located in the protein-like region and the soluble microbial by-product-like region. The EOM matrix shows a peak at the humic-like region (i.e., region V) that is not present in the IOM matrix. This implies that cells excrete marine humic-like substances during growth. The quality of the proteins released with EOM remains the same during growth; only the quantity increases until reaching 31% of the total DOC in EOM samples and up to 66% of the total DOC in IOM samples (Fang et al. 2010). Parlanti et al. (2000), working on seawater samples collected from nine different spots of the Gulf of Saint Malo, observed that the marine humic-like/tyrosine-like ratio was the only ratio that remains constant at all stations and they proposed that these compounds could be the result of biological activities. When degrading an algal bloom sample by mixing the solution with nutrient-free natural, artificial seawater or MilliQ water, they found that the decrease in the tyrosine-like peak was coupled with an increase in the marine humic-like peak. They hypothesized that tyrosine-like compounds may be protein-like material from algae, and that marine humic-like may have another origin such as bacterial origin. Jørgensen et al. (2011) also associated protein-like compounds with biological activities and humic-like compounds with microbial oxidation and degradation of organic matter. Parlanti et al. (2000) proposed to use these two parameters as markers to estimate biological activities in coastal zones, as it could give information on the age of the algal bloom.

AOM was also characterized using solid state analysis such as Fourier Transform InfraRed spectroscopy (FTIR) (Sandin et al., 2013), Pyrolysis-Gas Chromatography coupled with Mass Spectroscopy (Py-GC-MS) (Gillam et al., 1985) or Nuclear Magnetic...
Resonance - either $^{13}$C-NMR (Gillam et al., 1985; Benner et al., 1992; Repeta et al., 2002; Hedges et al., 2002; Nguyen et al., 2005) or $^1$H-NMR (Gillam et al., 1985; Repeta et al., 2002). Figure 1-7 plots the FTIR profile of the exopolymers secreted by Scenedesmus sp. during growth (Sandin et al., 2013).

\[\text{Figure 1-7: FTIR analysis of algal exopolymers substances from Scenedesmus sp. culture} \text{ (Sandin et al., 2013)}\]

In addition to the major band at 3282 cm$^{-1}$ characteristic of the hydrogen bonding, two bands relative to amide I and amide II (1627 cm$^{-1}$ and 1533 cm$^{-1}$, respectively), and one peak relative to carbohydrates (1063 cm$^{-1}$) are observed. These results confirm the strong proportion of protein-like and carbohydrate-like compounds in the AOM excreted by algal cells.

Py-GC-MS profiles of two different algal culture solutions ($D$. pulchellum and $S$. quadricauda) are presented in Figure 1-8. Samples were prepared by concentrating the solution using low temperature rotary evaporation (Widrig et al., 1996).
Figure 1-8: Py-GC-MS profiles of monocultures (a) D. pulchellum and (b) S. quadricauda. Solutions were collected from the reactor culture, concentrated using low temperature rotary evaporator and air-dried for 2 days (Widrig et al., 1996)

Pyrochromatograms of AOM are usually characterized by the presence of pyrroles, furans, nitriles and phenols (Gillam et al., 1985; Widrig et al., 1996). Pyrroles and nitriles molecules are produced from the pyrolysis of proteins and nucleic acids; furan-like molecules are polysaccharides by-products; phenols are the result of the thermal degradation of lignin, proteins or polycarboxylic acids (Leenheer, 2009; Gillam et al., 1985; Widrig et al., 1996). In Figure 1-8, pyrochromatograms are mainly described by nitrogen containing pyrolysis fragments and very few fragments associated to polysaccharides. Widrig et al. (1996) suggested that the lack of polysaccharide fragment or the strong amount of nitrogen containing fragments can be explained by a rapid algal cell division, such as during the exponential phase of growth.

NMR techniques have also been used in AOM samples larger than 1.6 μm (Hedges et al., 2002), in AOM with a size comprised between 0.2 μm and 1 kDa (Benner et al., 1992; Repeta et al., 2002; Aluwihare et al., 1997), and in XAD resins (XAD-2 and XAD8) extracted AOM samples (Gillam et al., 1985; Nguyen et al., 2005). $^{13}$C-NMR profiles of colloidal AOM (Hedges et al., 2002) and AOM fraction with a size comprised between 0.2 μm and 1 kDa (Repeta et al., 2002) are presented in Figure 1-9.
Figure 1-9. $^{13}$C-NMR of (a) colloidal AOM and (b) AOM fraction with a size comprised between 0.2 μm and 1 kDa. (Hedges et al., 2002; Repeta et al., 2002)

$^{13}$C-NMR profiles of seawater AOM are characterized by strong resonances in the alkyl carbon region (0-45 ppm), in the carbohydrate region (O-alkyl: 60-95 ppm and di-O-alkyl: 95-110 ppm), in the aromatic carbon region (110-160 ppm) and in the carbonyl region (160-215 ppm) (Gillam et al., 1985; Repeta et al., 2002; Nguyen et al., 2005; Hedges et al., 2002; Benner et al., 1992; Leenheer, 2009). The strong resonance at 175 ppm is characteristic of carbon in amide, carboxyl and/or ester (Hedges et al., 2002; Benner et al., 1992). Gillam et al. (1984), working on AOM fraction isolated on XAD-2 resin, observed that the IOM of the *P. tricornutrum* culture was showing a strong peak at 180 ppm than the EOM. $^{13}$C-NMR analyses are confirming the complex nature of the AOM composed by a mixture of proteins and carbohydrates. The fraction of AOM from
the Woods Hole seawater, North Pacific (Figure 1-9b) was also analyzed using $^1$H-NMR (Repeta and al., 2002) (Figure 1-10).

Figure 1-10: $^1$H-NMR of the Woods Hole seawater fraction comprised between 0.2 μm and 1 kDa (Repeta et al., 2002)

Resonances observed between 0.5 and 1.8 ppm are assigned to alkyl proton attached to carbon removed from aromatic rings or carboxylic groups. This region is attributed to the lipids by Aluwihare et al. (1997). From 1.8 to 3 ppm, the resonance corresponds to protons attached mostly to carbon positioned on α to aromatic ring and carboxylic groups, and are characteristic of proteins. Region from 3 ppm to 4.7 ppm (alcohol and ether H attached to carbon positioned on α to oxygen), and from 5 to 5.5 ppm correspond to the carbohydrate compounds. From 6.4 to 9 ppm, the resonances are assigned to aromatic and olefinic protons (Gillam et al., 1985; Aluwihare et al., 1997; Repeta et al., 2002). The $^1$H-NMR profile of the Woods Hole seawater fraction comprised between 0.2 μm and 1 kDa is characterized by strong resonances for carbohydrates, proteins and lipids.
1.2. Ultrafiltration

1.2.1. General

In water treatment, membrane processes are widely used. Four types of membranes can be distinguished according to their separation range: Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO). Membranes are semi-permeable structures that allow the separation of particles (i.e., colloids, dissolved organic matter, bacteria and even viruses) from a solution, depending on their size pore/molecular cutoff characteristic. Figure 1-11 summarizes the different separation characteristics of each type of membrane and the range of pressure needed to operate them (Meyn, 2011).

![Figure 1-11: Domain of separation for membrane processes (Meyn, 2011)](image)

The good membrane operation is mainly threatened by the fouling phenomena. Fouling is defined by the adsorption or deposition of material on the surface or within the pores of the membrane. Non-dissolved, colloidal or biologic matter accumulates at the membrane surface, building an additional layer on the top of the membrane. This
additional layer increases the hydraulic resistance of the membrane and more energy is required to operate the membrane. For porous membranes (MF and UF), the formation of a cake layer on the membrane surface modifies the rejection efficiency of the membrane by reducing the effective pore size of the membrane. Different fouling mechanisms have been identified in MF/UF. They are classified in three categories: the particulate fouling, the organic fouling and the biofouling, and will be developed in the following sections.

1.2.1.1. Particulate fouling

The particulate fouling is mainly due to colloids and biological inert particles present in solution (Pearce, 2009; Jiang, 2007). It is the accumulation of small particles on the surface of the membrane. This accumulation forms a thin film that increases the hydraulic pressure of the membrane and requires applying a higher transmembrane pressure in order to maintain the filtration flux. This fouling is generally reversible by hydraulic cleaning measures such as backflush or/and air scrubbing.

The particulate fouling can be predicted by measuring the Silt Density Index (SDI) or the Modified Fouling Index (MFI). The colloid concentration of the feed solution, the particle size distribution, and the compressibility of the colloids are affecting the fouling. To prevent particulate fouling, pretreatments such as coagulation can be implemented.
1.2.1.2. Organic fouling

Organic fouling is caused by the adsorption of dissolved organic substances on the membrane surface or in its pores due to the interaction between the membrane surface material and the natural organic matter (Figure 1-12).

![Figure 1-12: Different layers of Organic Fouling (a) Non-interpenetrated layers, (b) Interpenetrated layers (Guizard et al., 1996)](image)

Strong NOM foulants can be divided in four categories: proteins, amino-sugars, polysaccharides and aromatics. Makdissy et al. (2003) observed that the most important foulant for polymeric membrane was the organic colloidal fraction of NOM, mainly composed of bacterial cell wall residue rich in sugars and amino-sugars. Different studies indicated that the most problematic foulants for low pressure membrane were the polysaccharide-like and the protein-like fractions (Amy et al., 1999; Kimura et al., 2004; Lozier et al., 2008). However, other studies such as Jucker et al. (1994) and Aoustin et al., (2009) found that humic substances had an important role in the organic fouling of the UF polymeric membranes. They reported that humic acids tend to cause irreversible fouling and fulvic acids seem to be a weaker foulant and responsible of a more reversible fouling. Physical-chemical characteristics of the feed such as NOM concentration,
hydrophobicity, charge, pH, ionic strength and calcium concentration are affecting the organic fouling (Pearce, 2009; Jiang, 2007). Coagulation and pH adjustment are treatment options to reduce the organic fouling.

1.2.1.3. Biofouling

Biofouling is the unwanted adhesion of microorganisms at the membrane surface and growth of biofilm (Matin et al., 2011). The first stage of a biofilm formation is the deposition of single cells in the surface of the membrane (attachment). Once the cells are attached, they can move across the surface and agglomerate. This phase can take few seconds. Cells are then excreting exopolymers, which bind the biofilm to the surface of the membrane. It is then protected and irreversibly attached to the membrane. A few days later, the biofilm grows and creates micro-colonies (growth of the biofilm). During the third and last stage of the biofilm formation (detachment and dissemination), the micro-colonies are releasing young cells that will be able to attach to virgin membrane surface area and create a new and fresh biofilm. This stage can last days to months (Mansouri et al., 2010; Davies, 2003). Biological analyses such as Assimilable Organic Carbon (AOC) and Biofilm Formation Rate (BFR) are good biofouling indicators. The different stages of a biofilm formation are presented in Figure 1-13.
Figure 1-13: Biofilm formation: (1) individual cells populate the surface and produce Extracellular polymeric substances. Attachment becomes irreversible (sec-min) (2) biofilm architecture develops and matures (hours-days) (3) single cells are released from the biofilm (days-months). (Davies, 2003)

Once the biofilm is well established, chemical cleaning with disinfectant is often only partially efficient and dead cellular matter released during the disinfection are becoming fresh nutrients for living microorganisms, which leads to an intensive biological re-growth (Fritzmann et al., 2007). Biofouling is a major problem for RO membrane process due to its self-replicate nature and its rapid adaptation to physical and chemical changes (Khan et al., 2013).

1.2.2. Polymeric membrane

Most of the UF membranes used for water treatments are polymeric membranes. Two types of material membranes can be distinguished: (1) membranes characterized by their hydrophilicity (i.e., made of cellulose, polyacrylonitrile, hydrophilized polyethylene, hydrophilized polysulfone, polyethersulfone – PES,…) and (2) membranes characterized by their high strength and durability (made of polyvinylidene fluoride – PVDF) (Kubota
et al., 2008). In the past decade, PVDF membrane production and applications have increased to become the main type of membrane used for water treatment, due to their long lifetime of up to ten years (Kubota et al., 2008). Modules of hollow fibers are most commonly used. They can be operated with different filtration modes (Figure 1-14): (a) the inside-out, the feed solution is inside the membrane and the permeate is collected outside the membrane; (b) the outside-in mode, the feed solution is outside the membrane and the permeate is collected inside the polymeric fibers.

![Figure 1-14: Filtration modes: (a) Inside-out mode and (b) Outside-in mode](image)

Polymeric hollow fibers can be operated in cross-flow or dead-end modes (Figure 1-15); however, dead-end filtration is most commonly used in water treatment for energy consumption reasons.
1.2.3. Ceramic membrane

Ceramic membranes are composed of optional porous layers (metal oxide, glass) on a porous support (metal oxide), which has larger pore size (Burggraaf, 1996). The most common architecture for ceramic membrane is presented in Figure 1-16.

Figure 1-16: Asymmetric Ceramic membrane  (1) Porous support (pore diameter dp = 1000 - 15000 nm); (2) Intermediate layer(s) (dp = 100-1500 nm); (3) Top layer (dp = 3-100 nm); (4) modification of the top layer (Burggraaf, 1996)
The support layer is characterized by large pore size, to reduce flow resistance and allow high filtration flux. The top layer is the active separative layer providing the retention properties of the membranes. Its thickness should be as thin as possible, not to add any flux resistance. The separative layer can also be modified to improve the membrane rejection. The intermediate layer (optional) prevents the penetration of the precursor of the top layer material into the pores of the support. Furthermore, it helps regulate the pressure drop across the top layer of the membrane during filtration. In many cases, the intermediate layer is also used to improve the quality of the support system. To produce a graded system, the intermediate layers are added with gradually decreasing layer thickness and pore size from the bulk support to the separative layer. The separative layer is usually made of metal oxides such as alumina, titanium oxide, zirconium oxide, ceria and silicate (Burggraaf, 1996; Meyn, 2011; Bhave, 1991). Electrochemical properties of ceramic membranes influence the selectivity of the membranes. Due to the amphoteric behavior of the metal oxides, the surface sites of the separative layer are pH-dependent. The point of zero charge is an important parameter that permits to predict the charge of the membrane surface and the interaction between NOM and the membrane. When the pH of the solution is higher than the pH of zero point charge (pH_{zpc}), the hydroxyl groups present at the surface of the membrane are deprotonated and the surface is negatively charged. On the contrary, when the pH is lower than pH_{zpc}, the hydroxyl groups are protonated and the surface is positively charged (Mullet et al., 1997).

The pore size and the pore shape also have an important role on the separative properties of a membrane (Figure 1-17) (Burggraaf, 1996).
The pore network of a ceramic membrane can present different types of pore, determined by the size of the crystallites forming the network. During the heat treatment, the primary particles and their aggregates can greatly vary in morphology. The resultant pore network has varying degrees of randomness comprising isolated pores, dead-end pores and tortuous pores. An ideal membrane is a membrane without any dead-end pore to avoid any dead volume and have a higher filtration flux.

It is also essential to know the space that the pores occupy and the pore distribution in the membrane. The porosity parameter permits to evaluate the free space of the membrane. It is defined as the ratio between the void space and the total volume of the membrane: the higher the porosity, the higher the flux. The stability of the ceramic membrane to high pressure permits the measurement of the pore size distribution and the porosity by the bubble point test. This method is based on the Darcy law that links the pressure $P$ and the pore diameter $dp$:

$$dp = \frac{4 \times \gamma \times \cos(\theta)}{P} \times 0,75$$
with \( \gamma \), the surface tension of the wetting liquid; \( \theta \), the contact angle of the wetting liquid and 0.75 a correctional factor (used for non-tubular pores like in ceramic membrane).

The porosity is usually comprised between 30-40\% of the volume of the membrane and the pore size of the membranes can vary from macropores (> 500 nm to nanopores (< 2 nm) (Burggraaf, 1996).

In many applications the unique thermal, chemical and mechanical properties of ceramic membrane give them significant advantages over polymeric membranes, stainless steel membranes and conventional filtration technique (for example decantation, centrifugation and media filtration) (Sondhi, 2003). All the advantages that the ceramic membranes offer are summarized below (Bhave, 1991):

1. High temperature stability (> 1000°C)
2. Mechanical stability under large pressure gradients (non-compressible, no creep)
3. Chemical stability (especially in organic solvents)
4. “No ageing”, long lifetime
5. Rigorous cleaning operation allowable (steam sterilization, high backflush capability, use of strong acids or bases)
6. (Electro) catalytic and electrochemical activity easily realizable
7. High throughput volume and diminished fouling
8. Good control of pore dimension and pore distribution

1.2.4. Ultrafiltration of seawater

The efficiency of the conventional pretreatments such as coagulation-flocculation-sedimentation, Dual Media Filter (DMF) or Powder Activated Carbon (PAC) is limited
when applied to high fouling potential waters (Brehant et al., 2002; Kim et al., 2011; Voutchkov, 2010; Park et al., 2013; Guastalli et al., 2013; Zhang et al., 2011b). DMF is still dominating the Seawater Reverse Osmosis (SWRO) pretreatment technology over the world (Voutchkov, 2010), and Figure 1-18 displays pictures of DMF operated in normal condition and during an algal bloom (Park et al., 2013). Highly concentrated algal solution caused an early exhaustion of the filter due to a thick floating sludge or scum accumulation on the top. In this condition, DMF could only be operated for 10-12 hours before a breakthrough, which would lead to high SDI value and RO contamination.

![Figure 1-18: Pictures of DMF operated during normal operation and during an algal bloom (Park et al. 2013)](image)

Several studies (Brehant et al., 2002; Voutchkov, 2010; Guastalli et al., 2013) compared DMF pretreatment and low membrane pressure pretreatment. They concluded that for long-term operation and during algal bloom event, low-pressure membranes were more suitable than DMF for the pretreatment of seawater. Low-pressure membranes allow the production of a more stable water quality with a better removal of algal cells, foulant
material. Kim et al. (2011) studied the potential of three different pretreatments: DMF and Filter Absorber (FA). An activated carbon layer was built on the top of the FA and permitted to give to this process a larger organic content reduction and particle removal compared to DMF. However, they are characterized by a similar breakthrough behavior. Interest for UF filtration for SWRO pretreatment has strongly increased over the last decade. Figure 1-19 shows the evolution over time of SWRO plants using UF pretreatment (Busch et al., 2011). The three largest plants implementing UF as Reverse Osmosis pretreatment were Fukuoka (Japan, 50 000 m$^3$/d), Jeddah Islamic Port (Saudi Arabia, 26 800 m$^3$/d) and Yuhuan (China, 34 500 m$^3$/d) (Busch, 2010). The two last treatment plants are dealing with very challenging feed water and are needing efficient pretreatment. Within the next months (Freyberg, 2014), the largest SWRO plant (500 000 m$^3$/d) located in Magtaa, near Oran (Algeria) will be operating. This supersized desalination plant will use polymeric UF membranes to protect their RO membranes (Busch, 2010).
Due to the increasing interest of low-pressure membrane for seawater pretreatment, the fouling potential of marine water on polymeric membrane has been intensively studied in the past few years. A large majority of the published work deals with polymeric membranes, but few studies on ceramic membranes were also conducted. In all cases of algal solutions and independently of the water matrix (i.e., freshwater or seawater), a strong, rapid, and hardly reversible fouling has been reported on both, polymeric membranes (Babel et al., 2011; Lee et al., 2004; Castaing et al., 2010; Castaing et al., 2011; Chiou et al., 2010; Lee et al., 2006; Jeong et al., 2011; Kwon et al., 2005; Ladner et al., 2010; Park et al., 2013; Pearce et al., 2004; Qu et al., 2012; Qu et al., 2012; Rickman et al., 2012; Schurer et al., 2013; Yu et al., 2014; Alazmi et al., 2010; Villacorte, 2013; Zhang et al., 2011a; Zhang et al., 2013a) and ceramic membranes (Cui et al., 2013; Cui et al., 2011; Zhang et al., 2013b; Zhang et al., 2013c; Xu et al., 2010b; Matsui et al., 2012).
The same trends and observations can be made for the fouling potential of AOM on either polymeric or ceramic membranes. As a consequence, conclusions from studies using polymeric and ceramic membranes will be discussed in this same section and membrane material will always be mentioned.

1.2.4.1. Ultrafiltration fouling mechanisms

Lee at al. (2006) reported a strong fouling for the polymeric filtration of freshwater reservoir affected by an algal bloom in comparison to different fractions (hydrophobic, hydrophilic and transphilic) of freshwater sources. UF and MF fouling caused by marine or fresh AOM is governed by the three following mechanisms: cake layer formation, pore constriction and strong adhesion between the AOM and the membrane for either polymeric (Babel et al., 2011; Castaing et al., 2010; Castaing et al., 2011; Ladner et al., 2010; Qu et al., 2012; Yu et al., 2014; Villacorte, 2013) or ceramic membranes (Zhang et al., 2013b; Zhang et al., 2013c). Figure 1-20 summarizes the different fouling mechanisms governing the membrane fouling by algal EOM on hydrophobic PES membrane (Qu et al. 2012). Cases (a) and (b) describe the formation of a cake layer on the surface of the membrane. Cases (c) and (d) illustrate the electrostatic repulsion between the molecule and the membrane surface: negatively charged compounds are repulsed by the PES UF membrane. Case (d) shows the breakthrough of the neutral compounds without interaction with the membrane. Cases (e) and (f) represent the hydrophobic attraction/repulsion between the AOM and the membranes.
1.2.4.2. Importance of the algal cells on the fouling potential of marine solution

The role of algal cells in the polymeric UF fouling has been studied by Villacorte (2013). He studied two algae responsible for algal bloom (\textit{Chaetoceros affinis} and \textit{Microcystis sp.}). UF experiments were performed with the culture solution and after prefiltration through 5 μm and 1 μm for \textit{Chaetoceros affinis} and \textit{Microcystis sp.}, respectively. Results showed a better correlation between the fouling rate and the Transparent Exopolymer (TEP) concentration than between the fouling rate and algal cells. He suggested that algal cell concentration was not the main driver for polymeric UF fouling, despite a good removal of algal cells provided by low-pressure membranes. Castaing et al. (2010) also reported a great cell removal efficiency of polymeric MF and UF membranes with a minimal removal of 99%.

Few studies have been conducted on AOM excreted by algal cells (i.e., EOM) and bounded to it (bounded-EOM). Chiou et al. (2010) studied the fouling potential of three different freshwater algae of similar cell size (\textit{Chlorella vulgaris}, \textit{Chodatella sp.} and \textit{Microcystis sp.}) on polymeric UF. They isolated the cells by filtering the culture solution.
through 0.45 μm and re-suspended the retentate (i.e., cells) in a solution of 0.003 N NaClO₄ at pH7. The final cell concentration for each algal solution was 2x10⁶ cells/mL. Figure 1-21 displays an image of *Microcystis sp.* and the bounded-EOM associated (Chiou et al., 2010).

![Image of Microcystis sp.](image)

**Figure 1-21: Measurement of bounded-EOM volume and cell volume for *Microcystis sp.*

(scale bar = 10 μm) (Chiou et al., 2010)**

The volume of bounded-EOM was species-specific and was the more important for *Microcystis sp.* FTIR analysis revealed that bounded-EOM was mainly composed of polysaccharides and proteins for the three algae, with different relative abundance. *Microcystis sp.*, which was characterized by the higher amount of polysaccharides per mg of DOC, was responsible for the strongest fouling toward cellulose membrane. They concluded that the size of the cells was not a major parameter for the fouling potential of an algal solution, but the quality of the bounded EOM and its proportion of polysaccharides could be.
1.2.4.3. Importance of algal organic matter on fouling potential of marine solution

1.2.4.3.a. Role of the HMW structures on the fouling potential of algal solutions

Different studies conducted on surface water organic matter (SWOM) and AOM highlighted the important role of High Molecular Weight (HMW) compounds on the fouling of polymeric and ceramic membranes (Lee et al., 2004; Lee et al., 2006; Fan et al., 2001; Qu et al., 2012; Qu et al., 2012; Villacorte, 2013; Zhang et al., 2013c). Fraction of SWOM larger than 30 kDa was reported to be responsible for the greater flux decline for PVDF membrane (Fan et al., 2001). Qu et al. (2012) pre-filtered *Microcystis* sp. solution through 2 μm and 0.45 μm before polymeric UF filtration using PES membrane characterized by a 100 kDa cutoff. They observed that compounds larger than 0.45 μm had a relatively negligible role in the membrane fouling. However, compounds passing through 0.45 μm but retained by a 100 kDa cutoff membrane seemed to highly contribute to the polymeric UF fouling. In another study, using 100 nm pore-sized ceramic membranes, Zhang et al. (2013b), prefiltered a freshwater *Microsytis* sp. solution through 5 μm, 1 μm and 0.45 μm before UF. They found that prefiltration of the feed helped to minimize the fouling. However, it was unexpected to see that the best pretreatment was not provided by the lowest pore size filtration but by the prefiltration through 5 μm (Figure 1-22).
They hypothesized that the strong fouling of the algal solution was caused by the bounded AOM, which strongly and irreversibly attached to the membrane. For compounds lower than 1 μm, the cake layer would be denser and small compounds would interpenetrate the pores, which would cause a strong and irreversible fouling. On the other hand, for compounds with a size comprised between 1 μm and 5 μm, the particulate layer would help to protect the interpenetration of the pores by building a porous layer with a lower hydraulic resistance.

1.4.2.3.β. Impact of the age of the bloom on the fouling potential of algal solutions

The quality of the AOM changes during an algal bloom and the fouling can be affected by this change. Zhang al. (2013b) studied the fouling potential of an AOM solution produced by Microcystis sp. at three different stages of growth (early exponential phase, late exponential phase and stationary phase). Ceramic MF membrane (ZrO₂-TiO₂, 0.1
μm) was used to filter the AOM solution at same initial DOC of 5 mg/L. At stationary phase, fouling was exacerbated and irreversible. It was suggested that the biopolymer concentration and more specifically the hydrophilic biopolymers could be responsible for the stronger fouling potential at the late phase of growth.

Several studies agree to give an important role to the nature and the hydrophilic character of the AOM (and most particularly the HMW fraction) for the fouling of polymeric (Lee et al., 2004; Lee et al., 2006; Fan et al., 2001; Ladner et al., 2010; Qu et al., 2012a; Qu et al., 2012b; Her et al., 2004; Yu et al., 2014; Alazmi et al., 2010; Zhang et al. 2013a) and ceramic membrane (Zhang et al. 2013b; Zhang et al. 2013c). Polysaccharides appear to be mainly hydrophilic and proteins, more hydrophobic (Qu et al., 2012a; Qu et al., 2012b; Yu et al., 2014; Zhang et al., 2013c; Henderson et al., 2008). Qu et al. (2012b), working on PES UF membrane, found that the hydrophilic fraction (HPI) of AOM was characterized by a high fouling rate, but the fouling caused by the hydrophobic fraction (HPO) was more irreversible. In contrast, Yu et al. (2014) found that irreversible fouling of PES UF membrane was mainly driven by the hydrophilic fraction. Yu et al. (2014) suggested that, because the former study had focused on the filtration of hydrophobic and hydrophilic fractions separately, conclusion could not be applied to a natural solution were both fractions could interact and compete for membrane surface and pore. They also proposed that the polysaccharide fraction contains more LMW molecules that could enter and block the pores, inducing the strong irreversibility of the fouling caused by a polysaccharide-rich solution. Zhang et al. (2013b) separated and characterized three different layers of fouling material from the ceramic UF filtration of Microcystis sp. The
outer and middle layers were essentially composed of hydrophobic HMW compounds (i.e., proteins), whereas the inner layer was characterized by lower biopolymers with hydrophilic character (i.e., polysaccharides).

To summarize this section, in natural AOM solution, fouling is mainly due to HMW compounds (i.e., polysaccharides and proteins). When studying the hydrophilic compounds (polysaccharides) and hydrophobic compounds (proteins) separately, it was found that protein leads to a stronger irreversible fouling, however, when a natural solution was studied, it was found that polysaccharides, that are smaller molecules, would have a major role in the irreversibility of the fouling due to pore blocking. Hydrophobic compounds (proteins) would foul by interacting with the membrane surface, as they are considered of bigger size.

1.2.4.4. Importance of pH and calcium content on the fouling potential of marine solution

Parameters such as pH and calcium concentration can also affect the fouling of low-pressure membranes. Xu et al. (2010a) and Yu et al. (2014) studied the impact of the pH on the filtration of AOM solution through ceramic UF and polymeric UF membrane, respectively. These two studies demonstrated that DOC removal was higher at neutral-alkaline pH. Because the surface of both membranes were negatively charge at neutral/alkaline pH, the repulsion between the AOM and the membrane was enhanced. Regarding the effect of calcium concentration, conclusions are more controversial. Several studies observed a decrease in the resistance flux and an increase in the
irreversibility of the fouling by adding Ca\textsuperscript{2+} (Qu et al., 2012a; Yu et al., 2014; Zhang et al., 2013b; Alazmi et al., 2010). Yu et al. (2014) considered that calcium screened the negative charge of the membrane, and permitted a better aggregation of foulants, which form a denser cake layer, and that aggregation would preferentially involve polysaccharides due to their high content of carboxylic groups complexing with Ca\textsuperscript{2+}. The same observations were made with ceramic membranes: Zhang et al. (2013a) also observed a fouling reduction of the ceramic membrane with an increase in the irreversibility of the fouling when Ca\textsuperscript{2+} was added. Large AOM-calcium complexes could be formed at the surface of the membrane and not easily backwashed. Nonetheless, improvement in fouling was not proportional to the Ca\textsuperscript{2+} concentration. When adding large amounts of Ca\textsuperscript{2+}, the AOM-calcium complexes would start to build up a thick cake layer and would increase the resistance flux. An optimal calcium dose is necessary to lower the fouling potential of ceramic membrane. On the contrary, some studies observed little effect on the fouling of polymeric (PES) membrane by adding calcium (Lee et al., 2004; Lee et al., 2006). Lee et al. (2006) studied the Ca\textsuperscript{2+} effect on a solution of freshwater HPO (humic substances) fraction and a model protein solution (albumin). No change in fouling potential was observed in both solutions. The authors hypothesized that the size of the HPO compounds and albumin compound (<10 kDa and 66 kDa, respectively) were too small in comparison to the pore size of the membrane (100 kDa), and that even if they were interacting with Ca\textsuperscript{2+}, aggregates would not be big enough to block the 100 kDa pores of the PES membrane.
1.3. Pretreatments before membrane filtration

Different pretreatments such as Power Activated Carbon (PAC) or coagulation-flocculation have been studied for the UF pretreatment of AOM solutions. Zhang et al. (2011) studied PAC followed by UF for an algal-rich solution. Removal of cells was total for either PAC-UF system or UF alone. Even though PAC permitted to increase the EOM removal by 10%, polysaccharides and proteins were not significantly removed, and PAC-UF is not suitable for RO pretreatment.

Coagulation-flocculation (CF) is viewed as a treatment of choice before low pressure membrane to ensure a good membrane operation, mostly during algal bloom event (Zhang et al., 2013b; Schurer et al., 2013). Coagulant can be added in-line before the membrane process, or followed by flocculation-decantation, or followed by flocculation-flotation (also called Dissolved Air Flotation - DAF). CF permits to keep the integrity of the cells as no cell damage were observed during either coagulation or flocculation (Chow et al., 1999), and thus ensures a minimum release of IOM in the solution.

Morphology, motility, surface charge and EOM composition have an impact at the optimum coagulation conditions (Eldridge et al., 2012; Henderson et al., 2008; Widrig et al., 1996). Eldridge et al. (2012) compared the coagulation efficiency of five different algal species (Tetraselmis suecica, Chlorococum sp., Nannochloropsis salina, Dunaliella tertiolecta and Isochrysis galbana). The coagulant dose was proportional to the total surface area of suspended particles and a higher amount of cells would require a higher dose of coagulant. The dose of coagulant would also be impacted by the concentration of proteins and polysaccharides in the AOM sample. Biopolymers playing a coagulant-aid role, the coagulant demand decreases with an increase of the biopolymers concentration.
(Henderson et al., 2010). Kuroiwa et al. (2013) studied the impact of CF on DOM concentration and composition of a solution of *Cochlodinium polykrikoides* using FEEM analyses (Figure 1-23).

![Figure 1-23: FEEM spectra of Cochlodinium polykrikoides: (a) culture, (b) after coagulation-flocculation, sedimentation (Kuroiwa et al., 2013)](image)

A decrease in intensity was observed for all chromophore peaks after CF; however, the DOC of the solution remained similar. CF might preferentially remove chromophoric compounds such as proteins that, in this case, represents a small proportion of the DOC. Widrig et al. (1996) also found that CF preferentially eliminates “the parent material producing aliphatic nitrogen-containing fragments in pyrolysis”. This parent material might correspond to peak A and peak B in Figure 1-23 (i.e., protein-like compounds), which is well removed after CF.

Xu et al. (2013) observed a reduction of the fouling of ceramic membrane by implementing in-line ferric coagulation, due to a good removal of turbidity and DOC.
Coagulation allows the aggregation of molecules to form larger assemblage, but also neutralizes the negative charges of the colloids and decrease the interactions between AOM and metal oxide, which permits to minimize the fouling. Jeong et al. (2011) observed that even if the turbidity removal was similar between a conventional pretreatment (coagulation – flocculation – sedimentation – DMF) and a Coagulation – Flocculation- Sedimentation (CFS) followed by MF treatment, the RO efficiency (recovery, flux and salt rejection) was better after CFS-MF pretreatment. Ceramic membranes are prone to stronger fouling caused by AOM than polymeric membranes, and the filtration of high DOM content and algae-rich seawater cannot be performed in a sustainable manner without coagulation-flocculation (Cui et al., 2013; Cui et al., 2011; Meyn, 2011). In-line coagulation-flocculation followed by a natural sedimentation permitted to greatly reduce the fouling of the Tianjin Bohai Bay (China) seawater (Figure 1-24) (Cui et al., 2011.).

![Figure 1-24: Permeability of multi-channel ceramic membrane (ZrO2, Al2O3, 50 nm)](Cui et al. 2011)
DAF is also known to be a potential option for low pressure membrane pretreatment during an algal bloom (Anderson et al., 2012). DAF is an interesting technique as it uses the natural algal buoyancy property of algal cells. DAF efficiency is known to be impacted by the morphology and the mobility of the algal species (Henderson et al., 2008). The algal cell removal achieved with DAF is high (84% to 99%), and biopolymers are usually well removed as they play the role of coagulant aid, with a total AOM removal of 46 up to 71% (Henderson et al. 2010b). After DAF, turbidity, Total Suspended Solids and SDI values meet the RO requirements (Guastalli et al., 2013), and the Shuwaikh SWRO (Kuwait) was able to run during algal bloom event thanks to its pretreatment configuration composed of DAF – UF (Park et al., 2013).

The CF operation can also be conducted with an addition of clay. Clay is widely used to mitigate algal bloom in the sea, enforcing the algal cells to sediment (Beaulieu et al. 2005). This property of clay could possibly enhance the sedimentation of algal cells after coagulation. Ladner et al. (2010) studied the impact of Kaolinite (KAO) on the FeCl₃ CFS before low pressure membrane filtration of the *Heterocapsa pygmaea* culture.

During CFS the addition of KAO (200 mg/L) improved the removal of algal cells but increased the turbidity of the produced water, leading to a stronger membrane fouling. The solution treated with KAO + FeCl₃ exerted stronger but more reversible fouling than the solution treated with FeCl₃ alone. They suggested that the cake layer produced by KAO + FeCl₃ had a looser arrangement, and that the formed colloids had less interaction with the membrane. The addition of clay showed two different advantages for the CFS – low-pressure membrane system: a better algal cell removal and a more reversible fouling layer.
Regarding the type of coagulant, ferric chloride at acidic pH should preferentially be used instead of aluminum coagulant due to the stronger scaling potential of the aluminum coagulant toward RO membrane (Edzwald et al., 2011; Meyn, 2011).
2. Material and Methods

2.1. Algae culture

2.1.1. Algae species and Culture Protocol

Four different ubiquitous seawater algae responsible for algal bloom were studied during this project. Strains were provided by the Oceanographic Observatory of Banyuls-sur-Mer (ARAGO), France. Microscopic pictures and corresponding algal blooms are presented in Figure 2-1.

*Skeletonema costatum* (SKC): *Skeletonema costatum* belongs to the diatom group. Diatom is among the most common type of phytoplankton existing in the sea. It can form chains of 3 to 15 cells. It is characterized by a cell wall made of silica. Its length can vary between 2 to 60 μm and its diameter between 2 to 21 μm. SKC blooms usually appear during winter-spring and summer season (Naik et al., 2010; Anon). Algal bloom caused by SKC causes hypoxia of co-occurring species (Xu, 2012; Chen, 2003).

*Tetraselmis sp.* (TET): *Tetraselmis sp.* belongs to the prasinophyceae group. It is a unicellular flagellate. TET doesn’t form colonies and is about 10-20 μm long. It contains a chloroplast, essential for the photosynthesis of the cell. Its high concentration of Chlorophyll contained into the chloroplast gives it its green color (Algabase). *Tetraselmis sp.* is blooming every summer in the coast of California since 2010 (SCCOOS; Oceandatacenter). Algal bloom caused by TET is characterized by a green foam, but causes no health hazard.

*Hymenomonas sp.* (HYM): *Hymenomonas sp.* belongs to the coccolithophorid group “round-stone-bearers” (Monterrey Bay Aquarium Research Institute). The cell wall is
composed by coccoliths made of calcium carbonate. Cells are spherical with a diameter comprised between 8 to 30 μm. Coccolithophorids are responsible for late spring bloom in the Celtic Sea (North East Atlantic) (Van Oostende et al., 2012).

*Synechococcus* (SYN): *Synechococcus* is a marine cyanobacteria. The cells are relatively small (below 2 μm) and form chains. SYN is very abundant in nutrients rich environments. It is among the most common type of picoplankton existing in the open sea (Wang et al., 2011). Algal blooms caused by SYN mostly happen in summer time (Wang et al., 2011; Beardall, 2008).
Figure 2-1: Microscopic images of algae species and example of bloom. (a) *Skeletonema costatum* (bloom in Kiawah Island, USA), (b) *Tetraselmis sp.* (bloom in San Diego, USA), (c) *Hymenomonas sp.* (cocolithophorid bloom in Alaska and the Bering Sea), (d) *Synechococcus* (bloom in Dewees Island, USA). SEM and bloom images from NCCOS; Oceandatacenter; NASA; Barlow; Alfred Wegener Institute for Polar and Marine Research; Sciencephoto
Algae were cultured in F/2 Guillard medium. Seawater was sampled in the Red Sea, filtered through 0.45 μm and stored in a dark room. The medium was then prepared by adding nutrients to the seawater. The final solution was autoclaved at 120 °C for 20 minutes. After cooling down, the algae culture was inoculated to a new medium. A new inoculation, in a 50 mL tubes, was conducted every two weeks to keep the algal culture at exponential phase of growth.

Table 2-1: Composition of F/2 medium for 1L (NCMA)

<table>
<thead>
<tr>
<th>Component</th>
<th>Stock Solution</th>
<th>Quantity</th>
<th>Molar Concentration in Final Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO₃</td>
<td>75 g/L dH₂O</td>
<td>1 mL</td>
<td>8.82 x 10⁻⁴ M</td>
</tr>
<tr>
<td>NaH₂PO₄. H₂O</td>
<td>5 g/L dH₂O</td>
<td>1 mL</td>
<td>3.62 x 10⁻⁵ M</td>
</tr>
<tr>
<td>Na₂SiO₃. 9H₂O</td>
<td>30 g/L dH₂O</td>
<td>1 mL</td>
<td>1.06 x 10⁻⁴ M</td>
</tr>
<tr>
<td>trace metal solution</td>
<td>(see recipe below)</td>
<td>1 mL</td>
<td>---</td>
</tr>
<tr>
<td>vitamin solution</td>
<td>(see recipe below)</td>
<td>0.5 mL</td>
<td>---</td>
</tr>
</tbody>
</table>

Trace metal solution:

<table>
<thead>
<tr>
<th>Component</th>
<th>Primary Stock Solution</th>
<th>Quantity</th>
<th>Molar Concentration in Final Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl₃. 6H₂O</td>
<td>---</td>
<td>3.15 g</td>
<td>1.17 x 10⁻⁵ M</td>
</tr>
<tr>
<td>Na₂EDTA. 2H₂O</td>
<td>---</td>
<td>4.36 g</td>
<td>1.17 x 10⁻⁵ M</td>
</tr>
<tr>
<td>CuSO₄. 5H₂O</td>
<td>9.8 g/L dH₂O</td>
<td>1 mL</td>
<td>3.93 x 10⁻⁸ M</td>
</tr>
<tr>
<td>Na₂MoO₄. 2H₂O</td>
<td>6.3 g/L dH₂O</td>
<td>1 mL</td>
<td>2.60 x 10⁻⁹ M</td>
</tr>
<tr>
<td>ZnSO₄. 7H₂O</td>
<td>22.0 g/L dH₂O</td>
<td>1 mL</td>
<td>7.65 x 10⁻⁸ M</td>
</tr>
<tr>
<td>CoCl₂. 6H₂O</td>
<td>10.0 g/L dH₂O</td>
<td>1 mL</td>
<td>4.20 x 10⁻⁸ M</td>
</tr>
<tr>
<td>MnCl₂. 4H₂O</td>
<td>180.0 g/L dH₂O</td>
<td>1 mL</td>
<td>9.10 x 10⁻⁷ M</td>
</tr>
</tbody>
</table>

Vitamin solution:

<table>
<thead>
<tr>
<th>Component</th>
<th>Primary Stock Solution</th>
<th>Quantity</th>
<th>Molar Concentration in Final Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>thiamine HCl (vit. B₁)</td>
<td>---</td>
<td>200 mg</td>
<td>2.96 x 10⁻⁷ M</td>
</tr>
<tr>
<td>biotin (vit. H)</td>
<td>0.1 g/L dH₂O</td>
<td>10 mL</td>
<td>2.05 x 10⁻⁹ M</td>
</tr>
<tr>
<td>cyanocobalamin (vit. B₁₂)</td>
<td>1.0 g/L dH₂O</td>
<td>1 mL</td>
<td>3.69 x 10⁻¹⁰ M</td>
</tr>
</tbody>
</table>
Cultures were illuminated 12 h a day with artificial light for 4 to 6 weeks and the temperature was set to 18°C. Culture growths were conducted in large volume (10 L) to evaluate the composition of the culture solution at different phases of growth. Aeration with ambient air was continuously provided to prevent algae sedimentation, ensure an equal exposition to light for all cells, and permit good air exchange. Cultures were grown in non-axenic conditions to avoid a large antibiotic addition that does not match with environmental conditions.

**Figure 2-2: Culture setup for marine phytoplankton: Skeletonema costatum, Tetraselmis sp., Hymenomonas sp., Synechococcus (from left to right)**

Every two days, 100 mL of the culture solutions was sampled to monitor the culture growth by following the cell count (Flow cytometry and Fluorescence) and the evolution of the AOM content and characteristics (DOC, LC-OCD, UV, Fluorescence, pH).
2.1.2. Isolation of Algal High Molecular Weight Compounds

At the decline phase of growth (approximately 20 days of culture), 8 L of culture solution was centrifuged at 3000 g for 15 min to separate the AOM and the algal cells. The supernatant composed of AOM was analyzed by flow cytometry (FCM) to control the absence of algal cells and then filtered through 0.7 μm for SKC, TET, HYM and SYN. The solution volume was then reduced by a factor of 2, using a rotary evaporator, with a bath temperature of 30 °C.

All the algal cells are concentrated at the bottom of the 50 mL centrifuge tube. This solution was sonicated (QSONICA Q700) at 350 Watts for 10 minutes. The final solution was filtered through 0.7 μm for SKC, TET, HYM and SYN. These solutions contain the Intracellular Organic Matter (IOM) of the algae.

High Molecular Weight (HMW) compounds of both types of solutions (i.e., EOM and IOM) were then separated by 3.5 kDa dialysis against MilliQ water. EOM corresponds to the AOM of the culture solution after cell removal (0.7 μm porosity membrane) and IOM corresponds to the AOM contained inside the cells and released after sonication of the cells. MilliQ water was changed every two days until reaching a permeate conductivity lower than 10 μS/cm. Concentrate solution (i.e., inside the dialysis bag) was then considered to be HMW EOM or HMW IOM. Samples were freeze-dried for analytical purpose. Figure 2-3 summarizes the harvesting protocol for HMW EOM and HMW IOM.
AOM coming from two other algal strains (Spirulina – SPR and Chlorella vulgaris – CLV), cultured in freshwater were studied. *Spirulina* is the common term for the genus *Arthrospira*. It is a cyanobacteria mainly living in hot water. Chlorella vulgaris belongs to the Chlorophyta group. They are both responsible for blooms and are found in marine and fresh environment. Due to their dietary properties (high amount of proteins), they are largely cultivated and used as dietary supplements. After 3.5 kDa dialysis, High Molecular Weight (HMW) fraction and Low Molecular Weight (LMW) fractions were isolated.
2.2. Water Matrices

2.2.1. Natural Waters

Three different natural seawater sources were studied in this project.

Seawater from the Red Sea was sampled at 3 km offshore of Thuwal, Saudi Arabia (Figure 2-4), at two different periods (October 2011 and January 2012). Solutions were filtrated through 0.7 μm before experiments. The two seawater samples showed similar DOC of 0.8 mg/L, conductivity of 59.3 mS/cm and pH 8.2.

Seawater from the Arabian Sea was also collected at the Jubail RO plant (Figure 2-4), in July 2011, during an algal bloom. The solution was filtered through 0.7 μm before experiment. The DOC was 1.70 mg/L with a conductivity of 62.5 mS/cm at pH 8.2.

Figure 2-4: Sampling sites in the Red Sea and the Arabian Sea
Another seawater source originated from a mesocosm experiment, taking place at KAUST bay, Saudi Arabia (Figure 2-5), was studied. Waterproof mesocosms of 8 000 L were built in the Red Sea, in a coastal area of KAUST. A brief enrichment of nutrients (NO$_3^-$, PO$_4^{3-}$, SiO$_4^{-}$) was added to the mesocosms. 20 L of seawater was sampled everyday to monitor the growth of the algal population during 20 days. This experiment has been performed in collaboration with the Red Sea Research center at KAUST. Seawater was sampled on day 0, day 8 and day 14 and pre-filtered through 100 μm, for ultrafiltration experiment. For DOC analyses, samples were filtered through 0.7 μm, and some algal cells were passing through the porosity of the membrane. DOC varied between 0.7 mg/L +/- 0.2. The pH was increasing from 8.17 to 8.55 from day 0 to day 14.

Figure 2-5: Mesocosms experiments at KAUST, Saudi Arabia
2.2.2. Water Spiked with Organic Matter

2.2.2.1. Natural Seawater spiked with Algal Solutions

In order to keep a natural seawater matrix, seawater from the Red Sea, collected offshore of the KAUST bay, was spiked with different types of AOM. The DOC of the Red Seawater was constant over time (0.8 mg/L +/-0.1).

The Red Sea water was enriched with the HMW and LMW fractions of SPR and CLV AOM. The final solutions were characterized by a DOC concentration of 1 mg/L +/-0.1.

All solutions were pre-filtered through 0.45 μm before use.

Natural seawater from the Red Sea was also spiked with HYM and TET cultures at the decline phase of growth. Culture solutions were directly used without pre-filtration through 0.7 μm to emphasize the presence of algal cells. The final solutions were defined by a constant Chlorophyll-a concentration of 20 μg/L (19.9 μg/L +/- 2.83 and 20.23 μg/L +/-1.53 for HYM and TET, respectively). For AOM analyses, solutions were filtered through 0.7 μm.

2.2.2.2. Synthetic Seawater spiked with Algal Solutions and Algal Organic Matter

Synthetic seawater was prepared following the recipe developed by Grasshoff (1967) two different solutions. Table 2-2 summarizes the composition of each solution. The final conductivity was 59 mS/cm and pH8.1.
Table 2-2: Composition of synthetic seawater (after Grasshoff, 1967)

<table>
<thead>
<tr>
<th></th>
<th>Solution 1 for 1L MilliQ water (gram)</th>
<th>Solution 2 for 910mL MilliQ water (gram)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Chloride</td>
<td>47.8</td>
<td>Magnesium Chloride</td>
</tr>
<tr>
<td>Sodium Sulfate</td>
<td>8.0</td>
<td>Hexahydrate</td>
</tr>
<tr>
<td>Potassium Chloride</td>
<td>1.4</td>
<td>Calcium Chloride Dihydrate</td>
</tr>
<tr>
<td>Sodium Bicarbonate</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Potassium Bromide</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Boric Acid</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Sodium Fluoride</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>Magnesium Chloride</td>
<td>21.6</td>
<td></td>
</tr>
<tr>
<td>Calcium Chloride Dihydrate</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

Synthetic seawater (SSW) was used to focus on the fouling caused by algal culture solutions only. At the three different stages of growth (exponential, stationary and decline phase), all algal monocultures were diluted with SSW to achieve a final DOC of approximately 0.5 mg/L, corresponding to the variation of DOC during an algal bloom. Experiments were conducted right after verification of the final DOC. Algal cells did not suffer a different change of osmotic pressure when diluted into synthetic seawater, and remained alive in the solution. These solutions were filtered to study the impact of algal cells and AOM on UF filtration. Three different types of ultrafiltration experiments were conducted, with an initial DOC of 0.5 mg/L:

- experiment 1: with synthetic solutions prepared with direct dilution of the algal culture collected during the three different phases
- experiment 2: with synthetic solutions prepared with algal culture prefiltered through 0.7 μm in order to remove the algal cells

2.2.2.3. Synthetic Brackish Water spiked with Terrestrial Organic Matter

In order to compare the fouling potential of AOM to terrestrial NOM, an isolated Humic Substances (i.e., XAD-8 resin) from treated (i.e., clarification and ozonation)
Colorado River, USA (Col-HS) was used. Col-HS has a very low SUVA value (i.e. 1.58 L.mg⁻¹.m⁻¹), indicative of a relatively low hydrophobic character. Because high molecular weight humic substances precipitates in high conductivity water (estuary conditions), it was decided to dissolve the sample into synthetic brackish water. The synthetic brackish water was produced following the recipe of synthetic seawater proposed by Grasshoff (1967) with a dilution by a factor 2. The final salinity of the brackish water is around 17.5g/kg. All samples were prefiltered through 0.7 μm and the DOC was set to 10 mg/L.

2.3. Coagulation-flocculation experiments

Coagulation-Flocculation followed by Sedimentation (CFS) or Flotation (CFF) were studied. Two different algal cultures were used (TET and HYM), at different phases of growth. The Jar-test unit was composed of three 1 L jars and was equipped with a pressurized container to allow flotation.

2.3.1. Coagulation - Flocculation

Coagulation was performed with ferric chloride (FeCl₃), with doses varying from 1 mg Fe/L to 10 mg Fe/L. To ensure a good homogenization and an effective destabilization of the colloids, a rapid agitation of 200 rpm was maintained for 2 minutes. Flocculation was operated at 30 rpm for 10 minutes. The impact of the pH was also tested by adding drops of concentrated HCl (5 M) to achieve pH values of 5.5, 6, 6.5 and 7. The pH of the coagulation performed at free pH was around 8.4.
For some CFS experiments, the coagulation was performed with an addition of clay. Clay was added together with ferric chloride as coagulant aid or used alone to evaluate its coagulant efficiency. The addition of bentonite (BEN) was studied and the BEN dose varied from 10 mg/L to 200 mg/L.

2.3.2. Sedimentation

The sedimentation time was set to 30 minutes. After this time, the upper three fourth of the solution (800 mL) was collected by aspiration, using a 50 mL pipette and the concept of communicating vessel. The tip of the pipette was cut to enlarge the suction opening and avoid blockage with suspended large flocs.

2.3.3. Flotation

Flotation was performed by adding pressurized seawater (5 bars) at the bottom of the solution. Pressurized seawater forms microbubbles of approximately 40 μm, which attach to the formed flocs and make them float. This technic is commonly called DAF (Dissolved Air Flotation). The volume of pressurized seawater was set at 10% of the treated volume (i.e., 100 mL). Different flotation times were studied: 5 min, 8 min, 10 min and 15 minutes. When the flotation was completed, the produced water was recovered from the bottom of the jar. The first 100 mL were used to rinse the line and the last 100 mL were thrown away (due to its high concentration of flocs).
2.4. Ultrafiltration experiments

2.4.1. Ceramic Ultrafiltration

2.4.1.1. Disk membranes

Disk membranes with a diameter of 47 mm and an effective filtration area of 12 cm\(^2\) were used. Two different pore sizes and metal oxides were studied: 80 nm in alumina and 30 nm in titanium oxide. Pure water permeability at 20 °C +/- 0.5 and point of zero charge (evaluated with the acid base titration method) are presented in Table 2-3. Microscopic images of the ceramic membranes are displayed in Figure 2-6.

<table>
<thead>
<tr>
<th>Separative layer</th>
<th>Pore size (nm)</th>
<th>pH(_{zpc})</th>
<th>Filtration area (cm(^2))</th>
<th>Pure water permeability @20 °C (LMH/bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina (Al(_2)O(_3))</td>
<td>80</td>
<td>8.9</td>
<td>12</td>
<td>1244 +/- 55</td>
</tr>
<tr>
<td>Titanium oxide (TiO(_2))</td>
<td>30</td>
<td>6.5</td>
<td>12</td>
<td>788 +/- 36</td>
</tr>
</tbody>
</table>

Figure 2-6: SEM image of the ceramic membranes (a) Al\(_2\)O\(_3\)-80 nm and (b) TiO\(_2\)-30 nm
After the experiments, membranes were rinsed with MilliQ water and calcinated at 500 °C for 4 hours to remove any organic fouling. Initial permeability was recovered and the ceramic membranes were re-used.

2.4.1.2. Constant pressure experiments

The first set of filtration experiment was operated at constant pressure. Filtrations were performed in a dead-end filtration mode, at room temperature (20°C +/- 0.5). Figure 2-7 presents a scheme of the setup used for direct filtration experiments. The flux was recorded every 5 seconds by a digital balance connected to a computer. To remove noise, flux values were averaged every 20 sec.

![Figure 2-7: Constant-pressure UF ceramic setup](image)

Two different sets of dead-end filtration experiments were performed. For the brackish synthetic solutions (i.e., terrestrial organic matter), a sequence of three filtrations in series
separated by chemical cleaning using NaOH (0.1M) was conducted at 2 bars (both filtration and cleaning). The membrane was rinsed with MilliQ water after each chemical cleaning until reaching a stable permeability.

For UF experiments using algal culture or AOM solution, the same filtration sequence was performed but at lower pressure (0.7 bar). Backflush with MilliQ water was operated at 2 bars. A final chemical cleaning was applied using NaOH (0.1M) at 2 bars.

2.4.1.3. Constant flux experiments

For the second part of the work, dead-end filtration experiments were operated at room temperature (20°C +/- 0.5) and at constant flux. The pressure was recorded every second with a Pressure Transmitter (Cole Parmer, EW-68072-34). A scheme of the setup is displayed in Figure 2-8.

![Figure 2-8: Constant-flux ceramic UF setup](image)
For all feed solutions, constant-flux filtration experiment (250 LMH and 430 LMH) consisted of a set of five 5.5 min-long filtrations separated by backwash. Backwash was performed with permeate solution at a flux two times higher than the filtration flux for 1.5 min. After 5 cycles of filtration a chemical cleaning was established using NaOCl (2 000 mg/L Cl₂) for 2 minutes at a flux two times higher than filtration flux (i.e., 500 LMH or 860 LMH) and allowing soaking for 4 minutes. The setup was carefully rinsed with MilliQ water before resuming the filtration sequence, to remove any algal material or chemical cleaning solution from the pipes. In case of severe fouling, backwash was implemented before 5 filtration cycles. When the specific flux loss reached 70%, the filtration was stopped and a backwash was applied at the end of the filtration.

2.4.2. Polymeric Ultrafiltration

2.4.2.1. Hollow fiber membranes

Inside-out polymeric fibers with a nominal pore size of 30 nm and made of Hydrophilic-Polyvinylidene fluoride (H-PVDF) were used for our study. The internal diameter of the fiber was 0.7 mm and the outer diameter 1.3 mm.

Filtration modules were prepared with six fibers of 25 cm long (Figure 2-9). The total filtration surface was 70 cm² +/- 2. Permeability with MilliQ water was recorded before each experiment. Calculated permeability was 400 LMH/bar +/- 80. The main characteristics are summarized in Table 2-4.
Table 2-4: Polymeric membrane characteristics

<table>
<thead>
<tr>
<th>Separative layer</th>
<th>Pore size (nm)</th>
<th>Internal diameter (mm)</th>
<th>Outer diameter (mm)</th>
<th>Filtration area (cm²)</th>
<th>Pure water permeability @20°C (LMH/bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-PVDF</td>
<td>30</td>
<td>0.7</td>
<td>1.3</td>
<td>70</td>
<td>400 +/- 80</td>
</tr>
</tbody>
</table>

2.4.2.2. Constant flux experiments

Polymeric ultrafiltration experiments were performed using an automated setup (OSMO Inspector, Convergence) (Figure 2-10). This setup allowed us to program sequences including filtration, backwash and chemical cleaning.
Each filtration sequence included 10 cycles of 30 minutes of filtration and 2 minutes of hydraulic backwash operated with permeate. The permeate fluxes were 70 LMH +/- 5 and 120 LMH for filtration and hydraulic backwash, respectively. Filtration module was flushed with feed water before each filtration cycle to remove the remaining algal material detached during backwash.

2.4.3. Unified Modified Fouling Index (UMFI)

Fouling was quantified using a resistance-in-series approach (Nguyen et al., 2011). For low-pressure membrane, the flux, \( J \) (LMH) can be described as:

\[
J = \frac{\Delta P}{\mu R}
\]

Where \( \Delta P \) is the transmembrane pressure, \( R \) is the resistance to flow through the membrane and \( \mu \) is the water viscosity.

\( R \) represents the total resistance. It has two resistance components: the resistance of the clean membrane (\( R_{\text{memb}} \)) and the resistance due to the foulant accumulation on/into the membrane (\( R_{\text{foul}} \)).

\[
R = R_{\text{memb}} + R_{\text{foul}}
\]

Resistance due to fouling is considered to increase linearly with the volume of solution filtered (Nguyen et al., 2011). Thus, it can be expressed as a function of the volume filtered:

\[
R_{\text{foul}} = r_{\text{foul}} \cdot V,
\]

where \( r_{\text{foul}} \) is the rate constant for the resistance increase and \( V \) is the specific volume (L/m²).

The specific flux, \( J_s \) can then be expressed by:

\[
J_s = \frac{J}{\Delta P} = \frac{1}{\mu (R_{\text{memb}} + r_{\text{foul}} \cdot V)}
\]
For a new membrane, $J_{so} = 1/(\mu R_{memb})$. We can normalize the specific flux ($J_s$) by dividing $J_s$ by $J_{so}$. The equation obtained is the following:

$$J'_s = \frac{J_s}{J_{so}} = \frac{1}{1 + (r_{foul}V)/R_{memb}}$$

And the Unified Modified Fouling Index is defined by $UMFI = r_{foul}/R_{memb}$ and:

$$\frac{1}{J_s} = 1 + UMFI \cdot V$$

During a filtration experiment, UMFI can be used to characterize different properties of the membrane fouling. When calculated for each filtration, UMFI is called Total Fouling Index (TFI). It characterizes the fouling rate of one single filtration. When calculated after several sequences of filtration – backwash, it is called Hydraulic Irreversible Fouling Index. It characterizes the irreversibility of the fouling toward backwash process. Figure 2-11 summarized the different UMFI types during an operating cycle.

**Figure 2-11: Operating cycle and UMFI Determination** (Nguyen et al. 2011)
During the ultrafiltration experiment, feed quality remains constant. All UMFI can then be expressed as a function of the mass of organic carbon filtered:

\[ \text{UMFI}_m = \frac{\text{UMFI}}{[\text{DOC}]} \]

and the normalized specific flux can be calculated with the following equation:

\[ \frac{1}{J_{ns}} = 1 + \text{UMFI}_m.m_{\text{DOC}} \]

with \( m_{\text{DOC}} \) the mass of DOC filtered by \( m^2 \) (mg DOC/m²).

2.5. Algal Characterization

2.5.1. Algal Cell Analysis

To monitor the algal growth, cultures were sampled every two days, at the same time of the day. The culture solution was mixed before sampling to ensure a homogenous solution and obtain a representative sample. Two different tools were used to quantify the algal growth:

- Flow cytometry (FCM) (FACSVersette™, BD) was used to evaluate the concentration of cells in the culture. 200 μL of sample were excited with a blue laser at 488 nm. The combination of the right-angle light scattering (SSC, related to cell size) and red emission fluorescence (i.e., 700-754 nm) was used to discriminate and enumerate the different populations. Analyses were operated at high flow rate for SKC, TET and HYM, and medium flow rate for SYN. Acquisition was completed after 60 sec or 1,000,000 counted events.
- Fluorometer (10AU™ Fluorometer, Turner Designs) was used to measure the Chlorophyll-a (Chl-a) concentration at an emission excitation of 488 nm. A calibration curve was performed using Chlorophyll-a (free of Chlorophyll-b) standard, following the EPA method 445.0 (Arar & Collins 1997). Standard solution was diluted with aqueous acetone solution (90% acetone/10% MilliQ water). Two different ranges of concentration were used: from 0 μg/L to 100 μg/L Chl-a and from 0 μg/L to 400 μg/L Chl-a. Figure 2-12 displays the calibration curve for low and high Chl-a concentration. 25mL of homogenous culture solution was needed to measure the Chl-a concentration.

![Calibration curve for Chlorophyll-a concentration](image)
2.5.2. Algal Dissolved Organic Matter

To monitor the change in the quality and quantity of AOM, analyses of the culture solution (AOM during growth -AOM\textsubscript{g}, mainly EOM at the beginning of the growth) and of the sonicated solution (mixture of EOM and IOM) were performed every two days. AOM\textsubscript{g} was collected by filtering the culture solution through 0.7 μm porosity glass filter (GFF). The mixture of AOM\textsubscript{g} and IOM was collected by sonicating the culture solution at 350W for 10 minutes. After sonication, the solution was filtered through 0.7 μm and FCM was used to ensure the absence of algal cells in all permeate solutions.

Dissolved Organic Carbon (DOC) was measured for all samples using Shimadzu VCSH TOC analyzer. This equipment was calibrated every 2 weeks with Potassium Hydrogen Phthalate for concentration up to 3 mg/L DOC. Algal samples were diluted into MilliQ water to reach a DOC concentration within the range 0.5-3 mg/L DOC. The Shimadzu VCSH TOC analyzer allows an in-situ acidification using HCl (2M) (3% of the sample

Figure 2-12: Calibration of Fluorometer with Chlorophyll-a solution for (a) a concentration comprised between 0 and 20 μg/L, (b) a concentration comprised between 0 and 400 μg/L.
volume) and a sparging time of 4 minutes. Three injections were performed. If the Coefficient of Variation was higher than 2%, a fourth injection was analyzed. The final concentration is given by the average of the closest three concentration values. Liquid Chromatography coupled with Organic Carbon Detector and UltraViolet Detector (LC-OCD-UVD) is an excellent tool to monitor the change on the DOC quality. Analyses were performed on Model 8. LC-OCD requires 10 mL of sample and a DOC concentration of maximum 5 mg/L. The manufacturer (DOC-Labor) recommends a new calibration of the unit every 6 months. The calibration consists of (1) a calibration of the chromatogram, using two standards (Suwannee River Humic Acid and Suwannee River Fulvic acid) and (2) a calibration of the detectors (i.e., OCD and UVD) using Potassium Hydrogen Phthalate (Fluka 60359) and Potassium Nitrate (Fluka / Riedel de Haen 31263) standards. The calibration is carried out within 24 hours after standard preparation to avoid any degradation of the standards. Figure 2-13 presents the LC-OCD-UVD scheme of the equipment. During analysis, 10% of the sample is bypassing the chromatographic column and is directly injected into the detectors and 90% of the sample is passing the chromatographic column (Toyopearl HW-50), which ensures the size separation of the dissolved matrix before reaching the detectors. LC-OCD-UVD measurements and processing were developed by Huber et al. (2011).
Two different spectroscopy tools were also employed: UV-visible spectroscopy (Shimadzu UV-25500) and 3D-Fluorescence Spectroscopy (Horiba Fluoromax-4). UV spectrum covered the range 600-200 nm, with a 1 nm step. 3D-Fluorescence operated with excitation wavelengths from 240 to 500 nm and emission wavelengths from 250 to 650 nm. Increment and slit for both excitation and emission wavelength were set at 5 nm. Fluorescence Emission Excitation Matrix (FEEM) spectra were identified following Coble et al. (1996) (Figure 1-6a). A program, using Python, has been developed to calculate the volume of each identified chromophoric region. The different regions of the FEEM are presented in Figure 2-14.
2.5.3. Characterization High Molecular Weight Algal Dissolved Organic Matter isolates (HMW AOM)

Different solid-state analytical tools were used to characterize isolated fractions of HMW AOM. Concentration of Carbon, Hydrogen and Nitrogen was determined using an elemental analyzer (Perkin Elmer 2400 Series II CHNS/O Analyzer). 2 mg of sample was precisely weighted for each analysis. Each analysis was conducted in triplicate and the mean value was considered for the final result. The sample was combusted in pure oxygen environment to produce elemental gases (CO₂, H₂O, N₂ and SO₂). A thermal conductivity detector measures the gas concentration for each species. The initial weight is then used for percentage calculation of each element in the sample. Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR), Pyrolysis - Gas Chromatography - Mass Spectroscopy (Py-GC-MS), ¹H-Nuclear Magnetic Resonance
($^1$H-NMR) and $^{13}$C-Nuclear Magnetic Resonance ($^{13}$C-NMR) were used to identify complex organic molecules in AOM samples.

The potassium bromide (KBr) pellet method was used for ATR-FTIR analyses. A few mg of AOM powder was mixed to analytical grade KBr to form a transparent pellet. To remove background noise, a blank prepared with KBr alone was measured prior to analyses. Spectra covered a range of wavenumber from 400 cm$^{-1}$ to 4 000 cm$^{-1}$.

Py-GC-MS allows the identification of molecules arising from thermal degradation of the polymeric structures. Each molecules can be assigned to a given (bio)polymer (e.g., proteins, polysaccharides, lipids). AOM samples were analyzed according to the method described by Christy et al. (1999). 1 – 2 mg of AOM sample was degraded using flash pyrolysis (CDS Pyroprobe 5150) with the following temperature program: 50 °C for 1 sec then 650 °C for 20 sec with a ramp of 20 °C/msec. The compounds produces were then separated by GC (Agilent Technology, 7890A GC System) on DB-WAX column 0.25 micron (Agilent Technologies), and detected by Mass Spectroscopy (Agilent Instruments, 5975 inert MSD). The range of mass detection was set between 50 and 550 una.

For $^1$H-NMR, the sample was prepared by dissolving the compounds in 600 µl of deuterated water D$_2$O and then 550 µl of the solution was transferred to NMR tubes of 5 mm diameter. NMR spectra were acquired at 298 K using Bruker 700 AVANAC III spectrometer or Bruker 950 AVANAC III spectrometer equipped with 5 mm Bruker TCI CryoProbe (BrukerBioSpin, Rheinstetten, Germany). To achieve high signal to noise ratio, the $^1$H NMR spectra were recorded by collecting 1k scans with a recycle delay time of 3s. Chemical shifts were adjusted using 3-Trimethylsilylpropane sulfonic acid (DSS,
Sculpting pulse sequence using standard program (zgesgp program) from Bruker pulse library. The free induction decay (FID) data were collected with spectral width of 15243 Hz digitized into 64k data points. The FID signals were zero-filled and amplified by an exponential line-broadening factor of 0.3 Hz before Fourier transformation. Bruker Topspin 2.1 software was used in all experiments to collect and analyze the data. Solid-state $^{13}$C-NMR spectra were recorded with Bruker AVANAC III 400 MHz spectrometer equipped with a triple-resonance 4 mm Bruker MAS probe. $^{13}$C-Cross Polarization-Magic Angle Spinning-NMR ($^3$C-CP-MAS-NMR) spectra were recorded at a resonance frequency of 100.622 MHz under 14 kHz spinning rate. The temperature for all experiments was kept at 298 K. Bruker Topspin 3.0 software was used for data collection and for spectral analysis.

**2.5.4. Atomic Force Microscopy**

Chemical Force Microscopy (CFM) provided by Atomic Force Microscopy (AFM) is a powerful tool to study adhesion properties of substances on surfaces (Aubry et al. 2013). It is based on measuring the forces that a probe coated (functionalized) with a compound, undergoes when approaching, touching and leaving a surface, in function of the distance. Measurements are performed in liquids, and parameters that could influence the adhesion (e.g. pH, ionic strength, solution composition) can be taken into account.
The probe is constituted of a silica spherical colloid (Polyscience Inc, USA) glued at the end of the cantilever of a commercial AFM probe (SICON model, AppNana, USA). Colloid radii were measured with optical microscope (Olympus BX61, Japan) and were chosen to be in the 30 µm range. The probes were cleaned with an alkaline solution (HellmanexIII from Hellma, Germany), rinsed with DI water and then were immediately immersed overnight into a concentrated organic matter solution to perform the coating. The concentrated organic matter solution was prepared by dissolving 100 mg/L of HMW AOM into MilliQ water. This method was derived from the method developed by Aubry et al. (2013). CFM was performed in synthetic seawater (SSW).

Experiments were conducted on Agilent AFM 5500. Cantilever spring constant was measured in air by the method proposed by Hutter et al., (1993) and using thermal K module (Agilent, USA). The probe was then immersed and 40 adhesion force curves were performed by set of 10 curves done on 4 different areas selected by moving randomly the sample. For each measurement the probe was placed at a distance of 2 µm
above the surface and moved with a velocity of 400 nm/s, consistent with previous studies (Aubry et al. 2013; Cail & Hochella 2005; Lower et al. 2000). The maximum load during contact was set to 5 nN. For each curve, 10⁴ data points were recorded and were next treated with macros developed on Excel software.

Adhesion Force Curve can be divided in two parts, approach and retraction, from which relevant parameters can be calculated. Negative force values recorded during adhesion measurements are assigned to attractive force and positive values to repulsive force.

2.5.4.1. Important parameters during approach

2.5.4.1.a. Gradient Force

For a better interpretation of the approach part of curve forces, the Gradient Force method, as developed by Li and Logan (2004), was used. Gradient Force curve was obtained by calculating the slope of each points of the approach curve (using the surrounded six points). The Gradient Force curve can be divided in 4 different regions. As the measurement starts, the probe is too far away from the sample and no interactions are possible. Thus the gradient force is equal to zero. Then long-distance interactions start to appear and the gradient force curve is changed, showing a non-linear behavior (non-contact phase). These long-distance interactions could be electrostatic in nature or associated with the presence of long molecular chains extended away from the probe (steric repulsion). Note that, depending on the electrical charge of both surface and probe, electrostatic interaction could be attractive (opposite charges) or repulsive (same charges). The gradient force curve shows an approximately linear phase, suggesting that the probe is in contact with the membrane and the coating layer is compressed (contact
phase). Finally, the gradient force curve reaches a plateau at a non-null value, indicating a linear response of the cantilever when the coating layer is fully compressed (noncompliance phase). Figure 2-16b displays the adhesion curve force of *Tetraselmis sp.* AOM coated probe on Al$_2$O$_3$ ceramic membrane in 100mM NaCl and its Gradient Force (for more clarity, we plotted –GF).

![Figure 2-16: Approaching curve force of Tetraselmis sp. AOM coated probe on Al$_2$O$_3$ ceramic membrane in 100 mM NaCl and its Gradient Force (N-C: Non-Contact)](image)

### 2.5.4.1. β. Jump-at-contact and Tendency

When strong attractive interactions exist between the coated-probe and the surface, a jump-at-contact can be observed during the approach (Figure 2-17). The amplitude of this jump-at-contact is defined as the minimum value reached during the approach-part of force curve.
Tendency is a statistical tool to monitor the number of times a jump-at-contact happens in one experiment. Tendency is defined as the arithmetic average of jump-at-contact amplitude multiplied by the ratio of force curve showing jump at contact (e.g., if for 40 adhesion curves, only 12 of them showed a jump-at-contact with an average value of 0.5 nN, then the tendency would be 0.5*12/40 = 0.15). Note that for some NOM samples, the low number of jump at contact events did not allow the use of lognormal distribution and the arithmetic average was chosen for all cases.

2.5.4.2. Adhesion Energy (AE) needed for retraction

The Adhesion Energy is the energy needed to detach the probe from the surface. In the retraction plot displaying the adhesion force as a function of the distance to the probe surface, it corresponds to the area between the negative values of the force curve and the
x-axis. The integration was calculated using the trapezoidal method (Gordesli at al., 2012). Figure 2-18 presents the retraction curve force of *Hymenomonas sp*. EOM coated probe on Al$_2$O$_3$ ceramic membrane and illustrates the corresponding Adhesion Energy (AE).

![Figure 2-18: Retraction curve force of *Hymenomonas sp*. EOM coated probe on Al$_2$O$_3$ ceramic membrane in 0.33 mM CaCl$_2$](image)

Figure 2-18: Retraction curve force of *Hymenomonas sp*. EOM coated probe on Al$_2$O$_3$ ceramic membrane in 0.33 mM CaCl$_2$
3. Characterization of four algal monoculture solutions during growth

3.1. Algae characterization during growth

The growth of the four different algae (*Skeletonema costatum* – SKC, *Tetraselmis sp.* – TET, *Hymenomonas sp.* – HYM and *Synechococcus sp.* – SYN) was monitored by flow cytometry (FCM) and Chl-a concentration (Figure 3-1).
Figure 3-1: Culture growth control of (a) SKC, (b) TET, (c) HYM and (d) SYN by FCM and Chl-a fluorescence.

Three different phases can be distinguished: the Exponential Phase (EP), the Stationary Phase (SP) and the Decline Phase (DP). Before the algal culture starts to grow, a lag-phase can be noticed in the culture of SKC and SYN. During this phase, the number of cells is slowly increasing. When the cell population has reached a certain density, the growth is accelerated and the EP starts. Chl-a and cell count increase linearly during this period. Nutrients are in excess and there is no limiting factor for the growth. At the SP, nutrients were consumed, and the number of newly born cells is comparable to the number of cells dying. This steady state phase remains for a couple of days, depending on the algal species. When nutrients are lacking, more cells are dying and the DP begins: Chl-a and cell count decrease. The transition between EP and SP is observed at day 12 +/- 2, day 18 +/- 2, day 18 +/- 2 and day 20 +/- 2 for SKC, TET, HYM and SYN, respectively. DP starts at day 18 +/- 2, day 28 +/- 2, day 30 +/- 2 and day 27 +/- 2 for SKC, TET, HYM and SYN, respectively. The different transition days are summarized in Table 3-1.

<table>
<thead>
<tr>
<th></th>
<th>Transition day between EP and SP</th>
<th>Transition day between SP and DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>SKC</td>
<td>12 +/-2</td>
<td>18 +/-2</td>
</tr>
<tr>
<td>TET</td>
<td>18 +/-2</td>
<td>28 +/-2</td>
</tr>
<tr>
<td>HYM</td>
<td>18 +/-2</td>
<td>30 +/-2</td>
</tr>
<tr>
<td>SYN</td>
<td>20 +/-2</td>
<td>27 +/-2</td>
</tr>
</tbody>
</table>
Cell count and Chl-a concentration are linearly correlated (Figure 3-2), with a high linear regression coefficient ($R^2$) of 0.96, 0.95, and 0.98 for SKC, TET and HYM, respectively. For the cyanobacteria SYN, the linear regression coefficient is only 0.64, which is due to the nature of the cyanobacteria cells. Their Chl-a content is lower than the three other species ($0.05 \times 10^{-8} \mu g$ Chl-a/cells) increasing the incertitude value for low Chl-a analysis. SKC and HYM are similar in terms of Chl-a content per algal cell ($7.36 \times 10^{-8} \mu g$ Chl-a/cells and $8.17 \times 10^{-8} \mu g$ Chl-a/cell, respectively), and TET is the specie producing the largest amount of Chl-a with a rate of $16.10 \times 10^{-8} \mu g$ Chl-a/cell.

![Figure 3-2: Linear regression between cell count and Chl-a concentration during the EP of SKC, TET, HYM and SYN](image_url)
3.2. Culture solution characterization during growth

3.2.1. Algal organic matter released in solution

Algal Organic Matter (AOM) was analyzed after filtration of the algal cultures through 0.7 μm. Filtration through 0.7 μm was performed with the objective to remove algal cells and quantify the dissolved organic matter. For seawater analysis, 0.7 μm glass fiber filter is preferred over 0.45 μm cellulose acetate filter. TOC measurements were not possible due to cell debris in the solution, which could damage the analytical equipment. Two different analytical tools were used to quantify the AOM concentration: the Shimadzu TOC meter and the LC-OCD system. Measurements from the two analytical tools are linearly correlated (Figure 3-3). The LC-OCD analyzer is slightly underestimating the DOC concentration in comparison with the Shimadzu TOC meter. Catalytic thermal oxidation process (i.e., Shimadzu TOC meter) seems to be slightly more efficient than UV oxidation process (LC-OCD) for AOM analyses.
During growth, the DOC content of the culture solution increases gradually (Figure 3-4), however, each algal species is characterized by a singular DOC evolution.
The amount of DOC released in the solution depends on the origin of the algal species. TET is releasing the largest quantity of DOC with a rate of 0.48 mg/L of DOC per day ($R^2 = 0.94$). SYN, with a release rate of 0.22 mg/L of DOC per day ($R^2 = 0.90$), is the alga producing the lowest amount of DOC. The cell size of SYN is much smaller (below 2 μm) than the three other species (between 2 to 60 μm), which could justify this finding. The DOC concentration of the culture solution is also linked to the Chl-a content, i.e., the number of cells present in the solution (Figure 3-5).
The three different phases of growth are observed in Figure 3-5. The first phase (i.e., EP) is characterized by a linear correlation between Chl-a concentration (i.e., cell concentration) and DOC. Cells are multiplying and excreting AOM, i.e., Extracellular Organic Matter (EOM). This linear correlation between DOC and Chl-a is verified below a Chl-a concentration of 90 μg/L, 180 μg/L, 130 μg/L and 12 μg/L for SKC, TET, HYM and SYN, respectively. These Chl-a values characterize the transition phase between EP and SP (day 12, day 16, day 18 and day 20 for SKC, TET, HYM and SYN, respectively). During this phase of growth, the AOM excretion rate is the highest for TET and the lowest for SYN (Figure 3-6). Algae can be classified on their AOM excretion rate during the EP as the following: TET > HYM > SKC > SYN.
Figure 3-6: AOM excretion rate during the EP (i.e., EOM excretion rate) four SKC, TET, HYM and SYN (R^2 is labeled on the top of each bar)

The second phase of growth (i.e., SP) is characterized by an increase of the DOC content with no change of Chl-a concentration. During SP, the cell concentration reaches a plateau and Intracellular Organic Matter (IOM) is released to the culture solution and contributes to the total AOM. AOM of the culture solution is then a mixture of EOM and IOM. The third phase of growth (DP) is characterized by the decrease of the Chl-a concentration due to cell lysis and an increase in DOC due to continuing IOM release. The filtration through 0.7 μm was necessary to avoid analytical misuse; thus, the characterization and quantification of large colloidal organics (> 0.7 μm) in the solutions could not be investigated. For HYM, microscopic images are revealing large AOM clusters (Figure 3-7) that are removed by the filtration through 0.7 μm. These large aggregates are very specific to HYM species at DP and are not observed for the three other species. In this case, the AOM is probably underestimated and only partially characterized.
3.2.2. Composition of the dissolved algal organic matter

The composition of the DOC was monitored using the LC-OCD analyzer. Organic Carbon profiles and UV (at 254 nm) profiles of the culture solution at the different phases of growth are shown in Figure 3-8. Only few chromatograms are plotted in order to provide a clearer picture of the gradual evolution of the organic composition of the solution during growth.
Three different fractions of Organic Matter can be identified from the LC-OCD profiles:

- The High Molecular Weight compounds (HMW) with elution time below 40 min, including essentially non-aromatic compounds. This fraction is generally named the biopolymer fraction, and is characterized as a mixture of polysaccharide and proteins in the surface waters and treated wastewaters (Croué, 2004; Filloux et al., 2012). No absorption at 254 nm was recorded except for TET for SP and DP periods. Note that these signals can also be attributed to inorganic colloids present in solution as proposed by the processing protocol of DOC Labor. Referring to the molecular weight estimation of DOC-Labor, HMW compounds are larger than 20 kDa.

- The Intermediate Molecular Weight compounds (IMW), which incorporate structures that slightly absorb at 254 nm and are retained in the chromatographic column between 40 to 55 minutes. They correspond molecular weight structures comprised
between 10 and 0.3 kDa. In terrestrial surface waters, this fraction refers to humic substances showing strong UV signal related to the incorporation of oxidized lignin and tannin structures. We deliberately did not want to use the term humic substances for AOM.

- The Low Molecular Weight compounds (LMW), which are non-aromatic compounds, eluted after 55 minutes of analysis. They have a molecular weight below 0.3 kDa.
The UV@254 peak at 70 minutes is attributed to residual nitrate coming from the F/2 medium solution (75 mg NaNO₃/L).

A unique HMW (i.e., biopolymer) peak is observed at a retention time of 27 minutes for SKC and HYM and at 26 minutes for SYN. In contrast, TET is characterized by two biopolymer peaks with retention time of 25 and 30 minutes, respectively. In size exclusion chromatography (SEC), the higher the retention time the lower the molecular weight. Because the void volume of the SEC column is detected at 25 minutes, the HMW resolution between 25 and 30 minutes is relatively weak. However, species can still be classified as a function of their retention time or molecular weight and the HMW biopolymers corresponding to the first peak of TET can be considered larger than the HMW of the three other species. The relative abundance of the three fractions evolves differently during growth (Figure 3-9).
Figure 3-9: Evolution of the concentration of the different fractions of DOC during the growth of (a) SKC, (b) TET, (c) HYM and (d) SYN

For the four algae, the HMW compounds of AOM showed the largest increase during growth: initially representing the minor fraction of the DOC, the HMW structures later become the most abundant constituents of the organic carbon pool. The HMW structures represent 46 to 80 % of the DOC produced during growth. The IMW fraction exerted a moderate increase over time (12 to 21% of the DOC produced); its concentration was raised by a factor of 1.5 (SKC and SYN) to 2.5 (TET and HYM) during the whole period.
of growth. The concentration of LMW fraction remained almost constant with the exception of SKC (almost ¼ of the organic carbon produced). It suggests that the algal cells are mainly producing HMW compounds, which is in agreement with numerous studies (Benner et al., 1992; Boehme et al., 2006; Henderson et al., 2008; Myklestad, 1995). Villacorte (2013) also observed an increase of the HMW molecules during the growth of three different algae (i.e., *Alexandrium tamarense*, *Chaetoceros affinis* and *Microcystis sp.*). For TET, which is characterized by two distinct HMW peaks, the ratio between the first peak (larger HMW referred to as HMW 1) and the second peak (HMW 2) constantly increased during growth (Figure 3-10).

![Figure 3-10: Ratio between the first and the second peak of HMW during TET growth](image)

Figure 3-10: Ratio between the first and the second peak of HMW during TET growth
3.2.3. Aromatic character of the dissolved algal organic matter

Several studies have highlighted the low absorbance of AOM at 254 nm (Fang et al., 2010; Henderson et al., 2008; Nguyen et al., 2005; Pivokonsky et al., 2014; Villacorte, 2013). LC-OCD profiles (Figure 3-8) are characterized by a small absorbance at 254 nm located between 40 and 70 minutes. The UV spectra were recorded every two days on samples pre-filtered through 0.7 μm during the DP (Figure 3-11).

![Figure 3-11: UV spectra at DP for the four algal cultures](image)

A band with small intensity centered at 260 nm is observed at DP for SKC, TET and SYN. This absorbance at 260 nm could represent a signal from DNA and nucleic acids (Bricaud et al., 1981; Schmid et al., 2001; Wozniak et al., 2007). Proteins can also absorb at this UV range but to a lower extent (Schmid et al., 2001; Wozniak et al., 2007). HYM is characterized by a unique and singular peak centered at 290-299 nm.
FEEM highlighting the presence of chromophores are plotted in Figure 3-12 for the four species at the DP.

Four distinct regions are defined, inspired by Chen et al. (2003). Proteins containing amino acids such as tyrosine and tryptophan are typically located in regions I and III. Chromophores in region III are related to more complex molecules such as soluble microbial by-products. Region II is characteristic of fulvic acid-like structures and region IV is considered as humic acid-like structures. For SYN, a singular peak is observed between regions II and IV and for processing SYN data, these regions were merged. Each
algae is characterized by a unique FEEM profile. For SKC, TET and HYM, the main fluorescence signal is located in region I and region III, and a smaller response is observed in region IV. For SYN, the main chromophores are located in the merged region (II+IV). The evolution of the fluorescence intensity in the different regions during growth is displayed in Figure 3-13.

Figure 3-13: Evolution of the different FEEM regions over growth for (a) SKC, (b) TET, (c) HYM and (d) SYN
The fluorescence response of region IV increased significantly over time for SKC, TET and HYM, which suggests that AOM is getting more and more enriched in humic acid-like structures. For SYN, marine fulvic acid-like structures (absorbance in the merged region II+IV) are released in the solution. The fluorescence response of the region III is also increasing for the four algae, with a stronger evolution for SKC and TET, and AOM released by these species could contain more proteinaceous material than HYM and SYN.

The evolution of these specific regions can be associated with the strong increase of HMW fraction, and to a lower extent to the IMW structures. For SYN, the HMW compounds respond in the merged region II+IV, which corresponds the marine fulvic acid-like structures.

3.2.4. Reproducibility of the algal culture protocol

For each algal species, the evolution of two cultures was monitored over time. Figure 3-14 presents the DOC concentration of two culture batches of each strain, taken at the same phase of growth. The culture SYN-2 was stopped before DP for ultrafiltration experiment purposes.
Figure 3-14: DOC content representing three phases of growth for two batches of culture (N.B. the culture SYN-2 was stopped before reaching the DP)

Solutions sampled at similar time of growth are defined by a comparable DOC concentration. The differences are more pronounced during SP and DP due to differences in the final cell concentration. The DOC composition of the two batches at different phases of growth is presented in Figure 3-15.
These results show that under similar experimental conditions, the evolution of dissolved AOM composition during growth of a given alga gives acceptable (qualitative and quantitative) reproducibility. For our study, several batches of algal culture were grown using similar conditions to conduct ultrafiltration experiments for a period of 3 years.

Figure 3-15: DOC composition at three different growth phases for two culture batches for (a) SKC, (b) TET, (c) HYM and (d) SYN
3.2.5. Total algal organic matter in culture solution: Importance of the intracellular organic matter

The Total dissolved Algal Organic Matter ($\text{AOM}_T$) is defined by the sum of the AOM released during growth ($\text{AOM}_g$) and the entire IOM content. The $\text{AOM}_T$ ($<0.7 \, \mu\text{m}$) was analyzed every second day after sonication of the solution. Sonication permits to destroy the algal cells and release the IOM to the culture solution. Figure 3-16 presents the relationship between the $\text{AOM}_g$ and the $\text{AOM}_T$.

![Figure 3-16: Relationship between the $\text{AOM}_g$ and the $\text{AOM}_T$](image)

The DOC of $\text{AOM}_T$ is 10 times higher than the DOC released during growth (i.e., $\text{AOM}_g$) for SKC and HYM ($R^2 = 0.97$ for both SKC and HYM). A total cell lysis would increase the DOC concentration by 4 for TET ($R^2 = 0.95$) and by 2.7 for SYN ($R^2 = 0.89$). Figure 3-17 presents the composition differences between the $\text{AOM}_g$ and the $\text{AOM}_T$. 
Figure 3-17: Proportion of the different fractions of DOC in the AOM$_T$ as compared to the AOM$_g$. (a) HMW, (b) IMW and (c) LMW

The proportion of HMW compounds in AOM$_T$ is higher than in AOM$_g$ for SKC, TET and HYM, indicating that IOM is composed by a higher amount of HMW structures than EOM. The IMW structures are more abundant in AOM$_g$, and should be mainly released by the algal cells during growth as part of the EOM. The LMW contribution is slightly higher in AOM$_T$ than in AOM$_g$ for TET, HYM and SYN, (no significant difference for
SKC), which suggest that the IOM is more concentrated in LMW compounds than the EOM.

The FEEM fingerprint (normalized by the DOC concentration) of the AOM$_T$ is very similar to the fingerprint of AOM$_S$ (Figure 3-18), and no significant difference in the quality of the total chromophoric AOM was noticed for EOM and IOM.

Figure 3-18: FEEM comparison between the AOM$_S$ and AOM$_T$ for (a) SKC, (b) TET, (c) HYM and (d) SYN
3.3. Conclusion

(1) Three different stages of growth are distinguished in an algal culture: the Exponential Phase (EP), the Stationary Phase (SP) and the Decline Phase (DP). During the EP, the AOM content is linearly correlated with the cell concentration and the AOM of the culture solution mainly corresponds to the EOM. When the SP begins, the IOM is released to the solution due to cell lysis and the AOM of the culture solution is a mixture of EOM and IOM. At the DP, the proportion of IOM increases with the death of the algal cells. The composition of AOM is divided in three parts: the HMW, the IMW, which is slightly aromatic and the LMW fraction.

(2) During growth, the proportion of HMW moieties increases and becomes dominant at DP. The HMW is getting enriched in proteinaceous material and marine humic acid-like structures for SKC, TET and HYM, and the proportion of marine fulvic acid-like structures (i.e., fluorescence intensity) increases during growth for SYN.

(3) The IOM is richer in HMW and LMW structures than the EOM, however the chromophoric character of IOM is similar to EOM.

(4) Under similar experimental conditions, the evolution of dissolved AOM composition during growth of a given alga gives acceptable (qualitative and quantitative) reproducibility.
4. Algal HMW biopolymers of three different algal species: isolation and structural characterization

4.1. Isolation of HMW biopolymers

4.1.1. Impact of the centrifugation on the integrity of the algal organic matter

Algal cells are separated from AOM by centrifugation at 3,000g. The separation was performed at the end of the stationary phase of growth, when the organic content was sufficient to isolate the HMW compounds, and when the IOM contribution to the AOM was still limited.

To ensure that centrifugation does not destroy the algal cells and release IOM in the culture solution, a comparison was performed between the culture solution centrifuged and filtered through 0.7μm and a culture solution only filtered. LC-OCD profiles are displayed in Figure 4-1.
No significant difference between the culture solution centrifuged and filtered and the culture solution filtered can be observed on LC-OCD profiles. The centrifugation is apparently not destroying cells since the LC-OCD profile is not modified when centrifugation was operated in addition to filtration (i.e., undetected IOM contribution).

To be able to characterize the EOM (supernatant) and IOM fractions of the algal suspensions, the twenty liters of culture solution were centrifuged at 3,000g for 15 minutes. The cells recovered from the bottom of the flasks were concentrated down to 50 mL and sonicated to release all the IOM in the solution. The EOM (supernatant) and IOM solutions were finally filtered through 0.7 μm. The EOM solution is further concentrated by rotary evaporation at low temperature down to nine liters (factor of 2) (see Figure 2-3).
4.1.2. Size separation by dialysis

Based on the literature information, the most interesting fraction of AOM in term of fouling potential of algal solutions is the HMW fraction. Table 4-1 presents the proportion of HMW for all studied AOM solutions. The SYN suspension did not contain enough AOM material to develop the isolation procedure and characterize the HMW compounds.

<table>
<thead>
<tr>
<th></th>
<th>EOM</th>
<th>IOM</th>
</tr>
</thead>
<tbody>
<tr>
<td>SKC</td>
<td>27 %</td>
<td>6 %</td>
</tr>
<tr>
<td>TET</td>
<td>38 %</td>
<td>55 %</td>
</tr>
<tr>
<td>HYM</td>
<td>45 %</td>
<td>37 %</td>
</tr>
<tr>
<td>SYN</td>
<td>na</td>
<td>21 %</td>
</tr>
</tbody>
</table>

HMW material (< 0.7 μm) represents from 27 to 45 % of the dissolved organic carbon of SKC, TET and HYM EOM solutions; HYM being the most enriched. The proportion of HMW compounds in the IOM is more variable since it represents 6 to 55 % of the DOC; TET being the most enriched.

3.5 kDa dialyses of the EOM and IOM solutions against MilliQ were conducted with the objective to isolate HMW compounds (previous tests showed that 3.5 KDa dialysis bag is appropriate) and separate the organics from the inorganics. Several dialyses in series were conducted by renewing the MilliQ water every two days until the permeate conductivity was lower than 10 μS/cm. The dialysis retentate were collected, and LC-OCD profiles were compared to the original solutions (Figure 4-2).
Figure 4-2: Initial solution and dialysis concentrate, i.e. HMW biopolymers for (a) SKC, (b) TET, (c) HYM and (d) SYN.
LC-OCD profiles show that the dialysis protocol was very efficient to isolate the HMW fraction from the EOM and IOM solutions. The HMW solutions were lyophilized and the recovered material (powder) was used for further characterization i.e., Elemental Analysis, FTIR, Pyrolysis-GC-MS, $^{13}$C-NMR and $^1$H-NMR.

4.2. Characterization of HMW biopolymers

4.2.1. Elemental analysis

Elemental analysis was performed in triplicate for each sample. Table 4-2 gives the relative abundance (percent of mass) of C, H, N and the C/N and C/H atomic ratios. The C/N ratio is an indicator of the presence of nitrogenous structures such as proteins or similar biogenic material. The C/H ratio is an indicator of the degree of unsaturation (i.e., aromatic character).

<table>
<thead>
<tr>
<th></th>
<th>%C (Std. dev.)</th>
<th>%H (Std. dev.)</th>
<th>%N (Std. dev.)</th>
<th>C/N atomic ratio</th>
<th>C/H atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>SKC EOM</td>
<td>33.72 (0.05)</td>
<td>6.54 (0.05)</td>
<td>3.97 (0.17)</td>
<td>9.92</td>
<td>0.43</td>
</tr>
<tr>
<td>SKC IOM</td>
<td>51.03 (0.55)</td>
<td>7.84 (0.10)</td>
<td>6.44 (0.08)</td>
<td>9.24</td>
<td>0.54</td>
</tr>
<tr>
<td>TET EOM</td>
<td>35.99 (0.08)</td>
<td>6.44 (0.07)</td>
<td>2.80 (0.14)</td>
<td>15.01</td>
<td>0.46</td>
</tr>
<tr>
<td>TET IOM</td>
<td>35.51 (0.40)</td>
<td>6.44 (0.10)</td>
<td>5.82 (0.16)</td>
<td>7.11</td>
<td>0.46</td>
</tr>
<tr>
<td>HYM EOM</td>
<td>37.88 (0.03)</td>
<td>6.62 (0.07)</td>
<td>1.63 (0.14)</td>
<td>27.17</td>
<td>0.47</td>
</tr>
<tr>
<td>HYM IOM</td>
<td>30.73 (0.02)</td>
<td>6.10 (0.13)</td>
<td>1.94 (0.03)</td>
<td>18.44</td>
<td>0.42</td>
</tr>
<tr>
<td>SYN IOM</td>
<td>38.79 (0.02)</td>
<td>6.79 (0.12)</td>
<td>4.91 (0.10)</td>
<td>9.21</td>
<td>0.47</td>
</tr>
</tbody>
</table>
The carbon content of the isolated organics varied from 31% to 39%, with the exception of SKC IOM (i.e., 51%). Low carbon content is synonym of high polarity. It is interesting to note that HMW compounds isolated from freshwater (i.e., biopolymers) using the same protocol (Hwang et al., 2001) are showing slightly higher carbon content (i.e., 37 to 43%). C/H atomic ratios are very low (i.e., 0.42 to 0.47), even for SKC IOM (0.54), in the same order of magnitude as freshwater biopolymers and much lower (i.e., 0.7 to 0.8) than humic substances (Hwang et al., 2001). HMW organics from algal EOM and IOM are characterized by low unsaturated carbon content (low aromaticity). For all species, the C/N atomic ratio is lower for IOM than for EOM. For TET and HYM, IOM is described by a C/N almost two times higher than EOM, whereas SKC IOM and EOM have relatively similar C/N.

The C/N atomic ratios of the different algae EOM are following the sequence HYM > TET > SKC and IOM, the sequence HYM > SKC ≈ SYN > TET. HYM is characterized by the highest C/N ratio, which implies that it is least enriched in proteinaceous material, similar to humic substances (Hwang et al., 2001). The ratio is magnified by 1.5 and 2 between IOM and EOM for HYM and TET, respectively, whereas SKC IOM and EOM are defined by a similar C/N ratio; values that are in the order of magnitude of freshwater NOM (> 10) (Nguyen et al., 2005; Repeta et al., 2002). TET IOM has the lowest C/N and is probably rich in protein-like structures.

4.2.2. Fourier Transform Infrared (FTIR) spectroscopy

FTIR analysis was performed for each AOM samples and FTIR spectra are presented in Figure 4-3. FTIR analysis permits to highlight the predominant structural features of an
NOM sample. Identification of infrared (IR) absorption peaks was carried out in accordance with the data published by Leenheer (2009).

Figure 4-3: FTIR spectra for the different HMW AOM
The strong adsorption band at 3400 cm\(^{-1}\) is characteristic of the hydrogen bonding. Amide-A (3294 cm\(^{-1}\)), amide-B (3090 cm\(^{-1}\)), amide-I (1650 cm\(^{-1}\)), amide-II (1555 cm\(^{-1}\)), and amide-III (1410 cm\(^{-1}\)) signals were assigned to proteins. Presence of polysaccharides/sugars was assessed through detection of a broad band near 1037 cm\(^{-1}\) (stretching vibration of C-O). A sharp peak at 1384 cm\(^{-1}\) (symmetric bending vibration of CH\(_3\) of N-acetyl group) along with amide-I, amide-II peaks, and sugar bands, is characteristic of N-acetyl aminosugars, degradation product of bacterial cell wall peptidoglycans (Coates et al., 2000; Leenheer, 2009). Bands at 2960 cm\(^{-1}\) to 2850 cm\(^{-1}\) assigned to aliphatic groups (CH\(_3\), CH\(_2\)) (Igisu et al. 2009). The COOH band at 1730 cm\(^{-1}\) and CH\(_2\) band at 1454 cm\(^{-1}\) along with the band at 2960-2850 cm\(^{-1}\) could be attributed to lipids/aliphatic acids (Leenheer, 2009). The band at 1240 cm\(^{-1}\) is attributable to the stretching vibration of phosphodiester backbone of nucleic acids (Naumann et al. 1996).

Presence of mentioned biogenic material in all the AOM (i.e., EOM and IOM) samples was suggested by their characteristic IR bands. Relatively high intensities of bands assigned to carbohydrates and protein-like structures revealed that AOM samples were mainly consisted of these two biopolymers. The relative intensities of proteins signals were always higher for IOM than for EOM samples as compared to that of carbohydrates, for all HMW AOM samples. It means that IOM contents of all four algae were richer in proteinaceous/nitrogenous substances material than their counterpart EOM contents. Khan et al. (Khan et al., 2013a; Khan et al., 2013b; Khan et al. 2014) found that recent RO biofilms developed on RO desalination membrane populated with higher number of active micro-organisms contain a larger proportion of proteinaceous material and lower
polysaccharides content than mature biofilms characterized by lower microbial and higher exopolymeric substances (i.e., EPS mainly polysaccharides) contents. Their findings support our results indicating that IOM is more enriched in proteins. Moreover, it was also observed that AOM of HYM was mainly characterized by the presence of carbohydrates.

As expected, the intensity ratio between the amide I peak (at 1650 cm$^{-1}$) and the carbohydrate peak (at 1037 cm$^{-1}$) is correlated with the C/N atomic ratio measured with the elemental analysis (Figure 4-4), which confirms the use of C/N atomic ratio as an indicator of proteinaceous content.

![Figure 4-4: Correlation between the C/N atomic ratio and the intensity ratio between the amide I peak and the carbohydrate peak](image)

4.2.3. Pyrolysis-GC-MS (Py-GC-MS)

Pyrochromatograms of the different algal HMW are presented in Figure 5-2.
The different pyrolysis fragments were identified using data published by Leenheer et al., (2003) (Table 4-3).
Table 4-3: Specific pyrolysis fragments of biopolymers (Leenheer et al., 2003)

<table>
<thead>
<tr>
<th>Type</th>
<th>Common pyrolysis fragments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysaccharides</td>
<td>Methylfuran, furfural, acetyl furan, methylfurfural, levoglucosanone, hydroxypropanone, cyclopentanone, methyltetrahydrofuran, acetic acid</td>
</tr>
<tr>
<td>Aminosugars</td>
<td>Acetanilide, N-methylacetamide, propionamide, acetic acid</td>
</tr>
<tr>
<td>Proteins</td>
<td>Acetonitrile, benzonitrile, phenylacetonitrile, pyridine, methylpyridine, pyrrole, methylpyrrole, indole, methylindole (from tryptophan), toluene, styrene (from phenylalanine), phenol, p-cresol (from tyrosine)</td>
</tr>
<tr>
<td>Polyphenolic compounds</td>
<td>Phloroglucinol, α-, m-, p-cresol, methylphenols, dimethylphenols</td>
</tr>
<tr>
<td>Lignins</td>
<td>Methoxylphenols</td>
</tr>
<tr>
<td>Tannins</td>
<td>Catechol</td>
</tr>
<tr>
<td>DNA</td>
<td>Furfuryl alcohol</td>
</tr>
<tr>
<td>Polyhydroxybutyrates</td>
<td>Butanoic acid</td>
</tr>
</tbody>
</table>

All HMW AOM samples were characterized by a similar pyrolysis GC/MS fingerprint, however, the relative abundance of the different biopolymers (i.e., polysaccharides, proteins, polyhydroxybutyrates, lipids) varies from one species to another and from EOM to IOM.

The first important remark is that a large majority of the pyrolysis by-products (i.e., furans, furfural, cyclopentenones, levoglucosanone) of the EOM isolates of the three algae originate from polysaccharide moieties. This observation indicates that polysaccharides probably represent the dominant biopolymer group of algal EOM. The signature for proteins is also clear with the presence in the EOM pyrochromatograms of pyrroles, pyridines and the series of toluene, styrene characteristic of phenylalanine. For these samples the existence of phenol and p-cresol can be attributed to the pyrolysis of
tyrosine because in general these two peaks show similar intensities. Higher phenol signal suggest the predominance of polyhydroxyalkanoates (PHAs), whereas equal or higher p-cresol suggests predominant presence of tyrosine (Bruchet et al., 1990; Christy et al., 1999). In the case of TET EOM the presence of another methylphenol associated with the very intense toluene peak may refer to humic-like substances. However the relative abundances of all these protein related peaks are significantly lower than for the polysaccharide derivatives. EOM do contain lipids indicated by the identification of fatty acids, hexadecanoic acid (C16) characteristic of microbial lipids is predominant. HYM EOM shows relatively low peak intensity fatty acids as compared to SKC EOM and TET EOM. Overall the pyrolysis fingerprint of HYM EOM confirms the results of the previous characterization tools showing polysaccharides as the predominant biopolymer entering in the composition of this AOM fraction.

TET IOM and SKC IOM samples exhibited very specific pyrochromatograms with intense isocrotonic and crotonic acid peaks produced from the pyrolysis of polyhydroxybutyrates (PHBs) which are known as energy storage molecules synthesized by microbial cells under growth-limiting conditions (Ackermann et al., 1995). As a consequence the relative abundance of the polysaccharide and protein peaks for these two IOM fractions is decreased, however lipids (fatty acid derivatives) remain a major biopolymer constituent especially for SKC IOM (more intense peaks of the pyrochromatogram). It is interesting to observe that HYM EOM and HYM IOM produced very similar pyrochromatograms, both indicating the predominance of polysaccharides pyrolysis derivatives.
Increase in phenol/p-cresol peak area ratios from EOM to IOM fractions, in case of all studied algal species, is an evidence of the relatively lower presence of tyrosine containing proteins in algal exudates than in cellular contents. SYN IOM pyrochromatogram (only fraction analyzed for SYN) is characterized by intense fatty acids peaks and distinct fingerprints related to the incorporation of polysaccharides and proteins to much lower relative abundances.

4.2.4. $^{13}$C-NMR

$^{13}$C-NMR analyses were performed to further investigate the nature of each HMW AOM. The different spectra are plotted in Figure 3.
Figure 4-6: $^{13}$C-NMR spectra of the different HMW AOM
All $^{13}$C-NMR spectra are dominated by a strong resonance at 72 ppm (i.e., alcohol band) associated with a well resolved band centered at 100 ppm (i.e., anomeric C) characteristic of carbohydrates (Gillam et al., 1985; Nguyen et al., 2005; Benner et al., 1992). The peak at around 174 ppm can be attributed to carboxyl group present in carbohydrate moieties (Hedges et al. 2002; Benner et al. 1992). Profiles recorded for HYM EOM and IOM correspond to almost pure carbohydrates (Leenheer, 2009) in accordance with all the other characterization tools used in this project.

The peak at 174 ppm can also refer to amide as an indicator of proteins with the peaks in the 45 and 60 ppm region corresponding to the N-alkyl linkage and amino-acid groups (Hedges et al., 2002; Leenheer, 2009). The spectrum obtained for SKC IOM incorporates clear signatures of proteins with a strong signal in the 45-60 ppm region in addition to peaks at 130 and 169 ppm that correspond to aromatic aminoacids (i.e, tyrosine). The band at 174 ppm is more prominent suggesting a contribution of both, carboxyl and amide.

A distinct peak observed for some AOM fractions round 30 ppm refer to methylene carbons included in lipids or long straight carbon chain present in proteinaceous structures.

4.2.5. $^1$H-NMR

In order to obtain more information on the linkage of hydrogen, $^1$H-NMR was used and spectra are presented in Figure 4-7.
Resonances observed between 0.5 and 1.8 ppm are assigned to alkyl proton attached to carbon removed from aromatic rings or carboxylic groups. This region is attributed to the lipids by Aluwihare et al. (1997). From 1.8 to 3 ppm, the resonance corresponds to
protons attached mostly to carbon positioned on α to aromatic ring and carboxylic groups, and are characteristic of proteins. Region from 3 ppm to 4.7 ppm (alcohol and ether H attached to carbon positioned on α to oxygen), and from 5 to 5.5 ppm correspond to the carbohydrate compounds. From 6.4 to 9 ppm, the resonances are assigned to aromatic and olefinic protons (Gillam et al., 1985; Aluwihare et al., 1997; Repeta et al., 2002).

AOM samples are characterized by strong resonances in the carbohydrates, proteins and lipid regions. IOM is enriched in proteins for all algal species and in lipids for SKC and HYM, and contains fewer carbohydrates than EOM. HYM is characterized by the strongest signal in the carbohydrate region (3.2 to 4.3 ppm) and SKC, by the strongest signal in the lipid region (0.8 to 1.5 ppm). Surprisingly, no band characterizing the lipids are present for SYN IOM, despite the lipid signature in the pyrochromatogram.

4.2.6. Conclusion on the composition of the HMW AOM samples

Globally, the HMW AOM samples are defined by a higher polarity and a similar aromaticity than the freshwater biopolymers. The HMW AOM are mainly consisting of polysaccharides and proteins but their relative abundances vary from one alga to another. HYM is described as the richest polysaccharide-like NOM, whereas SKC and TET are a mixture of protein and polysaccharides. The higher protein content is observed for TET HMW samples. SKC and SYM HMW samples are also defined by higher lipid content. For all cases, the HMW IOM is enriched in protein-like structures, probably coming from the DNA contained in the algal cells.
4.3. Interactions between AOM fractions isolated from algal monocultures and Al$_2$O$_3$ membrane surface: an AFM study

The interactions between Al$_2$O$_3$ membrane surface and AOM fractions (i.e., EOM and IOM) isolated from SKC, TET, and HYM monocultures collected during decline phase were studied by Atomic Force Microscopy (AFM). In addition the Gartempe River HPOA fraction (i.e., Terrestrial Organic Matter or TOM) was selected for comparison. The alumina membrane was selected because of its hydrophilic characteristics, conferred by hydroxyl groups present in its structure which promotes interaction with water molecules (Sah et al., 2004; Tressaud et al., 2009). The isoelectric point of alumina has been previously measured between 8 and 9 by streaming potential, and has been suggested to be highly influenced by ionic strength and the presence of ions in solution (Sander et al., 2004). AFM was used because it is a sensitive technique that allows the study of specific and nonspecific interactions at the very interface (Butt et al., 2005). In addition, AFM can be adapted to closely mimic environmentally relevant aquatic systems (e.g., sea water). The colloidal probe technique was used to accurately quantify the interactions at a sub-nano Newton resolution between the NOM isolates and membrane surface.

AFM colloidal probe was coated with each NOM isolate following the layer-by-layer procedure using iron oxide as an intermediate layer (Aubry et al., 2013). Experiments were conducted in synthetic seawater. A minimum of forty force vs. distance curves were generated per each NOM isolate. Approaching and retracting regimes were individually analyzed and statistically processed. The main goal of this study was to elucidate the dominant interacting mechanisms that govern NOM-Al$_2$O$_3$ membrane surface.
interactions as a function of NOM characteristics under seawater conditions. It was developed to tentatively support the ceramic membrane fouling results obtained in this work and advance our fundamental understanding of AOM membrane fouling.

4.3.1. Gradient analysis of approaching force curves

Approaching force vs. distance curves (Figure 4-8) provided important information regarding range and type of interactions between NOM isolates and alumina membrane as a function of NOM characteristics. A gradient analysis was conducted on the approaching curves following the method previously described (Li et al., 2004).
Figure 4-8: Representative approach gradient curves for (a) SKC IOM and SKC EOM, (b) TET IOM and TET EOM, and (c) HYM IOM and HYM EOM

Each gradient curve was individually analyzed for the following three phases: 1) Non-Interaction phase (N-I): the NOM-coated AFM probe is at a considerable separation distance from the membrane surface where no interaction is detected; 2) Non-Contact phase (N-C): the NOM-coated AFM probe interacts through electrosteric mechanisms with the membrane surface; and 3) Contact Phase (C): the NOM-coated AFM probe is in contact with the membrane surface.
During SKC EOM, TET EOM, HYM EOM (i.e., EOM fractions), and HYM IOM approach to the alumina membrane surface only repulsive forces were detected. In contrast, during SKC IOM and TET IOM approach to the alumina membrane surface, 60% and 88% of the generated approaching curves displayed jump-in to contact events (i.e., strong attractive forces with a gradient exceeding the spring constant of the cantilever) (Figure 4-8). The occurrence of repulsive forces or jump-in to contact events indicates that the characteristics of the AOM isolates were highly influential during approach. Specifically, the characterization of the AOM isolates indicates that HYM sample have the highest relative abundance of carbohydrates, while SKC and TET samples have a more equilibrated protein/carbohydrate distribution. In addition, IOM fractions are more enriched in proteins and lipids, whereas EOM fractions are characterized by a higher abundance of carbohydrates.

Evidently, the fractions with higher content of carbohydrates in their structures solely displayed repulsive forces during approach and could be explained as follows. At the ionic strength (IS= 0.7 M) of synthetic seawater, the double layer is expected to be suppressed. In fact, at low IS and long separation distances, classic DLVO theory results in very good approximations when describing electrostatic forces. Nevertheless, when the IS of the solution reaches 100 mM, electrostatic repulsive forces (and theoretical Debye Length) quickly approaches to zero (Israelachvili, 2011). Therefore, at high IS and short separation distances, other non-DLVO forces (i.e., of attractive, repulsive, or even of oscillating nature) would play a fundamental role during interactions. In the specific case of the AOM fractions with large carbohydrates content, hydration and steric forces would cause this repulsive regime during approaching. Hydration forces occur at very
hydrophilic surfaces such as carbohydrates, which have a high capability of three-dimensional hydrogen bonding and high interaction with the surrounding solution. Water molecules and counter-ions (i.e., Na\(^+\) and Ca\(^{2+}\) are hydrated cations) would be expected to structure and accumulate in the vicinity of the carbohydrates structure forming a dense hydration layer, giving rise to hydration forces. In addition, steric forces due to the polymeric nature of these AOM isolates would also contribute to the repulsion observed. These two mechanisms would efficiently shield Van Der Waals attractive forces. Results from gradient analysis support this hypothesis. The longest N-C distances were observed for SKC EOM and TET EOM (15.7 +/- 0.2 nm and 15.1 +/- 0.7 nm, respectively) (Figure 4-9). Interestingly, all the measured N-C distances significantly deviates from theoretical DLVO (i.e., double layer is expected to be screened) therefore indicating polymeric structure interaction. Similarly, the longest C distances were measured for SKC EOM, TET EOM, HYM IOM, and HYM EOM, indicating a higher compression of the NOM layer than the samples with higher protein/lipid content (SKC IOM and TET IOM).
On the other hand, proteins have been described as complex mixtures highly dependent on their origins (Xu et al., 2005). Therefore, proteins interaction with surfaces would be influenced by their characteristics. Previous studies have remarked the importance of hydrophobicity and electrosteric mechanisms on protein interactions (Xu et al., 2005). Specifically, SKC IOM and TET IOM (i.e., highest protein and lipid content) displayed attractive (jump-in to contact) and repulsive forces during approaching. The oscillating nature of the interaction of these two fractions (i.e., observed in previous studies) (Xu et al., 2005) with alumina membranes would be explained as follows. The hydrophobic nature of these fractions (i.e., conferred by the presence of proteins and lipids) would not induce as strong hydration layers in the vicinity of their structures as the fractions with a high content of carbohydrates. In addition, the gradient force curve analysis showed the shortest C and N-C distances compared to their corresponding EOM fractions, indicating less compaction of their polymeric structures. This result also suggests that IOM fractions
would interact in a lesser extend with the surrounding solution than EOM fractions. These results support the hypothesis that deviations from classic DLVO theory arises on very hydrophilic or very hydrophobic surfaces. Interestingly, TOM (Gartempe River HPOA) interactions with alumina membrane were similar to those of SKC IOM and TET IOM. TOM has been previously characterized as a typical river humic substance of considerable aromatic structure and a high content of carboxyl functional groups. During TOM approaching to alumina membrane, 47% of the generated curves displayed jump-in to contact events. Likewise, at the high IS of the synthetic seawater used in this study, the double layer of TOM is expected to be completely screened. In addition, due to the hydrophobic nature of this river NOM fraction, no strong hydration layer would also be expected in the vicinity of its structure, favoring the occurrence of jump-in to contact events. Also, the N-C and C distances were significantly shorter than SKC EOM and TET EOM, suggesting more compaction of its polymeric layer than polysaccharide-rich fractions.

4.3.2. Analysis of NOM adhesion on alumina membrane surface during retracting regime

Force profiles during retraction provided information regarding the strength of the bond and energies of adhesion between AOM isolates and alumina membrane surface. Adhesion energies were calculated by integrating the adhesion forces with the separation distances using the trapezoidal rule as described elsewhere (Gordesli et al., 2012). The adhesion energies SKC EOM, TET EOM and HYM EOM were clearly higher than their corresponding IOM fraction, indicating stronger adsorption of carbohydrate-rich NOM to alumina surface (Figure 4-10).
Interestingly, previous studies have directly correlated the occurrence of jump-in to contact events to higher adhesion forces (Xu et al., 2005). Nevertheless, results from this investigation showed the opposite trend. EOM fractions displayed higher adhesion energies than IOM fractions (i.e., the latter showed jump-in to contact events), indicating that the attraction between IOM proteins and alumina membrane surface did not result in higher adhesion energies. Although hydrophobic interactions have been suggested as important for proteins (Schäfer et al., 2011), they did not play an important role during the adhesion to alumina membrane surface. Conversely, the higher adhesion of EOM fractions to alumina membrane surface would be explained by the hydrophilic nature of these carbohydrate-rich NOM isolates, suggesting the importance of hydrogen bonding during retraction as previously suggested (Aubry et al., 2013; Azmi et al., 2013). In addition, TOM adhesion energy to alumina membrane was lower than polysaccharide-rich AOM fractions, indicating the influence of its structure during interactions with the
membrane surface. The hydrophobic character of TOM would play a fundamental role during adhesion, similarly to SKC IOM and TET IOM (i.e., fractions rich in protein/lipids).

4.3.3. Conclusions on the adsorption properties of the different HMW AOM on Al₂O₃ membrane

Each AOM is characterized by a unique composition and HMW IOM and HWM EOM are different materials. IOM is enriched in proteins and lipids, whereas EOM has a higher abundance of carbohydrates. Additionally, HYM is described with the strongest carbohydrate content, and SKC and TET by a more equilibrated distribution protein/carbohydrate. Carbohydrate-rich NOM fractions (SKC EOM, TET EOM, HYM EOM, and HYM IOM) showed repulsion forces during approach, possibly attributed to steric and hydration forces. Conversely, a significant number of jump-in to contact events was observed in the most protein/lipid-rich AOM fractions (SKC IOM and TET IOM). These phenomena could be attributed to the hydrophobic nature of proteins and lipids present in the structure of these samples, which do not allow strong hydration layers at the vicinity of their structures, and therefore not efficiently overruling Van Der Waals forces. Interestingly, the occurrence of jump-in to contact events did not directly correlate to the magnitude adhesion energies. The highest adhesion energies were observed for the EOM samples, and can be attributed to their hydrophilicity (i.e., possibly originated by hydrogen bonding mechanisms). Finally, TOM interactions with alumina membrane were conducted as control experiments and the results obtained were in good agreement with similar hydrophobic fractions (i.e., SKC IOM and TET IOM). Jump-in to contact
events were present during TOM approaching to alumina membrane in 47% of the generated curves. Furthermore, the adhesion of TOM to alumina membrane was lower than polysaccharide-rich AOM fractions, suggesting the influence of its hydrophobicity during interactions.
5. Algal solutions fouling ceramic ultrafiltration membranes: A comprehensive study

5.1. Feed water quality

In order to understand the impact of the change in quality of the culture solution, ultrafiltration experiments were performed with SKC, TET, HYM and SYN monocultures during the Exponential Phase (EP) and the Decline Phase (DP) of growth. Experiments were conducted with diluted culture solutions prepared with organic free synthetic seawater. The prepared culture was then analyzed to insure a final DOC concentration of 0.5 mg/L. However, it is important to note that the dilution factor needed to reach the desired final DOC concentration of the feed solutions (i.e., 0.5 mg/L) was determined based on the analysis of the culture solution filtered through 0.7 μm. Colloidal AOM larger than 0.7 μm was present in the feed solution but were not quantified due to some restrictions on the use of our analytical tools.

The fouling potential of AOM was compared with the fouling potential of Terrestrial NOM and a one-cycle filtration experiment was performed using humic substances isolated from the Colorado River (Col-HS). Feed solution was prepared with organic free synthetic brackish water to avoid coagulation/flocculation observed at very high ionic strength (i.e., seawater). The synthetic seawater was diluted by a factor of two to produce the synthetic brackish water, and the LC-OCD profile is shown in Figure 5-1. The Col-HS isolated from treated water is a low aromatic DOM (SUVA$_{254}$ = 1.58 L.mg$^{-1}$,m$^{-1}$). The LC-OCD profile is typical of treated surface water composed of intermediate
molecular weight humics (i.e., fulvic acids), and low molecular weight acids and neutrals. Col-HS is more aromatic in nature than AOM.

Table 5-1 presents the DOC concentration of the UF feeds. The same feed solution was used for Al₂O₃-80 nm and TiO₂-30 nm membranes.

Table 5-1: Water quality of the feed waters during EP and DP

<table>
<thead>
<tr>
<th></th>
<th>DOC (mg/L)</th>
<th>HMW (mg/L)</th>
<th>IMW (mg/L)</th>
<th>LMW (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Proportion of the DOC)</td>
<td>(Proportion of the DOC)</td>
<td>(Proportion of the DOC)</td>
</tr>
<tr>
<td>Col-HS</td>
<td>9.66</td>
<td>+/- 0.29</td>
<td>Not quantifiable</td>
<td>5.90 (61%)</td>
</tr>
<tr>
<td>SKC</td>
<td>0.64</td>
<td>+/- 0.02</td>
<td>0.07</td>
<td>0.15</td>
</tr>
<tr>
<td>TET</td>
<td>0.61</td>
<td>+/-0.00</td>
<td>0.10</td>
<td>0.26</td>
</tr>
<tr>
<td>HYM</td>
<td>0.56</td>
<td>+/- 0.16</td>
<td>0.01</td>
<td>0.13</td>
</tr>
<tr>
<td>SYN</td>
<td>0.64</td>
<td>+/- 0.02</td>
<td>0.06</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Figure 5-1: LC-OCD profile of the Col-HS feed
The DOC content of the Col-HS was approximately twenty times higher than the AOM feed solution and as expected no HMW were present. The DOC concentrations of the AOM feed solutions were relatively similar, however the proportion of HMW is very different between the algal cultures and the phases of growth (i.e., EP and DP). The HMW contribution is magnified by 2.4 for SKC, 1.6 for TET, 10 for HYM and 3.7 for SYN between EP and DP.

5.2. Fouling property of algal solutions at different stage of growth

Two different ceramic membranes were studied: an alumina membrane characterized by a nominal pore size of 80 nm and a titanium oxide membrane characterized by a nominal pore size of 30 nm. UF experiments were performed at constant pressure fixed at 0.7 bar, which corresponds to a specific flux of 870 and 550 LMH for the alumina and titanium oxide membrane, respectively. Backwash pressure was three times higher than the filtration pressure (i.e., 2.0 bars), and was conducted with MilliQ water. One filtration experiment consists of three successive filtration cycles, i.e., filtration followed by a MilliQ backwash. For the third cycle, the MilliQ backwash was replaced by a Chemical Enhanced Backwash (CEB) using NaOH (0.1 M). The pure water permeability was measured after CEB. Feed solution (i.e., non-filtered culture solution diluted with SSW) was freshly prepared and the same feed solution was used for the two membranes.
5.2.1. Hydraulic performances

The hydraulic performances of the two membranes were assessed by monitoring the flux decline, and by calculating the Total Fouling Index of the first cycle (TFI -1) (Nguyen et al., 2011). Flux declines for both membranes are displayed in Figure 5-2.

Figure 5-2: Flux decline of the UF experiments performed at EP and DP for Al₂O₃-80 nm and TiO₂-30 nm membranes (Constant filtration pressure = 0.7 bar)
For similar initial DOC concentration, the fouling caused by algal solution depends on the algal species, the phase of growth and the UF membrane used. Algal solutions are characterized by a strong fouling potential as compared to Col-HS solution, and the flux decline is mainly occurring during the first filtration cycle of the experiment. As reported by Zhang et al. (2013b), the fouling potential of AOM solutions toward ceramic membrane are exacerbated with the age of the bloom, and the fouling is stronger at DP. The fouling potential of the different feed solutions are compared based on the calculation of the Total Fouling Index for the first cycle (TFI -1) expressed by m²/mg DOC filtered (Table 3). When normalizing the TFI -1 by the mass of DOC filtered, the small differences between the DOC concentration of the different feed solutions (which are not visible in Figure 5-2) are taken into account for a better comparison.

Table 5-2: Total fouling Index for the first cycle (TFI -1) for UF experiments through Al₂O₃-80 nm and TiO₂-30 nm at EP and DP. R² is specified under parenthesis.

<table>
<thead>
<tr>
<th></th>
<th>Al₂O₃ 80 nm</th>
<th>TiO₂ 30 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Col-HS</td>
<td>0.48 (1.00)</td>
<td>0.81 (0.99)</td>
</tr>
<tr>
<td>SKC</td>
<td>6.16 (1.00)</td>
<td>7.06 (0.99)</td>
</tr>
<tr>
<td></td>
<td>20.33 (0.99)</td>
<td>11.74 (0.99)</td>
</tr>
<tr>
<td>TET</td>
<td>3.49 (0.94)</td>
<td>3.49 (0.99)</td>
</tr>
<tr>
<td></td>
<td>23.00 (0.97)</td>
<td>11.68 (0.99)</td>
</tr>
<tr>
<td>HYM</td>
<td>3.16 (0.99)</td>
<td>2.40 (0.99)</td>
</tr>
<tr>
<td></td>
<td>31.27 (0.99)</td>
<td>44.91 (0.99)</td>
</tr>
<tr>
<td>SYN</td>
<td>4.51 (1.00)</td>
<td>8.43 (1.00)</td>
</tr>
<tr>
<td></td>
<td>10.23 (1.00)</td>
<td>57.10 (0.99)</td>
</tr>
</tbody>
</table>
The TFI -1 of the Col-HS solution is between 7 and 65 times and 3 to 55 times lower than TFI -1 of the AOM solutions for Al₂O₃-80 nm and TiO₂-30 nm, respectively.

During the EP, the most problematic fouling is observed for SKC with Al₂O₃-80 nm (TFI -1 = 6.16 x 10⁻³ m²/mg C), and for SYN with TiO₂-30 nm (TFI -1 = 8.43 x 10⁻³ m²/mg C). HYM induces the lowest fouling for both membranes (TFI -1 = 3.16 x 10⁻³ m²/mg C and 2.40 x 10⁻³ m²/mg C for Al₂O₃-80 nm and TiO₂-30 nm, respectively). At the EP, no major difference in TFI-1 fouling was recorded for all alga species, between Al₂O₃-80 nm and TiO₂-30 nm.

When the culture reaches the DP, the TFI -1 is globally increased. This increase is probably due to the higher HMW content and the change in the AOM composition (i.e., enrichment in proteins and lipids). The flux decline reaches a plateau at approximately 15-20% of the initial fluxes for both membranes. This finding may correspond to the formation of a porous cake layer that increases the hydraulic resistance of the membrane but does not totally block the pore network. At the DP, SKC and TET exerted higher TFI-1 fouling with Al₂O₃-80 nm as compared to TiO₂-30 nm; the opposite trend was observed of HYM and SYN, which might correspond to a higher affinity between polysaccharides and TiO₂ surface.

The most problematic fouling is caused by HYM (TFI -1 = 44.91 x 10⁻³ m²/mg C) and by SYN for TiO₂-30 nm (TFI -1 = 57.10 x 10⁻³ m²/mg C). The strong fouling potential of HYM at the DP is possibly due to the formation of large organic aggregates (Figure 4-7) that cannot be measured by our analytical tools. These large aggregates may induce a denser fouling leading to larger flux reduction. The high HMW content of SYN at the DP might explain the strong fouling potential of SYN toward TiO₂-30 nm.
membrane. However, the initial HMW content of SYN cannot explain the relatively low fouling of the Al₂O₃-80 nm membrane and other mechanisms developed later should be taken into account.

The irreversible nature of the fouling is also an important aspect of the fouling potential of AOM solutions. Flux decline (%), and proportion of reversible and irreversible fouling (RF and IF, respectively) are plotted in Figure 5-3. The reversible fouling corresponds to the flux that was recovered after backwash for the first and second filtration cycle, and after CEB for the third filtration cycle. It is calculated based on the initial flux, i.e, if the RF is 100 %, the initial permeability of the membrane is totally recovered.
Figure 5-3: Flux decline (%) and proportion of reversible and irreversible fouling for
(a) the first, (b) the second after backwash and (c) the third filtration cycle, after CEB.
As mentioned earlier, the first cycle is the most important in terms of flux decline, and the fouling is always higher at the DP compared to the EP. The lower and higher decline fluxes are observed for TET - EP (27.3%) and HYM – DP (70.4%) for Al₂O₃-80 nm, and for TET - EP (14.6%) and SYN – DP (63.3%) for TiO₂-30 nm, respectively.

Globally, for SKC, TET and HYM, the flux decline is higher for the filtration through Al₂O₃-80 nm than for the filtration through TiO₂-30 nm, whereas the opposite happens for SYN. This phenomenon could be explained by the size of the AOM that would be small enough to interpenetrate the pores of the Al₂O₃-80 nm membrane but not the pores of the TiO₂-30 nm membrane, which would lead to a stronger fouling. The filtration experiments were operated at pH8.1, which is close to the pHₚ𝒛c of Al₂O₃-80 nm (pHₚ scrollTop="false"="8.9") and higher than the pHₚ𝒛c of TiO₂-30 nm (pHₚ scrollTop="false"="6.5"). With these operating conditions, the surface of Al₂O₃-80 nm membrane was slightly positively charged whereas it was negatively charged for the TiO₂-30 nm, and the electrostatic repulsions were more important with the latest membrane, which permits a better filtration flux. However, this hypothesis does not corroborate results presented by Zaouri (2013) that found that the pH of the solution had no effect on the adsorption of algal HMW on alumina and zirconium oxide. It is also interesting to notice that, overall, the fouling is more reversible for Al₂O₃-80 nm (at best, 60% of the flux recovery, for the filtration of TET – EP), than for TiO₂-30 nm (at best, 30% of the flux recovery, for the filtration of HYM – EP), which could imply a stronger reactivity between the AOM and the titanium oxide.
The reversibility of the fouling was more important for the EP than the DP with SKC, TET and SYN through Al₂O₃-80 nm. HYM is characterized by a singular behavior and the flux recovery decreases between the EP and the DP, which is once again, probably due to the large AOM present in the solution at the DP that were not measured and increase the AOM content of the HYM solution. For TiO₂-30 nm, the irreversible fouling at the DP remains similar for SKC, is exacerbated for HYM and SYN and is reduced for TET. These opposite behaviors toward the two membranes could be explained by the interaction AOM – metal oxide and the change in quality of AOM when aging. During growth, AOM is enriched in HMW, which is a mixture of polysaccharides, proteins and lipids (Chapter 4, Henderson et al., 2008; Huber et al., 2011; Lancelot, 1984; Myklestad, 1995; Villacorte, 2013) and lead to higher fouling at the DP. In case of pore blocking, we can postulate that the large pores of the Al₂O₃-80 nm membrane could be more easily cleaned than the small pores of the TiO₂-30 nm membrane. The large HMW structures of TET would remain at the surface of the membrane and would be more easily backwashed, which confers to better reversibility of the fouling caused by TET.

Higher flux recovery is obtained with CEB using NaOH (0.1M) than MilliQ backwash; however, its efficiency remains limited. For both membranes and both phases of growth, the best recovery is observed for the filtration of TET, with a final permeability of 71% and 66% of the initial Al₂O₃-80 nm flux and of 78% and 55% of the initial TiO₂-30 nm flux, for the EP and the DP respectively. It is interesting to notice that TET is also characterized by the higher protein content, which suggest that the interaction between the protein-like structures and metal oxides are relatively weaker than the interactions
between the polysaccharide-like structures and the metal oxides, and it is in accordance with the AFM results discussed in the Chapter 4. The AOM is strongly bounded to the metal oxide and a solution of NaOH at 0.1M is not sufficient to wash out these organics from the membrane.

**5.2.2 Permeate quality**

The permeate was collected at the end of the ultrafiltration experiment and represents the total permeate (i.e., mixture of the permeate from the different filtration cycles). Good cell removal was achieved with ceramic UF filtration (Table 5-3). Algal cell removal is higher than 99.6% except for SYN – DP was 98.1%. Algal cell size is around 10 μm for SKC, TET and HYM and below 2 μm for SYN, which is relatively large as compared to the nominal pore size of the membranes, and cells should not be found in the permeate. The presence of a few algal cells in the permeate confirmed the non-homogeneity of the membrane pore size. Defects in the surface layer permit a limited amount of cells to breakthrough the membrane. Compared to SKC, TET and HYM, SYN cells are the smallest and they might more easily breakthrough the membrane porosity.
Table 5-3: Algal cell removal by Al$_2$O$_3$-80 nm and TiO$_2$-30 nm membranes for SKC, TET, HYM and SYN at EP and DP

<table>
<thead>
<tr>
<th></th>
<th>Feed</th>
<th>80 nm Permeate</th>
<th>Removal</th>
<th>30 nm Permeate</th>
<th>Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SKC</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP</td>
<td>15.5</td>
<td>&lt; 0.05</td>
<td>&gt; 3-log</td>
<td>&lt; 0.05</td>
<td>&gt; 2-log</td>
</tr>
<tr>
<td>DP</td>
<td>2.89</td>
<td>&lt; 0.05</td>
<td>&gt; 3-log</td>
<td>&lt; 0.05</td>
<td>&gt; 2-log</td>
</tr>
<tr>
<td><strong>TET</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP</td>
<td>2.58</td>
<td>&lt; 0.05</td>
<td>&gt; 4-log</td>
<td>&lt; 0.05</td>
<td>&gt; 4-log</td>
</tr>
<tr>
<td>DP</td>
<td>1.99</td>
<td>&lt; 0.05</td>
<td>&gt; 2-log</td>
<td>&lt; 0.05</td>
<td>&gt; 4-log</td>
</tr>
<tr>
<td><strong>HYM</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP</td>
<td>3.24</td>
<td>&lt; 0.05</td>
<td>&gt; 2-log</td>
<td>&lt; 0.05</td>
<td>&gt; 2-log</td>
</tr>
<tr>
<td>DP</td>
<td>5.20</td>
<td>&lt; 0.05</td>
<td>&gt; 2-log</td>
<td>&lt; 0.05</td>
<td>&gt; 2-log</td>
</tr>
<tr>
<td><strong>SYN</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP</td>
<td>583.95</td>
<td>0.13</td>
<td>&gt; 3-log</td>
<td>0.15</td>
<td>&gt; 3-log</td>
</tr>
<tr>
<td>DP</td>
<td>1066.50</td>
<td>1.64</td>
<td>&gt; 2-log</td>
<td>20.78</td>
<td>&gt; 1-log</td>
</tr>
</tbody>
</table>

LC-OCD profiles presented in Figure 5-4 are showing that the DOC removal is mainly due to the removal of the HMW fraction.

Figure 5-4: LC-OCD profiles of feed and permeate at the EP and the DP for (a) SKC, (b) TET, (c) HYM and (d) SYN for the filtration through Al$_2$O$_3$-80 nm and TiO$_2$-30 nm
Figure 5-4: LC-OCD profiles of feed and permeate at the EP and the DP for (a) SKC, (b) TET, (c) HYM and (d) SYN for the filtration through Al$_2$O$_3$-80 nm and TiO$_2$-30 nm (end)
The removal of IMW and LMW fractions is negligible when compared to the removal of the HMW compounds for the filtration through Al\textsubscript{2}O\textsubscript{3}-80 nm and TiO\textsubscript{2}-30 nm. It is interesting to notice that for TET, which is characterized by two HMW peaks, the first peak (i.e., the largest HMW) is better removed than the second peak. This finding is in accordance with numerous results (Fan et al., 2001, Lee et al., 2006, Qu et al. (2012) for polymeric UF and Zhang et al., 2013a, and 2013b for ceramic UF) which demonstrate the preferential removal of HMW during UF filtration. Figure 5-5 plots the HMW concentration in the feed and in the permeate of each filtration experiments.

![Figure 5-5: HMW fraction concentration in the feed and in the permeate of Al\textsubscript{2}O\textsubscript{3}-80 nm and TiO\textsubscript{2}-30 nm](image)

The HMW organics removal is globally higher for TiO\textsubscript{2}-30 nm than for Al\textsubscript{2}O\textsubscript{3}-80 nm, which can explain by the smaller pore size of the TiO\textsubscript{2}-30 nm membrane but also by the
higher affinity of the TiO$_2$ for the polysaccharide biopolymers. The HMW permeate concentration also depends on the algal species and the phase of growth. The best HMW removal is achieved for SKC – EP for both membranes and the removal decreases for the DP. Size exclusion cannot explain this evolution by itself, and interactions between AOM and membrane surface should be involved. When the HMW moieties concentration in the feed increases, the concentration in the permeate increases too, which suggests a breakthrough of the compounds probably due to the unavailability (membrane surface coated by AOM) of the binding sites of the membrane surface.

Table 5-4 summarized the species responsible for the strongest flux decline and the highest HMW removal.

### Table 5-4: Algal species responsible for the strongest flux decline versus algal species with the highest HMW removal

<table>
<thead>
<tr>
<th></th>
<th>Al$_2$O$_3$-80 nm</th>
<th>TiO$_2$-30 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Strongest flux decline</strong></td>
<td>SKC</td>
<td>SYN</td>
</tr>
<tr>
<td><strong>Highest HMW removal</strong></td>
<td>SKC</td>
<td>SYN &amp; SKC</td>
</tr>
<tr>
<td><strong>Strongest flux decline</strong></td>
<td>HYM</td>
<td>SYN</td>
</tr>
<tr>
<td><strong>Highest HMW removal</strong></td>
<td>TET</td>
<td>SYN</td>
</tr>
</tbody>
</table>

For the filtration through Al$_2$O$_3$-80 nm at the DP, the strongest fouling is obtained by filtering HYM solution, but the highest HMW removal is observed for TET solution. It is probably due to the underestimation of the AOM content in the HYM feed solution due to the necessary prefiltration through 0.7 μm prior to analysis, which leads to the underestimation of the HMW removal. These AOM aggregates are probably responsible of the strong fouling of HYM – DP (TFI = 44.91 x 10$^{-3}$ m$^2$/mg C with the lowest HMW
removal = 52.3%). SYN is responsible for the strongest fouling and HMW removal with TiO$_2$-30 nm, for the two phases of growth. It is possible that SYN AOM has a stronger affinity with the titanium oxide or could also more easily interpenetrate the pore network.

5.3. Ultrafiltration fouling due to AOM below 0.7 μm

5.3.1. Fouling properties

In order to estimate the impact of the algal cells and large organic colloids, UF experiments were performed with 0.7 μm pre-filtered solutions. A large volume of the culture solution was filtered through 0.7 μm in order to remove the algal cells and organic colloids larger than 0.7 μm, and the initial DOC was measured. The pre-filtered solution was then diluted with organic free synthetic seawater to achieve a final DOC of 0.5 mg/L. Experiments were performed during the most problematic phase of growth, i.e., the DP, the day after the filtration of the non-filtered culture solution. The same feed solution was used for both membranes (Al$_2$O$_3$-80 nm and TiO$_2$-30 nm). All chemical analyses were performed after filtration through 0.7 μm for either non-prefiltered or prefiltered solutions. Figure 5-6 compares the flux decline of the AOM solutions with and without 0.7 μm prefiltration (w/ PF and w/o PF, respectively), during DP through Al$_2$O$_3$-80 nm and TiO$_2$-30 nm.
Figure 5-6: Flux decline of the AOM solution with and without prefiltration, during the DP, through 80 nm and 30 nm: (a) SKC, (b) TET, (c) HYM and (d) SYN

The prefiltration through 0.7 μm slightly reduces the fouling of HYM and SKC for both membranes, but it has limited impact for SYN and TET. TFI -1 is presented in Table 5-5 and expressed by m²/mg DOC filtered. The calculated TFI -1 reduction is defined by the difference between the TFI -1 of the algal solution w/o PF and the TFI -1 of the algal solution w/ PF divided by the TFI -1 of algal solution w/o PF.

Table 5-5: Total fouling Index (TFI -1) for UF experiments through Al₂O₃-80 nm and TiO₂-30 nm of 0.7 μm prefiltered AOM solution and reduction (%) as compared to AOM UF experiments without prefiltration. R² is specified under parenthesis.

<table>
<thead>
<tr>
<th></th>
<th>Al₂O₃-80 nm</th>
<th>TiO₂-30 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TFI -1 (x10⁻³ m²/mg C)</td>
<td>Reduction (%)</td>
</tr>
<tr>
<td>SKC w/ PF</td>
<td>10.95 (0.97)</td>
<td>46.1</td>
</tr>
<tr>
<td>TET w/ PF</td>
<td>19.34 (0.99)</td>
<td>15.9</td>
</tr>
<tr>
<td>HYM w/ PF</td>
<td>15.90 (0.99)</td>
<td>49.2</td>
</tr>
<tr>
<td>SYN w/ PF</td>
<td>8.79 (0.98)</td>
<td>14.1</td>
</tr>
</tbody>
</table>
For the filtration of TET through TiO$_2$-30 nm the reduction is negative, however, TFI -1 values for both experiments are relatively similar (11.68 x 10$^{-3}$ m$^2$/mg C and 14.92 x 10$^{-3}$ m$^2$/mg C) and the prefiltration through 0.7 μm does not have any significant effect on the fouling tendency. It suggests that the fouling behavior of TET is mainly caused by AOM smaller than 0.7 μm. The strongest prefiltration effect is observed for SKC and HYM, with TFI -1 reductions comprised between 40 and 60 % for Al$_2$O$_3$-80 nm and TiO$_2$-30 nm. These results confirm the presence of large aggregates in the culture of HYM at DP (Figure 4-7) that are playing a major role in the fouling of UF ceramic membranes.

Regarding SKC, at the DP, the IOM input is important and, as seen in Chapter 4, SKC IOM is very rich in proteins and lipids. These more hydrophobic biopolymers might play an important role in the fouling mechanism of ceramic membranes and might have been removed during the prefiltration through 0.7 μm, which permits to reduce the TFI -1 value.

The impacts of the prefiltration on the reversibility of the fouling, flux decline (%) and proportion of reversible and irreversible fouling (RF and IF, respectively) are displayed in Figure 5-7.
Figure 5-7: Influence of the prefiltration for the flux decline (%) and proportion of reversible and irreversible fouling for (a) the first filtration cycle, (b) the second filtration cycle and (c) the third filtration cycle, after CEB.
In comparison with Figure 5-6, the fouling potential of the AOM solution is reduced when the feed solution is prefiltered through 0.7 μm. However, the flux decline is still important and still mainly happening during the first cycle. As discussed earlier, the fouling is stronger for the filtration Al₂O₃-80 nm than for and TiO₂-30 nm and could be explained by the interpenetration of large AOM with a size comprised between 0.7 μm and 30 nm into the 80 nm porosity membrane.

The removal of algal cells and AOM larger than 0.7 μm influences the reversibility of the fouling of the two membranes but different behaviors are observed for the two types of membrane. When the 0.7 μm prefiltration of TET and SYN enhances the irreversibility of the fouling for Al₂O₃-80 nm, no significant differences are noticed for the filtration through TiO₂-30 nm. The very large structures of TET and SYN could protect the membrane from pore blocking, phenomenon that should be more significant for large pore sizes (i.e., Al₂O₃-80 nm). On the contrary, the 0.7 μm prefiltration of SKC and HYM has minor effect on the reversibility of the fouling of Al₂O₃-80 nm, but the irreversibility is stronger for TiO₂-30 nm. The removal of large structures may permit to the biopolymers (< 0.7 μm) to more easily access the membrane surface and bind the fouling sites (i.e., polysaccharides for HYM). The different oxide material composing the Al₂O₃-80 nm and TiO₂-30 nm might have different affinity with AOM constituents.

After CEB, the recovery is slightly deteriorated by the prefiltration of the feed solution, which suggest that the algal cells and large colloids (> 0.7 μm) could form a protective surface layer, which limits the interpenetration of the pore network by the dissolved AOM.
5.3.2. Permeate quality

The HMW organic fraction removal for Al\textsubscript{2}O\textsubscript{3}-80 nm and TiO\textsubscript{2}-30 nm membranes (Figure 5-8) is diminished after the prefiltration through 0.7 \textmu m for SKC, TET and SYN. The prefiltration of a large volume (for the feed of the UF experiment w/ PF) through GFF 0.7 \textmu m porosity membrane would cause the formation of a cake layer at the surface of the filter that would play the role of an additional filter and remove more AOM than when filtering short volume of solution (i.e., for the UF experiment w/o PF). For HYM, the HMW is enhanced by the prefiltration through 0.7 \textmu m. The large aggregates in the HYM culture might serve as an additional separative layer, and permit a better HMW removal.

![Graphs showing HMW removal during UF for experiments](image)

**Figure 5-8:** HMW removal during UF for experiments performed with and without prefiltration through 0.7 \textmu m for (a) Al\textsubscript{2}O\textsubscript{3}-80 nm and (b) TiO\textsubscript{2}-30 nm membranes

For the experiments performed with prefiltration, the strongest HMW compounds removal is correlated with the strongest TFI -1 for both membranes (Figure 5-9). The
filtration through 80 nm of TET with prefiltration is characterized by the strongest HMW removal (67%) and the highest TFI -1 (19.34 x 10^{-3} m^2/mg C), and the filtration through 30 nm of the SYN solution with prefiltration is characterized by the strongest HMW removal (82%) and the highest TFI -1 (39.14 x 10^{-3} m^2/mg C). The TFI -1 of the different filtration experiments performed at different stage of growth are linked with the HMW concentration in the feed water.

**Figure 5-9:** Linear correlation between the HMW concentration in the feed water and the TFI -1 (a) for the filtration through Al₂O₃-80 nm and (b) for the filtration through TiO₂-30 nm

For one species and for the same feed preparation (i.e., with or without prefiltration), the TFI -1 increases linearly with the increase in the HMW concentration. The strongest fouling potential is attributed to HYM for both membranes. No notable differences are observed for prefiltered and raw AOM solution for SKC and SYN for Al₂O₃-80 nm and TiO₂-30 nm membrane. For TET, the prefiltration is greatly diminishing the TFI -1 of the Al₂O₃-80 nm membrane but no impact is observed with the TiO₂-30 nm membrane. The
prefiltration of HYM permits to significantly reduce the TFI-1 value for the two membranes, which corroborates the presence of large AOM aggregates in the HYM culture at the SP and the DP, which enhances the fouling. When considering the UF experiments performed on dissolved AOM (i.e., w/ PF), for the same HMW concentration, the TFI -1 is species –specific. The nature of the HMW should play a major role on the interactions with the metal oxide of the ceramic membrane. The HMW of the different species have been characterized in Chapter 4 and it seems that the relative abundance of each biopolymers (i.e., polysaccharides, proteins and lipids) are a key parameter for the fouling of ceramic membrane, along with the molecular weight of the HMW structures. Further investigations on the fouling and the characterization of different algal HMW are needed to understand the fouling mechanism of algal solution on ceramic membranes.

5.4. Conclusion

(1) For all phases of growth, the fouling of the ceramic UF filtration of AOM solutions is strong and severe. The most problematic fouling is observed during the DP for the four species. The species responsible for the strongest fouling is HYM for the filtration through Al₂O₃-80 nm and SYN for the filtration through TiO₂-30 nm. Chemical enhanced cleaning using NaOH (0.1M) had very little effect to recover the hydraulic performance of the membrane.

(2) Different fouling mechanisms are involved such as (a) cake layer formation, which remains porous and allows 10 to 20 % of the initial flux; (b) pore blockage, which leads
to a fast and irreversible fouling and (c) strong affinity between AOM and membrane surface which contribute to the irreversible fouling.

(3) Apart of HYM, where large AOM aggregates are observed at the DP, algal cells and AOM aggregates larger than 0.7 μm are only slightly impacting the mechanical properties of the membranes and the fouling remains significant after 0.7 μm prefiltration. The little improvement in terms of flux decline is however accompanied with stronger fouling irreversibility. Algal cells and large AOM probably form a cake layer at the surface of the membrane that prevents the pore blockage.

(4) The fouling potential of algal solution depends on the HMW organics concentration of the feed solution. For a given alga, the fouling of AOM solution is linearly correlated with the concentration of HMW compounds in the feed solution. This species-specific character of the fouling highlights the importance of the HMW quality and the affinity AOM-metal oxides. Polysaccharide relative abundance is among the key parameters driving the fouling mechanisms, however, other contributors (i.e., proteins and lipids) are involved in the fouling caused by algal solutions and further investigations are needed.

(5) At the DP of an algal bloom, the more severe fouling is attributed to the higher HMW structure concentration but the impact of the change of composition of these HMW moieties (i.e., enrichment of proteins and lipids), due to a larger contribution of the IOM, should not be underestimated. Studies on polymeric membranes, using model compounds such (i.e., bovine serum albumin, dextran and commercial humic substances) or algal solutions (Xiao et al., 2011; Qu et al., 2012a) have associated the more hydrophobic compounds (i.e., proteins) with a low reversible fouling, and the role of lipids is generally not approached in these works. In Chapter 4, we have observed a significant number of
jump-to-contact events for the most protein/lipid-rich AOM (i.e., SKC IOM and TET IOM), which suggests a strong attraction between these biopolymers and the ceramic membrane.

(6) The fouling of ceramic membranes by AOM solutions is extremely complex, and the structural characterization of the main foulants (i.e., HMW structures) is not sufficient to explain the different mechanisms involved.
6. Algal bloom growth in Red Sea mesocosms: Characterization and Ultrafiltration

6.1. Growth control

Different parameters such as temperature and Chl-a concentration (i.e., algal cell density) were monitored in situ during the period of experiment (Figure 6-1). After the nutrient enrichment, the temperature decreased from 25°C to 22°C at day 9, and then increased progressively to reach 26-27°C at day 14. When the temperature was the lowest, the Chl-a concentration reached its maximum value in the water column (day 8). Local Chl-a concentration spots were monitored below 20-meter depth. However, the samples for ultrafiltration experiments were collected in the 0 to 5 m depth zone, so these phenomena will not be discussed in this study.
Figure 6-1: In situ control of the mesocosm experiment: (a) temperature and (b) Chlorophyll-a (Chl-a) concentration over time.

Solutions from the sampling zone were collected every day. Microbial control and physical chemical analyses (Figure 6-3) were performed on these samples in order to follow changes in the phytoplankton and bacterial communities, and in the water quality. Prior to analysis, the samples were filtered through 100 μm. Flow cytometry was used to assess the number of phytoplankton cells and bacteria cells in the mesocosms during the experimental period (Figure 6-2). Three types of phytoplankton can be distinguished from the flow cytometry analyses: *Synechococcus sp.*, picoplankton and nanoplankton. *Synechococcus sp.* is the smallest cyanobacteria present in the sea with a size of around 1
to 2 μm. The picoplankton community is characterized by a size comprised between 0.2 and 2 μm, and the nanoplankton community by a size comprised between 2 to 20 μm. The bacteria size is typically comprised between 0.5 to 5 μm. Low Nucleic Acid (LNA) content and the High Nucleic Acid (HNA) bacteria were monitored (Figure 6-2).

Figure 6-2: Microbial growth control of the sampling zone: FCM and evolution for (a) phytoplankton and (b) bacteria.
At day 3, the *Synechococcus sp.* cell concentration started to increase and reached its maximum value at day 4, this event was the first algal bloom of the experiment. The picoplankton community started to increase at the same time as the *Synechococcus sp.*, but reached its maximum 2 days later (i.e., picoplankton bloom) at day 6. From day 6, the picoplankton community decreased and the nanoplankton community increased simultaneously, to reach its maximum at day 7, characterizing the nanoplankton bloom and the last major bloom episode of the experiment. At day 8, all blooms were terminated and the nanoplankton community decreased slowly to the initial concentration at day 11. From day 14 to 16, a small increase in the picoplankton community was observed, however, this increase was relatively small in comparison with the earliest three blooms. An overall increase in the bacteria community was observed during the whole period of the mesocosm experiment. A bacteria bloom occurred with a maximum concentration at day 7. This bacterial bloom was certainly the consequence of the decline of the *Synechococcus* community and was majorly composed of HNA bacteria.

Physical chemical parameters such as pH, turbidity, Chl-a concentration and DOC were monitored during the mesocosm experiment and are displayed in Figure 6-3. The DOC measurement was performed after filtration through 0.7 μm in order to protect the analytical equipment against clogging.
The pH of the sampling zone varies from 8.17 to 8.55. The increase observed at day 3 is probably due to an increase in the CO₂ consumption by the phytoplankton community. The turbidity strongly increases at day 7, and the same peak is observed for the Chl-a concentration, which suggests that the evolution of the turbidity is due to the higher concentration of algal cells. As expected, the Chl-a concentration is linearly correlated with the total phytoplankton cell count due to its presence in living algal cells. The DOC
(i.e., AOM) concentration slightly decreases from day 2 to day 4 (1.56 to 1.10 mg/L). At day 5, the first peak of DOC is detected, which coincides with the decline phase of the *Synechococcus sp.* bloom. The DOC concentration reached 1.77 mg/L probably due to the release of AOM from the *Synechococcus sp.* bloom. At day 2, the second peak of DOC is observed and corresponds to the decline phase of the three major blooms: the algal cells have lysed and the IOM was released to the mesocosm solution, which increased the concentration of AOM to 2.47 mg/L. To estimate the change in the DOC quality, samples were analyzed with LC-OCD every day (Figure 6-4a). The evolution of the different fractions during the experimental period is displayed in Figure 6-4b and Figure 6-4c.
Figure 6-4: Evolution of the water quality of the mesocosm: (a) LC-OCD profiles and (b) the evolution of the three fractions over time and (c) the evolution of the three fractions as a function of the DOC.
The HMW and the IMW fractions are increasing during growth, whereas the LMW fraction remains stable. From day 10, the HMW fraction increases more rapidly, which corresponds to the end of the three main algal blooms. This stronger increase is well correlated with the increase of DOC starting at day 10, which suggests that from this day, the DOC contains a higher proportion of HMW structures. Figure 6-4c confirms the DOC enrichment of HMW and IMW as this two fractions are linearly correlated with the DOC concentration.

6.2. Ceramic ultrafiltration of the mesocosm water samples

6.2.1. Feed characteristics

Ceramic UF experiments were performed at the very beginning of the mesocosm experiment (day 0), after the Synechococcus and the picoplankton bloom (day 8) and at the end of the three major blooms (day 14). The solutions were filtered through 100 μm prior filtration to remove large particles such as macro-algae and sand particles present in the open-air mesocosm. LC-OCD profile of each UF feeds (filtered through 0.7 μm porosity membrane for analysis) is presented in Figure 6-5 and feed characteristics are summarized in Table 6-1.
Figure 6-5: LC-OCD profile of the feed at day 0, day 8 and day 14 of the mesocosm culture.

Table 6-1: Feed chemical characteristics at day 0, day 8 and day 14 of the mesocosm experiment.

<table>
<thead>
<tr>
<th></th>
<th>Day 0</th>
<th>Day 8</th>
<th>Day 14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chl-a (μg/L)</td>
<td>0.09</td>
<td>0.96</td>
<td>0.34</td>
</tr>
<tr>
<td>pH</td>
<td>8.18</td>
<td>8.45</td>
<td>8.55</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>0.50</td>
<td>1.68</td>
<td>0.88</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>1.56</td>
<td>1.41</td>
<td>1.76</td>
</tr>
<tr>
<td>HMW (mg/L)</td>
<td>0.13</td>
<td>0.18</td>
<td>0.26</td>
</tr>
<tr>
<td>Proportion (%)</td>
<td>8.3</td>
<td>12.8</td>
<td>14.8</td>
</tr>
<tr>
<td>IMW (mg/L)</td>
<td>0.65</td>
<td>0.69</td>
<td>0.85</td>
</tr>
<tr>
<td>Proportion (%)</td>
<td>41.7</td>
<td>48.9</td>
<td>48.3</td>
</tr>
<tr>
<td>LMW (mg/L)</td>
<td>0.78</td>
<td>0.54</td>
<td>0.65</td>
</tr>
<tr>
<td>Proportion (%)</td>
<td>50.0</td>
<td>38.3</td>
<td>36.9</td>
</tr>
</tbody>
</table>

Day 0 is characterized by the lowest phytoplankton cell concentration (0.09 μg/L Chl-a), the lowest pH value (8.18) and turbidity value (0.50 NTU). At day 8, the nanoplanckton bloom is occurring and the feed solution shows the highest algal cell concentration of the
three dates of sampling. pH value increased to 8.45 and turbidity is 1.68, due to the high algal cell concentration. At day 14, algal blooms have declined, and the Chl-a concentration has decreased to 0.34 μg/L. Cells fragments have settled, reducing the turbidity to 0.88 NTU. The DOC concentration did not significantly change during growth (+/- 0.35 mg/L), however the composition did. Between day 0 and day 14, the HMW concentration doubled, whereas the concentrations of the two other fractions (i.e., IMW and LMW) remained similar.

6.2.2. Fouling property at different periods of the mesocosm culture

Two different ceramic membranes were studied: an alumina membrane characterized by a nominal pore size of 80 nm (Al₂O₃-80 nm) and a titanium oxide membrane characterized by a nominal pore size of 30 nm (TiO₂-30 nm). UF experiments were performed at constant pressure fixed at 0.7 bar, which corresponds to a specific flux of 870 and 550 LMH for the alumina and titanium oxide membranes, respectively. Backwash pressure was three times higher than the filtration pressure (i.e., 2.0 bars) and was conducted with MilliQ water. One filtration experiment consists of three successive filtration cycles, i.e., filtration followed by a MilliQ backwash. For the third cycle, the MilliQ backwash was replaced by a Chemical Enhanced Backwash (CEB) using NaOH (0.1 M). The pure water permeability was measured after CEB. Feed solution was freshly prepared and the same feed water was used for the two types of membranes. The hydraulic performances of the two membranes were assessed be monitoring the flux
decline and by calculating the Total Fouling Index of the first cycle (TFI -1) (Nguyen et al., 2011). Flux decline for both membranes is displayed in Figure 6-6.

![Figure 6-6: Flux decline of the filtration of the mesocosm solution through (a) 80 nm and (b) 30 nm.](image)

As expected and observed in Chapter 5 and by Zhang et al. (2013b), the strongest fouling is observed at the end of the blooms (i.e., day 8 and day 14) and the flux decline is mainly happening during the first filtration cycle. After the first filtration cycle, and because backwash showed limited efficiency, the flux decline is progressively reaching a plateau (2\textsuperscript{nd} and 3\textsuperscript{rd} cycle) at around 25\% of the initial flux for both membranes. This observation was also made for the filtration of the algal monoculture in Chapter 5 and it suggests the formation of a porous cake layer at the surface of the membrane that does not totally block the filtration flux and allows a restricted flow to pass through.
The fouling potential of the different feed solutions are compared based on the calculation of the Total Fouling Index for the first cycle (TFI -1) expressed by $m^2/mg$ DOC filtered (Table 3). When normalizing the TFI -1 by the mass of DOC filtered, the small differences between the DOC concentration of the different feed solutions (which are not visible in Figure 6-6) are taken into account for a better comparison.

Table 6-2: Total Fouling Index for the first filtration cycle through Al$_2$O$_3$-80 nm and TiO$_2$-30 nm. R-squared are specified under parenthesis.

<table>
<thead>
<tr>
<th>TFI -1 $(x 10^{-3} m^2/mg C)$</th>
<th>Al$_2$O$_3$-80 nm</th>
<th>TiO$_2$-30 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 0</td>
<td>3.96 (0.99)</td>
<td>2.26 (0.99)</td>
</tr>
<tr>
<td>Day 8</td>
<td>15.18 (1.00)</td>
<td>9.73 (1.00)</td>
</tr>
<tr>
<td>Day 14</td>
<td>11.19 (1.00)</td>
<td>13.62 (1.00)</td>
</tr>
</tbody>
</table>

For both membranes, the TFI-1 strongly increases between day 0 and day 8 (by a factor of 5), which corresponds to the end of the *Synechococcus sp.* and picoplankton blooms. Feed solutions at day 0 and day 8 are characterized by a similar DOC (1.56 mg/L and 1.41 mg/L) and only a change in the AOM quality can explain this TFI -1 increase. In Chapter 5, we demonstrated the strong relation between the TFI -1 and the initial HMW organics concentration. The higher proportion of HMW compounds in the feed solution at day 8 (12.8% versus 8.3%) probably induced the higher membrane fouling. At day 14, once the three blooms (i.e., *Synechococcus sp.*, picoplankton and nanoplankton blooms) were terminated for already few days, the TFI -1 remained relatively similar for the filtration through Al$_2$O$_3$-80 nm despite a DOC increase of 0.30 mg/L and an increase in HMW structures of 0.08 mg/L. On the contrary the TFI -1 increased for the filtration through TiO$_2$-30 nm. Two hypotheses can explain these different behaviors: (1) above a
certain amount of HMW compounds, the fouling of the Al$_2$O$_3$-80 nm membrane remains unchanged; (2) the HMW composition changes and the affinity between the AOM and the metal oxides become stronger for TiO$_2$. In Chapter 5, the TFI -1 of monoculture solutions through Al$_2$O$_3$-80 nm and TiO$_2$-30 nm membranes was linearly correlated for HMW moieties concentration comprises between 0.001 to 0.4 mg/L. During the mesocosm experiment, different algal blooms are taking place and the AOM released by each species are different (Chapters 3 and 4), which could lead to different reactivity with the metal oxide composing the membrane.

The irreversible nature of the fouling is also an important aspect of the fouling potential of AOM solutions. Flux decline (%) and proportion of reversible and irreversible fouling (RF and IF, respectively) are plotted in Figure 6-7. The reversible fouling corresponds to the flux that was recovered after backwash for the first and second filtration cycle, and after CEB for the third filtration cycle. It is calculated based on the initial flux, i.e, if the RF is 100 %, the initial permeability of the membrane is recovered.
Figure 6-7: Flux decline (%) and proportion of reversible and irreversible fouling for
(a) the first filtration cycle, (b) the second filtration cycle and (c) the third filtration cycle, after CEB.
As mentioned earlier and also observed in Chapter 5, the first cycle is the most important in terms of flux decline. It is also interesting to notice that, as for the filtration of the monoculture solutions, the flux decline was always higher and the fouling always more reversible for the filtration through Al2O3-80 nm than for the filtration through TiO2-30 nm. Two hypotheses were proposed in Chapter 5: (1) the size of the AOM that could interpenetrate the 80 nm pores but not the 30 nm and could lead to a faster fouling and (2) the stronger affinity of the AOM toward titanium oxide than toward alumina, which could cause the stronger irreversible property of the fouling of the 30 nm membrane.

For Al2O3-80 nm, the hydraulic irreversibility of the membrane is enhanced with the ageing of the mesocosm solution, whereas the fouling becomes slightly more reversible for the first filtration cycle through TiO2-30 nm. Surprisingly, the opposite trend was observed for the filtration of the *Synechococcus sp.* (SYN) solution in Chapter 5. The quality of the AOM present in the mesocosm is probably more complex than the AOM present in the SYN solution, due to the variety of algal corresponding AOM composition.

With time, the mesocosm solution is getting enriched in proteins and lipids coming from the decline of the algal bloom and these biopolymers are considered to increase the irreversibility of the fouling of polymeric membranes (Xiao et al., 2011; Qu et al., 2012a).

As expected from Chapter 5, the CEB using NaOH (0.1 M) did not permit to recover the hydraulic performance of the membranes. The recovery is within the range of the recovery for the algal monoculture filtration experiments. The CEB efficiency increases with the ageing of the bloom for Al2O3-80 nm, whereas it decreases for TiO2-30 nm.
This evolution was also observed for the CEB performance of SYN culture at the EP and the DP (Figure 5-3). The adhesion between Al$_2$O$_3$-80 nm and polysaccharides is much stronger than with lipids/protein-rich solutions, and enrichment in these biopolymers could explain the higher CEB efficiency. AFM study on TiO$_2$-30 nm membrane could help us to understand its opposite behavior.

6.2.3. Permeate quality

The permeate was collected at the end of the ultrafiltration experiment and represents the total permeate (i.e. mixture of the permeate from the different filtration cycles). Ceramic UF filtration achieved relatively high cell removal (Table 6-3). Because algal cells are relatively large as compared to the nominal pore size of the membranes they should not be found in the permeate. The presence of a few algal cells in the permeate is a proof of the non-homogeneity of the membrane porosity. Defects in the surface layer would permit to a limited amount of cells to breakthrough the membrane.

<table>
<thead>
<tr>
<th>Cell density</th>
<th>Feed</th>
<th>Al$_2$O$_3$-80 nm</th>
<th>TiO$_2$-30 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Permeate Removal</td>
<td>Permeate Removal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Permeate Removal</td>
<td>Permeate Removal</td>
</tr>
<tr>
<td><strong>Synechococcus</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Day 0</td>
<td>22.78</td>
<td>&lt; 0.05</td>
<td>&gt; 3-log</td>
</tr>
<tr>
<td>Day 8</td>
<td>1.30</td>
<td>&lt; 0.05</td>
<td>&gt; 2-log</td>
</tr>
<tr>
<td>Day 14</td>
<td>0.52</td>
<td>&lt; 0.05</td>
<td>&gt; 2-log</td>
</tr>
<tr>
<td><strong>Pico-plankton</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Day 0</td>
<td>1.34</td>
<td>n.q.*</td>
<td>&gt; 4-log</td>
</tr>
<tr>
<td>Day 8</td>
<td>0.51</td>
<td>&lt; 0.05</td>
<td>&gt; 2-log</td>
</tr>
<tr>
<td>Day 14</td>
<td>0.13</td>
<td>&lt; 0.05</td>
<td>&gt; 1-log</td>
</tr>
<tr>
<td><strong>Nanoplankton</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Day 0</td>
<td>1.29</td>
<td>&lt; 0.05</td>
<td>&gt; 4-log</td>
</tr>
<tr>
<td>Day 8</td>
<td>1.41</td>
<td>&lt; 0.05</td>
<td>&gt; 2-log</td>
</tr>
<tr>
<td>Day 14</td>
<td>1.58</td>
<td>&lt; 0.05</td>
<td>&gt; 1-log</td>
</tr>
</tbody>
</table>

*n.q. = not quantifiable
The LC-OCD profiles of the permeates from the filtration through Al₂O₃-80 nm or through TiO₂-30 nm are showing a decrease in the HMW fraction (Figure 6-8). The chromatogram remains similar than the feed in the IMW and LMW domains. This finding confirms, once again, the fact that ceramic UF is very efficient for HMW biopolymers removal (Fan et al., 2001, Lee et al., 2006, Qu et al. (2012) for polymeric UF and Zhang et al., 2013a, and 2013b for ceramic UF).

Figure 6-8: LC-OCD profiles of the feed solution and the permeates of the filtration through Al₂O₃-80 nm and through TiO₂-30 nm for (a) day 0, (b) day 8 and (c) day 14
Table 6-4 presents the HMW organics removal by Al$_2$O$_3$-80 nm and through TiO$_2$-30 nm at the three different dates.

<table>
<thead>
<tr>
<th></th>
<th>Feed</th>
<th>Permeate</th>
<th>Removed</th>
<th>80 nm</th>
<th>Day 0</th>
<th>Day 8</th>
<th>Day 14</th>
<th>30 nm</th>
<th>Day 0</th>
<th>Day 8</th>
<th>Day 14</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HMW (mg/L)</strong></td>
<td>0.13</td>
<td>0.12</td>
<td>0.03</td>
<td>0.13</td>
<td>0.12</td>
<td>0.06</td>
<td>0.07</td>
<td>0.04</td>
<td>0.09</td>
<td>0.10</td>
<td>0.14</td>
</tr>
<tr>
<td><strong>IMW (mg/L)</strong></td>
<td>0.66</td>
<td>0.7</td>
<td>0.66</td>
<td>0.66</td>
<td>0.68</td>
<td>0.79</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
</tbody>
</table>

As seen in Figure 6-8, the ultrafiltration through Al$_2$O$_3$-80 nm and TiO$_2$-30 nm has no effect on the IMW compounds and the DOC decrease is mainly due to HMW removal. The HMW concentration in the permeate increases with the initial HMW concentration for both membranes, which indicates a breakthrough of the HMW probably due to the unavailability (membrane surface coated by AOM) of the bounding sites of the membrane surface or due to changes in the composition of the AOM. As expected from Chapter 5, the TFI -1 is linked with the initial HMW content and the higher the HMW content, the higher the fouling (Figure 6-9).
6.3. Conclusions

(1) The most problematic fouling was observed once the three major blooms have declined (day 14) and released their IOM. The fouling caused by the mesocosm solution was highly hydraulically irreversible but, in most cases, a CEB using NaOH (0.1M) was efficient enough to recover the initial permeability of the membrane.

(2) The three main mechanisms of the AOM fouling of ceramic membranes are the cake layer formation, the pore blockage and the adhesion between AOM and the metal oxides. These mechanisms were already observed in different studies using polymeric membranes (Castaing et al., 2011; Castaing et al., 2010; Ladner et al. 2010; Qu et al., 2012; Villacorte, 2013; Yu et al., 2014) and ceramic membranes (Zhang et al., 2013b; Zhang et al. 2013c).

(2) The DOC removal is mainly achieved by a strong HMW removal and the initial concentration of the HMW greatly impacts the fouling potential of an algal solution,
which suggests that the affinity between the AOM (and more particularly the HMW) and the metal oxide is depending on the nature of the HMW and the nature of the metal oxide.
7. Coagulation Flocculation as a pretreatment before UF filtration during and algal bloom

7.1. Optimization of coagulation-flocculation protocol during an algal bloom

Two different modes have been studied in this work:

- coagulation-flocculation-flotation (CFF)
- coagulation-flocculation-sedimentation (CFS)

The optimization was performed using two different algal cultures: Tetraselmis sp. (TET) and Hymenomonas sp. (HYM) cultures collected at stationary phase and dilute in Red Sea water to reach a final Chl-a content of 20 μg/L.

In this chapter, solutions were analyzed using LC-OCD analyzer, TOC-meter (Shimadzu), turbidimeter and fluorometer (Chl-a concentration).

7.1.1. Physicochemical characterization of the two algal species

The average characteristics of HYM and TET solutions used for all conducted experiments are summarized in Table 7-1.

<table>
<thead>
<tr>
<th></th>
<th>Turbidity (NTU)</th>
<th>Chl-a (μg/L)</th>
<th>DOC (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HYM</td>
<td>4.60 +/- 0.70</td>
<td>19.9 +/- 2.8</td>
<td>3.71 +/- 0.49</td>
</tr>
<tr>
<td>TET</td>
<td>7.06 +/- 0.70</td>
<td>20.2 +/- 1.5</td>
<td>1.36 +/- 0.06</td>
</tr>
</tbody>
</table>

For a similar Chl-a concentration, HYM and TET solutions are defined by very different turbidity and DOC values. The turbidity is 1.5 times higher for TET feed solution than
for HYM solution, and the DOC concentration is 2.7 higher for HYM than for TET solution. The difference in DOC content can be explained by a larger number of cells for HYM, leading to a higher amount of excreted organic matter. As discussed in Chapter 3, Chl-a concentration and cell count are linearly correlated. For a same Chl-a concentration, HYM cell count is higher than TET cell count. HYM and TET cells have relatively similar size (8-30 μm and 10-20 μm for HYM and TET, respectively), and it suggests that a higher cell concentration would naturally lead to a higher amount of excreted organics and a higher DOC concentration released in the solution.

7.1.2. Coagulation-Flocculation-Flotation (CFF)

CFF experiments have been conducted in duplicate. The experimental conditions used as reference, were:

- coagulation at 200 rpm for 2 minutes
- flocculation at 30 rpm for 10 minutes
- flotation for 10 minutes with addition of 10% of pressurized seawater
- pH adjusted to 6.8 +/- 0.2
- coagulant dose of 2.5 mg Fe/L

7.1.2.1. Impact of the coagulant dose

The impact of the coagulant dose on the CFF performances was conducted with ferric chloride (FeCl₃), because, aluminum coagulant is prone to a stronger scaling potential toward RO membranes and is less suitable for CF of seawater (Edzwald et al., 2011).
Four different coagulant doses were studied: 1.0 mg Fe/L, 2.5 mg Fe/L, 5.0 mg Fe/L and 10.0 mg Fe/L. Turbidity, DOC and Chl-a concentration of the clarified water and removals are plot in Figure 7-1.
Figure 7-1: Impact of the coagulant dose on the CFF performances: (a) turbidity, (b) Chl-a and (c) DOC. The first column displays the concentration in the produced waters and the second column, the calculated removals (%). CFF conditions: coagulation at 200 rpm for 2 minutes at pH6.8, flocculation at 30 rpm for 10 minutes, flotation for 10 minutes with addition of 10% of pressurized seawater

With the exception of the experiment performed with HYM at 1 mg Fe/L, an increase in the coagulant dose leads to an increase in the turbidity removal. The turbidity decreases from 6.10 +/-1.08 NTU to 4.28 +/- 0.15 NTU for HYM using 2.5 mg Fe/L to 10.0 mg Fe/L; and from 6.13 +/- 0.62 NTU to 3.93 +/- 0.31 NTU for TET using 1.0 mg Fe/L to 10.0 mg Fe/L. The best but relatively low turbidity removal was achieved with 10.0 mg Fe/L for HYM with a removal of 15.3% +/- 2.9, and with 5.0 mg Fe/L for TET with a removal of 53.5% +/- 6.07. Similar turbidity removal was observed with 5.0 mg Fe/L and 10.0 mg Fe/ TET (48.9% +/- 4.0 and 53.5% +/-6.07, respectively). In terms of cell removal (i.e., Chl-a removal), the coagulant dose has an important impact. Indeed, from 1.0 mg Fe/L to 10.0 mg Fe/L, the removal increases from 15.7% +/- 0.6 to 89.1% +/- 1.2 for HYM and from 20.9% +/- 2.9 to 85.7% +/- 2.6 for TET. At 10.0 mg Fe/L, the concentration of Chl-a in the clarified water is comparable for HYM and TET with 2.6
+/- 0.3 μg/L and 3.1 +/- 0.6 μg/L, respectively. The DOC removal increases with an increase of the coagulant dose for HYM (18.1% +/-0.5 to 36.1% +/- 0.1) whereas no significant impact is noticed for TET (24.9% +/- 1.0 to 19.4% +/- 8.3). The DOC reduction is mainly attributed to the removal of the HMW organic fraction (Figure 7-2), (i.e., biopolymers). The initial composition of the DOC was approximately 45% HMW and 55% non-HMW compounds for HYM and 29% of HMW and 71% of non-HMW for TET, but after CF at 10 mg Fe/L, the HMW structures only represented 30 and 15% of the DOC for HYM and TET, respectively.

Figure 7-2: LC-OCD profiles of the raw and clarified waters at different coagulant doses for (a) HYM and (b) TET

Figure 7-3 incorporates all the results obtained from the CFF experiments conducted with the same experimental conditions (i.e., coagulation at 200 rpm for 2 minutes at pH6.8, flocculation at 30 rpm for 10 minutes, flotation for 10 minutes with addition of 10% of pressurized seawater). Removal efficiencies are plotted as a function of the coagulant expressed as mg Fe/mg DOC.
Figure 7-3: Relationship between (a) turbidity removal, (b) Chl-a removal, (c) DOC removal and ratio Fe/DOC (mg/mg) for all the CFF experiments. CFF conditions: coagulation at 200 rpm for 2 minutes at pH6.8, flocculation at 30 rpm for 10 minutes, flotation for 10 minutes with addition of 10% of pressurized seawater.
Removal efficiencies are well correlated with the applied Fe/DOC ratio. Above 2.5 and 1.5 mg Fe/mg DOC for HYM and TET, respectively, 90% of the algal cells are removed during CFF. Overall, the DOC removal increases with the increase of the Fe/DOC ratio, but the linear correlation is weak. In terms of turbidity, HYM is showing a singular behavior: the turbidity is slightly decreasing for low (<0.5 mg Fe/mg DOC) and high (>1.7 mg Fe/mg DOC) doses, but is increasing for intermediate doses (0.5 to 1.7 mg Fe/mg DOC). It can be explained by the formation of large aggregates at intermediate doses that are not easily floating.

HMW and non-HMW compound removals are presented in Figure 7-4. The HMW fraction is clearly preferentially removed toward the non-HMW fraction. It is interesting to notice that TET HMW, which is characterized by a stronger proportion of proteinaceous material than HYM HMW (as discussed in Chapter 4) is better removed than HYM HMW for a similar Fe/DOC ratio. These results corroborate suggestions from Kuroiwa et al. (2013) and Widrig et al. (1996), who observed a preferential removal of the proteinaceous material during CF and the HMW removal observed during CF could be driven by the protein-like removal.
Figure 7-4: Relationship between (a) HMW removal, (b) non-HMW removal and Fe/DOC ratio. CFF conditions: coagulation at 200 rpm for 2 minutes at pH6.8, flocculation at 30 rpm for 10 minutes, flotation for 10 minutes with addition of 10% of pressurized seawater.
Coagulation is known to be sensitive to pH conditions. Four different pH were investigated: 5.5, 6.0, 6.5, and 7. The pH was achieved by adding drops of concentrated HCl (5 M). Standards conditions were applied for these experiments (described in section 8.1.2). The coagulant dose, set at 2.5 mg Fe/L is lower than the optimum dose but it is more realistic in terms of cost for a treatment plant process. Concentrations of the clarified water and removals are plotted in Figure 7-5.

The pH of the coagulation only slightly impacts the CFF performances for the treatment of marine algal solutions, and the two algal species behave differently. For TET, the evolution of the turbidity and the Chl-a concentration is similar, which suggests that the turbidity is principally coming from the TET cells. The best turbidity and Chl-a removal is obtained for a pH higher than 6. The DOC removal slightly decreases with the pH value (19 to 13%). For HYM, above pH6.5, the coagulation permits to reduce the Chl-a (relatively similar for this pH range) but add turbidity to the solution, as observed at intermediate coagulant dose (Figure 7-3). On the other hand, the DOC increases with the pH value. The optimum pH is specie-dependent and is set at 5.5 for TET and 7 for HYM, for the maximum DOC removal.
Figure 7-5: Impact of the pH on the CFF performances: (a) turbidity, (b) Chl-a and (c) DOC. The first column displays the concentration in the produced waters and the second column, the calculated removals (%). CFF conditions: coagulation at 200 rpm for 2 minutes with a coagulant dose of 2.5 mg Fe/L, flocculation at 30 rpm for 10 minutes, flotation for 10 minutes with addition of 10% of pressurized seawater.
7.1.2.3. Impact of the flocculation time

Four different flocculation times were studied to evaluate the impact of the flocculation on the process performances: 5 min, 8 min, 10 min and 15 min. Standards conditions were applied for these experiments (described in section 8.1.2). Concentrations of the clarified water and removals are plot in Figure 7-6.

A flocculation above 10 minutes permits to increase the turbidity, Chl-a and DOC removal for TET. Once again, the Chl-a evolution is closely related to the turbidity for this alga and, as suggested earlier, the turbidity is mainly due to TET algal cells. For HYM, the impact of the flocculation time is more uncertain. The turbidity of HYM has increased but does not seem to be impacted by the flocculation time. Low (< 5 min) and high (> 10 min) flocculation time permits a greater algal cell removal (i.e., Chl-a removal). The DOC removal is not flocculation time-dependent and the removal is comprised between 19 and 27% for HYM. The optimum flocculation time is depending on the algal species, it is comprised between 10 to 15 minutes for TET and no optimum flocculation time was highlighted for HYM.
Figure 7-6: Impact of the flocculation time on the CFF performances: (a) turbidity, (b) Chl-a and (c) DOC. The first column displays the concentration in the produced waters and the second column, the calculated removals (%). CFF conditions: coagulation at 200 rpm for 2 minutes with a coagulant dose of 2.5 mg Fe/L at pH6.8, flocculation at 30 rpm, flotation for 10 minutes with addition of 10% of pressurized seawater.
7.1.2.4. Impact of the flotation time

Four different flotation times were analyzed to evaluate the optimum flotation time: 5 min, 8 min, 10 min and 15 min. Standards conditions were applied for these experiments (described in section 8.1.2). Concentrations of the clarified water and removals are plot in Figure 7-7.

The flotation time does not seem to greatly impact the performance of the CFF with algal solutions. For the rest of the study a flotation time of 10 minutes was implemented.
Figure 7-7: Impact of the flotation time on the CFF performances: (a) turbidity, (b) Chl-a and (c) DOC. The first column displays the concentration in the produced waters and the second column, the calculated removals (%). CFF conditions: coagulation at 200 rpm for 2 minutes with a coagulant dose of 2.5 mg Fe/L at pH 6.8, flocculation at 30 rpm for 10 minutes, flotation with addition of 10% of pressurized seawater.

7.1.3. Coagulation-Flocculation-Sedimentation (CFS) with clay as coagulant aid

Clay is widely used to mitigate algal bloom in the sea, enforcing the algal cells to sediment (Beaulieu et al., 2005). This property can be interesting to enhance the sedimentation of algal cells after coagulation-flocculation. For this application, flotation was replaced by sedimentation and the chosen clay was bentonite (BEN). The experimental conditions used as reference for CFS are:

- coagulation at 200 rpm for 2 minutes
- flocculation at 30 rpm for 10 minutes
- sedimentation for 30 minutes
- pH adjusted at 6.8 +/- 0.2
7.1.3.1. Impact of the clay dose

Standards conditions were applied for these experiments (described in section 8.1.3).

Figure 7-8 displays the turbidity, the Chl-a and the DOC removals for (a) HYM and (b) TET feed solutions.

An increase in the BEN dose leads to an increase in the turbidity removal and Chl-a removal. It is interesting to notice that the addition of BEN as coagulant aid permits a better removal of the turbidity and Chl-a but has minor impact (slight reduction) on the DOC removal for both feed solutions (HYM and TET) in comparison with the produced water of CFF without BEN (11.6%, 15.7%, 18.1% for HYM and 20.3%, 20.8%, 24.9% for TET, for turbidity, Chl-a and DOC removals). Best turbidity removal is achieved with a BEN dose of 200 mg/L for either HYM solution (53.2%) or TET solution (67.5%). The

Figure 7-8: Impact of the BEN coagulant aid on the performance of CFS for the treatment of (a) HYM solution and (b) TET solution. CFS conditions: coagulation at 200 rpm for 2 minutes with a coagulant dose of 1 mg Fe/L at pH6.8, flocculation at 30 rpm for 10 minutes, sedimentation for 30 minutes.
Chl-a removal is also highly impacted by the BEN dose: the higher BEN dose, the higher Chl-a removal. The Chl-a removal reaches 96.2% and 93.2% with 200 mg BEN/L for HYM and TET, respectively. The DOC concentrations of the clarified water remain very similar with all BEN doses, and close to the result obtained in absence of clay (with a standard deviation of 0.04 mg/L for HYM and 0.05 mg/L for TET), which suggests that BEN is not efficient in terms of DOC removal.

7.1.3.2. Impact of the coagulant dose on the CFS with clay (BEN) as coagulant aid

For the CFS treatment of HYM solution, different coagulant doses were studied (0 mg Fe/L, 1.0 mg Fe/L and 2.5 mg Fe/L) along with different BEN doses (10 mg/L, 50 mg/L and 200 mg/L). For the rest of the operation conditions, standards conditions were applied as described in section 8.1.3. Figure 7-9 presents the turbidity removal, the Chl-a removal and the DOC removal for the different combinations (a) BEN = 10 mg/L, (b) BEN = 50 mg/L and (c) BEN = 200 mg/L.
Figure 7-9: Impact of the coagulant dose on the performances of CFS for HYMculture, with coagulant aid (clay) for (a) BEN = 10 mg/L, (b) BEN = 50 mg/L and (c) BEN = 200 mg/L. CFS conditions: coagulation at 200 rpm for 2 minutes at pH6.8, flocculation at 30 rpm for 10 minutes, sedimentation for 30 minutes.

When BEN is used in absence of ferric chloride, the turbidity and Chl-a removals are linearly correlated with the BEN dose and reached 39.8% and 92.6%, respectively for 200 mg BEN/L. However, BEN alone does not eliminate any DOC, at any applied dose. When ferric chloride is added, all removals are increased (i.e., turbidity, Chl-a and DOC) and the DOC removal raises from 0% to 28% for a coagulant dose of 2.5 mg Fe/L, whatever the BEN dose. This suggests that the DOC removal is only achieved by the ferric chloride coagulant and BEN has not effect on it.
7.1.4. Comparison between CFF and CFS with BEN aid

In order to compare the three different coagulation-flocculation configurations (i.e., CFF - Fe, CFS - Fe + BEN and CFS - BEN), experiments were performed with the most problematic algal species (in terms of fouling and CF treatment), HYM at decline phase with a fixed DOC concentration of 2 mg/L. The comparison study was conducted in triplicate. The characteristics of the HYM solution for the three comparison studies is presented in Table 7-2.

<table>
<thead>
<tr>
<th></th>
<th>Turbidity (NTU)</th>
<th>Chl-a (μg/L)</th>
<th>DOC (mg/L)</th>
<th>HMW (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HYM</td>
<td>4.25 +/- 1.92</td>
<td>17.62 +/- 6.94</td>
<td>1.97 +/- 0.26</td>
<td>0.62 +/- 0.16</td>
</tr>
</tbody>
</table>

The HYM solution for each comparison study is relatively similar in terms DOC and HMW concentration, with a standard deviation of 0.26 and 0.16, respectively. The Chl-a concentration differs more with a standard deviation of 6.94 μg/L. Fluctuation in the turbidity is also expected at decline phase, due to cells debris.

The standard experimental conditions were applied with the optimum coagulant dose of 2.5 mg Fe/mg DOC for coagulation-flocculation (coagulation at 200 rpm for 2 min at pH6.8 +/- 0.2, flocculation at 30 rpm for 10 minutes). The flotation duration was 10 minutes for CFF, and the sedimentation, 30 minutes for CFS. 200 mg/L of BEN was added for CFS configurations. Figure 7-10 plots the LC-OCD chromatograms of the feed and clarified waters along with the performances of the different CF configurations.
CFS – BEN is a good pretreatment to remove algal cells (i.e., Chl-a) and turbidity, however it has poor efficiency for the removal of DOC, with only 4.4% +/-5.9 removal. DOC is partially eliminated only when ferric chloride is used as a coagulant and it is mainly due to HMW removal as observed in Figure 7-10a. The DOC removal remains similar when BEN is added to the coagulant, however, the HMW removal slightly decreases from 70.4 % to 60.2 %. The best CF treatment for DOC and HMW removals is achieved using ferric chloride only.

7.1.5. Partial conclusion

The two studied algae (TET and HYM) are showing different behavior during coagulation-flocculation. This observation is in agreement with numerous studies that
concluded that morphology, motility, surface charge and AOM composition were impacting the coagulation-flocculation performances (Eldridge et al. 2012; R. K. Henderson et al. 2008b; Widrig et al. 1996). For the same coagulant dose (mg Fe/ mg DOC), the quality of the TET clarified water is better than the HYM clarified water. The higher performance of CF on TET can be explained by its richer protein-like content (Chapter 4, Kuroiwa et al. (2013) and Widrig et al. (1996) found that the coagulation-flocculation preferentially removes protein-like compounds. HYM, which is mainly composed, of carbohydrates, is then harder to treat by coagulation flocculation. Clay used without coagulant is a good approach for algal cell and turbidity removal but have very little impact on DOC reduction.

7.2. Efficiency of coagulation – flocculation – ultrafiltration sequence for the treatment of *Hymenomonas sp.* solution at decline phase: comparison between polymeric and ceramic membranes

7.2.1. Reduction of UF fouling after coagulation-flocculation of HYM solution at decline phase

The clarified solutions obtained from the comparison study (CFF, CFS with and without BEN) (section 8.1.4.) were filtered through polymeric and ceramic UF membranes. Polymeric dead-end UF experiments are performed with a hydrophilic PVDF membrane with a nominal pore size of 30 nm. Ceramic dead-end UF experiments were performed with an alumina membrane with a nominal pore size of 80 nm (Al₂O₃-80 nm membrane).
The polymeric UF filtration setup available in the laboratory was operated at constant flux, and to be able to compare the two types of membranes (i.e., polymeric and ceramic), all UF experiments were performed at constant flux. The filtration flux was set at 9 +/- 1 mL/min for both membranes. However, because of the difference in filtration surface of the polymeric and ceramic membranes (70 cm² and 12 cm², respectively), the specific flux was 75 +/- 7 LMH for polymeric and 430 +/- 30 LMH for ceramic UF experiments. Ceramic membrane allows a higher operating flux than polymeric (Bhave 1991) and the two membranes were operate with the same flux but higher specific flux for ceramic membrane. The filtration duration was then calculated in order to filter the same volume per filtration surface (i.e., 30 minutes and 5.5 minutes for polymeric and ceramic UF experiments, respectively). In order to evaluate the impact of the specific filtration flux on the fouling and the permeate quality, a lower flux of 250 +/- 20 LMH was then applied to ceramic UF filtration. After five filtration cycles (i.e., filtration – backwash), a

In the previous chapters (Chapter 5 and 6), Chemical Enhanced Backwash (CEB) using NaOH showed very poor efficiency to recover the hydraulic performances of the membranes and in this study, CEB was implemented with a solution of NaOCl (350 mg Cl₂/L for polymeric and 2000 mg Cl₂/L for ceramic membrane). The DOC and HMW compounds concentration of the raw and clarified solutions are presented in Table 7-2 and Table 7-3, respectively.
Table 7-3: Characteristics of the clarified seawater obtained after CFF and CFS with and without BEN

<table>
<thead>
<tr>
<th>Pretreatments</th>
<th>DOC (mg/L)</th>
<th>HMW (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFF – Fe</td>
<td>1.20 +/- 0.14</td>
<td>0.15 +/- 0.03</td>
</tr>
<tr>
<td>CFS – Fe+BEN</td>
<td>1.30 +/- 0.16</td>
<td>0.27 +/- 0.15</td>
</tr>
<tr>
<td>CFS – BEN</td>
<td>1.70 +/- 0.18</td>
<td>0.48 +/- 0.36</td>
</tr>
</tbody>
</table>

The flux declines recorded for the raw and clarified solutions obtained after CFF, CFS with and without BEN are plotted in Figure 7-11. The flux declines of only one comparison study is plotted for a clearer picture but for the rest of the discussion, the fouling indexes and permeate qualities are calculated on average of the three comparison studies.
Figure 7-11: Typical flux declines during the filtrations of the raw and clarified HYM solutions obtained after CFF, CFS with and without BEN.
For the filtration of the raw HYM solution, the fouling is rapid and severe as observed in Chapter 5. However, a very low permeability is preserved for both types of membrane (polymeric or ceramic) (around 10% of the initial flux). This suggests the formation of a porous cake layer that increases the hydraulic resistance of the membrane but still allow the passage of the solution.

The best fouling reduction is observed in the presence of ferric chloride (i.e., CFF – Fe and CFS – Fe+BEN) for both types of membrane. The use of BEN (i.e., CFS – BEN) alone permits to greatly reduce the fouling of the polymeric membrane, and a slight but significant reduction is observed for the ceramic membrane, which confirms the higher sensitivity of the ceramic membrane toward biopolymers. The fouling reduction could be due to the removal of large AOM aggregated present in the HYM culture at the DP (Figure 3-7) that were not quantified because of the prefiltration through 0.7 μm prior to analyses.

The CF pretreatment efficiency will be divided in three sections:

1) the fouling during the first filtration cycle (TFI -1)
2) the hydraulically reversible/irreversible character of the fouling (HIFI)
3) the CEB efficiency

7.2.1.1. Fouling during the first filtration cycle (TFI -1)

The different raw HYM solutions were slightly different from one comparison study to another (Table 7-2), which lead to different fouling potential. In order to evaluate the
impact of the different CF pretreatments on the polymeric and ceramic ultrafiltration performances, the percentage of reduction of TFI-1 (m²/mg C) was determined (i.e., TFI-1 with and without CF pretreatment). The TFI-1 reduction is displayed in Table 7-4.

Table 7-4: TFI-1 reduction (%) for each CF pretreatments (MF: Moderate Flux; HF: High Flux)

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Polymeric UF</th>
<th>Ceramic UF - MF</th>
<th>Ceramic UF - HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFF - Fe</td>
<td>83.8 +/- 14.2</td>
<td>86.4 +/- 2.4</td>
<td>90.2 +/- 0.8</td>
</tr>
<tr>
<td>CFS – Fe+BEN</td>
<td>80.8 +/- 5.3</td>
<td>70.5 +/- 0.4</td>
<td>86.3 +/- 8.7</td>
</tr>
<tr>
<td>CFS - BEN</td>
<td>16.8 +/- 17.5</td>
<td>23.2 +/- 4.7</td>
<td>17.7 +/- 20.4</td>
</tr>
</tbody>
</table>

The reduction of the TFI-1 (expressed as m²/mg C filtered) is the highest after CFF – Fe pretreatment, with a reduction of 83.8% +/- 14.2, 86.4% +/- 2.4 and 90.2% +/-0.8 for the polymeric UF, the ceramic UF at MF and the ceramic UF at HF, respectively. The CFS – Fe+BEN also permits a significant TFI-1 reduction, whereas the fouling of the CFS – BEN clarified water is poorly improved. The TFI-1 reductions for the two ceramic UF modes (operated at MF and HF) are relatively similar which suggests that the fouling depends on the mass of DOC filtered and not on the filtration flux. The large removal of HMW organic fraction (mainly polysaccharides for HYM) should support these results for the two pretreatment modes implementing ferric chloride.

The TFI-1 of the clarified waters after the best CF configurations (i.e. CFF – Fe and CFS – Fe+BEN) are presented in Table 7-5.
Table 7-5: TFI -1 (m²/mg DOC) of the clarified waters

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Polymeric UF</th>
<th>Ceramic UF - MF</th>
<th>Ceramic UF - HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFF - Fe</td>
<td>1.07 x 10⁻³ +/- 0.09</td>
<td>5.65 x 10⁻³ +/- 0.10</td>
<td>3.94 x 10⁻³ +/- 0.93</td>
</tr>
<tr>
<td>CFS – Fe+BEN</td>
<td>2.00 x 10⁻³ +/- 0.47</td>
<td>1.27 x 10⁻² +/- 0.37</td>
<td>6.1 x 10⁻³ +/- 2.82</td>
</tr>
</tbody>
</table>

Even if the CF pretreatment with ferric chloride permits to reduce the fouling potential of marine algal solutions, the fouling of ceramic membranes remains at least three times more severe than the fouling of the polymeric membranes, and strong interactions between the metal oxide and the AOM should be involved.

7.2.1.2. Hydraulically reversible/irreversible character of the fouling (HIFI)

The percent reduction of the Hydraulically Irreversible Fouling Index (HIFI) expressed as m²/mg C filtered, was also calculated as an indicator of the backwash (Table 7-6). For polymeric UF experiments, the HIFI was calculated for the first five filtration cycles and for the ceramic UF at moderate flux (i.e., MF), HIFI was only calculated for the first two filtration cycles to be able to compare with the HIFI of the raw HYM solution. No comparison was possible for ceramic UF at high flux (i.e., HF).

Table 7-6: HIFI (%) reduction for each CF pretreatments. HIFI is calculated for the first five filtration cycles (before CEB) for the polymeric UF and for the first two filtration cycles for the ceramic UF.

<table>
<thead>
<tr>
<th>Pretreatments</th>
<th>Polymeric UF</th>
<th>Ceramic UF - MF</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFF - Fe</td>
<td>95.7 +/- 1.6</td>
<td>87.7 +/- 7.7</td>
</tr>
<tr>
<td>CFS - Fe+BEN</td>
<td>97.1 +/- 1.1</td>
<td>63.9</td>
</tr>
<tr>
<td>CFS - BEN</td>
<td>92.7 +/- 5.1</td>
<td>30.8 +/- 0.7</td>
</tr>
</tbody>
</table>
The better HIFI reduction is achieved when the solution was pretreated with CFF – Fe +BEN. It is interesting to note that for the polymeric UF, the fouling of the CFS – BEN clarified water is highly reversible too, showing similar HIFI reduction than the other CF configurations. The reversibility could be due to flocs of BEN and AOM deposited in the surface of the polymeric membrane (pore size = 30 nm) and washed out during the backwash process. The high irreversibility of the ceramic membrane for the filtration of the clarified water after CFS – BEN is probably due to the strong sensitivity of Al2O3-80nm with the polysaccharides. The filtrations of the CFF – Fe and CFS – Fe+BEN clarified solutions are characterized by a strong irreversibility for both polymeric and ceramic membranes. Yu et al. (2014) suggested that hydrophilic compounds (such as polysaccharides), which are generally not well removed by CF, are responsible for irreversible fouling due to their lower MW, which allow them to interpenetrate the pores of the membranes. Zhang et al. (2013c) also found that the inner layer of the fouling material of a ZrO2 membrane was mostly composed by hydrophilic materials such as polysaccharides. Because CF reduces the proteinaceous material content responsible for the strong flux decline, the proportion of polysaccharide-like material increases, leading to a strong fouling irreversibility. The stronger fouling of the ceramic membrane refers to a higher affinity of AOM with metal oxides than with organic polymers.

The HIFI for the filtration of the clarified waters obtained after the two best CF treatment is more than five times higher for ceramic membrane (Table 7-7), which confirms the strong adhesion of polysaccharides and Al2O3 surface, measured on our AFM study. AFM measurement should be performed with H-PVDF polymeric membrane in order to
compare the adhesion forces between polysaccharides and H-PVDF and polysaccharides and Al₂O₃.

Table 7-7: HIFI (m²/mg DOC) of the clarified waters. HIFI is calculated for the first five filtration cycles (before CEB)

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Polymeric UF</th>
<th>Ceramic UF - MF</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFF - Fe</td>
<td>0.88 x10⁻³ +/- 0.18</td>
<td>5.93 x 10⁻³ +/- 0.52</td>
</tr>
<tr>
<td>CFS – Fe+BEN</td>
<td>0.60 x10⁻³ +/- 0.14</td>
<td>5.36 x 10⁻² +/- 0.44</td>
</tr>
</tbody>
</table>

7.2.1.3. The CEB efficiency

After CEB, the flux of the polymeric membrane is globally improved for all CF configurations, whereas the CEB at high dose (2 000 mg Cl₂/L) has no effect on the flux of the ceramic membrane, with confirms the strong very strong adhesion of HYM AOM on Al₂O₃-80 nm membrane measured by AFM (Figure 4-10). Hypochlorite oxidation efficiency is much slower than hypobromite in alkaline solutions (Varela 2003) and CEB using hypobromite could be an option for the cleaning of membranes fouled by AOM. The high efficiency of the CEB for the polymeric UF filtration of the clarified water obtained after CFS using BEN suggests the presence of microflocs of BEN and AOM that would remain at the surface and protect the polymeric membrane (with a porosity of 30 nm) from the adhesion of AOM with the membrane surface. These flocs would be large enough to interpenetrate the ceramic membrane (80 nm porosity), allowing the AOM to adhere to the membrane surface.
7.2.2. Permeate quality: comparison between polymeric and ceramic UF

The permeate of the ceramic UF is generally of better quality than the permeate of the polymeric UF. Table 7-8 presents the average DOC and HMW concentration for the filtration of CFF – Fe and CFS – Fe+BEN clarified waters. The average values were only calculated for these filtrations because of the similarity in the UF feed solutions. The Chl-a removal is not discussed as it has mainly been eliminated during CF.

Table 7-8: Permeate quality of the filtration of CFF – Fe and CFS – Fe+BEN clarified waters

<table>
<thead>
<tr>
<th>Filtration mode</th>
<th>DOC (mg/L)</th>
<th>HMW (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymeric UF</td>
<td>1.48 +/- 0.34</td>
<td>0.15 +/- 0.08</td>
</tr>
<tr>
<td>Ceramic UF – MF</td>
<td>0.93 +/- 0.31</td>
<td>0.03 +/- 0.02</td>
</tr>
<tr>
<td>Ceramic UF – HF</td>
<td>1.26 +/- 0.20</td>
<td>0.08 +/- 0.02</td>
</tr>
</tbody>
</table>

Overall, the ceramic UF permits a better removal of DOC and particularly HMW compounds. This selectivity can explain the stronger AOM fouling toward ceramic membrane than toward polymeric membrane.

The operation of the ceramic membrane at high flux degrades the quality of the permeate. It is possible that high filtration flux would force the passage of the smallest HMW compounds through the ceramic. This difference in permeate quality highlights the importance of the filtration flux for the ceramic UF operation mode.

7.3. Conclusion

In order to treat algal rich solution such as seawater during an algal bloom, a coagulation-flocculation prior UF is necessary. The configuration coagulation-flocculation-flotation...
using ferric chloride at pH6.5 and at high coagulant dose (>1.5 mg Fe/ mg DOC) appear to be the best treatment to remove HMW compounds and permits the best fouling reduction for either polymeric or ceramic UF. The addition of clay in the coagulation process only slightly impacts the DOC removal of the CF, but probably due to the lower HMW fraction removal, is not as efficient as the CFF – Fe. However, for polymeric UF, the addition of BEN increases the reversibility of the fouling toward polymeric as compared to ceramic UF membrane. The microflocs of BEN and AOM would remain at the surface, forming a porous layer and protecting the surface from pore blocking, and thus would be more easily backwashed. For ceramic membrane, the adhesion between the metal oxide and the polysaccharide-rich solution is too important and the backwash does not permit a significant flux recovery.

The clarified water impoverished in HMW (and more specifically proteinaceous material) permits a great fouling reduction for both polymeric and ceramic UF. The ceramic membrane is prone to a stronger AOM fouling than polymeric membrane, probably due to a stronger affinity between the metal oxides and the AOM. This stronger affinity permits a better removal of the DOC and more specifically HMW removal than polymeric membrane, and thus a better permeate quality. CEB using strong disinfectant agent (NaOCl at 2 000 mg Cl₂/L) is not sufficient to recover the initial flux of the ceramic membrane and other strong oxidants such as ozone, UV or advanced oxidation process should be studied to clean the membrane. Further investigation should also be performed on the impact of the flux reduction versus the quality of the permeate of the polymeric and ceramic UF membranes, on the RO filtration and RO fouling potential.
8. PUBLISHED PAPER: Ceramic membrane as a pretreatment for Reverse Osmosis: Interaction between marine organic matter and metal oxides

This paper has been published in *Desalination and Water Treatment*, 2013.

**DOI:** 10.1080/19443994.2012.714728. The work has been conducted while the algal monocultures were established in the laboratory and is considered as a preliminary work.

8.1. Introduction

Throughout the world, there is a trend to intensify the use of desalination as a mean to reduce current or future water scarcity. Water scarcity occurs mostly in arid regions, but not exclusively. Pollution and over exploitation of fresh waters (groundwater aquifers and surface waters) have significantly diminished the water quantity available for conventional treatment. At the same time, population, industrial activities and agriculture exploitations are growing fast, leading to higher water demand and higher water consumption. Alternative water resources are needed. Membrane desalination provides such an alternative source, offering water otherwise not accessible for industrial and municipal use. Reverse Osmosis is the most common membrane-based desalination option for seawater and brackish water. The water passes through the membrane while salts are almost completely retained. This technique presents an extremely good removal of colloids, dissolved organic matter and salts.

In Reverse Osmosis technology, fouling control is important as fouling results in increased energy consumption, decreased salts rejections and higher cleaning frequency, which shorten the lifetime of the membrane. Fouling concerns colloidal, organic fouling
and biofouling. To minimize RO fouling, pretreatment must be applied to efficiently remove particles, colloids and also precursors of the organic fouling and biofouling. Conventional pretreatments such as Dual Media Filtration (with coagulation) or Microfiltration/Ultrafiltration are usually performed. Both membrane types have proven their efficiency against particles (including bacteria) and colloidal material. Ceramic membranes (porous media composed by optional porous layers of metal oxides) offer several advantages for Micro and Ultrafiltration pretreatments because their initial properties can be recovered using more severe cleaning procedure (strong acids and bases, oxidants, high backflush capacity,) as compared to polymeric membranes. Furthermore, ceramic membranes offer other advantages such as: mechanical stability under large pressure gradients (noncompressible, no creep); long lifetime; (electro) catalytic and electrochemical activity easily realizable; high throughput volume; good control of pore dimension and pore distribution (Bhave, 1991).

Several works have been developed on the performance (pressure filtration, backwash frequency and backwash pressure, pore size) of ceramic membrane filtration (Xu J. et al., 2010; Khenakhem S. et al., 2009; Konicezny K. et al., 2006; Lerch A. et al., 2004; Bottino A. et al., 2001). Only few studies are considering the interaction of NOM with metal oxides in the ceramic filtration process. A few projects can be found, focusing on the interactions between natural metal oxides (such as goethite, iron oxides) with fresh water NOM under real conditions (Perez et al., 2011; Ghosh et al., 2010; Claret et al., 2008; Weng et al., 2007; Chen et al., 2006; Gu et al., 1995; Gu, 1994; Schlautman et al., 1994; Ochs et al., 1994; McKnight et al., 1992). NOM adsorption on mineral surface seems to depend both on the NOM origin and on the type of mineral. NOM is a
heterogeneous mixture of different organic molecules that may have different adsorption affinities for the mineral surface. These different organic compounds compete for adsorption when the surface adsorption sites are limited. In the majority of the studies, the NOM is usually treated as a single organic component representative such as Humic Substances (HS) or more precisely Humic or Fulvic Acids (respectively HA and FA). Different studies have been done on natural minerals present in solution, such as iron oxide, goethite and alumina oxides. It has been observed that the fraction of organic matter that fouled the most was the High Molecular Weight fraction with high aromatic moieties (Perez et al., 2011; Claret et al., 2008; Weng et al., 2007; Chen et al., 2006; Gu et al., 1995; Gu, 1994; Ochs et al., 1994; McKnight et al., 1992). The influence of the pH has been observed in all the studies: sorption decreases with increasing pH. For pH below the mineral pH\textsubscript{pzc}, anion exchange reaction is part of the whole process but is considered very insignificant at high pH. Results on the ionic strength dependence are more debatable. Gu et al. (1995) demonstrated that the ionic strength does not have real impact on the adsorption of NOM on iron oxide. This means that the electrostatic interactions are a minor mechanism. However Weng et al. (2007) found that an increase in ionic strength leads to a decrease in size of the HA structures. Thus the HA moieties get closer to the surface, which leads to a stronger competition with the anions that are adsorbed as ion pairs on the surface. The FA molecules are by nature smaller, so the conformational change is less important and their sorption is less ionic strength-dependent. Ghosh at al. (2010) and Chen et al. (2006) also showed that in the presence of cations such as Ca\textsuperscript{2+} and Na\textsuperscript{+}, the aggregation between humic acids and nano-alumina oxides is more important.
The quality and composition of the feed water has a great importance on the performance of high-pressure membrane filtration. Algal bloom events are of particular importance for RO desalination process because of the release of significant amounts of organic matter that leads to membrane fouling. RO desalination plants had to be shut down during major algal bloom event in the Middle East region during the past few years.

Our study focuses on the fouling of ultrafiltration ceramic membrane by marine organic matter. Special attention is given to algal exudates with the objective to simulate RO pretreatment during algal bloom event occurring in seawater.

8.2. Material and Methods

8.2.1. Sample description

The first part of the study focused on two different natural seawaters collected at different time of the year.

The first seawater was collected at the inlet of a Seawater Reverse Osmosis plant located in Jubail, Saudi Arabia on the Arabian Sea. Water samples were obtained during the summer season, on July 2011. It shows a DOC of 1.70 mg/L with a conductivity of 62.5 mS/cm (at 20.5°C) and a pH of 8.2.

The second seawater was collected 3km offshore of Thuwal (Saudi Arabia) in the Red Sea on October 2011 and January 2012. The two samples showed similar DOC around 0.8 mg/L. The conductivity of the Red Sea is 59.3 mS/cm (at 20.5°C) and a pH of 8.2.
The second part of the study investigated the influence of marine organic matter on the ultrafiltration. Algal exudates from *Chlorella vulgaris* species were studied. *Chlorella vulgaris* is a microalgae, living in all aqueous habitats—essentially cosmopolitan in both freshwater and marine habitats. It is known to be responsible for un-harmful algal bloom. This study focuses on the High Molecular Weight (HMW) compounds of *Chlorella* exudates isolated from dialysis (3.5 KDa) against MilliQ water. Red Seawater, collected on October 2011 was enriched with the *Chlorella* HMW compounds. Final conductivity was 45 mS/cm (at 20.5°C) and a pH 8.2.

### 8.2.2. Filtration experiment

Dead-end filtration experiments were conducted at room temperature (20.5°C +/- 0.5) and constant pressure (0.7 bar).

Two different ceramic membranes (47 mm diameter planar disk; effective filtration area: 12 cm²) were used. Both of them are made with a silica support coated with alumina or titanium oxide for nominal pore size of 80 nm and 30 nm, respectively. The pure water permeability determined at room temperature (20°C +/- 1) with MilliQ water was 1000 ± 50 L/m².h.bar and 680± 50 L/m².h.bar for the alumina and titanium membrane, respectively.

The permeate flux was recorded with a scale connected to a computer.

Three filtrations in series were performed at 0.7 bar separated by backflush with MilliQ water at 2 bars and a final chemical cleaning using NaOH (0.1M) at 2 bars.

Pure water permeability of the membrane was determined before and after all fouling tests.
UV, fluorescence, DOC and LC-OCD analyses were conducted on the permeate solutions, the backflush solutions and the cleaning solutions.

8.2.3. Unified Membrane Fouling Index (UMFI)

Fouling can be quantified using a resistance-in-series approach. For low-pressure membrane, the flux \( J, \text{L/m}^2\text{.h} \) can be described as:

\[
J = \frac{\Delta P}{\mu R}
\]

Where \( \Delta P \) is the transmembrane pressure, \( R \) is the resistance to flow through the membrane and \( \mu \) is the water viscosity.

\( R \) is the total resistance. It sums the resistance of the clean membrane \( (R_{\text{memb}}) \) and the resistance due to the fouling the membrane \( (R_{\text{foul}}) \):

\[
R = R_{\text{memb}} + R_{\text{foul}}
\]

The resistance of the fouling increases linearly with the volume of solution filtered. Thus, we can express \( R_{\text{foul}} \) as: \( R_{\text{foul}} = r_{\text{foul}} \cdot V \), which \( r_{\text{foul}} \) is a rate constant for the increase in the resistance and \( V \) is specific volume \( (\text{L/m}^2) \).

Combining the three equation, we obtain:

\[
J_s = \frac{J}{\Delta P} = \frac{1}{\mu \left( R_{\text{memb}} + r_{\text{foul}} \cdot V \right)}
\]

For a new membrane, \( J_{s0} = \frac{1}{\mu R_{\text{memb}}} \). We can normalize the specific flux \( (J_s) \) by dividing \( J_s \) by \( J_{s0} \). The equation obtained is the following:

\[
J' \cdot s = \frac{J_s}{J_{s0}} = \frac{1}{1 + \frac{r_{\text{foul}} \cdot V}{R_{\text{memb}}}}
\]

And:
\[
\frac{1}{J_s} = 1 + UMFI \cdot V
\]
Where UMFI = \( \frac{r_{fou}f}{R_{memb}} \).

Fouling can then be expressed by drawing the graph \( \frac{1}{J_s} = f (V) \). The slope of the curve will be the UMFI. UNFI for each filtration cycle is named Total Fouling Index (TFI).

8.3. Results and discussion

8.3.1. Natural Seawaters

The two seawaters are significantly different in term of DOC concentration. The Arabian Sea water presents a DOC that is almost the double of the DOC of the Red Sea water (1.70 mg/L and 0.74 mg/L). However, the DOC composition is qualitatively comparable. Figure 1 gives the LC-OCD chromatogram of the two seawaters (bottom: Arabian Sea, July 2011; top: Red Sea, October 2011). Table 1 summarizes the concentration of the different components of the marine organic matter and their relative abundance.
Figure 8-1: LC-OCD chromatogram of natural seawaters (bottom: Arabian Sea, July 2011; top: Red Sea, October 2011)

Table 8-1: Distribution of the DOC of the Arabian Sea and Red Sea

<table>
<thead>
<tr>
<th></th>
<th>DOC (mg/L)</th>
<th>Biopolymers (mg/L)</th>
<th>Humics (mg/L)</th>
<th>Building Blocks (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Sea</td>
<td>0.76</td>
<td>0.089</td>
<td>0.389</td>
<td>0.156</td>
</tr>
<tr>
<td>+/- 0.05</td>
<td>(11.7%)</td>
<td>(51.2%)</td>
<td>(20.5%)</td>
<td></td>
</tr>
<tr>
<td>Arabian Sea</td>
<td>1.70</td>
<td>0.214</td>
<td>0.671</td>
<td>0.236</td>
</tr>
<tr>
<td>+/- 0.05</td>
<td>(12.6%)</td>
<td>(39.4%)</td>
<td>(13.8%)</td>
<td></td>
</tr>
</tbody>
</table>

Results indicate that the biopolymers represent around 12% of the DOC of the two seawaters, however the Arabian Sea water is much more enriched than the Red Sea water in this fraction. The humics and building blocks are also two times higher in the
Arabian Sea water, than in the Red Sea, but their relative contribution is lower. One can notice the presence of a significant LMW neutrals peak, at around 75 minutes for the Arabian Sea water. The UV signal of the chromatogram has been magnified by 20.

Humic substances from marine water are known to exert low arolatic signature.

In this study, seawater samples are filtered through a 80nm alumina membrane. The relative permeate flux decline curves, recorded during the filtration of the Arabian Sea and Red Sea waters, are shown in Figure 2.

![Permeate flux decline during the filtration of the Arabian Sea and Red Sea waters through a 80nm alumina ceramic membrane](image)

**Figure 8-2: Permeate flux decline during the filtration of the Arabian Sea and Red Sea waters through a 80nm alumina ceramic membrane**

The permeate flux of the Arabian Sea water declines very rapidly. After only 6 minutes, the flux has already been reduced by 20% for the Arabian Sea and only 7% for the Red Sea water. In both cases the different backflushes showed only minor effect in
recovering the initial flux. Similar observation can be made after chemical cleaning with NaOH, at 2 bars, indicating that the severe irreversible fouling occurred.

Figure 8-3: Total Fouling Index of the filtration of Arabian Sea (A) and Red Sea (B) waters
The TFI for the first filtration (TFI -1) was 4.76 m².L⁻¹ for the Arabian Sea and only 1.18 m².L⁻¹ for the Red Sea. After backflush, in the successive filtrations, the TFI continued to rise.

From a qualitative point of view, the filtration on 80nm slightly reduced the DOC concentration for the Arabian Sea water (almost 20%), but no significant change was observed for the Red Sea water. Table 2 shows the concentrations of feed and permeate for each experiment.

| Table 8-2: Natural seawaters filtration: DOC concentrations of feed and permeate |
|--------------------------------|-----------------|-----------------|
|                               | Feed water      | 80 nm permeate  |
| Red Sea water (KAUST)         | 0.76 +/- 0.05   | 0.79 +/- 0.05   |
| Arabian Sea water (Jubail)    | 1.70 +/- 0.05   | 1.38 +/- 0.05   |

In terms of distribution of the DOC (figure 4), a reduction of the biopolymers can be observed in the filtration of the two different seawater samples. The filtration on 80nm showed a reduction in biopolymers of 30% for the Arabian Sea water and 20% for the Red Sea water. No particular trend can be found regarding humics and building blocks.
8.3.2. Algae exudates

To understand the role of HMW compounds on the filtration of seawaters, the Red Sea water (collected on October 2011) was enriched with HMW exudates isolated from a *Chlorella* cultures using 3.5 kDa dialysis bag.

Figure 5 shows the LC-OCD chromatogram of the algae exudates before (A) and after (B) dialysis.
Figure 8-5: LC-OCD chromatogram of the *Chlorella* exudates dialysis: feed, concentrate and permeate

Figure 6 presents the LC-OCD profiles of the raw Red Sea water (bottom) and the enriched one with *Chlorella* HMW compounds (top). Table 3 summarizes the concentration of the different components of the marine organic matter and their relative abundance.
Figure 8-6: LC-OCD chromatogram of the Red Sea water (bottom) and the Red Sea water enriched with *Chlorella* HMW compounds (top)

Table 8-3: Distribution of the DOC of the Red Sea water and the Red Sea water enriched with HMW compounds

<table>
<thead>
<tr>
<th></th>
<th>DOC (mg/L)</th>
<th>Biopolymers (mg/L)</th>
<th>Humics (mg/L)</th>
<th>Building Blocks (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Sea water</td>
<td>0.84</td>
<td>0.170</td>
<td>0.364</td>
<td>0.122</td>
</tr>
<tr>
<td>enriched with</td>
<td>+/- 0.05</td>
<td>(20.2%)</td>
<td>(43.1%)</td>
<td>(14.5%)</td>
</tr>
<tr>
<td>Chlorella HMW</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>compounds</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Red Sea water</td>
<td>0.76</td>
<td>0.089</td>
<td>0.389</td>
<td>0.156</td>
</tr>
<tr>
<td></td>
<td>+/- 0.05</td>
<td>(11.7%)</td>
<td>(51.2%)</td>
<td>(20.5%)</td>
</tr>
</tbody>
</table>
The DOC remains in the same range of concentration after the water was spiked with HMW exudates (9% increase i.e. 0.08mg/L). The different fractions of DOC remain in the same range of concentration except the biopolymer content, that was doubled for the Red Sea water enriched with *Chlorella* HMW compounds in comparison to the raw Red Sea water. Thus the two seawater samples mainly differ on the concentration of the biopolymers.

The relative permeate flux decline recorded during the filtration of the raw and the enriched in HMW exudates Red Sea water is displayed on figure 7.

![Permeate flux decline during the filtration of the Red Sea water and the Red Sea water enriched with *Chlorella* HMW compounds](image)

**Figure 8-7: Permeate flux decline during the filtration of the Red Sea water and the Red Sea water enriched with *Chlorella* HMW compounds**

The permeate flux of the Red Sea water enriched with *Chlorella* HMW compounds declines very rapidly. After 6 minutes, the flux has already been reduced by 15%. A decrease in the flux of only 7% is observed for the raw Red Sea water. Again, the
efficiency of the backflushes is limited. After chemical cleaning with NaOH, at 2 bars, the initial flux is not recovered. Table 4 shows the DOC concentration and the DOC distribution of the feed and the permeate for each Red Sea water experiment and the UMFI of the first filtration cycle.

Table 8-4: Distribution of DOC in the raw and enriched with *Chlorella* HMW compounds Red Sea water

<table>
<thead>
<tr>
<th>DOC (mg/L)</th>
<th>TFI 1 (m².L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>30 nm permeate</td>
</tr>
<tr>
<td>Red Sea water</td>
<td>0.76 +/- 0.05</td>
</tr>
<tr>
<td>Red Sea water enriched with HMW Chlorella</td>
<td>0.84 +/- 0.05</td>
</tr>
</tbody>
</table>

UMFI 1 for the Red Sea water enriched with *Chlorella* HMW compounds is more than twice the UMFI 1 for the raw Red Sea. The increase of the UMFI 1 relates to the increase in the biopolymers content. Figure 8 gives the composition of the feed and permeate of the two filtration experiments.
Figure 8-8: Distribution of DOC on the feed and permeate water for the filtration of raw and Red Sea water enriched with *Chlorella* HMW compounds.

Biopolymers are the group of compounds that are the most affected by the filtration on 30nm. 40% of the biopolymers are removed from the raw Red Sea water, and up to 60% for the Red Sea water enriched with HMW compounds. Thus we can clearly conclude that the HMW compounds play a major role on the fouling of the ceramic membranes.

The 30nm permeate was then filtered on a new 30nm membrane. Figure 9 displays the relative permeate flux decline recorded during the filtration of the 30nm permeates of the two waters filtered through 30nm.
A decline of the permeate flux is still observed during the repeated filtration of the Red Sea waters on 30nm. These results clearly indicate that size exclusion is not the only mechanism involved on the fouling phenomena of ceramic membranes with marine organic matter. Adsorption of low molecular weight molecules also occurs.

To understand the strong affinity of the HMW compounds with the membrane (no significant impact of the backflushes), HMW compounds have been lyophilized and characterized using pyrolysis-GC-MS analysis and FTIR analysis.
Figure 8-10: GC-MS pyrochromatogram of the HMW compounds

The pyrochromatogram (figure 10) is processed by assigning the pyrolysis products to one of the four categories: polysaccharides, proteins, N-acetylamino sugars and polyphenolic material (Bruchet, 1998). The pyrochromatogram obtained for the HMW compounds shows that most of the pyrolysis by-products are furan derivatives and cyclic ketones such as Methoxy furan (12.7 min), Cyclopentenone (19 min), Furfural (22 min), Furanone (22.5 min), Methyl Furfural (27.5 min), Furan methanol (31 min), Dimethyl hydroxyl furanone (37.9 min) and Methoxy furan carboxaldehyde (45 min). These compounds are known to originate from the pyrolysis of polysaccharides. Proteins are also present at a lower extent in the sample. The estimate of the proteins is based on the pyrrole derivatives such as pyrrole (26 min) and Acetyl methyl pyrrole (31 min).
The infrared spectrum of the algal HMW compounds (figure 11) shows distinct C-O vibration between 1100 and 1000 cm\(^{-1}\). These peaks can be assigned to polysaccharides. Amide 1, Amide 2 and CH\(_3\) peaks located at 1631 cm\(^{-1}\), 1544 cm\(^{-1}\) and 1408 cm\(^{-1}\) respectively are diagnostics of N-acetylamino sugars. Both characterization techniques indicate that HMW compounds are mainly composed by polysaccharides with a lower amount of proteins. The biopolymer composition can explain the lack of efficiency with the sodium hydroxide cleaning. Alkaline solutions do not strongly interact with polysaccharides.

8.4. Conclusion

Fouling property of marine organics especially algal exudates is very important in ceramic membrane filtration. The severe and irreversible fouling of algal exudates is mainly due to the biopolymers content. Algal biopolymers are essentially composed of polysaccharides. It is thus difficult to chemically clean the membrane using alkaline...
solutions such as sodium hydroxide. Additional work will be done on the characterization of those polysaccharides for different algae species. Different pretreatments will be studied such as coagulation, DMF or flotation, to remove and minimize the biopolymers impact on the filtration.
In the Middle East, and more specifically in the Gulf region, population growth is rapid and freshwater resource is very limited. Seawater desalination is a good alternative to supply the water demand and desalination market is rapidly growing in this region (Fritzmann et al., 2007a). In 2011, Saudi Arabia was the largest desalinated water producer, generating 25% of the worldwide output in its more than 2000 plants (Henthorne, 2009; Berktay, 2011). The production of desalinated seawater is threatened by an emergent phenomenon: the higher frequency of the algal bloom events. Episodic algal bloom events are affecting the seawater quality and can have strong consequences for the desalination plant production. In 2008, a Cochlodinium polykrikoides bloom occurred in the Arabian Gulf and Gulf of Oman, forcing the desalination plants to stop their production, before an irreversible fouling of the reverse osmosis membranes (Richlen et al., 2010). In this context, it is imperative to implement efficient pretreatment to prevent risk of major fouling of the reverse osmosis membranes. Membrane technology (Microfiltration – MF and Ultrafiltration – UF) are becoming of interest as they produce a permeate water with stable quality. Polymeric MF/UF membranes are widely used but ceramic MF/UF membranes can also be an alternative, as they offer different advantages (high filtration specific flux, strong acid, base and oxidant resistances, long lifetime) toward polymeric membranes (Xu et al., 2010a; Matsui et al., 2012; Cui et al., 2013; Cui et al., 2011; Condom et al., 2004; Massé et al., 2011; Bhave, 1991).

In this work, different marine algal solutions were studied (natural seawaters and four marine algal monocultures) along with two different ceramic membranes (an alumina
membrane with a pore size of 80 nm – Al₂O₃-80 nm, and a titanium oxide membrane with a nominal pore size of 30 nm – TiO₂-30 nm). Few experiments were also performed with H-PVDF UF hollow fibers for comparison. Different aspects were also studied such as: the algal specie impact, the age of the algal bloom, the impact of the algal cells and algal organic matter larger than 0.7 μm. Clarification (Coagulation-flocculation using ferric chloride) prior to UF was also conducted, and three different configurations were investigated: coagulation-flocculation-flotation and coagulation-flocculation-sedimentation with and without clay.

The five main findings and conclusions are discussed in the following sections.

1. AOM composition during algal bloom

Three different stages of growth are distinguished in an algal culture: the Exponential Phase (EP), the Stationary Phase (SP) and the Decline Phase (DP). During the EP, the Algal Organic Matter (AOM) content is linearly correlated with the cell concentration and the AOM of the culture solution mainly corresponds to the Extracellular Organic Matter (EOM). When the SP begins, the Intracellular Organic Matter (IOM) is released to the solution due to cell lysis and the AOM of the culture solution is a mixture of EOM and IOM. At the end of the bloom, the AOM is composed by more than 50 % of High Molecular Weight (HMW) structures, with an important relative abundance of polysaccharides. At the DP, the proportion of IOM increases with the death of the algal cells, which enriches the AOM with protein and lipid- like structures. Globally, the HMW AOM samples (isolated from AOM using dialysis) are characterized by a higher polarity and a similar aromaticity than the freshwater biopolymers. The HMW AOM are
mainly constituted of polysaccharides, proteins and lipids, but their relative abundances vary from one alga to another. HYM is described as the richest polysaccharide-like NOM, whereas SKC and TET are a mixture of protein and polysaccharides. The higher protein content is observed for TET HMW sample, and SKC and SYN IOM samples are also characterized by high lipid content. For all cases, the HMW IOM is enriched in protein and lipid-like structures.

Under similar experimental conditions, the evolution of dissolved AOM composition during growth of a given alga gives acceptable (qualitative and quantitative) reproducibility.

2. Fouling potential of marine solutions

Natural and algal-enriched seawaters are responsible for strong and irreversible fouling and, for the same mass of DOC filtered, their fouling potential is higher than the potential of terrestrial humic substances (from treated Colorado River) by a factor of 3 to 65. Chemical Enhanced Backwash (CEB) using NaOH at 0.1 M did not permit to recover the initial flux of the membrane, neither CEB using strong disinfectant agent (NaOCl at 2000 mg Cl₂/L) was sufficient to recover the initial flux of the ceramic membrane. Other oxidants should be studied. Experiments performed at the WDRC/KAUST as part of another PhD project showed that ozone could be a promising chemical. However, the necessity to generate ozone in situ is probably of concern for the operator.

The rapid flux decline caused by the UF of marine solution reaches a plateau at around 10 to 20 % of the initial flux, which suggests the formation of a porous cake layer at the membrane surface. The irreversible character of the fouling can be explained by the
interpenetration of the AOM inside the pore network of the membrane, which is not
easily washed out by hydraulic backwash, and by a strong affinity between the AOM and
the metal oxide (strong adhesion energy between polysaccharide-rich AOM and Al₂O₃
measured by AFM). Fouling of ceramic membranes is enhanced at the end of bloom (i.e.,
decline phase of growth of the culture), for similar initial DOC. The increase in fouling
potential corresponds to an enrichment of HMW structures, and to a relative enrichment
of protein and lipid-like compounds in the AOM composition. Polysaccharides, proteins
and lipids, which are the main components of the HWM compounds, are playing a major
role in the fouling of UF ceramic membranes. The fouling potential is linearly correlated
to the HMW concentration of the feed solution.

Algal cells and AOM aggregates larger than 0.7 μm are only slightly impacting the
mechanical properties of the membranes and the fouling remains significant after 0.7 μm
prefiltration. The little improvement in terms of flux decline is however accompanied
with stronger fouling irreversibility. Algal cells and large AOM probably form a cake
layer at the surface of the membrane that prevents the pore blockage.

The stronger fouling potentials were observe for the filtration of polysaccharide-rich
AOM, which suggests the preferential adhesion of polysaccharides in the surface of the
membrane. The AFM study on the adhesion/retraction of the different HMW AOM
toward alumina membrane, confirms the high adhesion of polysaccharide-rich AOM. The
adhesion of AOM with a high abundance of polysaccharides could be even more
important toward titanium membrane than alumina. However, AFM measurements on the
adhesion/retraction of HMW AOM should be performed to confirm this hypothesis. At
the decline phase of the algal bloom, the increase of the fouling potential, for the same
similar initial DOC, is probably also due to the higher relative abundance of more hydrophobic compounds (i.e., proteins and lipids), that are characterized by a strong attraction with the metal oxides (high number of jump-to-contact event during AFM measurement).

3. Coagulation-flocculation prior to UF for algal-rich seawaters

In order to treat algal-rich solution such as seawater during an algal bloom, a coagulation-flocculation prior to UF is necessary. The configuration coagulation-flocculation-flotation using ferric chloride (CFF – Fe) at pH6.5 and at high coagulant dose appeared to be the best treatment to remove HMW compounds and permits a good fouling reduction for either polymeric or ceramic UF. The addition of clay in the coagulation process only slightly impacts the DOC removal of the process, but probably due to the lower HMW fraction removal, is not as efficient as the CFF – Fe. However, for polymeric UF, the addition of BEN increases the reversibility of the fouling. The microflocs of BEN and AOM would remain at the surface, forming a porous layer and protecting the surface from pore blocking, and thus would be more easily backwashed. For ceramic membrane, the adhesion between the metal oxide and the polysaccharide-rich solution is too important and the backwash does not permit a significant flux recovery.
4. Comparison ceramic-polymeric

The ceramic membrane is prone to a stronger AOM fouling than polymeric membrane, due to a stronger affinity between the metal oxides and the AOM. This stronger affinity permits a better removal of the DOC and more specifically HMW removal than polymeric membrane, and thus a better permeate quality. However, for long-term filtration, the ceramic fouling is strongly irreversible and CEB using NaOCl at high dose (2 000 g Cl₂/L) did not permit to recover any flux, whereas CEB using a dose of oxidant three times lower (350 mg Cl₂/L), permitted to recover around 40 % of the initial flux (for the filtration of clarified water using ferric chloride, with and without clay). Ceramic membrane offers a better permeate quality that could be an advantage for downstream RO filtration, but further investigation should be performed on the cleaning of ceramic membranes after fouling by AOM.
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