Forward Osmosis/Low Pressure Reverse Osmosis for Water Reuse: Removal of Organic Micropollutants, Fouling and Cleaning

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ABSTRACT

Forward Osmosis/Low Pressure Reverse Osmosis for Water Reuse: Removal of Organic Micropollutants, Fouling and Cleaning

Rodrigo Valladares Linares

Forward osmosis (FO) is a natural process in which a solution with high concentration of solutes is diluted when being in contact, through a semipermeable membrane, with a low concentration solution. This osmotic process has been demonstrated to be efficient to recover wastewater effluents while diluting a saline draw solution. Nevertheless, the study of the removal of micropollutants by FO is barely described in the literature. This research focuses on the removal of these substances spiked in a secondary wastewater effluent, while diluting water from the Red Sea, generating feed water that can be desalinated with a low pressure reverse osmosis (LPRO) system. Another goal of this work is to characterize the fouling of the FO membrane, and its effect on micropollutants rejection, as well as the membrane cleaning efficiency of different methods. When considering only FO with a clean membrane, the rejection of the hydrophilic neutral compounds was between 48.6% and 84.7%, for the hydrophobic neutrals the rejection ranged from 40.0% to 87.5%, and for the ionic compounds the rejections were between 92.9% and 96.5%. With a fouled membrane, the rejections were between 44.6% to 95.2%, 48.7% to 91.5% and 96.9% to 98.6%, respectively. These results suggest that, except for the hydrophilic neutral compounds, the rejection of the micropollutants is increased by the fouling layer, possibly due to the higher hydrophilicity of the FO fouled

membrane compared to the clean one, the increased adsorption capacity and reduced mass transport capacity, membrane swelling, and the higher negative charge of the surface, related to the foulants. However, when coupled with low pressure reverse osmosis, the rejections for both, the clean and fouled membrane, increased above 98%. The fouling layer, after characterizing the wastewater effluent and the concentrated wastewater after the FO process, proved to be composed of biopolymers, which can be removed with air scouring during short periods of time, reaching a flux recovery of more than 90%, proving that this cleaning method is very effective; chemical cleaning was effective against transparent exopolymer particles (TEP) attached to the support layer of the membrane.

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TABLE OF CONTENTS

LIST OF ABBREVIATIONS

3-D FEEM – 3-dimensional fluorescence excitation emission matrix

AHA – Aldrich humic acid

AL – active layer

ATP – adenosine 5'triphosphate

BOD_5 – biochemical oxygen demand at 5 days

BSA – bovine serum albumin

CDOC – colored dissolved organic carbon

CFW – concentrated feed water

COD – chemical oxygen demand

CP – concentration polarization

CTA – cellulose triacetate

CWWE – concentrated wastewater effluent

DDS – diluted draw solution

DI – deionized

DO – direct osmosis

DOC – dissolved organic carbon

DS – draw solution

ECP – external concentration polarization

EDCs – endocrine disruptive compounds

EWWE – evaporated waste water effluent

FC – flow controller

FO – forward osmosis

FSW – filtered seawater

FW – feed water

GP – gear pump

HB – hydrophobic

HL – hydrophilic

ICP – internal concentration polarization

LC-OCD - liquid chromatography coupled with organic carbon detector

LMW – low molecular weight

LPRO – low pressure reverse osmosis

MBR – membrane biological reactor

MF – microfiltration

MP – micropollutants

MW – molecular weight

MWCO – molecular weight cutoff

NF – nanofiltration

NTU – nephelometric turbidity units

OCD – organic carbon detection

OND – organic nitrogen detection

OsMBR – osmotic membrane biological reactor

PDP – positive displacement pump

PhACs – pharmaceutical active compounds

PMMA – poly (methyl methacrylate)

POC – particulate organic carbon

PRO – pressure retarded osmosis

RLU – relative light units

RO – reverse osmosis

SBR – sequential batch reactor

SDDS – synthetic diluted draw solution

SEC – size exclusion chromatography

SS – synthetic solution

SWWE – secondary wastewater effluent

TC – temperature controller

TDS – total dissolved solids

TEP – transparent exopolymer particles

TN – total nitrogen

TOC – total organic carbon

TSS – total suspended solids

UVD – ultraviolet detection

VSS – volatile suspended solids

LIST OF FIGURES

LIST OF TABLES

I. Introduction

1.1 Background

A constant and reliable source of fresh water is a primary resource for the development of modern economies and settlements around the world. By the year 2025, between 2.4 billion and 3.2 billion people could live under water-scarce or water-stressed conditions, four-folding the number of people that lived in these situations at the beginning of the century. Water shortage is likely to grow especially acute in the Middle East and in much of Africa (Engelman et al. 2000). Besides the amount of water itself, the water quality must comply with the minimum standards set by each country's regulations to be considered as potable; diarrheal disease alone is responsible for the deaths of 1.8 million people every year, and it was estimated that 88% of these cases are attributable to unsafe water supply, sanitation and hygiene (Prüss-Üstün and Corvalá 2004).

Research has identified the potential for hybrid forward osmosis/reverse osmosis (FO/RO) systems for several applications, including seawater desalination (Choi et al. 2009). Recently, studies have shown the potential of these systems to produce high quality water using low pressure desalination, while recovering impaired water from a recycled feed water (Cath et al. 2009). Nevertheless, there are still concerns about the use of FO membranes as a barrier for rejecting organic micropollutants, besides the eventual fouling problems that can occur during the

dilution process, when the membrane is submerged in the recycled feed water, resulting in a poor water flux and an increase in the cost due to membrane cleaning and future replacement.

1.2 Hypothesis

- High rejection of micropollutants (MP) with a forward osmosis (FO) membrane, using a secondary wastewater effluent (SWWE) as feed water and seawater as draw solution (DS).
- Double barrier system for MP removal (>99%) with FO and low pressure reverse osmosis (LPRO) to obtain a clean permeate, involving both wastewater reclamation and low cost desalination.
- High flux recovery in the FO membrane using air scouring to remove fouling.
- Biopolymers are the main constituents in FO membrane fouling.
- Transparent exopolymer particles (TEP) fouling on the draw solution (DS) side of the FO membrane

1.3 Goal and Objectives

The main goal of this research was to analyze the removal of organic micropollutants from a feed solution consisting of either synthetic wastewater or a secondary effluent from a wastewater treatment plant from the city of Jeddah, spiked with selected micropollutants, using a FO membrane, to recover water in a concentrated solution (Red Sea water), for further application of LPRO.

The objectives were the following:

- Analysis of the flux of the FO membrane and fouling in different feed waters: clean deionized (DI) water with the ionic strength of a wastewater and secondary wastewater effluent from a treatment plant.
- Determination of the rejection percentage for each micropollutant, along with the rejection mechanisms, being able to designate a molecular weight cutoff (MWCO) for the membrane.
- Analysis of the fouling of the FO membrane; determination of the effect of fouling on MP rejection.
- Assessment of cleaning techniques for the FO membrane to recover flux
- Identification of the components causing fouling in the feed water and DS side of a FO membrane

II. Literature Review

2.1 Osmotically Driven Membrane Processes

Osmosis is simply defined as the transport of water through a semipermeable membrane caused by a difference in osmotic pressure of the solution on both sides of the membrane. Present-day applications of the osmosis phenomenon extend from water treatment and food processing to power generation and novel methods for controlled drug release (Cath et al. 2006). The osmotic pressure of a solution depends on the concentration of dissolved ions in solution and the temperature of solution (Cath et al. 2009).

The osmotic pressure can be calculated using the van't Hoff equation (Hoff 1887):

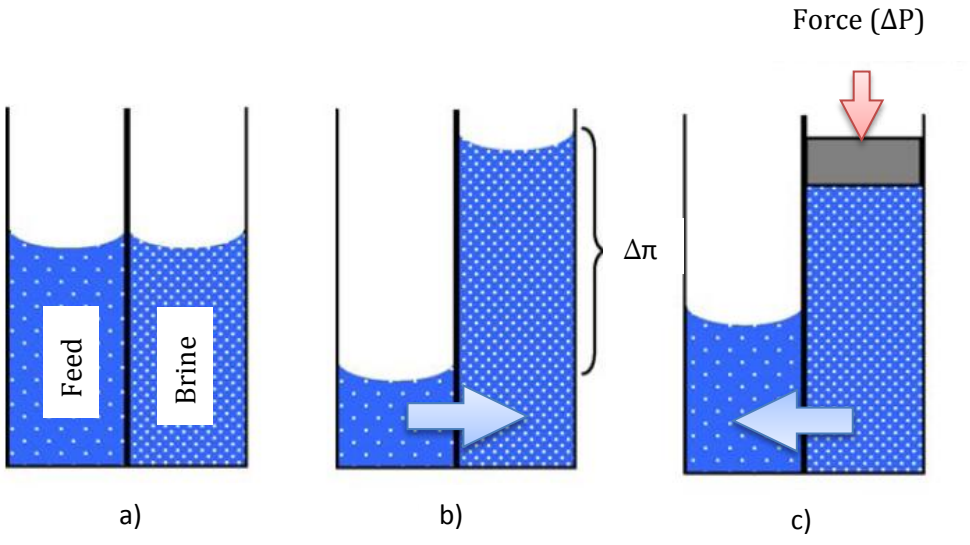
$$\pi = RT\sum iM \qquad (2\text{-}1)$$

where i is the dimensionless van't Hoff factor for the specific ion, M is the molarity of the specific ion, R is the gas constant (0.08206 $L{\cdot}atm{\cdot}mol^{-1}{\cdot}K^{-1}$), and T is the temperature in Kelvin.

The most common states of osmotically driven membrane processes are forward osmosis (FO), also known as osmosis or direct osmosis (DO), and reverse osmosis (RO), described in Fig. 2.1. The former processes occurs when one of the two

solutions separated by the semipermeable membrane has a high osmotic pressure and the other one has a low osmotic pressure; the water will start flowing from the diluted solution to the concentrated brine until equilibrium. The latter occurs when the osmotic pressure difference between the two solutions is overcome by a hydrostatic pressure applied to the brine, reversing the osmosis process, and thus, the definition of the process itself.

Fig. 2.1 – Osmotically driven processes. a) The low osmotic pressure solution is the feed, and the brine is the high osmotic pressure fluid. b) For the forward osmosis process, the flow through the membrane will go from the low feed to the brine. c) On the other hand, the natural osmotic flow will be reversed during reverse osmosis, due to the pressure applied to the brine (ΔP).



Source: Adapted from (Cath et al. 2006)

According to Lee et al. (1981), the general equation describing water transport through the membrane in RO is:

$$J_w = A(\sigma \Delta\pi - \Delta P) \qquad (2\text{-}2)$$

where J_w is the water flux, A the water permeation constant of the membrane, $\sigma\Delta\pi$ the effective osmotic pressure difference in reverse osmosis, σ being the reflection coefficient, and ΔP the applied pressure (Lee et al. 1981); for FO, ΔP=0; for RO, $\Delta P > \Delta\pi$ (Cath et al. 2006). This equation is not suitable for FO processes because the parameter A and the reflection coefficient are calculated considering that pressure is being applied to the brine; besides, the driving force considered is the difference between osmotic pressure and the force ΔP.

For FO, it is necessary to refer to the Lee's equation for low concentration solutions in the porous substructure side of the membrane (Lee et al. 1981):

$$\frac{J_1}{A\pi_{Hi}} = \frac{1-(\frac{C_{Low}}{C_{Hi}})\exp(J_1 K)}{1+\frac{B}{J_1}(\exp(J_1 K)-1)} \qquad (2\text{-}3)$$

where A is the water permeation constant for RO and B is the solute permeation constant for the RO, J_1 is the flux measured during the experiment, C the

concentration of the solutions, π_{Hi} the osmotic pressure of the high concentration solution, and K is the solute resistivity of the membrane.

Instead, Loeb et al. derived a formula (Eq. 2-4) from Lee's equation (Eq. 2-3) that can be applied to a case in which two different solutions, one with higher osmotic pressure, are kept in contact through a semipermeable membrane, making several important considerations for FO. The π_{Low} is always appreciably higher than zero; with this, A π_{Low} and, therefore, A π_{Hi} are much higher than B or J; the difference between the conductivity can be proportional to the relation between osmotic pressures ($(\gamma_{Hi} - \gamma_{Low})\alpha = (\pi_{Hi}/\pi_{Low})$) when restricting the condition of appreciable osmotic pressure on both sides of the membrane.

$$K = \frac{1}{J}\ln\left(\frac{\pi_{Hi}}{\pi_{Low}}\right) \qquad (2\text{-}4)$$

where K is the solute resistivity of the membrane, π_{Hi}/π_{Low} the ratio between the osmotic pressure of the high concentration solution and the low concentration solution, and J the flux. It is worth noting that the driving force in the case of FO keeps a logarithm ratio between the osmotic pressures, unlike the RO, where the driving force is only the difference between the osmotic pressures and the pressure generated by the applied force (Loeb et al. 1997).

2.1.1 Forward Osmosis

Forward osmosis (FO), or simply osmosis, uses a concentrated draw solution to generate high osmotic pressure, which pulls water across a semi-permeable membrane from the feed solution (Mi and Elimelech 2008). Typically, the FO process results in concentration of the feed stream due to water withdrawal, and the dilution of the draw solution (DS). As the salt concentration of feed water increases, the permeate flux decreases even at high draw solution concentrations (Choi et al. 2009).

The main advantage of using FO is the low energy required to extract the water from a wastewater or recycled feed, being only the energy used to recirculate the draw solution on the other side of the membrane (Adham et al. 2007). A major limiting factor of FO systems performance is an eventual flux decline due to concentration polarization (McCutcheon et al. 2005).

There are many applications that have been studied for FO membranes, including desalination (Low 2009), concentration of dilute industrial wastewater, concentration of landfill leachate, direct potable reuse for advanced life support systems, food processing, pharmaceutical industry processes (Cath et al. 2006), concentration of digested sludge liquids (Holloway et al. 2007), among others.

2.1.2 Reverse osmosis

Reverse osmosis (RO) is an osmotically driven membrane process in which water is recovered from saline water (brine) through a semipermeable membrane, by pressurizing the concentrated solution to a level above its osmotic pressure. In this way, the membrane rejects the salt ions, preventing them from permeating, getting as a result a highly concentrated solution, and a pure water feed on the other side (Miller and Evans 2006). The high pressure needed for overcoming the osmotic pressure of the brine solutions is the reason why this process (RO) requires such a high energy demand (Cath et al. 2009).

Since the minimum pressure required to achieve the separation is directly related to the dissolved salt concentration (dependent on the osmotic pressure), RO can be economically feasible and less energy intensive if it is applied to a low salinity water (brackish water), where pressures from 15 to 25 bar are enough to obtain a good flux through the membrane. This is the reason why the hybrid FO/RO systems have been investigated recently as a way to get a low cost dilution process of saline waters, using a low concentration water source, followed by LPRO to get pure water (Choi et al. 2009).

2.2 Organic Micropollutants

Organic micropollutants (MP), or emerging organic contaminants, are substances that include, but are not limited to, pharmaceutically active compounds (PhACs), endocrine disrupting compounds (EDCs), disinfection by-products and pesticides,

that are present in the environment and, due to the increasing concentration detected in recent studies, are an arising concern among researchers and regulatory agencies, because most of them are not yet regulated and their impacts on human life are not quite known.

There is an urgent need to understand their partitioning, accumulation and removal from water, soil, air and biota; unfortunately, there is not a clear idea of the exact risks of chronic exposure to a mixture of organic micropollutants, including quantities ingested through drinking water, leaving a big question yet to be answered (Yangali-Quintanilla et al. 2010b). There are current technologies that can remove these organic micropollutants from wastewaters, but generally they are energy intensive processes, such as nanofiltration (NF) and RO (Kimura et al. 2003, Bellona et al. 2004). Conventional wastewater treatment plants will not completely remove these chemicals, which will partition mainly into the sludge produced and the water effluent, generating a threat for the discharge site and the downstream areas.

Table 2.1 lists several different micropollutants with its properties, providing a classification based on hydrophobicity and their charge, two characteristics that are fundamental to determine the rejection of these compounds by membranes, along with the size of the molecule itself (associated but not always consistent with the molecular weight).

Table 2.1 – Classification and properties of selected organic micropollutants

Name	Molecular weight (g/mol)	Acid pK_a 20 °C[a]	Log K_{ow}[b]	Log D[a] (pH 7)	Dipole moment (debye)[c]	Molar volume[d] (cm^3/mol)	Molec. length (nm)[e]	Molec. width (nm)[e]	Molec. depth (nm)[e]	Equiv. width (nm)[e]	Classification[f]
Acetaminophen	151	10.2	0.46	0.23	4.55	120.90	1.14	0.68	0.42	0.53	HL-neutral
Phenacetine	179	N/A	1.58	1.68	4.05	163.00	1.35	0.69	0.42	0.54	HL-neutral
Caffeine	194	N/A	−0.07	−0.45	3.71	133.30	0.98	0.87	0.56	0.70	HL-neutral
Metronidazole	171	N/A	−0.02	−0.27	6.30	117.80	0.93	0.90	0.48	0.66	HL-neutral
Phenazone	188	N/A	0.38	0.54	4.44	162.70	1.17	0.78	0.56	0.66	HL-neutral
Sulfamethoxazole	253	5.7	0.89	−0.45	7.34	173.10	1.33	0.71	0.58	0.64	HL-ionic
Naproxen	230	4.3	3.18	0.34	2.55	192.20	1.37	0.78	0.75	0.76	HB-ionic
Ibuprofen	206	4.3	3.97	0.77	4.95	200.30	1.39	0.73	0.55	0.64	HB-ionic
Carbamazepine	236	N/A	2.45	2.58	3.66	186.50	1.20	0.92	0.58	0.73	HB-neutral
Atrazine	216	N/A	2.61	2.52	3.43	169.80	1.26	1.00	0.55	0.74	HB-neutral
17β-estradiol	272	10.3	4.01	3.94	1.56	232.60	1.39	0.85	0.65	0.74	HB-neutral
Estrone	270	10.3	3.13	3.46	3.45	232.10	1.39	0.85	0.67	0.76	HB-neutral
Nonylphenol	220	10.3	5.71	5.88	1.02	236.20	1.79	0.75	0.59	0.66	HB-neutral
Bisphenol A	228	10.3	3.32	3.86	2.13	199.50	1.25	0.83	0.75	0.79	HB-neutral

a ADME/Tox Web Software.
b Experimental database: SRC PhysProp Database.
c Chem3D Ultra 7.0.
d ACD/ChemSketch Properties Batch.
e Molecular Modeling Pro.
f HL = hydrophilic, HB = hydrophobic.

Source: Adapted from (Yangali-Quintanilla et al. 2010b)

2.2.1 Pharmaceutical Active Compounds

Pharmaceutically active compounds (PhACs) include complex pharmaceutical substances that form part of the active ingredients of personal care products, that are usually excreted and discharged to the wastewater by humans and animals, either unused as residuals or metabolized. The most common PhACs are active substances of over-the-counter medicines such as ibuprofen or acetaminophen, which are commonly and widely used throughout the world; nevertheless, there are other types of drugs that contain active substances that have toxic effects (analgesics and anti-inflammatory drugs, bacteriostatics, antiepileptic drugs, beta-blockers, blood lipid regulators, cytostatic drugs, oral contraceptives, etc.) (Heberer 2002). Other types of PhACs include antiseptics, sunscreens, antibiotics, fragrances,

among others (Sawyer et al. 2003). Studies in several countries around the world have revealed the presence of more than 80 varieties of PhACs in sewage, surface water, and ground water with μg/L levels (Heberer 2002).

PhACs activity as active compounds may last for an extended period of time, as they are intended to be absorbed by the body during medical treatments, which may lead to a high bioconcentration factor, turning the quantity of the compound less important than its presence itself, which would make even low amounts in the range of ng/l of concern.

Diverse effects have been studied that relate to the presence of PhACs in water. Strains of pathogenic bacteria can develop resistance to certain antibiotics due to the high amount of certain PhACs in the water analyzed, making it a public health concern as new drugs must be developed in order to treat patients affected by these new strains (Hirsch *et al.*, 1999). Studies in wastewater treatment plants with biological processes have shown that certain pharmaceuticals (diclofenac sodium, carbamazepine, etc.) can prevent the biodegradation process that occurs during the anaerobic digestion stage (Fountoulakis *et al.*, 2004). Based on the same study, it can be stated that the potential for the inhibition mechanism is directly correlated with the tendency of the compounds to adsorb on bacterial cells, which also highlights the tendency for bioaccumulation of PhACs.

2.2.2 Endocrine Disruptive Compounds

Endocrine disruptive compounds (EDCs) raise an important concern because they imitate, block or alter the functions of hormones, affecting the normal activities of the endocrine human system. Therefore, EDCs represent a human and wildlife threat (Bonefeld-Jørgensen et al. 2001).

In the last two decades researchers have found adverse consequences of EDCs that are currently in the environment in different concentrations varying from site to site. In humans, disruption of the thyroid function has been reported, affecting the development stage of young persons (Zoeller 2005). In recent years, EDCs have been found in sediments, marine mammals, fish, and bird eggs. Moreover, some of them (BPA, PCBs, PBDEs and other organobrominated compounds) have also been identified in human blood, adipose tissue, and breast milk (Lindström et al. 1999, Meneses et al. 1999, Covaci et al. 2002). For human milk, there are studies that reveal concentrations in breast milk for Swedish mothers that exponentially increased from 1972 to 1997 (Meironyte et al. 1999). Effects related to endocrine disruption have been reported in molluscs, crustacea, fish, reptiles, birds and mammals in various parts of the world (Sumpter and Jobling 1995).

Besides the effects in development due to the endocrine disruption, there is some evidence that these compounds may affect the immune system and can also function as neurotoxins; nevertheless, these effects´ mechanisms are yet to be discovered (Sumpter and Jobling 1995).

As the EDCs come from a wide variety of chemical compounds, ranging from highly hydrophobic to very soluble in water, it is really difficult to determine their concentrations and real effects on the biota. Current trends and future perspectives in chemical analysis are expected to serve in the assessment of several groups of EDCs that are of priority within European Union and US, such as alkylphenols, polybrominated diphenyl ethers, and phthalates (Petrovic et al. 2004).

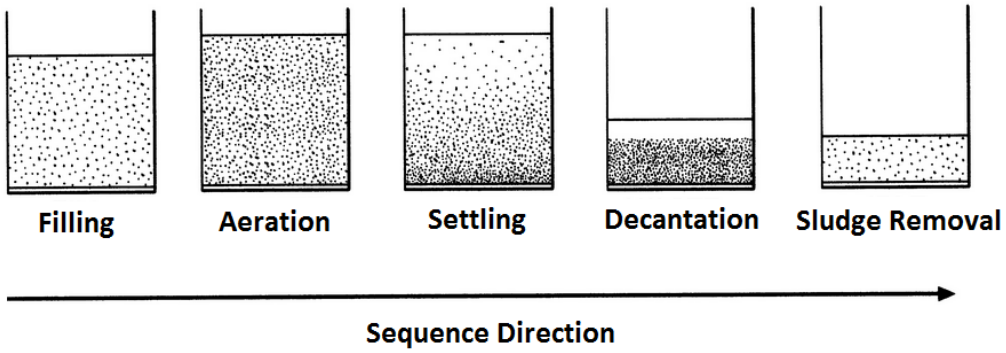
2.3 Complete-Mix Activated-Sludge Processes

2.3.1 Sequencing Batch Reactor

The sequencing batch reactor (SBR) is a biological nutrient removal and water treatment process based on a fill-and-draw activated sludge reactor with complete mixing, after which sedimentation takes place (in the same tank) and the effluent is removed, closing the loop filling the tank again with untreated influent. The SBRs consist of usually 5 steps: filling, aeration (mix), settling or clarification, decantation and removal of sludge (not performed in every cycle necessarily) (Metcalf and Eddy 2003). Fig. 2.2 shows the schematic diagram of a conventional SBR.

SBRs have been used as a technology to remove nitrate and phosphorous in one single process because of their flexibility. Both, nitrate and phosphorous are removed during the anaerobic reaction periods; nitrate is usually removed in an anoxic stage following the complete mix and before the settling, and phosphate-accumulating bacteria are free of competitors for the chemical oxygen demand (COD) during the filling and initial reaction period (Metcalf and Eddy 2003).

Fig. 2.2 – Sequencing batch reactor process



Source: Adapted from (Smith 2004)

The SBR cycle can be modified at any time relatively easily and fast according to the influent characteristics or effluent objectives that each cycle requires or due to a sudden change in wastewater composition (Pochana and Keller 1999).

2.3.2 Membrane Biological Reactor

In a membrane biological reactor (MBR), microfiltration (MF) membranes with nominal pore sizes in the range of 0.1 to 0.4 μm are used coupled with a bioreactor unit (activated sludge), extracting water through the membranes using negative pressure; suspended solids are retained in the system, leading to high levels of organic nutrients removal and low levels of turbidity (Judd 2010). Thereby, the clarification and effluent filtration processes are replaced, reducing the space needed to less than half for a conventional activated sludge wastewater treatment plant (Daigger 2005). There are two possible configurations: one that immerses the membrane in the bioreactor, and the other where the membrane is outside,

connected through a recirculation system that pumps liquor from the reactor to the MF system (Metcalf and Eddy 2003).

The effluent from an MBR process may be used for irrigation, aquifer recharge, and as an indirect source for potable water. There are several aspects that make the MBRs a more suitable option for wastewater treatment: reduction in the plant configuration footprint, effluent quality and consistency, very high removal of suspended solids, low sludge production; when aerobic and anaerobic cycles are alternated simultaneous removal of carbon and nitrogen can be achieved (Zhang et al. 2006). On the other hand, the main problem related with this process is the fouling of the membranes (Achilli et al. 2009).

Achilli et al. have studied a new alternative to MBRs, using an FO membrane inside the bioreactor to extract water with a high concentration DS, as a direct source of high quality water for a downstream RO process, called osmotic membrane bioreactor (OsMBR). Compared with MBR, this system requires substantially less backwashing, because the membrane is not operated under negative pressure, thus the suspended solids and organic matter will not be sucked towards the membrane surface. The OsMBR can achieve removals higher than 98% for both total organic carbon (TOC) and total nitrogen (TN) (Achilli et al. 2009).

2.4 Energy Demand in Desalination and Water Treatment Processes

High energy demand for current desalination technologies has limited their use in several regions, representing in more than 70% of the operating costs of the plant and up to 50% of the cost of the final product (potable water). Thus, one of the main goals of researchers is to reutilize the energy in high-pressure brine (Farooque et al. 2008). Another way to reduce energy demand is by diluting the feed water and reducing its concentration, using a FO membrane, and extracting water from an impaired source, which usually contains a low total dissolved solids (TDS).

One of the main advantages of FO is that it requires a limited amount of external energy to extract water from the feed, because it only needs a very low hydraulic pressure to recirculate the DS on one side of the membrane, while the feed is passively in contact with the other side (Cath et al. 2006). However, it should be noted that special attention must be taken into the water quality, because the dilution might contaminate the water and affect the downstream RO process (Shannon et al. 2008). This might turn into an energy intensive solution, having to add an advanced pretreatment process, which makes the research on contaminant removal with FO membranes critical.

For water treatment processes, more than 50% of the energy required is used for the activated sludge aeration; another significant fraction of the energy is used for

the pumping system in all the stages (Metcalf and Eddy 2003). There are several recommendations that require implementing operational changes and retrofitting equipment to reduce the energy consumption in wastewater treatment plants; however, all these measures represent a significant expenditure and cannot be applied in many cases.

The SBR configuration is in a general context simple and can assure the operator a direct hydrodynamic control of fouling, but there is a high energy demand due to the recirculation system of the effluent. When an MBR is used, recirculation is taking place in the same tank (bioreactor), using the same aeration energy to recirculate and prevent fouling; consequently, the energy demand for the immersed membrane system can be two orders of magnitude lower than for external membrane system (van Dijk and Roncken 1997). Unfortunately, submerged systems operate at a lower flux and thus, demand more membrane area which will increase the capital cost of the system (Chang et al. 2002).

2.5 Concentration Polarization in FO Membranes

Concentration polarization (CP) occurs when the difference in concentration across the active later is different than the difference in concentration in the bulk solutions (McCutcheon and Elimelech 2006). CP can refer to the formation of a concentration layer at the membrane surface, or in the porous structure of asymmetric membranes, that reduces the driving force (osmotic pressure), and thus, the flux. The former one is called external concentration polarization (ECP), and it is not only

a problem with FO, but with all types of membranes, including RO; there are several hydrodynamic techniques in which it can be controlled (i.e. crossflow velocity increased) (Sablani et al. 2001). The latter, which is present only in FO, is referred to as internal concentration polarization (ICP); it occurs within the support layer of the membrane, and is characterized by differing solute concentrations at the transverse boundaries of the porous layer (Gray et al. 2006).

Ng and Cath studied, in different experiments, the effects of ICP for a commercial FO membrane, tested with two different orientations, one in which the active layer is facing the draw solution (referred to as the normal configuration), and the other one where the active layer is in contact with the feed (reverse configuration). After several tests, they concluded that the flux decline can be up to 15% lower for the reverse configuration in comparison with the normal orientation (Ng et al. 2006) (Cath et al. 2006). ICP is very minimally affected by changing the hydraulic conditions in the membrane cell, but it is affected by the orientation of the dense layer of the membrane (McCutcheon and Elimelech 2006). Nevertheless, other studies conducted by Cornelissen et al. refer to the overall performance of the membranes and concludes that the best configuration to prevent membrane damage is the one in which the active layer is facing the feed solution, reducing the ICP in the support layer, because the direction of the water flow is opposite to the concentration of the bulk DS solution into this layer; this configuration is also effective against membrane fouling (Cornelissen et al. 2008).

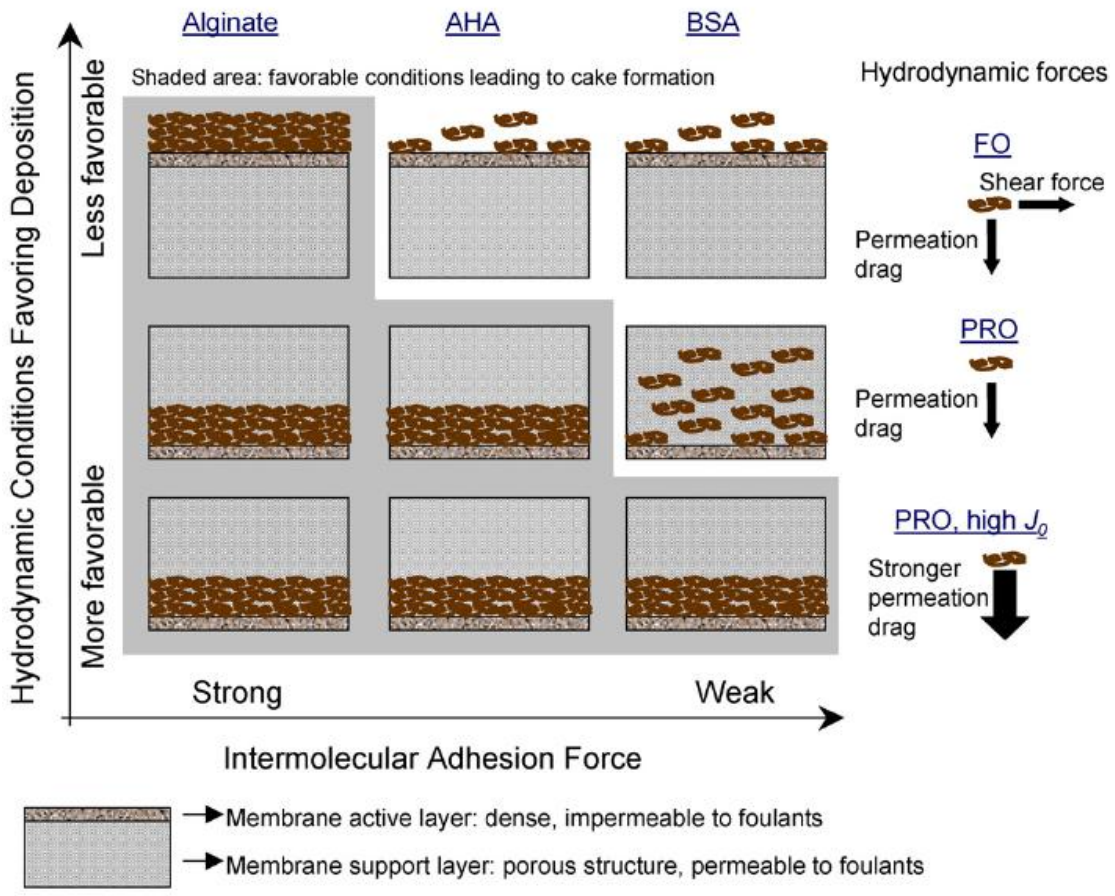
2.6 FO Membrane Fouling

Fouling is a severe problem in membranes, reducing the flux considerably; when wastewater is being treated, many organic contaminants commonly present can be potentially serious fouling agents. However, these problems are linked to the use of osmotic pressure processes, such as NF or RO, where the pressure applied against the membrane facilitates the fouling phenomena. Nevertheless, for FO membranes, water flux decline due to fouling is minimal, even with wastewater with high fouling propensity, because the process itself does not induce suspended solids and other organic contaminants into the membrane (Holloway et al. 2007). Because of this, FO processes require less frequent backwash, if even recommended.

During an 8h experiment realized by Cornelissen et al., both reversible and irreversible membrane fouling due to activated sludge was found to be negligible, suggesting that the operating conditions might be lower than the critical flux for fouling; however, it has been seen that when the active layer faces the feed solution, fouling is prevented (Cornelissen et al. 2008).

Fouling can change the surface characteristics of the membrane, either to improve or diminish the rejection capability and flux. There are studies that can prove both situations (Bellona et al. 2004, Xu et al. 2006) for NF and RO membranes, but there is no literature on the precise effects of organic contaminants and their rejection by FO membranes.

Fig. 2.3 – Coupled influence of intermolecular adhesion and hydrodynamic forces on membrane fouling by alginate, AHA, and BSA



Source: (Mi, B. 2008)

Cath et al. realized benchscale experiments for 14 days with an FO/RO hybrid system, using impaired water and DI water as feed for the FO process and salt concentrated solutions simulating sea water as DS. The results show the extremely low fouling propensity of the FO process, and the ability to treat large volumes of water with almost no need for a measure to recover flux (Cath et al. 2009).

Mi and Elimelech analyzed the fouling process of FO membranes with bovine serum albumin (BSA), Aldrich humic acid (AHA) and alginate. They related the influence of intermolecular adhesion and hydrodynamic forces on the two different orientations for the process. In this case, the FO mode is the one in which the top active layer is facing the feed, and the support is on the draw solution side. Pressure retarded osmosis (PRO) mode is the reverse configuration, with the support mesh facing the feed (Mi and Elimelech 2008). Fig. 2.3 shows a schematic relating the effects that are directly related with the fouling on the membrane for both configurations and the 3 compounds. The results confirm that the best mode to use the membrane and prevent fouling is the FO mode, independently from the compounds that may be causing the formation of the cake layer, because the active layer is impermeable to these foulants.

III. Materials and Methods

3.1 Materials

3.1.1 Membranes

The FO membranes used for this research were provided by Hydration Technology Innovations (HTI, Albany, OR, USA). The HTI membrane was originally received as flat sheet coupons, each one measuring 4" × 6", and then cut into the proper size for the membrane cell (see Section 3.1.5). It is a cellulose triacetate (CTA) membrane with a mesh support, in which the active layer is embedded, making it thinner than a porous support layer membrane with the active layer in the top, which gives the membrane a higher flux.

The RO membrane used is an aromatic polyamide membrane produced for desalination of brackish water by Dow-Filmtec (Midland, MI, USA) under the name BW30. The molecular weight cutoff (MWCO) of the membrane was reported as 98Da, with a sodium chloride rejection of 99.5%, a contact angle of 48° for the virgin membrane, and a zeta potential of -6.1mV at pH 8 (Nghiem and Coleman 2008).

3.1.2 Sample Water

Deionized (DI) water (Milli-Q water) was used for the preparation of every solution required, besides its use as diluting agent for stock solutions of micropollutants and synthetic solutions.

Secondary wastewater effluent was collected from the Al-Ruwais Wastewater Treatment Plant in the city of Jeddah (SWWE). In this facility, the wastewater (after primary treatment) is treated in activated sludge aeration tanks. The biochemical oxygen demand at 5 days (BOD_5) of the wastewater effluent was 20mg/L, the TOC was 4.60mg/L, the pH of 7.3, and the conductivity was 2850μS/cm and the turbidity was 0.387 NTU. The total suspended solids (TSS) and volatile suspended solids (VSS) of the water was 2.4 and 2.1 mg/L respectively. Calcium ions (Ca^{2+}) were found in a concentration of 108 mg/L. The specific ultraviolet absorbance (SUVA) was 2.45 L/mg m. The effluent sample was taken on March 2011.

The seawater used as a draw solution for the FO experiments was Red Sea water taken from the same pipe that feeds the desalination plant in KAUST, located in Thuwal, a town by the Red Sea coast. This water was pre-filtered with a 0.45μm pore size filter (see Section 3.1.4). The TDS were 40.5g/L and the conductivity of 57500μS/cm. pH of the water was 7.8. The TOC was 1.12mg/L. The TSS and VSS of the seawater were 10.3 and 7.1 mg/L respectively. The concentration of calcium ions was 571 mg/L. The SUVA was 1.07 L/mg m. These characteristics correspond to the sample taken on March 2011.

Table 3.1 shows the list of chemicals and the precise concentration to create an inorganic synthetic solution (SS) to simulate the ionic-strength of a wastewater effluent, avoiding the presence of suspended solids and fouling agents. It was calculated based on the results of the analysis done to the wastewater effluent from

Jeddah following the Standard Methods for the Examination of Water and Wastewater (Eaton et al. 2005), for ammonium, nitrate, nitrite, total nitrogen and phosphate. The results for this test can be found in Table 7.1 of the Appendix. The final balance of the total anions and cations was obtained using the Dow-Filmtec software ROSA.

Table 3.1 – Recipe for inorganic synthetic solution

Chemical	Purity (%)	Concentration (mg/L)
KCl	0.995	56.42
NH_4Cl	0.995	0.30
NaCl	0.995	2186.23
$MgCl_2.6H_2O$	0.995	547.19
$CaCl_2.6H_2O$	0.99	608.03
$Na_2CO_3.H_2O$	0.995	0.55
$NaHCO_3$	0.995	64.62
$NaNO_3$	0.99	3.58
Na_2SO_4	0.99	6.18

3.1.3 Chemicals

All the chemicals (inorganic and organic compounds) were purchased from Sigma Aldrich (Munich, Germany), including those listed in Table 3.1 for the preparation of the synthetic solution. The list of micropollutants used to prepare the stock solutions is presented in Table 3.2. Compounds were classified according to their speciation in water as hydrophobic when the logarithm of the octanol/water

distribution coefficient (log D) is higher than 2.6, and hydrophilic when log D ≤ 2.6. Ionic compounds shown in the table are negatively charged at pH 7, which was determined by using ADME/Tox Web Software. Physicochemical properties were calculated using Molecular Modeling Pro. All of the compounds, except for EE2, were prepared in a stock solution of 10mg/L with Milli-Q water; EE2 was diluted in 1% wt. ethanol solution, and then diluted to a concentration of 10mg/L with Milli-Q water.

Table 3.2 – List of micropollutants spiked to the FO feed water

Name	**Name ID**	**MW (g/mol)**	**log D [a] (pH 7)**	**Molec. length (nm)[b]**	**Width (nm)[b,c]**	**Depth (nm)[b]**	**Equiv. width (nm)[b]**
1,4-dioxane	DIX	88	-0.17	0.71	0.66	0.52	0.59
Acetaminophen	ACT	151	0.23	1.14	0.68	0.41	0.53
Metronidazole	MTR	171	-0.27	0.93	0.9	0.48	0.66
Phenazone	PHZ	188	0.54	1.17	0.78	0.56	0.66
Caffeine	CFN	194	-0.45	0.98	0.87	0.56	0.70
Bisphenol A	BPA	228	3.86	1.25	0.83	0.75	0.79
Carbamazepine	CBM	236	2.58	1.20	0.92	0.58	0.73
17α-ethynilestradiol	EE2	296	3.98	1.48	0.87	0.84	0.85
Ibuprofen	IBF	206	3.97	1.39	0.73	0.55	0.64
Naproxen	NPX	230	0.34	1.37	0.78	0.75	0.76
Fenoprofen	FNP	242	0.38	1.16	0.93	0.74	0.83
Gemfibrozil	GFB	250	2.3	1.58	0.94	0.65	0.78
Ketoprofen	KTP	254	-0.13	1.16	0.92	0.74	0.83

a. ADME/Tox Web Software; b. Molecular Modeling Pro; c. equivalent width = $(\text{width} \times \text{depth})^{0.5}$

3.1.4 Pre-filtration System

Seawater was pre-filtered using a microfilter with a pore size of 0.45mm composed-by a glass microfiber pre-filter and a nylon membrane (Whatman, USA). This was achieved by connecting the filter with stainless steel tubing (Swagelok BV, Netherlands) to a positive displacement pump (Hydra-Cell, MN, USA), working at a frequency of 17.9 Hz. The batch of filtered seawater was then stored in a cold room at 4°C to prevent bacterial growth.

3.1.5 FO Membrane Cell

The membrane cell was a custom-made plate and frame assembly made of poly (methyl methacrylate) (PMMA). The cell can hold two flat-sheet membranes each one with an area of 202 cm^2 in a plate-and-frame configuration, leaving a channel between them, where the draw solution will recirculate. A picture of the FO membrane cell used can be seen in Fig. 3.1.

This FO membrane cell offers a new configuration different from the FO membrane contactors described in previous publications for similar applications (Cath et al. 2005a, Cath et al. 2005b, Cath et al. 2010).

Fig. 3.1 – FO Membrane Cell

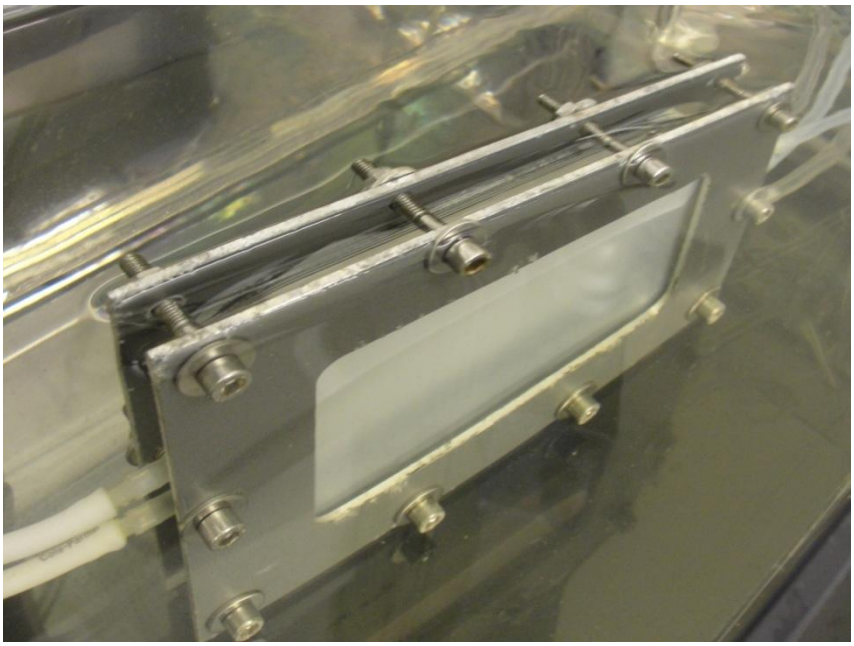
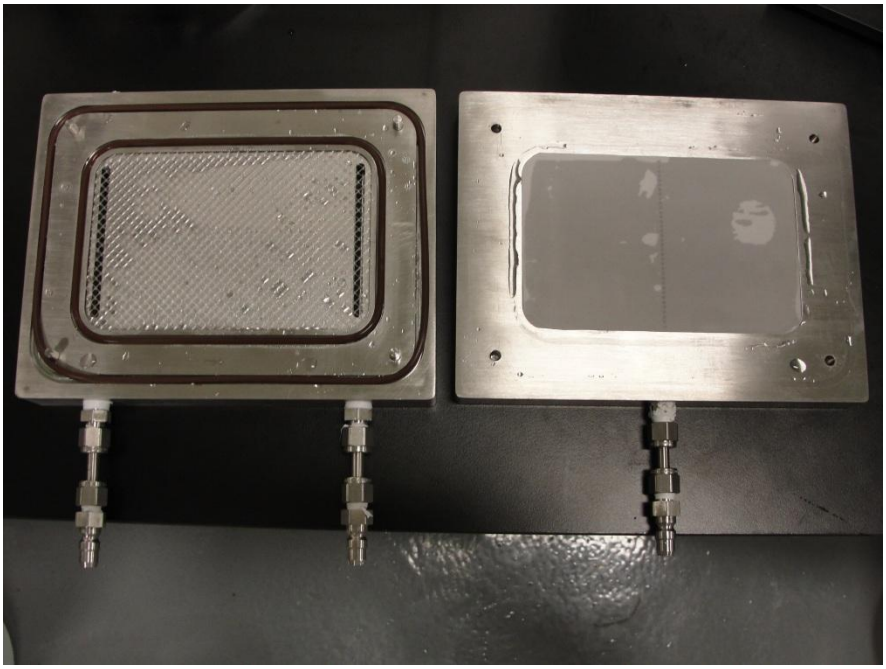


Fig. 3.2 – LPRO Membrane Cell



3.1.6 Low Pressure Reverse Osmosis System

The LPRO system consists of a positive displacement pump (PDP) (Hydra-Cell, MN, USA) working at 14.7 Hz, a crossflow filtration cell accommodating a 139cm^2 membrane (SEPA CF II, Sterlitech, Kent, WA, USA), needle valves, pressure gauges, a proportional pressure relief valve and stainless steel tubing (Swagelok BV, Netherlands). Fig. 3.2 shows a picture of the membrane cell for LPRO.

3.1.7 Water Analysis Kits

Hach Kits were used to analyze the amount of ammonium (LCK 302 and HACH 69 HR Ammonium), nitrate (LCK 340 and TNT 835), nitrite (LCK 342 and TNT 835), total nitrogen (LCK 238) and phosphate (LCK 350 and TNT 843) in water samples.

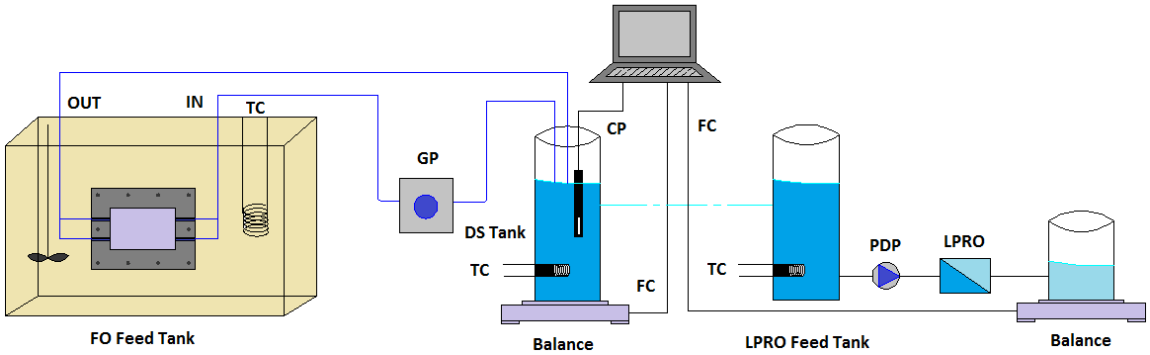
3.2 Experimental Methods

3.2.1 Hybrid FO/LPRO System Set-up

Fig. 3.3 describes the hybrid system and its configuration. The FO membrane cell is immersed in the feed tank, connected with tubing to the DS container; this DS is being recirculated by a gear pump (GP) (Coleparmer) inside the cell formed by the membranes and frame. The diluted DS is then transferred to the LPRO feed tank, conducted then through the crossflow filtration cell, where desalination takes place and the permeate is recovered at the end. A balance (TE6101, Sartorius AG, Göttingen, Germany) was used as flow controller (FC) when connected to a computer, for the DS tank (FO flux) and for the permeate tank (LPRO flux). The conductivity of the DS and the RO permeate were recorded with a conductivity

meter (conductivity probe - CP) (WTW, Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, Germany) connected to a computer. The temperature of the water solutions was kept constant 20±0.5 C° by using chiller/heater devices (temperature controller - TC) for the feed tanks, FO feed and LPRO feed, as well as for the DS tank.

Fig. 3.3 – Hybrid FO/LPRO System Layout



3.2.2 Hybrid FO/LPRO System Procedure

The seawater is filtered (see Section 3.1.4) and used as draw solution for all of the experiments. The feed water for the FO tank was changed accordingly so the comparison between an inorganic synthetic solution (SS) and a real secondary wastewater effluent (SWWE) could be made. No pretreatment was performed for the SWWE. A stirrer was set at a gradient velocity of $50s^{-1}$ to provide movement in the FO feed tank.

At the beginning, 500ml of seawater were poured in the DS tank; at the same time, the FO feed tank was being filled with 21L of inorganic synthetic solution with a conductivity of 5,000µS/cm. The two flat sheet FO membranes were set in the

membrane cell, which was then immersed in the FO tank. The recirculation pump was started at a flow rate of 50mL/min, along with the recording devices for flow (scale) and conductivity. This transversal flow through the inside of the membranes (channel) allowed the DS water to extract water from the synthetic solution with a lower concentration, the process only driven by osmotic difference, no negative pressure inside the cells was observed along the time of recirculation of draw solution. The dilution process takes 24 hours, increasing the level in the DS tank, while the synthetic solution concentrates (volume decreases). After this, the DS is transferred to the LPRO feed tank, where it is desalinated and the permeate is recovered. The parameters under which the LPRO system was operated are summarized in Table 3.3. The experiment is repeated filling the DS tank with fresh pre-filtered seawater, and replenishing the water extracted from the FO tank. The same exact procedure was followed with the SWWE collected in Jeddah.

Table 3.3 – LPRO operating parameters

Parameter	**Value**
Feed Pressure	15 bar
Permeate Flow	1.6 mL/min
Concentrate Flow	80 mL/min
LPRO Flux	7 L/m^2-h
Recovery	2%
Salt rejection	95%

3.2.3 Micropollutants Analysis

The organic micropollutants were spiked into the synthetic solution and the SWWE from the stock solution prepared with a concentration of 10mg/L. The target concentration in the FO feed of each micropollutant independently was 10µg/L. Samples of the FO feed water were taken before the experiment started, and control samples were taken before addition of the micropollutants.

For the diluted draw solution, a composite sample of the 2nd and 3rd day and 4th and 5th day of a continuous experiment were collected, allowing the steady-state saturation of the membrane during 3 days, estimating the adequate rejection and avoiding overestimation. The same procedure applies for the collection of samples from the LPRO permeate.

Table 3.4 shows the description of each sample taken for every experiment. A sample of blank DI water was taken as control.

The micropollutants in water samples were analysed by Technologiezentrum Wasser, (TZW, Karlsruhe, Germany). The information about the procedures for analyses of micropollutants in water samples are referenced in previous studies (Yangali-Quintanilla et al. 2010a). The uncertainty of measurement was ±20%, not determined for each compound individually sampled, but determined during method validation, for all of the compounds listed Table 3.2.

Limits of quantification and limits of detection for each compound can be found in the Table 7.2 on the Appendix.

Table 3.4 – List of the range of concentration, description and volume of samples for MP analysis

Spl. #	ID	Description	Volume (L)	Conc. (µg/L)
1	DS1-2	Diluted seawater synthetic solution (2st and 3rd day composite)	4	0 – 5
2	DS3-4	Diluted seawater synthetic solution (4rd and 5th day composite)	4	0 – 5
3	ROF	Reverse osmosis feed (diluted seawater with MP)	2	5 – 15
4	PE1-2	Permeate water of RO	4	0 – 1
5	SS1	Synthetic solution with MP (original concentration)	2	5 – 15
6	SS2	Synthetic solution with MP (concentrated after 5 days)	2	5 – 15
7	DS5-6	Diluted seawater wastewater effluent Jeddah with MP (2st and 3rd day composite)	4	0 – 5
8	DS7-8	Diluted seawater wastewater effluent Jeddah with MP (4rd and 5th day composite)	4	0 – 5
9	WWEJ1	Wastewater effluent Jeddah with MP (original concentration)	2	5 – 15
10	WWEJ2	Wastewater effluent Jeddah with MP (concentrated after 5 days)	2	5 – 15
11	BLK*	Blank DI water	4	0 – 1

*The results for these samples can be found in Table 7.3 on the Appendix

3.2.4 Total Organic Carbon Analysis

A Shimadzu TOC-V CPH total organic carbon analyzer (Japan) was used to determine the organic carbon present in water samples. The samples have to be pre-filtered with a 0.45μm filter into a 10ml glass vial, and diluted enough to have a TOC of maximum 5mg/L.

3.2.5 Zeta Potential (ZP) Analysis

An Anton Paar Zeta Potential Analyser (Austria) was used to determine the ZP of the FO membrane. It uses a clamping cell where two pieces of membrane are used to create a channel of 25mm of length and 5mm width, with the active layers facing each other, and then the charge of the membrane in mVolts is measured when an electrolyte flows through it. In this case, two electrolytes are used, 10mM KCl and SWWE. The ZP is measured in the pH range in which the membrane can operate (4 to 8), so the proper injection of acid (0.1M HCl) or base (0.1M NaOH) is added in the titration process. The results presented in this study were calculated with the Helmholtz-Smoluchowski equation.

3.2.6 Contact Angle Measurement

A KSV Theta Optical Tensiometer (Finland) was used to measure the contact angle of the FO membrane. The membrane sample was attached to the surface with double-sided tape to prevent absorption of the water drop into the material, in order to take a steady image of the drop and calculate with precision the contact angle. The volume of the drop was set to 5μl.

3.2.7 Liquid Chromatography coupled with Organic Carbon Detection

A Liquid Chromatography coupled with Organic Carbon Detector analyser (LC-OCD) Model 8, DOC LABOR DR. HUBER (Germany) was used to analyse the organic carbon content in the water samples. The process consists of three size exclusion chromatography (SEC) columns that divide the organic carbon into several fractions based on size and hydrophobic and ionogenic characteristics. Around 1000µL of sample are injected into the instrument and filtered in-line with a 0.45µm filter when using diluted wastewater effluent (2000µL for seawater). The deposit on the filter is backwashed after 5 min and directly analyzed with the TOC analyzer to determine the particulate organic carbon (POC) content. This process will take 130 minutes per sample. The organic carbon detector used is based on a thin film reactor principle ("Gräntzel" type). Inorganic carbon is removed with air stripping. The organic carbon is oxidized to CO_2 by UV radiation at 185 nm. The CO_2 is analyzed using nondispersive infrared detection. The detection limits are in the parts per billion concentrations. UV absorbance was also determined in parallel. CDOC is the chromatographable fraction of DOC, which refers to the hydrophilic fraction of DOC. Results were calculated using peak area. HOC is the hydrophobic fraction (Huber 1998). The recommended DOC concentration of the sample should not be higher than 5mg/L (in this case, a target of 2mg/L of DOC was used, based on TOC and DOC previous analysis).

3.2.8 3-Dimensional Fluorescence Emission-Excitation Matrix

Several 3-Dimensional Fluorescence Excitation Emission Matrixes (3-D FEEM) were obtained with a Fluoromax-4 Spectrofluorometer (Horiba, USA) for the different water samples. The preparation of the samples is simple, consisting only in the filtration of the water with a 0.45μm filter. No dilution was performed, nor pH adjustment.

A typical spectra response for a 3-D FEEM can be seen in Figure 7.3 in the Appendix.

3.2.9 Adenosine 5´Triphosphate Analysis

A A Celsis Advance Luminometer (Belgium) was used to calculate the amount of adenine 5´ triphosphate (ATP) on the FO membrane after 10 days of continuous use, as well as for the diluted draw solution (DDS) and the feed water (FW) (secondary wastewater effluent). The tubes with the samples of the fouling material scrubbed (diluted in 50ml) from the membrane sections with a total area of 9cm^2 were placed in an ultrasonic cleaning bath (Bransonic Model 5510, 40 KHz, USA) for 2 minutes, and then mixed on a vortex mixer (Fisher Scientific, 230 V, USA) for 10 seconds at speed 7. This operation was repeated three times.

Active biomass was determined in duplicate by measuring the ATP concentration from 50 μL samples. The luminometer added 100 μL of Celsis LuminEX-B reagent to a sample to release ATP from the bacterial cells. Subsequently, 100 μL of Celsis

LumATE-PM was added for light production. Finally the amount of light produced in the reaction was measured in relative light units (RLU).

3.2.10 Transmitted and Reflected Light Research Microscopy

In order to analyze the presence of transparent exopolymer particles (TEP) in the FO membrane, Alcian Blue dye is used in order to stain the particles and make them visible in the microscope. An Olympus BX61 Motorized Transmitted and Reflected Light Research Microscope (Japan) was used with different objectives (60x and 100x) to take images of a fouled membrane after a 10-day cycle FO process.

The cut pieces of membrane are submerged in a petri dish with DI water to rinse them for 2 minutes; afterwards, the pieces are immersed in a solution of Alcian Blue for 10 minutes to allow the dye to be absorbed by the TEP; finally, a second rinse is made with DI water before putting the samples under the microscope.

4. Results and Discussion

4.1 FO Flux and Conductivity

The results for the flux through the forward osmosis membrane are not a direct measurement. Nevertheless, the change in weight through time is the most straightforward way to determine flow, and the relation with the effective area of the membrane will give an accurate estimation of the flux (J_w) (Fig. 4.1 and 4.2), as equation 4-1 shows:

$$J_w = \frac{W_2 - W_1}{t_2 - t_1} / A_e \qquad (4\text{-}1)$$

where W_2 is the weight in t_2, W_1 is the weight in t_1 and A_e is the effective membrane area, considering the area lost (not working) because of air intrusion in the channel inside the cell. In this case, for the membrane cell used, the effective membrane area is 70% of the total membrane area.

Overtime the flux decreased due to the decrease of the driving osmotic pressure difference, which is demonstrated by the conductivity decrease; this assures that the experiment meets the conditions previously described for equation 2-4 in the literature review. Equation 4-1 will give the actual flux for the experiment. Based on tests realized with an osmometer (Osmomat 030, Gonotec, Germany), it can be considered that the relation between the conductivity and the osmotic pressure is

linear, and thus, the results provided for the experiment in terms of conductivity are consistent with Lee's and Loeb's equations described in section 2.1. Results for the linear relation can be observed in Fig. 7.1 in the Appendix. Both correlation factors R^2 are higher than 0.999. Fig. 4.1 shows the proportionality between conductivity and osmotic pressure, one of the assumptions that Loeb uses in his formula. Table 4.1 details the values for each parameter for the seawater and wastewater effluent. The transformation from osmolality to osmotic pressure was realized using equation 4-2, adapted from the osmometer manual (equation 7-1 in the Appendix) and an addendum from Dow Filmtec Membranes for osmotic pressures of sodium chloride (equation 7-2 in the Appendix).

$$\pi = 0.0262\theta - 0.0904 \qquad (4\text{-}2)$$

where π is the osmotic pressure in Bar and θ is the osmolality in milliOsmol/Kg H_2O.

This approach proved to be accurate for seawater, even though this water not only has sodium chloride as TDS, because the relation is almost the same for the osmolality (calculated directly from the apparatus) and the osmotic pressure (obtained through the equation 4-2) compared against the conductivity, which is also a direct measurement.

Fig. 4.1 proves that Loeb´s equation (equation (2-4)) can be used for the feed water (SWWE) and the draw solution (SW) proposed in this experiment; moreover, the

logarithm of the relation between osmotic pressures can be substituted with a proportionality constant with a value of 0.0001 affecting the difference in conductivity between the feed and the draw solution:

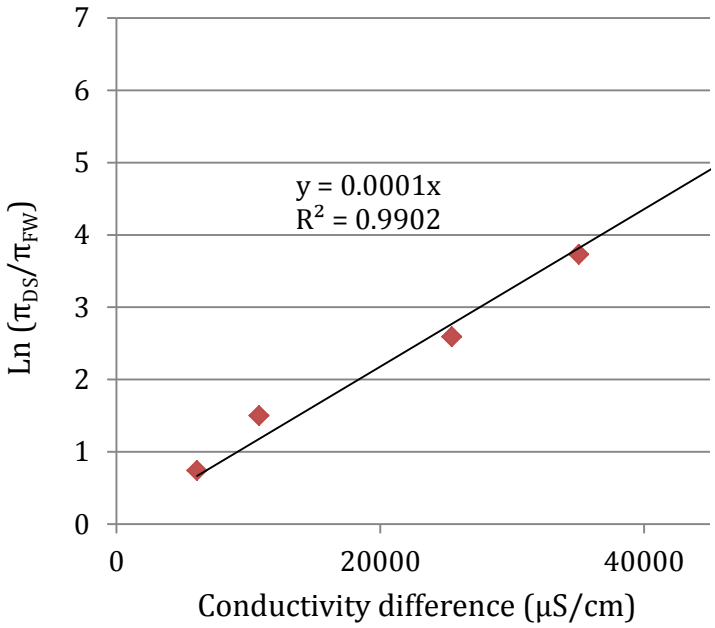
$$K = \frac{1}{J}\ln\left(\frac{\pi_{DS}}{\pi_{FW}}\right) \quad = \quad K = \frac{1}{J}\alpha(\gamma_{DS} - \gamma_{FW}) \qquad (4\text{-}3)$$

Eq. (4-3) can be used to determine the flux model for the experiments, or to estimate the fluxes when the conductivity of the solutions is known.

Table 4.1 – Conductivity, osmolality and osmotic pressure of water samples

Sample	**Conductivity (mS/cm)**	**Osmolality (mOsmol/Kg H_2O)**	**Osmotic Pressure (Bar)**
SW	54300	1160	30.3
SW	37600	777	20.3
SW	29400	584	15.2
SW	15820	279	7.2
SW	13700	233	6.0
SWWE	1810	7	0.1
SWWE	2550	22	0.5
SWWE	3970	47	1.1
SWWE	5010	65	1.6
SWWE	7590	113	2.9

Fig. 4.1 – Correlation between conductivity and osmotic pressure



After 1 day of running the FO, the results for the feed seawater (DS) and the DDS are compared. Table 4.2 shows the values for each sample. Note that the dilution changes the concentration of all of the dissolved solids in the water, reducing the TDS from 40,500 to 15,640 mg/L. It is also important to note that the pH is decreasing, from 7.8 to 7.6, and the UVA_{254} absorbance increases slightly from 0.012 to 0.025, due to the low molecular weight neutrals and acids that might be transported through the membrane from the SWWE to the DDS. This will be explained thoroughly in the next sections.

Table 4.3 shows the results for the amount of nitrate, nitrite, ammonium, phosphate and total nitrogen a sample of feed water (SWWE) and a sample of the diluted draw solution (DDS). The removal of nitrate is 73% going from 2.27mg/L to 0.62mg/L in

the DDS; ammonium is removed efficiently from the feed water, as the DDS value is 0.12mg/L, compared to 0.85mg/L in the feed water. For the nitrite, as well as for the total nitrogen, the removal cannot be compared since the results were both below the limit of detection of the test. Phosphate removal can be as high as 100%. The FO membrane proves to be a good barrier against the nitrogen and phosphorus species present in the wastewater effluent.

Table 4.2 – Composition of DS (feed seawater) and DDS (after 1-day FO cycle)

	DS	DDS
Conductivity (μS/cm)	57500	21900
Temperature (° C)	20.5	20.5
pH	7.8	7.6
DOC (mg/L)	1.12	1.19
UVA_{254} (1/cm)	0.012	0.025
SUVA (L/mg m)	1.07	2.10
TDS (mg/L)	40500	15640
SDI	2	n.a.
Barium (mg/L)	0.01	n.a.
Calcium (mg/L)	571	257
Magnesium (mg/L)	1458	639
Potassium (mg/L)	488	188
Sodium (mg/L)	12470	5620
Strontium (mg/L)	7	3.9
Bicarbonate (mg/L)	141	65
Boron (mg/L)	2.2	1
Carbonate (mg/L)	8.0	n.a.
Chloride (mg/L)	23073	10288
Fluoride (mg/L)	1.5	0.6
Sulphate (mg/L)	2400	1122

n.a. – not available

Fig. 4.2 and 4.3 show the plots for flux decline and conductivity for both FO feed waters (SS and SWWE). The results demonstrate that only osmosis took place between the thin-film layer of the FO membrane facing the feed water and the draw solution recirculating inside the cells. Fouling was accounted in the model by calculating solute resistivity of the membrane for each cycle; this phenomenon is further explained and characterized in section 4.2 and 4.5.

Table 4.3 – Nitrogen and phosphorus species in SWWE, DS and DDS

	SWWE (mg/L)	DS (mg/L)	DDS (mg/L)
Nitrate (NO_3^-)	2.27	1.56	0.62
Nitrite (NO_2^-)	<0.015	<0.015	<0.015
Ammonium (NH_4)	0.85	0.4	0.12
Phosphate (PO_4)	2.18	0	0
Total N	<5	<5	<5

Fig. 4.2 a) shows the FO flux through time. The cycles are similar to each other because there are no foulants in the feed water that can decrease the flux over time. Only the loss of osmotic pressure due to dilution of the DS (Fig. 4.2 b)) is causing the flux decline, which is why the values for the final conductivity for every cycle are almost equal. Although the water in the feed tank (SS) is concentrating, during this experiment the conductivity of the feed was maintained at around 5,000μS/cm to ensure that enough water was recovered through the FO process to obtain at least 2 liters of diluted DS for the MP analysis. The average flux for the 5-day experiment with SS as FO feed was 2.95 L/m^2-h, varying from 5.5 to 2 L/m^2-h.

For the FO process with the SWWE as feed, the fluxes varied from 6.2 to 2.6 L/m^2-h, with an average of 3.75 L/m^2-h. The draw solution was diluted from 52,000µS/cm to 22,000µS/cm in average. These results can be seen in Fig. 4.3 a) and b). The flux decline for a 5-day cycle is 19%. This is attributed partially to the increase in concentration of the feed in the tank (from 2850µS/cm to 4,230µS/cm). Nevertheless, fouling of the thin film of the membrane is also affecting the flux. This phenomenon is further analyzed.

From Fig. 4.3 b) it can be noted that even though the flux through the membrane is being reduced as the fouling affects the membrane, the dilution process continues and the seawater conductivity can be reduced to the same value in one cycle (1 day). Reducing the initial volume of the DS (500ml) will result in a lower final conductivity for the same cycle, reducing the energy consumption of the LPRO process. For the convenience of the measuring instruments for all of the parameters involved, the volume of the DS was not reduced during this experiment, but it is essential to manage the volume when scaling the project to full scale.

The recovery for the FO process, as discussed before, depends on the configuration of the system (tank size, number of cells, membrane area, volume of the DS, etc.). For this particular experiment, the recovery was calculated only by dividing the total feed volume in the tank by the volume extracted from the SWWE through the membrane (obtained by the difference in weight). The average recovery for all of the cycles is 7%, but it can be increased further than 30% if another 3 cells with the

same size are immersed in the tank (the feed volume will be reduced in the tank, but the system would still work with the same parameters).

Fig. 4.2 FO flux and conductivity decline of DS – SS as FO feed

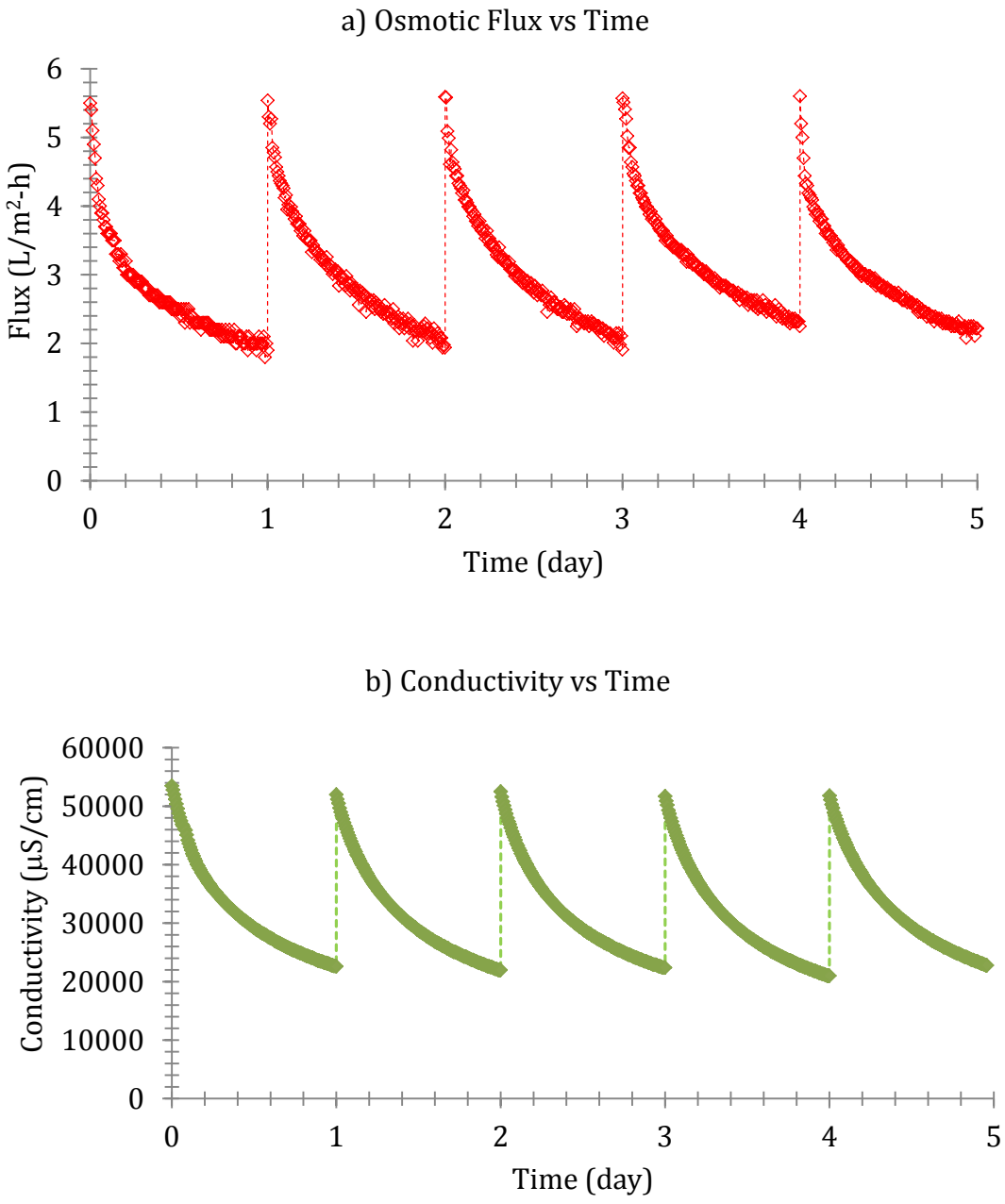
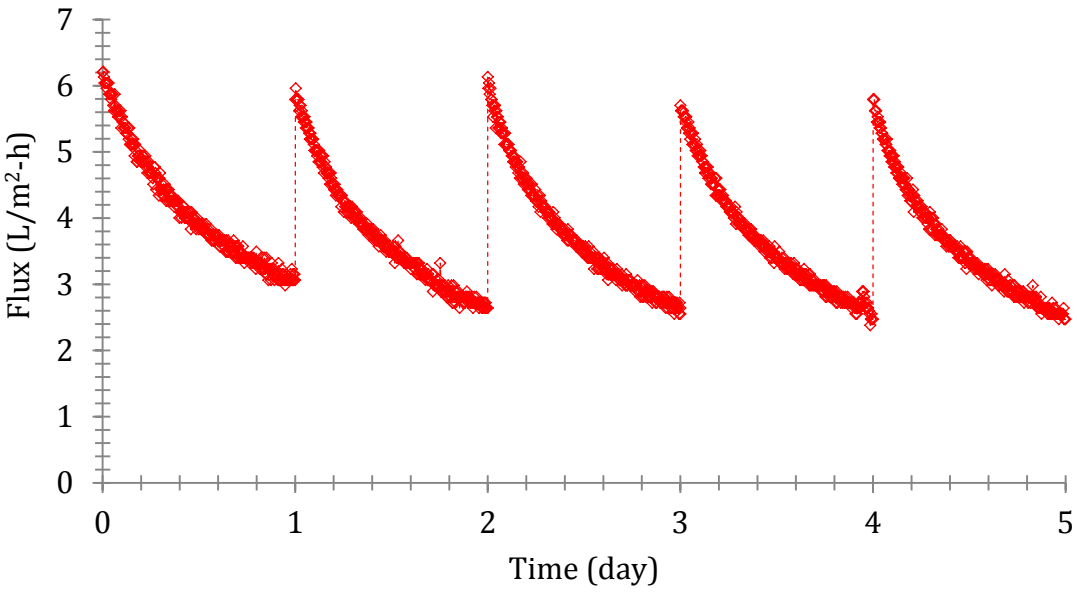
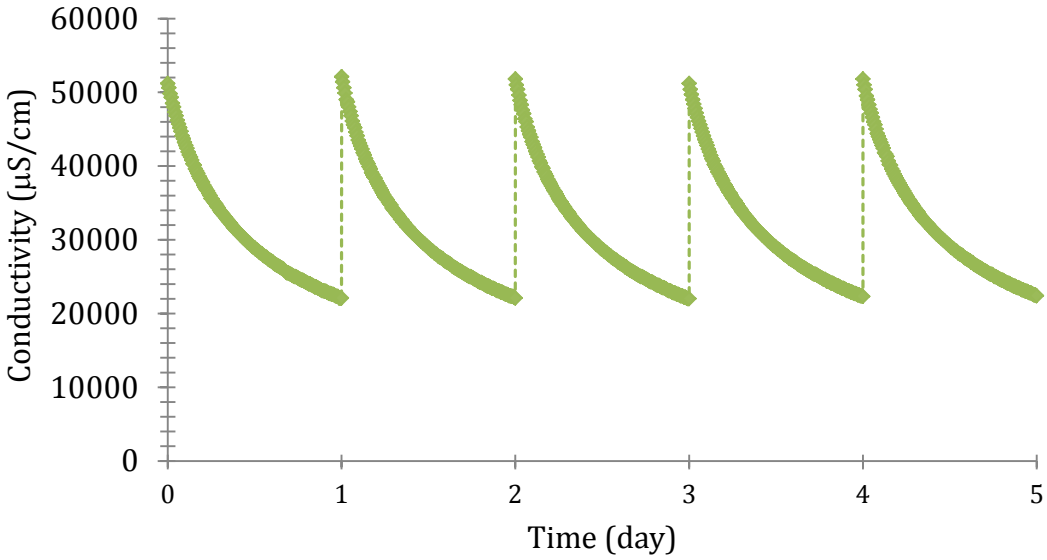


Fig. 4.3 FO flux and conductivity decline of DS – SWWE as FO feed

a) Osmotic Flux vs Time



b) Conductivity vs Time



The salt leakage of the FO membrane calculated with the initial and final TDS of the feed water and the draw solution initial TDS was set to 0.285 g/m²-h.

4.2 FO Membrane Fouling and Cleaning

Apart from the loss in osmotic pressure difference due to the dilution process (seen only in the 24-hour lapse, because the DS is changed for each cycle), another cause of flux decline in the process, seen throughout the experiment when comparing the decrease of the initial flux, is membrane fouling.

To characterize the fouling in the FO membrane and determine the percentage of irreversible fouling due to the continuous use of the system, a 15-day experiment was run with secondary wastewater effluent from Jeddah (SWWE). Fig. 4.4 shows the experiment done with SWWE and DI as feed water, with the purpose of determining the effectiveness of air scouring cleaning and chemical cleaning. During this set of tests, the FO membrane was first used with DI water as feed and FSW as the DS. After this, SWWE was used as feed, running the experiment for 11 days before the first cleaning (membrane cell submerged in the concentrated wastewater effluent (CWWE)) with air scouring for 15 minutes, at a cross flow rate of 250 L/h (flow rate of 12.5 L/h per Liter of feed water) on each side of the cell, after which a test with SWWE was made. The next day the feed water was changed to DI water, and air scouring was performed again for the same lapse of time in the same conditions. Later, a test with DI as feed water was made to compare both flux declines. After the 14th day, chemical cleaning was made with a washing solution at pH 8 to prevent membrane damage (adapted from cleaning protocols for ROGA RO spiral wound elements with CTA membranes), specified in Table 4.4, leaving the membrane cell immersed for 5 minutes on each side and rinsing both the tank and

the cell with tap water, besides recirculating DI water inside the channel to prevent membrane damage. It is important to note that when moving the membrane position upside down, most of the fouling is instantly cleaned due to the contact with the solution. Day 15 shows the results for the flux with DI after the chemical cleaning.

Table 4.4 – FO Membrane Cleaning Solution

ROGA RO Elements	**g/ L**	**g/5 L**
Trisodium phosphate	20	100
Sodium EDTA		
if powder	8	40
if 39% solution	20	100
Triton X-100	1	5

FO HTI	**g/L**	**g/5 L**
Alconox*	10	50
Sodium EDTA		
if powder	8	40
if 39% solution	20	100

*Sodium dodecylbenzenesulfonate (10-30%), sodium carbonate (7-13%), tetrasodium pyrophosphate (10-30%) and sodium phosphate (10-30%)

Fluxes of the FO process varied along the experiment between 2.0 to 7.2 L/m^2-h. The draw solution was diluted in average from 51500µS/cm to 22500µS/cm in one cycle (1 day). The average flux was 3.42 L/m^2-h for the SWWE as feed water. The

flux recovery when using the wastewater effluent is around 90% when compared to the first day of tests (for SWWE day 2 to day 13), similar to the recovery when comparing the new membrane used with DI water as feed and the cleaned membrane with the same feed (day 1 to day 14). The flux results for this analysis are presented in Table 4.5.

Cleaning with air scouring for 15 minutes (air flow rate of 12.5 L/h per L of feed water) proved to be very effective in removing the fouling of the membrane (even though not all of the fouling agents are visible), because the increase in flux recovery when compared to chemical cleaning is less than 3%.

After chemical cleaning, comparing with the flux with DI water as feed for the FO process (day 1 and day 15), the irreversible fouling can be defined as the flux that could not be recovered, in this case, 8.2%.

For Fig. 4.4 b), the conductivity decrease in each cycle can be seen. This represents the dilution of the seawater in the DS along the experiment. This diluted water will then be the feed for the LPRO process. It is noticeable in the graph that the final conductivity for each day varies, increasing as the experiment continues in time, because the flux was also decreasing and thus, in the same time, seawater will be less diluted. Nevertheless, after the cleaning processes, the conductivity goes back again to the same levels and even lower, due the use of DI water as feed water.

Fig. 4.4 – FO flux and conductivity decline of DS

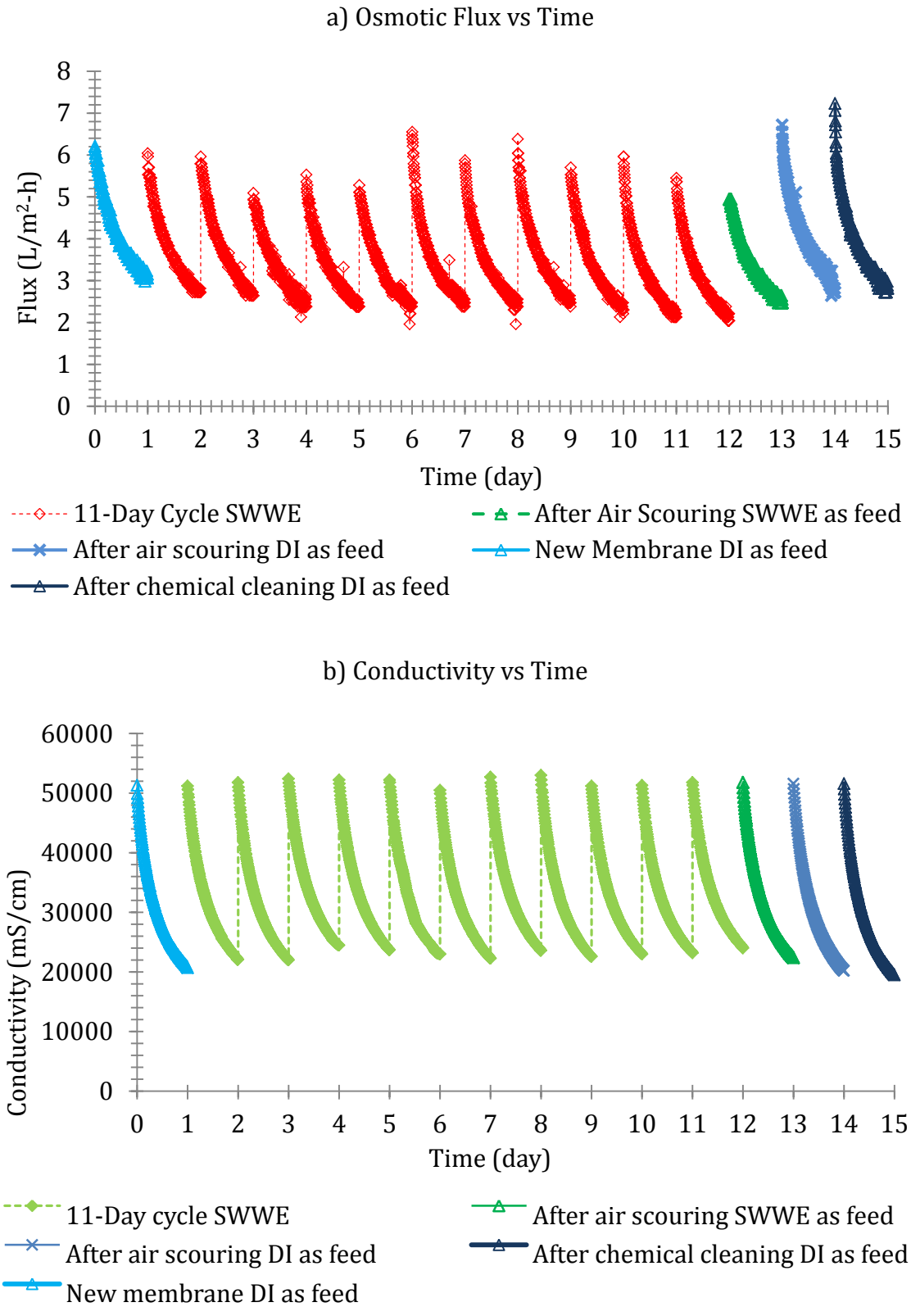


Table 4.5 – Characteristics of the flux

Parameter	Value
Flux decline	25.0%
Average flux	3.42 L/m^2-h
Flux recovery (air scouring CWWE)	90.8%
Flux recovery (air scouring DI)	88.9%
Flux recovery (chemical cleaning DI)	91.8%
Irreversible fouling	8.2%

4.3 TOC Analysis

Table 4.6 shows the results for the TOC analysis for the initial concentration and the final concentration in the FO feed water (SWWE and Concentrated FO Feed respectively) and in the draw solution (filtered seawater (FSW) and DDS respectively). These samples were pre-filtered with a 0.45μm filter, so the results are for the dissolved organic carbon (DOC). Note that there is an increase in the DOC measured for the seawater after dilution. The source of this organic carbon may not be the feed water, because the membrane rejects almost all of the organic carbon compounds; thereby, the bacteria growing in the tubing were responsible for the increment of the total organic carbon in the DS. Nevertheless, this change is not significant (less than 6.5% increment) for the scope of the experiment and it can be

considered that the water obtained from the FO process has almost zero mg/L of DOC.

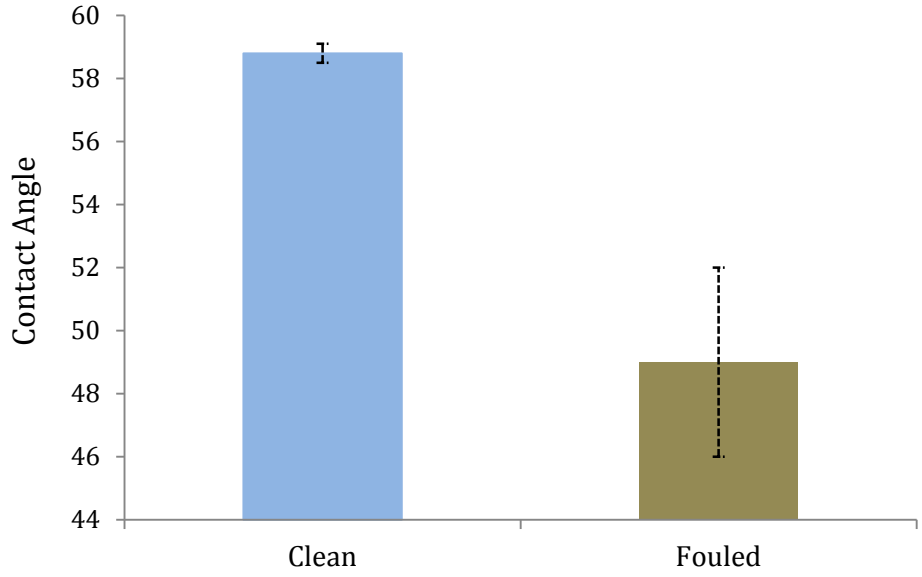
Table 4.6 – DOC values for 5-day cycle experiment

Sample	**DOC (mg/L)**
SWWE	4.60
Concentrated FO Feed	10.51
FSW	1.12
Diluted DS	1.19

4.4 Contact Angle

After the flux tests, the contact angle of the fouled membrane was measured, and the value was compared with the contact angle of a clean new membrane. The measured contact angle of the clean FO membrane was of 58.8° ±0.3, and that of the fouled membrane was of 49° ±3. Fig. 4.5 shows the results with the error bars, which suggest an increase in the hydrophilicity of the membrane. Nevertheless, it is important to consider that the contact angle may be an inexact parameter for quantifying hydrophobicity or hydrophilicity of a fouled membrane; compaction and composition of a dried foulant layer can erroneously produce results that do not reflect the true hydrophobicity of the composite foulant layer and the membrane itself.

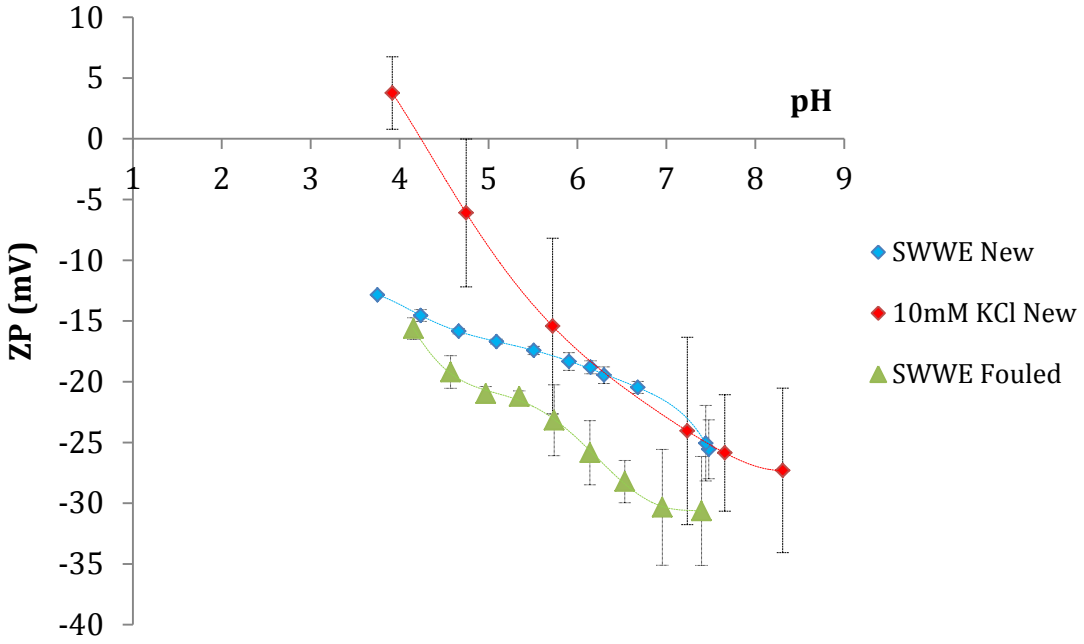
Fig. 4.5 – Contact angle of a clean and fouled FO membrane



4.5 Zeta Potential Determination

The ZP of the new membrane and the fouled membrane was determined. Fig. 4.6 shows the graph for the ZP in mVolts for each value of pH, using different electrolytes. The clean new membrane is generally negative for the experiments that have been done in this study, because the pH for the SWWE is 7.6, compared to the isoelectric point of the clean membrane, which corresponds to a pH of 4.1 (using Helmholtz-Smoluchowski equation). Table 7.4 in the Appendix shows the results for the ZP and the standard deviation of the calculated voltage for each electrolyte used in the clean and new membrane.

Fig. 4.6 – Zeta Potential of the FO membrane for varying pH values and electrolytes



The fouling layer after the FO process increases the negative charge in the membrane, shown clearly in Fig. 4.6. Nevertheless, whenever the membrane is in contact with the wastewater effluent, for the operational pH range of the membrane (4 to 8), the ZP is negative, which means that ionic MPs will be rejected due to electrostatic repulsion. This rejection is higher when the membrane is fouled, because the charge increases even more with the fouling layer, due to the presence of negatively charged compounds in the foulants, mainly coming from the NOM acids (carboxylic radicals) and the polysaccharide or polysaccharide-like substances as described in the literature (Cho et al. 1998, Fan et al. 2001, Shim et al. 2002).

4.6 Micropollutants Rejection

Two sets of experiments were conducted with the selected micropollutants (MP) in order to determine the rejection capability of the FO membrane, and the effect of fouling on the MP partitioning. The first experiment (Experiment 1) was realized using SWWE as feed water (spiked with the MPs), running the FO process in 5 1-day cycles; afterwards, the DDS was passed through a RO membrane. The second experiment (Experiment 2) was realized with a synthetic solution (SS) (same ionic strength as the SWWE) to eliminate fouling in the FO membrane; during this second experiment another test with SWWE was also completed to corroborate the data obtained in the first experiment (for FO and RO).

The results, along with the uncertainty measurements, can be seen in Tables 4.7 for the first set of experiments (Experiment 1), and in Tables 4.8, 4.9 and 4.10 for the second set (Experiment 2), showing the concentrations of the previously selected micropollutants, after being analysed by the laboratory in Germany, and the rejections for each part of the process:

a) FO rejection for the clean membrane (using SS as feed water)
b) FO rejection for the fouled membrane (using SWWE as feed water)
c) FO/RO rejection, considering the rejection of both processes together
d) DS/RO rejection, considering only the rejection for the RO after FO process

e) RO rejection, considering only the rejection for the RO with a synthetic diluted draw solution (SDDS) (diluted seawater with DI water, spiked with MP at the same concentration used for the other tests)

Rejections of the FO and RO membrane were calculated with equation 4-3.

$$\text{Rejection } (\%) = \left(1 - \frac{C}{C_0}\right) \times 100 \qquad (4\text{-}3)$$

For FO rejection, C_0 is the concentration of the feed water (spiked SWWE/SS), and C is the concentration of the diluted DS. For FO/RO rejection, C_0 is the concentration of the feed water (spiked SWWE/SS), and C is the concentration of the RO permeate. For DS/RO rejection, C_0 is the concentration of the diluted draw solution, and C is the concentration of the RO permeate. Finally, for the RO rejection, the C_0 is the concentration of the synthetic diluted draw solution (SDDS), consisting of prefiltered seawater diluted with DI to reach the FO DDS conductivity after one cycle, and the C is the concentration of the RO permeate.

Table 4.7 – MP concentration for water samples (SWWE as feed) and rejection of MP for FO, FO/RO and DS/RO *Experiment 1*

Compound (MW in g/mol)	Unit	Initial Feed	Final Feed	DS	DS-RO permeate	FO Rejection (%)	FO/RO (%)	DS/RO (%)
1,4-Dioxane (88)	µg/L	9.20	2.80	4.30	0.00	53.30	100.00	100.00
Acetaminophen (151)	µg/L	8.30	0.22	5.90	0.31	28.90	96.30	94.70
Metronidazole (171)	µg/L	7.50	7.40	4.10	0.08	45.30	98.90	98.00
Phenazone (188)	µg/L	7.60	1.26	2.30	0.01	69.70	99.90	99.60
Caffeine (194)	µg/L	13.00	9.80	3.20	0.03	75.40	99.80	99.10
Carbamazepine (236)	µg/L	9.90	13.60	2.50	0.02	74.70	99.80	99.20
Bisphenol A (228)	µg/L	7.60	6.40	7.00	0.06	7.90	99.20	99.20
EE2 (296)	µg/L	7.30	5.60	1.50	0.00	79.50	100.00	99.90
Naproxen (230)	µg/L	9.90	14.40	0.62	0.01	93.70	99.90	98.40
Fenoprofen (242)	µg/L	11.00	12.40	0.67	0.01	93.90	99.90	98.50
Gemfibrozil (250)	µg/L	12.00	19.80	0.62	0.01	94.80	99.90	98.40
Ketoprofen (254)	µg/L	7.90	13.80	0.39	0.01	95.10	99.90	97.40

Table 4.7 – MP concentration for water samples (SWWE as feed) and rejection of MP for FO, FO/RO and DS/RO

Experiment 1

(*Continuation*)

Error bars					
+ FO	- FO	+ DS/RO	- DS/RO	+ FO/RO	- FO/RO
15.54	23.41	0.00	0.00	0.00	0.00
23.71	35.53	1.80	2.58	1.21	1.90
18.26	27.30	0.70	0.93	0.39	0.50
10.12	15.09	0.11	0.25	0.01	0.10
8.19	12.32	0.28	0.51	0.05	0.15
8.46	12.58	0.27	0.40	0.07	0.10
30.70	46.06	0.25	0.44	0.29	0.34
6.80	10.32	0.06	0.00	-0.01	0.02
2.12	3.09	0.52	0.82	0.03	0.05
2.04	3.04	0.50	0.74	0.04	0.04
1.76	2.55	0.52	0.82	0.04	0.02
1.61	2.51	0.89	1.25	0.02	0.09

Table 4.8 – MP concentration for water samples (SS as feed) and rejection of MP for FO process
Experiment 2

						Error Bars	
Compound (MW in g/mol)	Unit	Initial Feed	Final Feed	DS	FO Rejection	+ FO	- FO
1,4-Dioxane (88)	µg/L	9.00	0.50	4.00	55.60	14.77	22.27
Acetaminophen (151)	µg/L	10.70	7.20	5.50	48.60	17.13	25.70
Metronidazole (171)	µg/L	8.70	8.90	2.60	65.50	11.51	17.22
Phenazone (188)	µg/L	11.80	10.00	1.80	84.70	5.13	7.58
Caffeine (194)	µg/L	9.60	7.60	1.90	80.20	6.61	9.89
Bisphenol A (228)	µg/L	8.50	6.90	5.10	40.00	20.00	30.00
Carbamazepine (236)	µg/L	10.00	9.40	3.30	67.00	11.00	16.50
EE2 (296)	µg/L	6.40	2.90	0.80	87.50	4.17	6.25
Ibuprofen (206)	µg/L	0.70	0.69	0.05	92.90	2.34	3.61
Naproxen (230)	µg/L	10.40	8.90	0.36	96.50	1.19	1.69
Fenoprofen (242)	µg/L	10.90	10.20	0.71	93.50	2.16	3.27
Gemfibrozil (250)	µg/L	11.30	10.50	0.50	95.60	1.45	2.24
Ketoprofen (254)	µg/L	9.20	8.10	0.32	96.50	1.18	1.72

Table 4.9 – MP concentration for water samples (SWWE as feed) and rejection of MP for FO, FO/RO and DS/RO
Experiment 2

Compound (MW in g/mol)	Unit	Initial Feed	Final Feed	DS	DS-RO permeate	FO Rejection	FO/RO	DS/RO
1,4-Dioxane (88)	µg/L	9.20	1.40	4.30	0.01	53.30	99.90	99.80
Acetaminophen (151)	µg/L	8.30	0.20	4.60	0.31	44.60	96.30	93.30
Metronidazole (171)	µg/L	7.50	10.00	2.80	0.08	62.70	98.90	97.10
Phenazone (188)	µg/L	7.60	12.00	1.60	0.01	78.90	99.90	99.40
Caffeine (194)	µg/L	13.00	9.00	0.62	0.03	95.20	99.80	95.20
Bisphenol A (228)	µg/L	7.60	1.60	3.90	0.06	48.70	99.20	98.50
Carbamazepine (236)	µg/L	9.90	11.60	2.30	0.02	76.80	99.80	99.10
EE2 (296)	µg/L	7.30	3.30	0.62	0.00	91.50	100.00	99.80
Ibuprofen (206)	µg/L	0.70	0.40	0.01	0.00	98.60	99.90	93.00
Naproxen (230)	µg/L	9.90	10.80	0.31	0.01	96.90	99.90	98.40
Fenoprofen (242)	µg/L	11.00	13.00	0.31	0.01	97.20	100.00	98.40
Gemfibrozil (250)	µg/L	12.00	12.00	0.35	0.01	97.10	100.00	98.60
Ketoprofen (254)	µg/L	7.90	10.00	0.24	0.01	97.00	99.90	97.90

Table 4.9 – MP concentration for water samples (SWWE as feed) and rejection of MP for FO, FO/RO and DS/RO

Experiment 2

(Continuation)

Error bars					
+ FO	- FO	+ DS/RO	- DS/RO	+ FO/RO	- FO/RO
15.54	23.41	0.04	0.15	0.03	0.06
18.45	27.73	2.21	3.41	1.21	1.90
12.41	18.70	1.00	1.39	0.39	0.50
7.06	10.48	0.18	0.34	0.01	0.10
1.62	2.35	1.57	2.46	0.05	0.15
17.09	25.67	0.51	0.73	0.29	0.34
7.71	11.65	0.32	0.40	0.07	0.10
2.84	4.24	0.09	0.04	-0.01	0.02
0.45	0.74	2.33	3.50	0.03	0.05
1.01	1.60	0.52	0.82	0.07	-0.02
0.92	1.43	0.52	0.82	-0.03	0.07
0.96	1.47	0.45	0.74	-0.03	0.06
0.97	1.56	0.71	1.02	0.06	-0.01

Table 4.10 – MP concentration for water samples (SDDS as feed) and rejection of MP for RO process *Experiment 2*

Compound (MW in g/mol)	Unit	RO feed	RO permeate	RO Rejection	Error bars	
					+ RO	- RO
1,4-Dioxane (88)	µg/L	5.30	0.50	90.57	3.14	4.72
Acetaminophen (151)	µg/L	10.40	1.10	89.42	3.53	5.29
Metronidazole (171)	µg/L	8.30	0.33	96.02	1.33	1.98
Phenazone (188)	µg/L	11.30	0.06	99.45	0.18	0.27
Caffeine (194)	µg/L	6.10	0.01	99.84	0.05	0.09
Bisphenol A (228)	µg/L	10.00	0.05	99.51	0.16	0.24
Carbamazepine (236)	µg/L	10.30	0.05	99.55	0.15	0.22
EE2 (296)	µg/L	8.00	0.01	99.88	0.05	0.06
Ibuprofen (206)	µg/L	0.84	0.01	99.40	0.20	0.29
Naproxen (230)	µg/L	10.40	0.04	99.62	0.12	0.20
Fenoprofen (242)	µg/L	10.60	0.05	99.54	0.15	0.23
Gemfibrozil (250)	µg/L	10.70	0.03	99.76	0.08	0.12
Ketoprofen (254)	µg/L	9.00	0.02	99.78	0.07	0.11

The rejections of all the processes were compared in Fig. 4.7 for the first set of experiments (Experiment 1). Hydrophilic neutral compounds (Dioxane, Acetaminophen, Metronidazole, Phenazone, Caffeine and Carbamazepine) showed rejections that can be related to their molecular weight (MW) as seen in Fig. 4.7 a) and Fig. 4.8. Considering the neutrality and low hydrophobicity of compounds such as Phenazone and Caffeine, the molecular weight cutoff (MWCO) of the FO membrane can be generally assumed to be around 200 Da. The MWCO of the membrane is shown in Fig. 4.8, where the rejection of the MPs are compared for both FO process and RO processes. Carbamazepine is neutral, but it is a compound in the boundary between hydrophobicity and hydrophilicity (log D = 2.58), so in this case it was considered among the hydrophobic compounds because of its relative low rejection in relation with the MWCO of the membrane (Fig. 4.8). Thereby, if a compound with a similar MW as the carbamazepine, but hydrophilic, is tested, then its rejection will be greater than 75%. Rejection of Dioxane was greater than rejection of Acetaminophen, but the error bars of both compounds overlap, leaving a possibility of a similar rejection or even lower for Dioxane than the one for Acetaminophen, which would be consistent with the MW.

It has been demonstrated that rejection of organic compounds by NF and RO membranes is related to the size of the compound and the hydrophobicity of the pollutant rather than the MW only (Yangali-Quintanilla et al. 2010b). This can help explain the rejection achieved for hydrophobic neutral compounds (Fig. 4.7 b), which is low, especially for small size compounds. Rejection of Bisphenol A was the

lowest achieved by the FO membrane with a range from 8 to 39%; this occurred due to the hydrophobicity of the compound and the slight hydrophobicity of the membrane. On the other hand, the rejection of 17α-ethynilestradiol was more favored by the size of the compound (size exclusion or steric hindrance). Although this compound is hydrophobic neutral (log D = 3.98), its rejection was increased by its size when trying to partition through the FO membrane (MW 296). In contrast, the smaller size of Bisphenol A combined with its hydrophobicity and the moderate hydrophobicity of the membrane, was detrimental in its rejection, the compound adsorbed, and after saturating the membrane, the compound partitioned across the thin-film layer. Cartinella et al. (2006) reported rejections greater than 99.5% for estrone (MW 270, log D 3.46) and estradiol (MW 272, log D 3.94) by an FO membrane under experimental conditions different of those carried out in this study.

The rejection results of negatively charged ionic compounds (Naproxen, Fenoprofen, Gemfibrozil, Ketoprofen) by the FO membrane can be explained by steric hindrance effects and electrostatic repulsion between the negative charge of the membrane surface as mentioned by Cartinella et al. (2006) and the negative charge of the compound at pH 7.3 (the feed water has a pH of 7.3). They all have rejections higher than 93%. Fig. 4.7 c) shows a comparison for the 4 ionic compounds.

Finally, for the FO/RO processes together, the rejections of all of the compounds are higher than 99%, except in the case of Acetaminophen (96.3%) and Metronidazole (98.9%), which also have very high rejection. For the DS/RO process, the rejections are slightly lower due to the low concentration left in the draw solution for some compounds, especially the ones that were highly removed by the FO membrane.

These results can be compared with the results presented by (Cath et al. 2011) who used a spiral wound configuration for the FO membrane, thus, utilizing considerable amounts of energy to circulate both the DS and the feed water. They use an impaired water source (MBR effluent) as FO feed and seawater as DS. The concentration of the micropollutants varied from 2 to 400ng/L; it is significant to mention that these contaminants were not added to the feed, they were actual concentrations in the effluent stream (even in some cases the compounds were below the limit of quantification). In the case of the experiments mentioned in this work, the concentrations of the spiked MPs are in the range of 1 to 10 μg/L, at least 2 orders of magnitude higher, and there is no crossflow velocity on the feed side, which means a higher concentration polarization effect, leading to the accumulation of micropollutants in the membrane surface; thereby, the rejections expected from the single FO process are considerably lower. Nevertheless, when the hybrid process is considered, the results of this work and that of Cath et al. are similar, achieving very high percentages of rejection (>99%).

Fig. 4.7 – (a) Rejection of hydrophilic neutral (HL Neutral) b) hydrophobic neutral (HB Neutral) and c) hydrophilic ionic MP for FO, DS/RO and FO/RO processes – *Experiment 1*

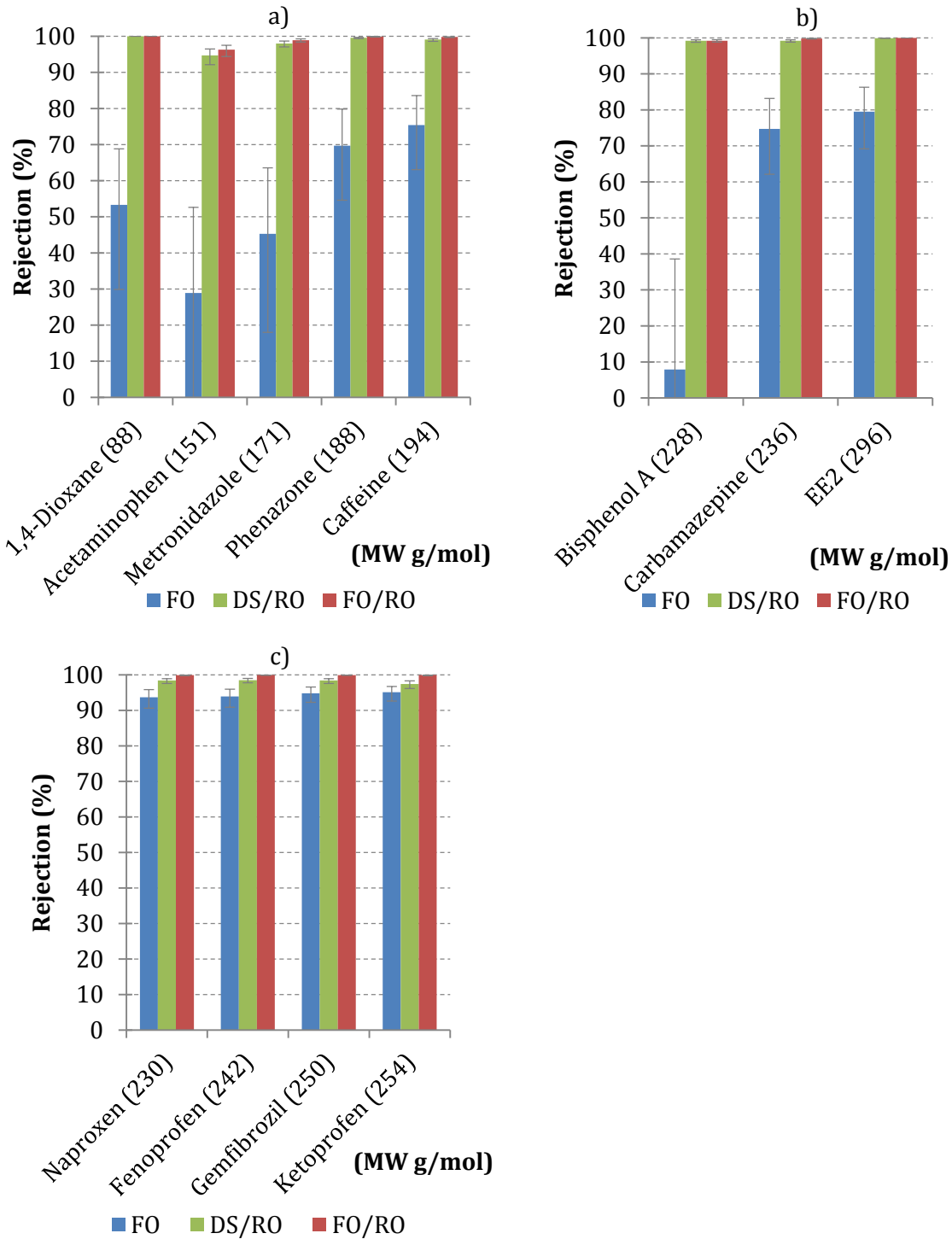
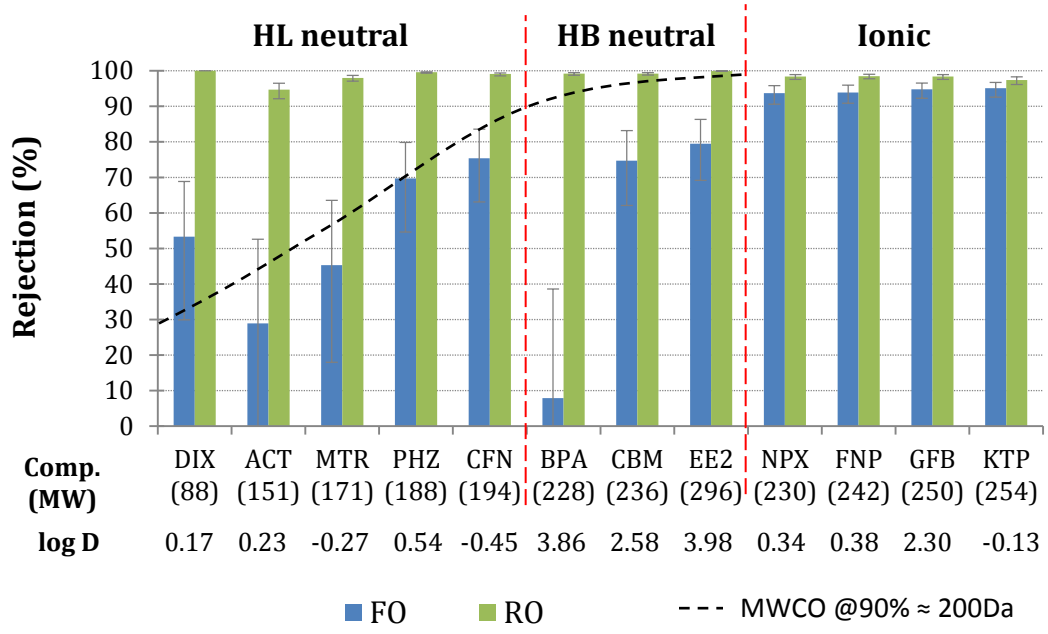


Fig. 4.8 – Rejection of selected MP vs. molecular weight (MW) vs. log D for FO and LPRO process – *Experiment 1*



For the second set of tests (Experiment 2), the objective was to reproduce the results obtained in the first experiment and analyse the difference in the rejection mechanisms of the MP with the clean and fouled membrane. Fig. 4.9 presents the results in terms of a comparison chart among the FO process with the SS (FO clean), FO process with the SWWE (FO fouled) as a confirmation of the first experiment, DS/RO, FO/RO and RO processes, divided by the hydrophobicity and the charge of the compounds, and in ascending order of their MW. An additional MP was spiked, Ibuprofen (MW 206), to determine the rejection of ionic compounds close to the determined MWCO of the membrane.

Fig. 4.9 – (a) Rejection of hydrophilic neutral (HL Neutral) b) hydrophobic neutral (HB Neutral) and c) hydrophilic ionic MP for FO, DS/RO, FO/RO and RO processes *Experiment 2*

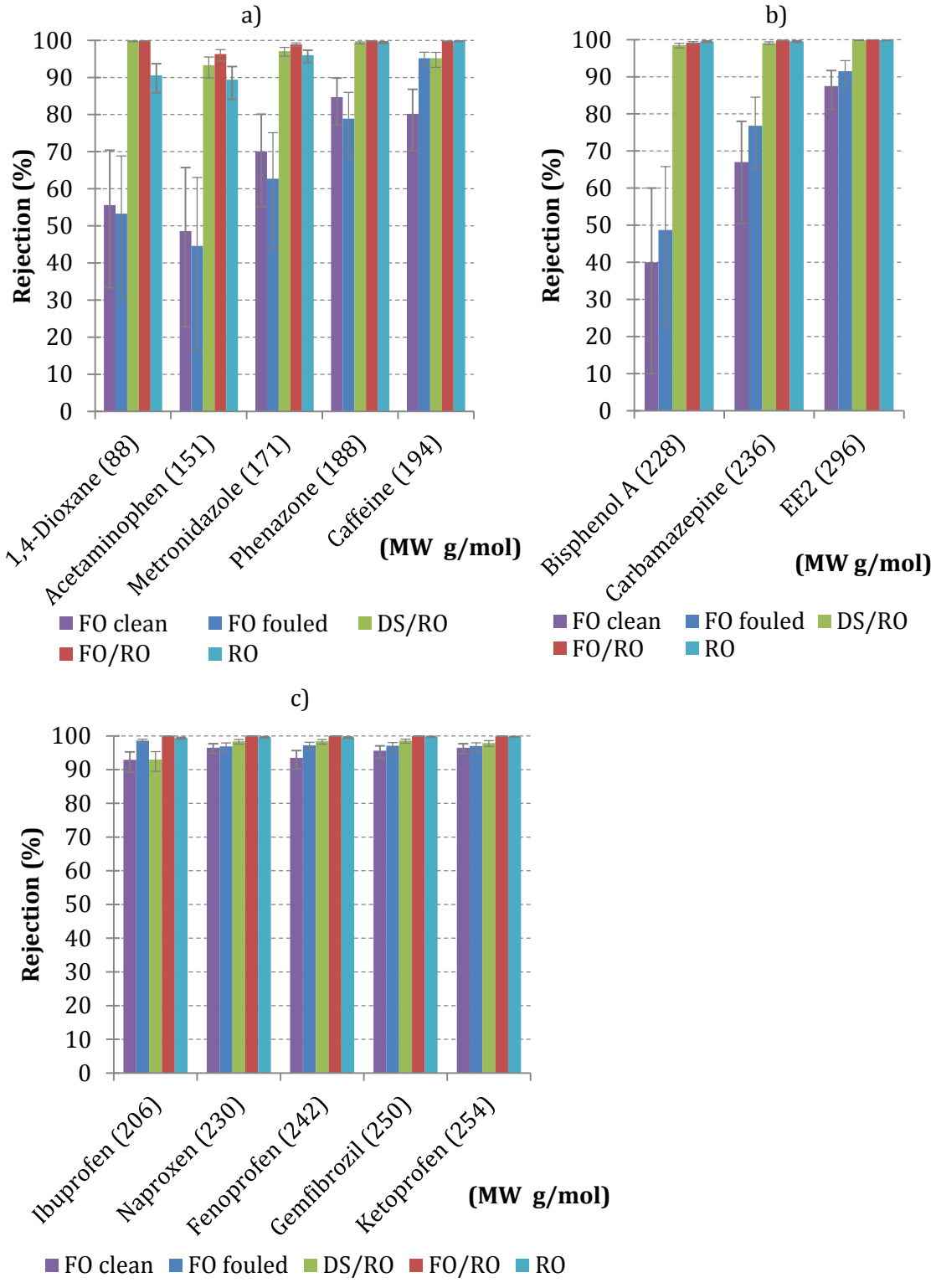
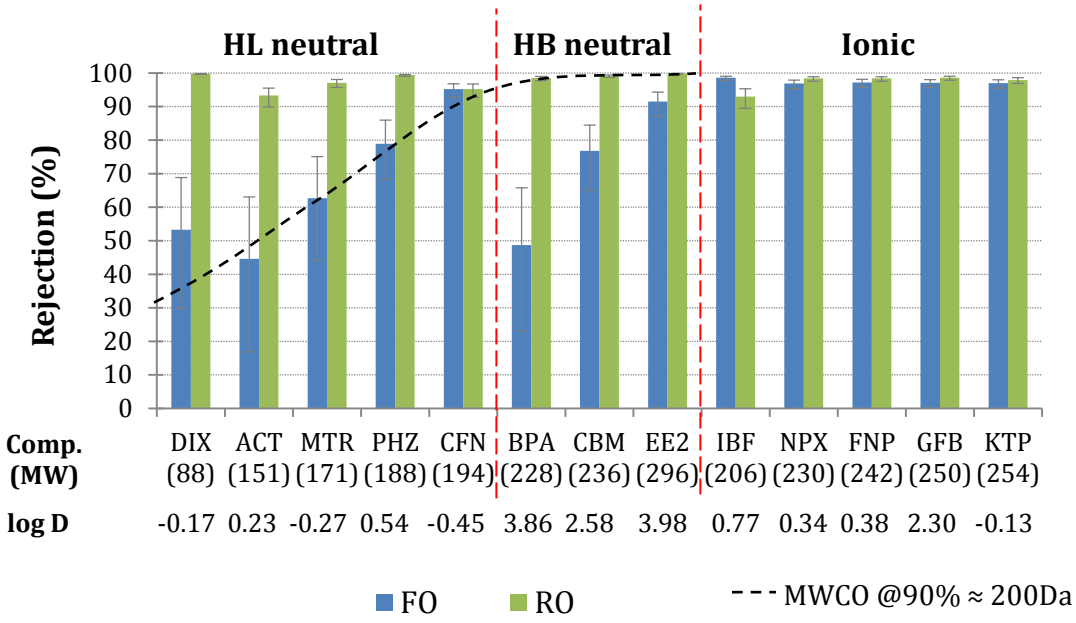


Fig. 4.10 – Rejection of selected MP vs. molecular weight (MW) vs. log D for FO and LPRO process – *Experiment 2*



From Fig. 4.9 a) it can be seen that for the hydrophilic neutral compounds the rejection with the SS as feed water (clean membrane) is higher than the rejection when SWWE is used as feed (fouled membrane), ranging from 2% for the Dioxane to 6% for the Phenazone, except for Caffeine. This can be explained by the increase in surface charge (ZP results in Section 4.5), which potentially results in a higher MWCO due to membrane swelling, as described by Xu et al. for NF and RO CTA membranes, along with a higher hydrophilicity generated by the fouling layer on the membrane (based on the results for contact angle described in Section 4.4), which will allow a higher amount of MPs to partition through the membrane, and eventually, decrease the rejection (Xu et al. 2006). In the case of Caffeine, the rejection for the fouled membrane increases 15% compared to the clean membrane; this can be explained by the high hydrophobicity of the compound (log D - 0.45),

being repelled by the cake layer formed in the membrane and thus, preventing the compound from partitioning through the membrane into the DS. Along with this hypothesis, the MWCO of the membrane is really close to the MW of this compound, and the foulants can be blocking (and ultimately reducing) the pore size of the membrane.

For hydrophobic neutral compounds and hydrophilic ionic ones, Fig. 4.9 b) and c), the rejections are increased with the fouled membrane. For the HB neutrals, the increase in rejections goes from 8.7% for the Bisphenol A, to a 9.8% for the Carbamazepine. In the case of the ionic contaminants, the increase goes from 0.4% for the Naproxen, to 6% for the Ibuprofen when the membrane is fouled.

This increase in the rejection of HB neutral MPs is due to the higher hydrophilicity of the membrane when the fouling cake layer is present (refer to Section 4.4); this phenomenon is also associated with an increased adsorption capacity and reduced mass transport capacity (diffusion and partitioning) of the membrane. For the ionic compounds, the negative charge of the membrane is greater when fouled (Section 4.5), increasing eventually the electrostatic repulsion (Donnan exclusion) between the negative charge of the membrane surface as mentioned by Cartinella et al. and Xu et al. (Cartinella et al. 2006, Xu et al. 2006) and the negative charge of the compound at pH 7.3. Nevertheless, the rejection is still low for the HB neutral compounds, with Bisphenol A again being the lowest with 48.7% rejection with the fouling layer.

For this second experiment (Experiment 2), higher rejections for the hydrophilic neutral compounds were obtained (Fig. 4.10). Nevertheless, the MWCO curve still fits the results, proving that the approach in the first experiment (MWCO of the FO membrane equals 200 Da) is accurate. For the Acetaminophen the rejection increases 15.7%, for the Metronidazole the rejection goes from 45.3% to 62.7% and the Phenazone has an increment of 9.2%. The same increase in rejection is observed for the hydrophobic neutral compounds, especially for the Bisphenol A, going from 7.9% in the first experiment to 48.7% in the second set of tests. This phenomenon is observed mainly because the determination of the precise concentration of a certain MP in the water samples is rather difficult, making the error bars go as far as ±20%, or even more for low MW compounds such as Dioxane, in which the values for the second experiment were not consistent between the initial concentration and the final concentration, so an estimate based on the first experiment was made.

Finally, when both processes are considered together (FO/RO), the results for rejection can go as high as 99.9% for Dioxane, 96.3% for Acetaminophen, 98.9% for Metronidazole and for the rest of the compounds the rejection is higher than 99%. If this is compared with the RO alone, the rejection is reduced for the low MW compounds, being 90, 89 and 96% for the already mentions compounds (Fig. 4.9 c)). Thus, the hybrid forward osmosis/low pressure reverse osmosis FO/LPRO system proves to be an effective double barrier against the 13 emerging contaminants tested.

4.7 FO Membrane Fouling Characterization

4.7.1 LC-OCD Analysis

A Liquid Chromatography coupled with Organic Carbon Detector analyser was used to detect and characterize the organic carbon in the effluent samples. To make the right interpretation of the results, a typical LC-OCD chromatogram is shown in Fig. 7.2 in the Appendix, where the peaks in the different curves are identified, analysed and associated with certain organic carbon compounds depending on the size (biopolymers, humic acids, building blocks, low molecular weight acids and low molecular weight neutrals), which are related to the retention time, as it is an indication of the molecular weight (MW) of the NOM fraction – the higher the retention time, the smaller the MW of the fraction (Villacorte et al. 2009).

Fig. 4.11 shows the results for the chromatogram from the LC- OCD test, where the chromatographable dissolved organic carbon (CDOC) in two samples is characterized. The first one (top) is the retention time versus the signal response of the FW before starting the experiment (original SWWE). The second one (bottom) is the concentrated feed water (CFW) after the 12-day test. The single response is visibly increased for biopolymers (associated with the peak in the organic nitrogen detection (OND)), humics (associated with the peak in ultraviolet detection (UVD)), building blocks and low molecular weight (LMW) acids as the water is concentrated when direct osmosis is occurring. The dilution factor of the samples is 4:1 for both waters, so the chromatographs are in the same scale. The results for the organic carbon present in the samples are consistent with the values obtained in the TOC

test. Table 4.11 summarizes the values obtained in mg/L of carbon for each type of substance in the samples analysed.

Fig. 4.12 shows the differences in the signal response for the organic carbon detection curves of both samples, noting that all the components in the wastewater effluent are being concentrated either in the membrane or in the tank, which means in a general sense that these compounds are not significantly contaminating the draw solution. In a further analysis, the draw solution and the diluted draw solution are analysed to determine the efficiency of the membrane to reject organic carbon compounds.

To analyse and determine which substances in the wastewater effluent are causing the fouling of the active layer of the membrane a test was done in which SWWE was evaporated at 30°C during two days to concentrate it to the same conductivity of the CFW analysed in the previous figures (Fig. 4.11 and Fig. 4.12) coming from the FO process. Afterwards, a LC-OCD test comparison was held to compare and determine which compounds were not present in the sample, suggesting that they were forming a cake layer on the membrane, and thus were not anymore part of the CFW. Again, the dilution factor for both samples was 4:1.

Fig. 4.11 – OCD, UVD and OND chromatograms for FW and CFW

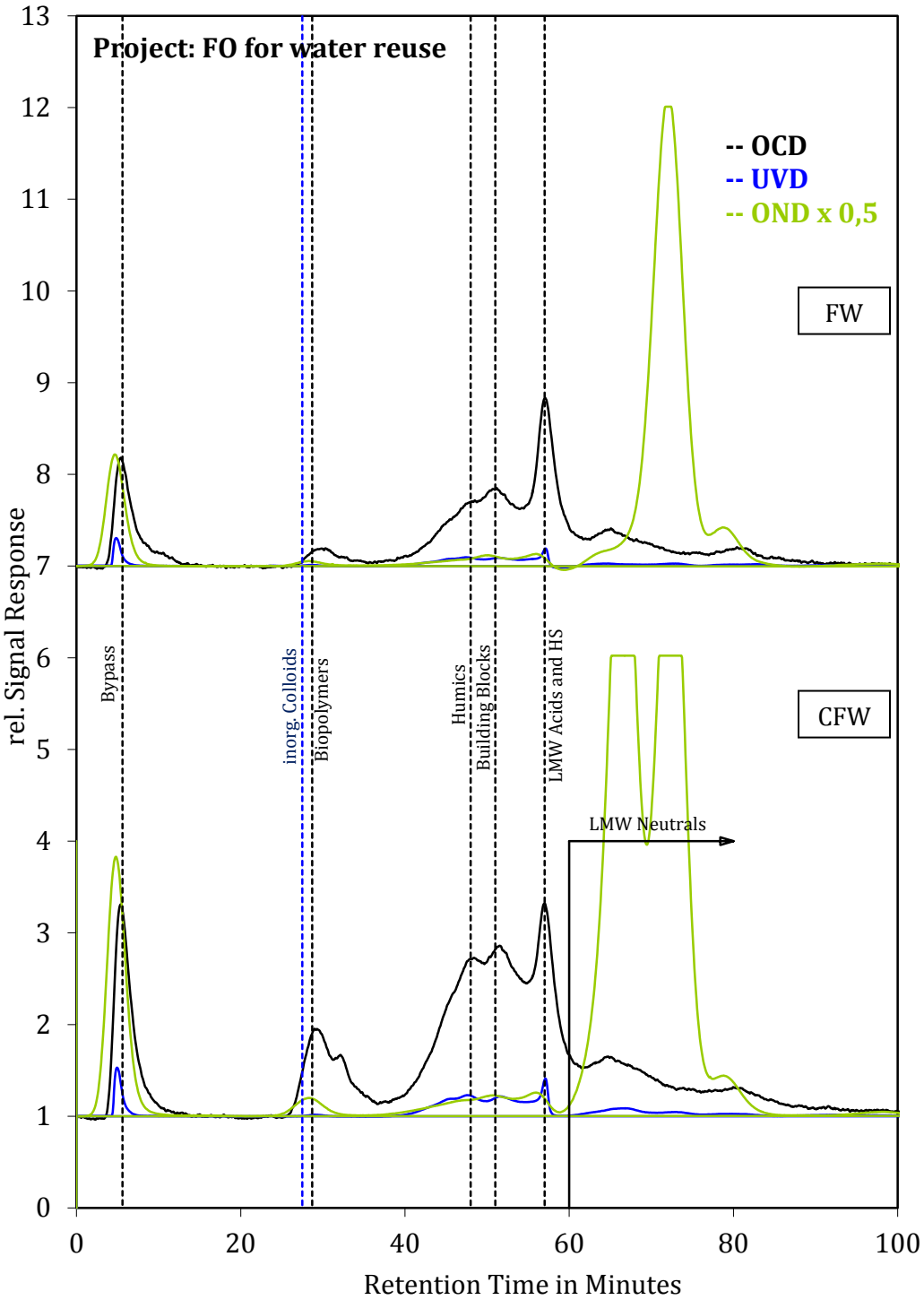


Fig. 4.12 – Difference in signal response in the chromatograms for FW and CFW

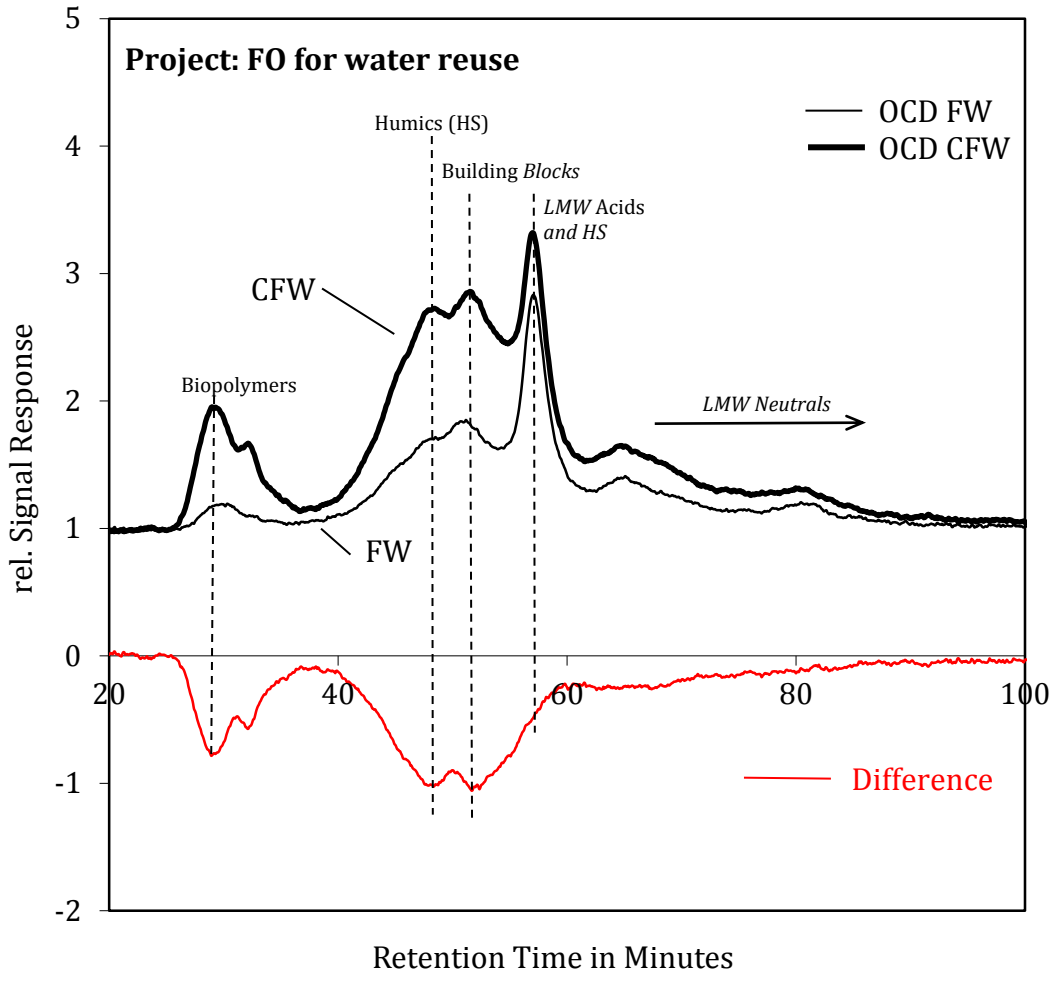


Table 4.11 – Composition of CDOC in FW and CFW

	CDOC (mg/L)	*Biopolymers (mg/L - C)*	*Humic Substances (mg/L - C)*	*Building Blocks (mg/L - C)*	*LMW Neutrals (mg/L - C)*	*LMW Acids (mg/L - C)*
FW	4.63	0.28	1.70	1.65	0.99	n.q.
CFW	9.67	1.14	4.79	1.99	1.74	0.02

Fig. 4.13 and Fig. 4.14 show the chromatograms and the differences when compared to a sample of CFW and the evaporated wastewater effluent (EWWE). It is evident that the peak in the OCD curve accounted for biopolymers (supported by a peak in the OND curve) is bigger in the EWWE than in the CFW, suggesting that these compounds are fouling the membrane. These biopolymers include polysaccharides and protein like compounds.

The results for the concentration in the samples for the second LC-OCD test are compared in Table 4.12. Note the high difference in concentration for the biopolymers which, instead of being similar for both samples, as the rest of the compounds, is significantly different. For the CFW the value in mg/L of biopolymers is 1.44, while the EWWE has 2.52 mg/L. The humic substances are present in a concentration of 5.40 and 5.25 mg/L respectively; building blocks are also similar in concentration for both samples, with 2.64 and 2.51 mg/L accordingly, and so are the LMW Acids (2.29 to 2.37 mg/L respectively). This can be taken as evidence that proves the hypothesis in which biopolymers are responsible for the fouling of the active layer in the FO process when SWWE is being fed.

From Table 4.11 and Table 4.12, the mass balance for the fouling can be calculated. Considering the initial and final volume of the FO feed water and the SWWE added for each cycle to refill the tank, the relation of biopolymers fouling the membrane was quantified as 0.04 mg/cm^2.

Fig. 4.13 – OCD, UVD and OND chromatograms for CFW and EWWE

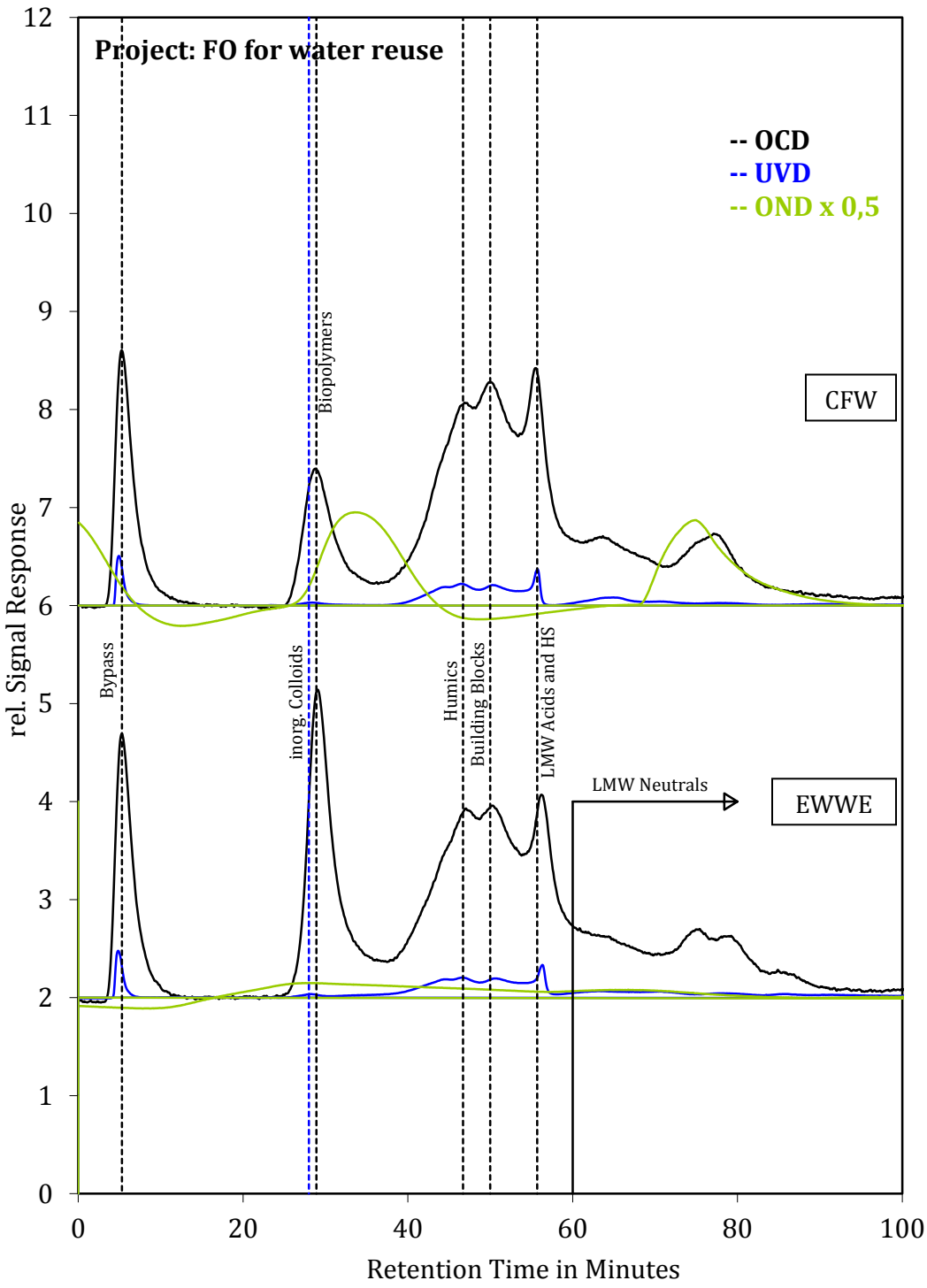


Fig. 4.14 – Difference in signal response in the chromatograms for CFW and EWWE

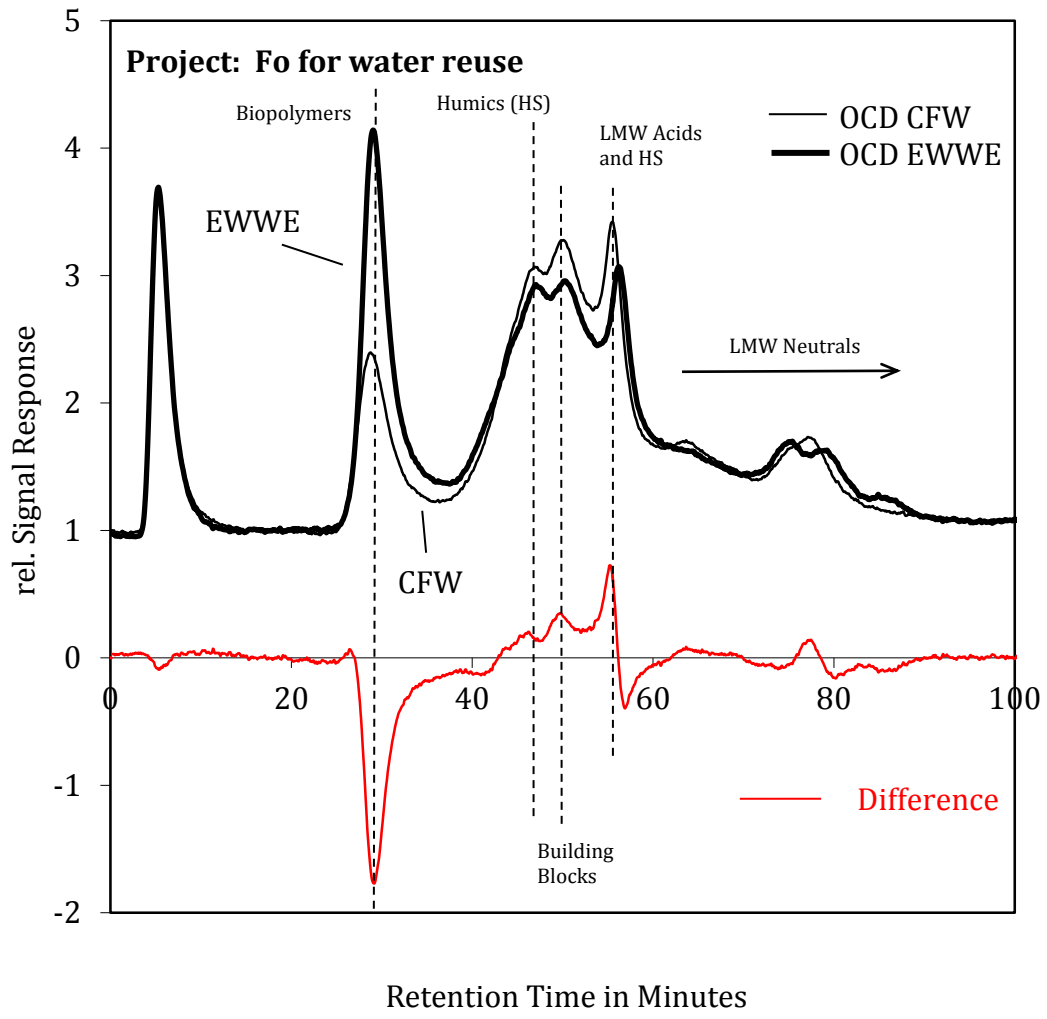


Table 4.12 – Composition of CDOC in CFW and EWWE

	CDOC (mg/L)	*Biopolymers (mg/L - C)*	*Humic Substances (mg/L - C)*	*Building Blocks (mg/L - C)*	*LMW Neutrals (mg/L - C)*	*LMW Acids (mg/L - C)*
CFW	11.76	1.44	5.40	2.64	2.29	n.q.
EWWE	12.65	2.52	5.25	2.51	2.37	n.q.

Among the biopolymers that might be associated with fouling that cannot be accounted with LC-OCD tests are the transparent exopolymeric particles (TEP), substances that have been studied and are probably responsible for the biofouling of membranes when the feed water or the draw solution used contains or was in contact with bacteria (Bar-Zeev et al. 2009). These substances are particularly found in seawater, so further analysis is made on both the active and support layer of the membrane with microscopy to determine the influence of TEP in the performance of the FO process.

Besides the analysis of the feed water to characterize the fouling in the membrane, it is also fundamental to know the quality of the water that is being extracted from the FO process, and determine the differences from the initial DS (seawater) and the diluted DS. An LC-OCD analysis was used to detect the different organic carbon components of the water before and after the FO dilution; with this result, the water quality can be compared. Fig. 4.15 shows the chromatograms for the filtered seawater (FSW) and the diluted draw solution (DDS) (dilution factor 1:1 for both samples). The difference in the signal response can be seen in Fig. 4.16. Note that for the biopolymers, the signal is almost similar; if dilution is taking place, a decrease is expected, however, the contamination coming from biofouling of the tubing of the system might be the responsible for the increase in biopolymers. For the low molecular weight compounds, there is a higher partition into the DDS as the size of the particles is reduced, leading to a high amount of LMW neutrals. This point is discussed later in this same section.

The values of the concentration of biopolymers, humic susbtances, building blocks, LMW acids and LMW neutrals are in Table 4.13. When comparing the results for the biopolymers, there is a reduction for the diluted draw solution (DDS), which means the water extracted from the FO feed does not contain polysaccharides and proteins, which also suggests that these compounds are being retained on the membrane (not in the concentrated feed water as Fig. 4.14 previously shows). For the humic substances, the building blocks and the LMW acids, the rejection of the membrane is significant, reducing the amount of these fractions in the DDS. Nevertheless, for the lowest molecular weight compounds (LMW neutrals), the rejection seems to be very poor, with a concentration 7 times higher in the DDS than the FSW; the difference in the OCD chromatograms can be seen in Fig. 4.16.

From Table 4.13, and comparing with the results of the DOC in Table 4.6, the results for the dissolved organic carbon vary, they are lower for the LC-OCD analysis (both for the FSW and DSS), but for both tests the values compared to the DOC on the feed water for the FO are low, which means the membrane is acting as a barrier for most of the components of the DOC. As mentioned before, the results for the LC-OCD analysis when focusing on the LMW compounds for these tests cannot prove that the contamination of the DDS is coming from the feed water, which is possible due to the high concentration of this fraction in the CFW, or from the membrane itself, which may contains LMW neutrals that might be partitioning into the DS for the whole testing time.

Fig. 4.15 – OCD, UVD and OND chromatograms for FSW and DDS

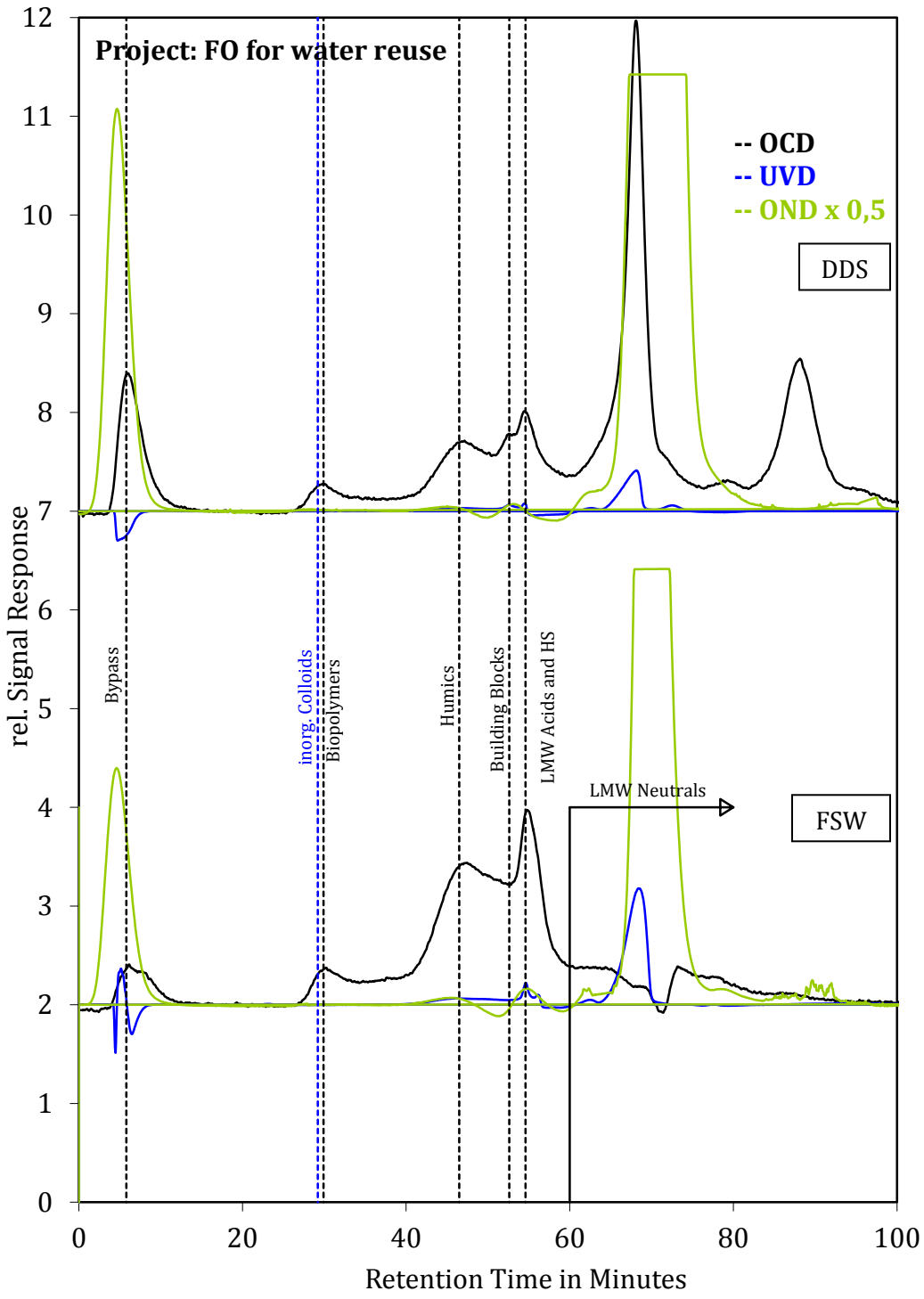


Fig. 4.16 – Difference in signal response in the chromatograms for FSW and DDS

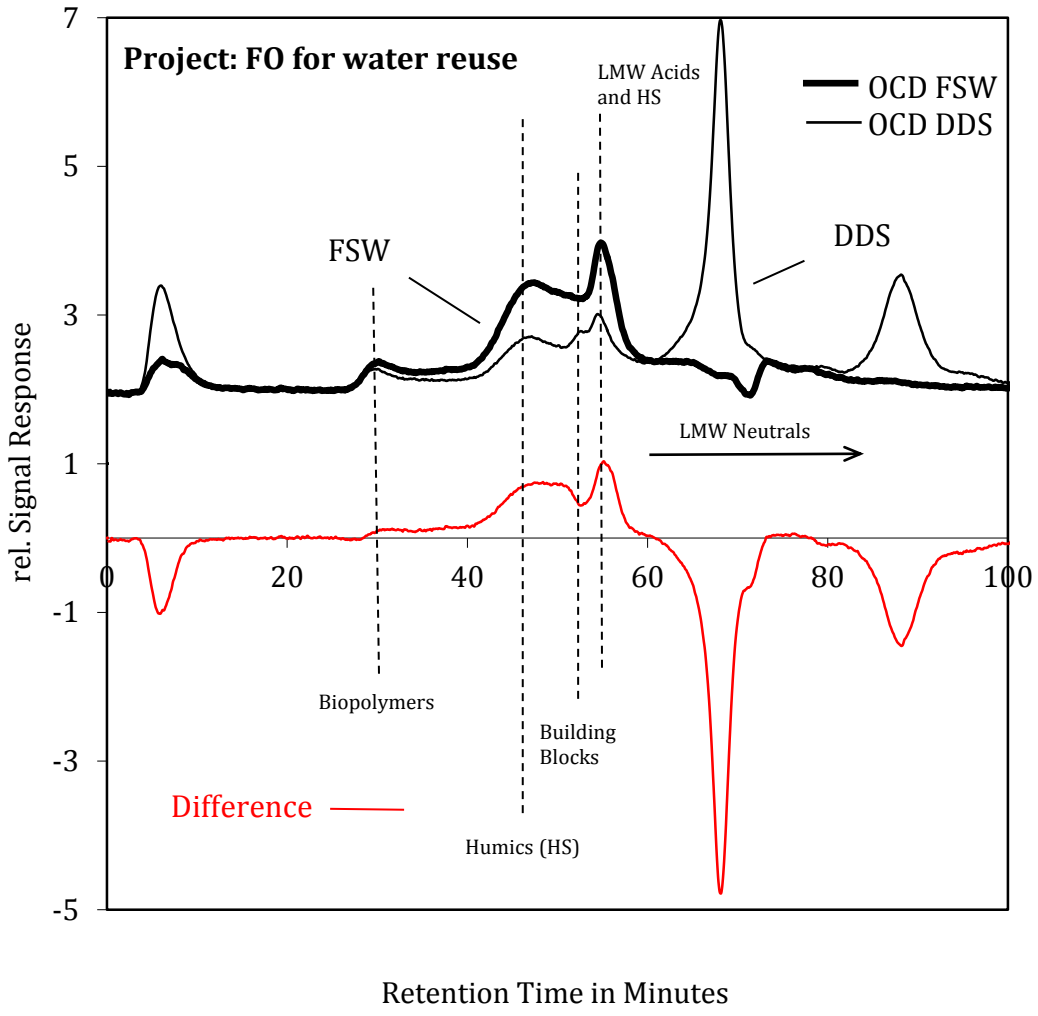


Table 4.13 – Composition of CDOC in FSW and DDS

	CDOC (mg/L)	*Biopolymers (mg/L - C)*	*Humic Substances (mg/L - C)*	*Building Blocks (mg/L - C)*	*LMW Neutrals (mg/L - C)*	*LMW Acids (mg/L - C)*
FSW	0.80	0.08	0.54	0.07	0.11	n.q.
DDS	1.10	0.05	0.18	0.13	0.74	n.q.

4.6.2 3-D FEEM Analysis

A 3-D Fluorescence Excitation Emission Matrix analysis was realized with a Fluoromax-4 Spectrofluorometer (Horiba, USA) to analyse the seawater used as draw solution (SW), the diluted draw solution coming from the FO process (DDS), the secondary wastewater effluent used as feed water (SWWE), the concentrated feed water after the FO process (CFW) and the evaporated wastewater effluent (EWWE) as a control sample.

Fig. 7.3 in the Appendix shows the typical spectra for an FEEM, relating the fluorescence intensity (color) with the emission wavelength and the excitation wavelength. In this way, there are certain 3-D peaks that can be identified, which belong to a certain type of organic carbon constituent (protein-like substances (biopolymers), fulvic humic-like matter, organic humic-like matter, etc.), similar to the LC-OCD analysis. With this figure, and Table 4.14, the results can be interpreted to determine the change in the concentration of these substances and, thus, define the effectiveness of the membrane for the FO process, relating both excitation-emission wavelengths.

Fig. 4.17 shows the results for the 3-D FEEM comparing the seawater with the diluted draw solution in the same scale. There is an increase in the fluorescence intensity for the protein-like substances, as well as for the organic humic-like matter, which can be attributed to the growth of bacteria in the tubing, because as discussed before, these types of substances are not crossing the membrane from the wastewater effluent feed. To prove this argument, Fig. 4.18 shows a comparison on

the same scale (different from the one used in Fig. 4.17) for the fluorescence intensity of the secondary wastewater effluent, the seawater and the diluted draw solution. The results prove that the membrane is significantly rejecting the dissolved organic carbon from being transported from the SWWE to the DDS, but there are still some substances that are either coming through the membrane or the tubing that are causing an increase in Fig. 4.17 when comparing the fresh seawater with the diluted one. These results are comparable to the ones obtained with the LC-OCD analyser, when proving the effectiveness of the FO membrane as a barrier against high molecular weight organic carbon fraction.

Fig. 4.19 shows the 3-D FEEM resulting from the analysis of the SWWE, the concentrated feed water after a 5-day cycle test (CFW) and an evaporated wastewater effluent (EWWE) with the same concentration as the CFW (similar conductivity), to support the results previously obtained with the LC-OCD test. Again, comparable to the mentioned tests, the 3-D FEEM shows a peak in the protein-like substances (biopolymers) in the EWWE, compared to the CFW, which suggests that these compounds are not in the feed water, so they are retained in the membrane and form a fouling layer, considering that the other possibility has already been discarded (transport through the membrane to the DDS).

Nevertheless, Fig. 4.19 also shows that some humic-like substances are not present in the CFW as they are in the EWWE, which suggests that the DDS is being

contaminated and would explain the results in Fig. 4.17, considering the fact that the membrane is not retaining this low molecular weight compounds.

Table 4.14 – Peak identification and description for a FEEM

Peak Description	Fluorescence Range	
	Excitation (nm)	Emission (nm)
Humic-Like (Primary)	330-350	420-480
Humic-Like (Secondary)	250-250	380-480
Protein-Like (Tyrosine)	270-280	300-320
Protein-Like (Tryptophan)	270-280	320-350
Protein-Like (Albumin)	280	320

Source: Adapted from (Amy et al. 2010)

Fig. 4.17 – 3-D FEEM of SW and DDS

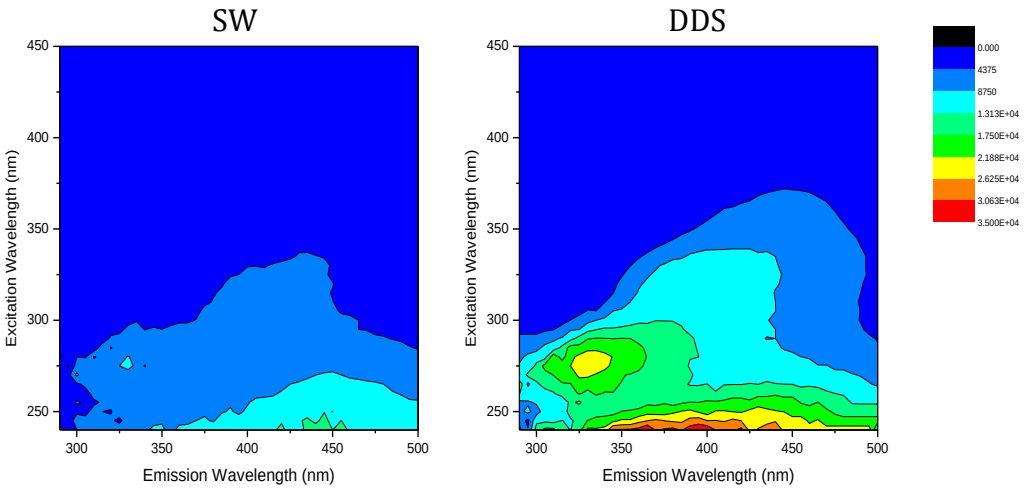


Fig. 4.18 – 3-D FEEM of SWWE, SW and DDS

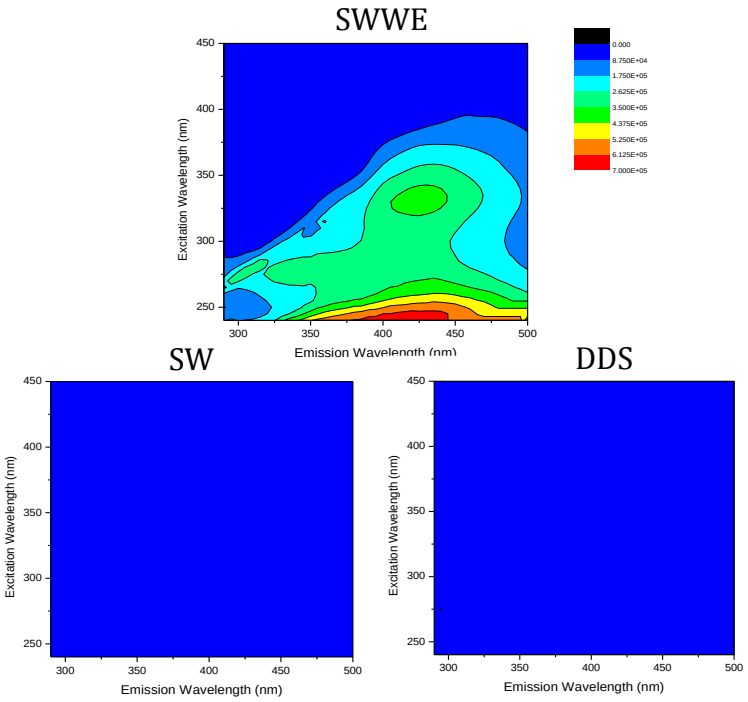
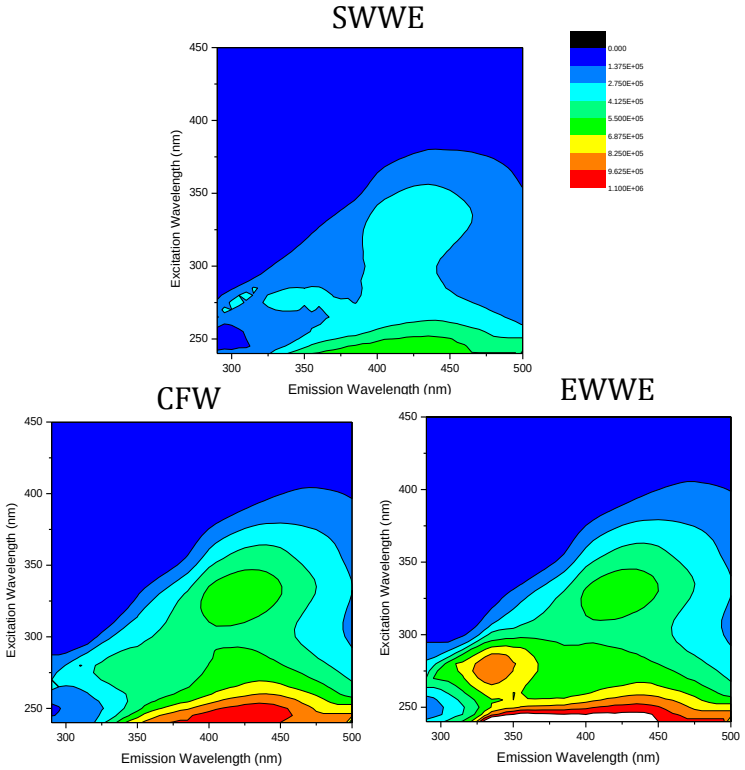


Fig. 4.19 – 3-D FEEM of SWWE, CFW and EWWE



4.6.3 ATP Quantification

A calibration curved was made for reference samples of ATP ranging from 0.1 μg/L to 100 μg/L in order to interpret the results for the fouling samples. The reference curve can be found in Fig. 7.3, and the results in Table 7.5, both in the Appendix. The results for the fouling material and DDS are shown on Table 4.15. An analysis of a fouled membrane immersed in a SBR is also included in the results as a comparison.

Table 4.15 – ATP measurements for the FO membrane, FW and DDS

Sample	**ATP (μg/L)**	**RLU**	**ng ATP cm^{-2}**
FO fouled membrane in SWWE	2.18	384,146	12.13
FO fouled membrane in MBR	89.02	14,794,754	494.54
FW (SWWE)	0.29	70,112	n.a.
DDS	< 0.1	8,139	n.a.

n.a. – not applicable, RLU – relative light units

Results in Table 4.15 show that the fouling layer in the FO membrane (when SWWE is used as feed water) has living microorganisms, and thus, it can be said that the membrane is affected by biofouling. Nevertheless, when compared to the fouled FO membrane inside the MBR, the value is more than 40 times higher, reaching almost 500 ng of ATP per cm^2. These living organisms are found in the feed water and not in the draw solution (seawater), as the results for the concentration of ATP in the

samples for the FW and DDS reveal. For the former, the concentration is 0.29 μg/L, and the latter has a concentration of less than 0.1 μg/L.

4.6.4 Transparent Exopolymer Particles Analysis

Transparent exopolymer particles (TEP) are deformable, gel-like, transparent particles of acid mucopolysaccharides suspended in the water mass that appear in many forms, usually in a microscopic range (>0.4 μm), and are ubiquitous to freshwater and marine environments (Bar-Zeev et al. 2009).

Fig. 4.20 and 4.21 show pictures of the FO membrane seen from the support layer, where the support mesh can be identified. The TEP are clearly affecting this side of the membrane, because there is a lot of material being accumulated. Based on this observations and the fact that the support layer is facing the draw solution, the TEP are coming from the seawater. In the literature, seawater has been identified as a major source of these particles. Problems associated with TEP fouling filtration membranes or RO desalination systems are attributable to the TEP found in the feed water itself, rather than TEP coming from the bacteria in the water, meaning that disinfection of the feed water is not useful to prevent these particles from causing fouling (Berman et al. , Bar-Zeev et al. 2009).

The cleaning potential of two solutions was tested to analyze the best option for TEP removal. The first solution (Solution 1) has the same composition as the one used for the chemical cleaning of the membrane fouling in section 4.2 (Table 4.2). The

second one contains 1% aqueous solution of NaOCl (pH 7.6) (Solution 2). The protocol was cleaning the membrane before staining the TEP with the dye, using petri dishes with the solution and cutting two pieces of the fouled membrane, one for each cleaning solution. After being submerged for 10 minutes, a quick 1-minute rinse with DI water was practiced before the dyeing process.

Fig. 4.22 and 4.23 show the images of the membrane cleaned with Solution 1. The solution effectively cleaned the TEP particles from the membrane, segregating the remaining ones into small particles instead of being clumped in big formations. For the Solution 2, almost no TEP can be found in the membrane (Fig. 4.24). Note that, unlike the Solution 1, in this case there are no small particles left after the cleaning, suggesting that the effectiveness of Solution 2 is greater.

Fig. 4.25 and 4.26 show an image from the active layer (AL) for the fouled membrane. It can be noted that no TEP is attached to the thin film layer of the membrane, not when the focus is set on the AL (Fig. 4.25), nor when the microscope focuses on the support mesh on the side of the AL (Fig. 4.26). Based on these images, it can be said that no TEP is crossing from the DS to the feed water, and no TEP is found in the SWWE, so the active layer is not being affected by TEP fouling.

Fig. 4.20 – TEP fouling in the support layer of an FO membrane (60x)

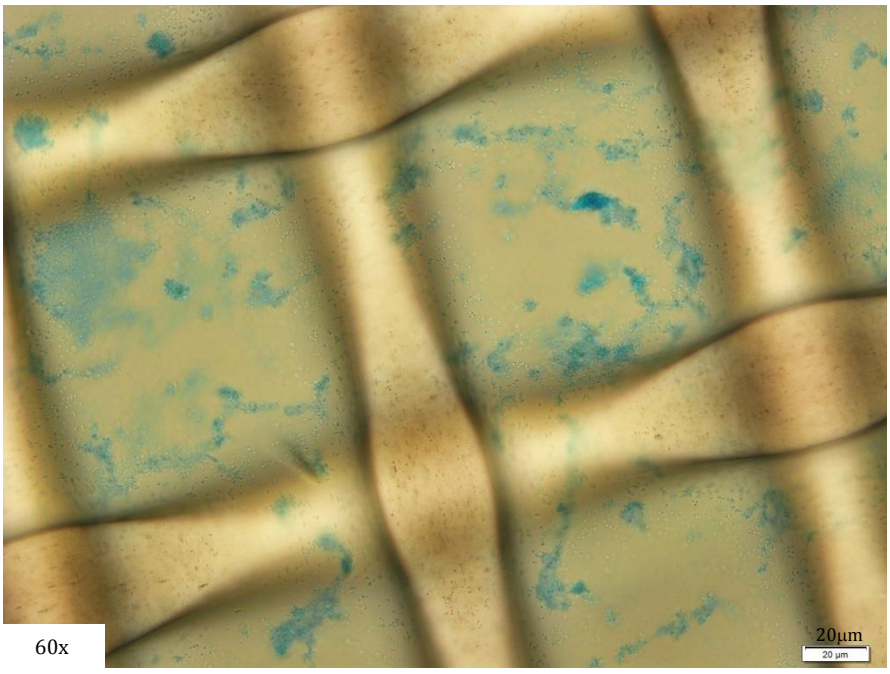


Fig. 4.21 – TEP fouling in the support layer of an FO membrane (100x)

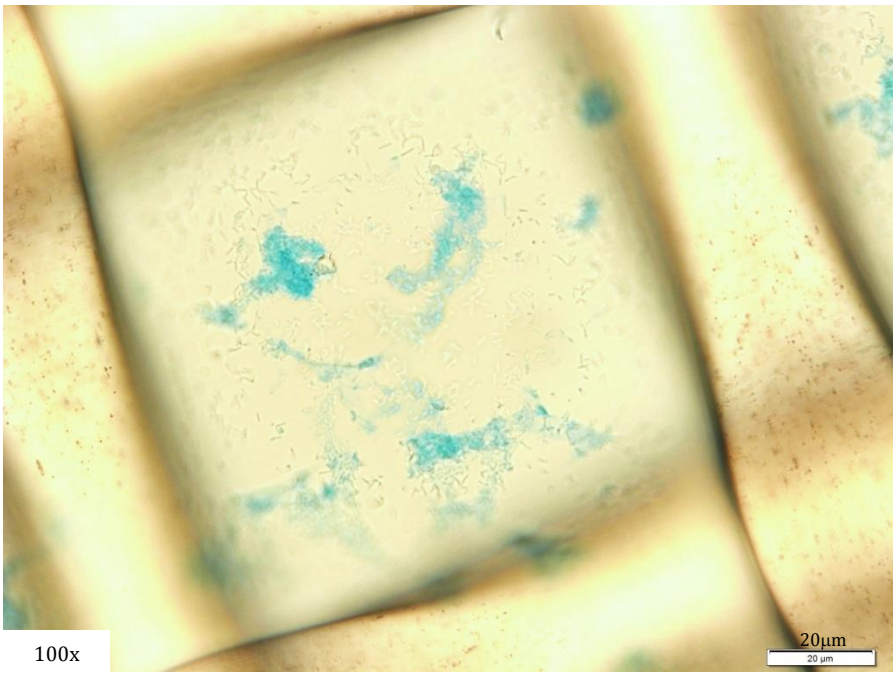


Fig. 4.22 – TEP fouling in the support layer of a cleaned FO membrane (60x) – (Solution 1)

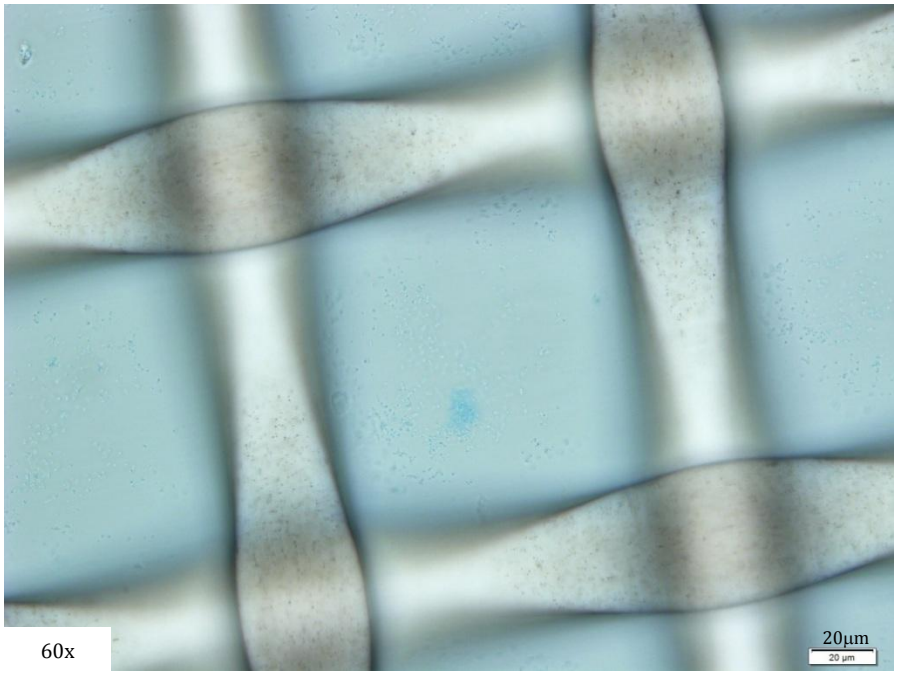


Fig. 4.23 – TEP fouling in the support layer of a cleaned FO membrane (100x) – (Solution 1)

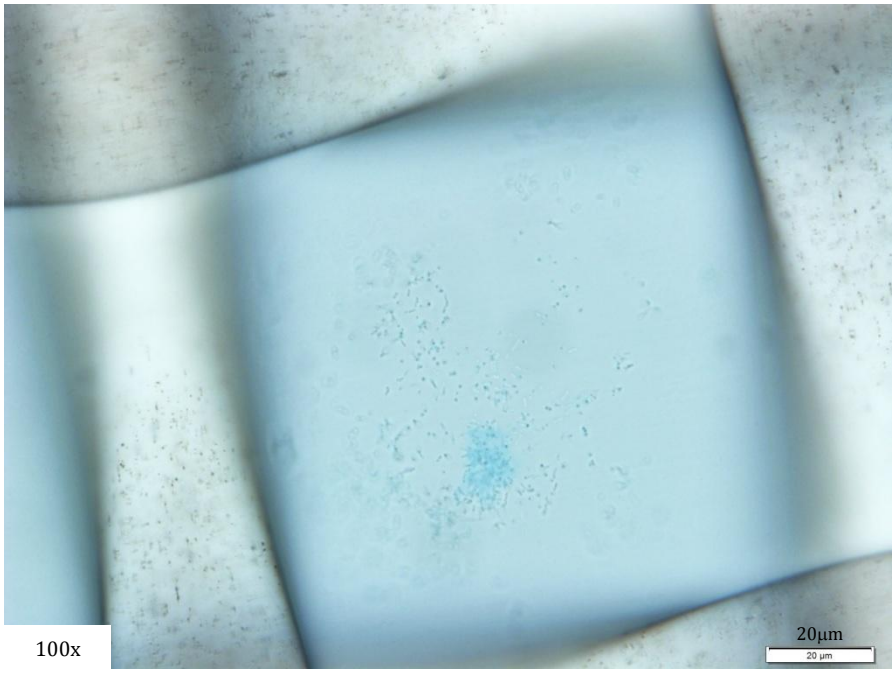


Fig. 4.24 – TEP fouling in the support layer of a cleaned FO membrane (60x) – (Solution 2)

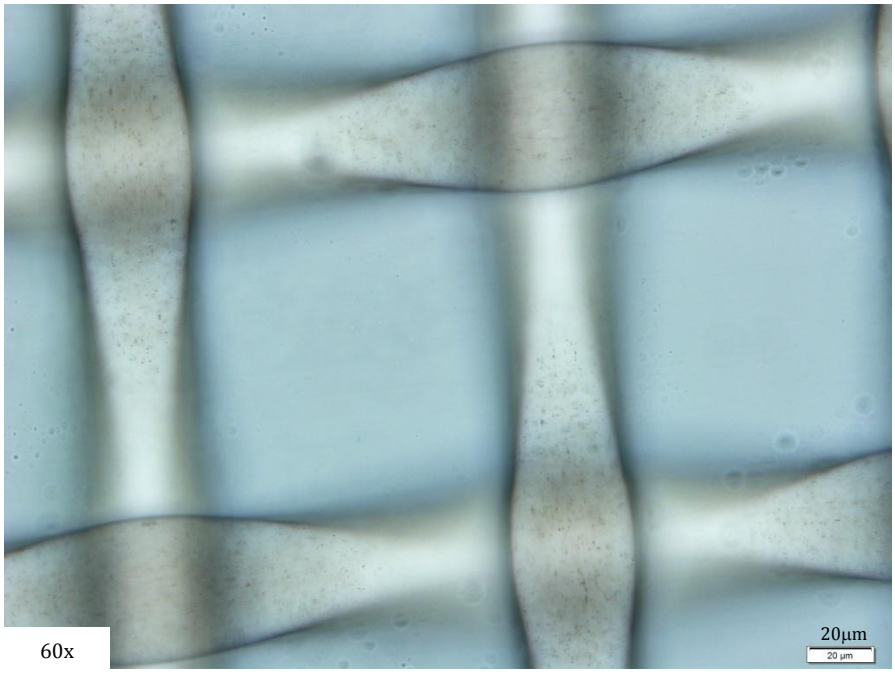


Fig. 4.25 – Focused active layer of a FO membrane (60x)

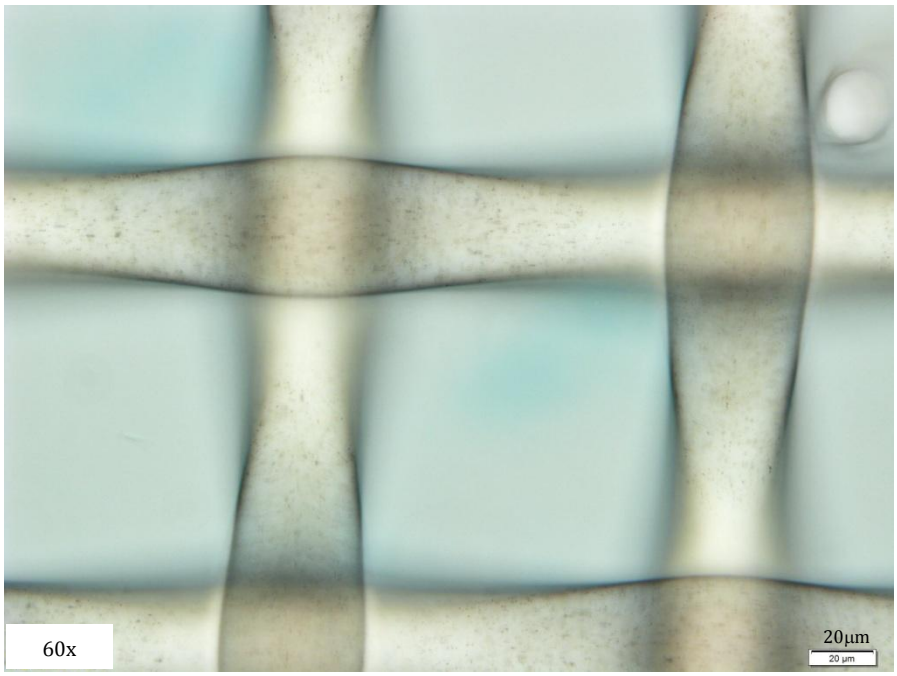
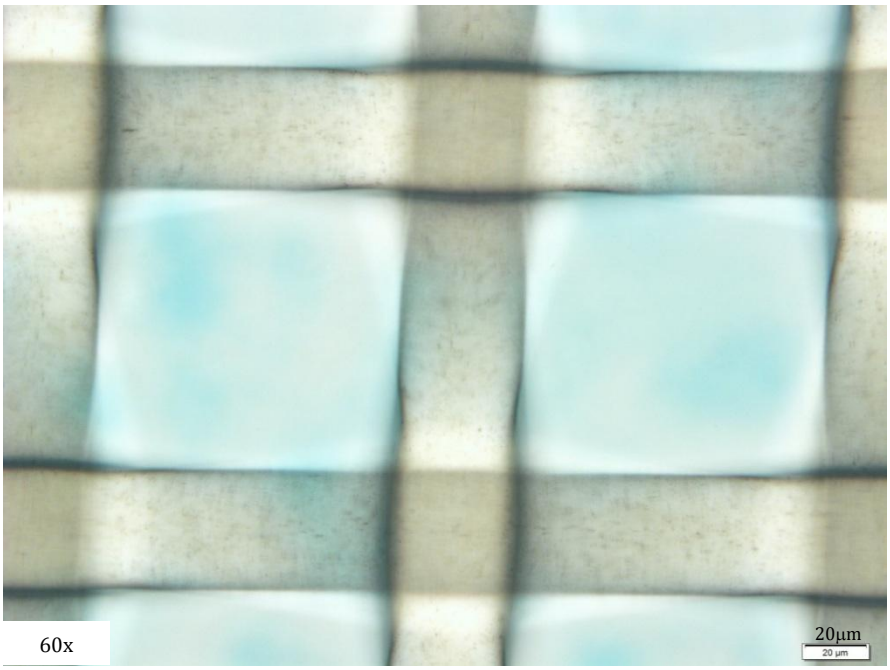


Fig. 4.26 – Focused mesh on the active layer side of a FO membrane (60x)



5. Conclusions and Recommendations

5.1 Conclusions

- The flux for the FO process using SWWE as feed and seawater as DS varies from 6.2 to 2.6 L/m^2-h, with an average of 3.75 L/m^2-h. The draw solution was diluted from 52,000µS/cm to 22,000µS/cm, creating a feed for the RO process that can be desalinated at low pressure (15 bars), producing a permeate with a conductivity lower than 500µS/cm.

- The average recovery for the FO cycles is 7% in this plate-and-frame configuration, but it can be increased further than 30% if another 3 cells with the same size are immersed in the tank.

- FO membranes proved to be an effective barrier against nitrogen and phosphorus species present in the SWWE. Phosphate removal was as high as 76%, and removal for nitrate and ammonium was 100%.

- The flux recovery when using the secondary wastewater effluent is around 90% when compared to the first day of tests, similar to the recovery when comparing the new membrane used with DI water as feed and the cleaned membrane with the same feed.

- Cleaning with air scouring for 15 minutes proved to be very effective in removing the fouling of the membrane (regardless that not all of the fouling agents are visible), because the increase in flux recovery when compared to chemical cleaning is less than 3%.

- After chemical cleaning, comparing with the flux with DI water as feed for the FO process, the irreversible fouling can be approximated as 8.2%.

- In real conditions of water reuse applications, FO membranes were able to reject most of the micropollutants; rejections were mainly moderate (29 – 75%) and high (95%), with one exception, BPA (8 – 49%).

- LPRO after FO was quite effective, rejecting micropollutants at more than 98%.

- Ionic and HB neutral compounds were rejected more effectively when the FO membrane was fouled due to the higher negative charge of the membrane and the higher hydrophilicity imparted by the fouling layer, along with an increased adsorption capacity and the reduced mass transport capacity. Rejection of HL neutral compounds decreased an average of 5% with the fouled membrane, caused by membrane swelling which results in a higher MWCO. Again BPA is the compound with the lowest rejection with 48.7%.

- The DOC in the DDS has no significant increment compared to the FSW, reflecting the ability of the FO membrane to reject dissolved organic carbon.

- LC-OCD chromatograms and the 3-D FEEM images suggest that biopolymers, including polysaccharides, proteins and protein-like substances, among other organic particles similar in size present in the feed water (SWWE), are forming a fouling layer in the thin film of the FO membrane, reducing the flux and thus, affecting the efficiency of the dilution process.

- TEP can be seen in the support layer of the FO membrane in contact with the seawater, which contains a significant amount of these particles, affecting the flux of the FO process. Chemical cleaning with a solution of 1% NaOCl during 10 minutes proved to be effective in removing the TEP.

5.2 Future Recommendations

- Flux recovery will be higher when cleaning the membrane in the support layer with chemical cleaning.

- Chemical cleaning in-line is recommended in the DS side (support layer) of the membrane with a solution of 1% NaOCl, effectively removing the TEP attached, and possibly removing other biopolymers causing fouling.

- Increasing the membrane area in the FO process by adding additional cells in the feed tank will increase the recovery of the system and its performance.

- An analysis of the energy and cost requirements of the system will be helpful to compare this new technology with the available options in the market.

- Development of a pilot plant of the hybrid system will reflect the applicability and advantages of the system to remove contaminants and obtain a low cost permeate from wastewater reclamation and low pressure desalination.

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APPENDIX

Table 7.1 – Characterization of the wastewater effluent from Jeddah (SWWE)

Nitrate (NO_3^-) (mg/L)	Nitrite (NO_2^-) (mg/L)	Ammonium (NH_4) (mg/L)	Phosphate (PO_4) (mg/L)	Total N (mg/L)
2.48	0.03	0.085	2.18	<5

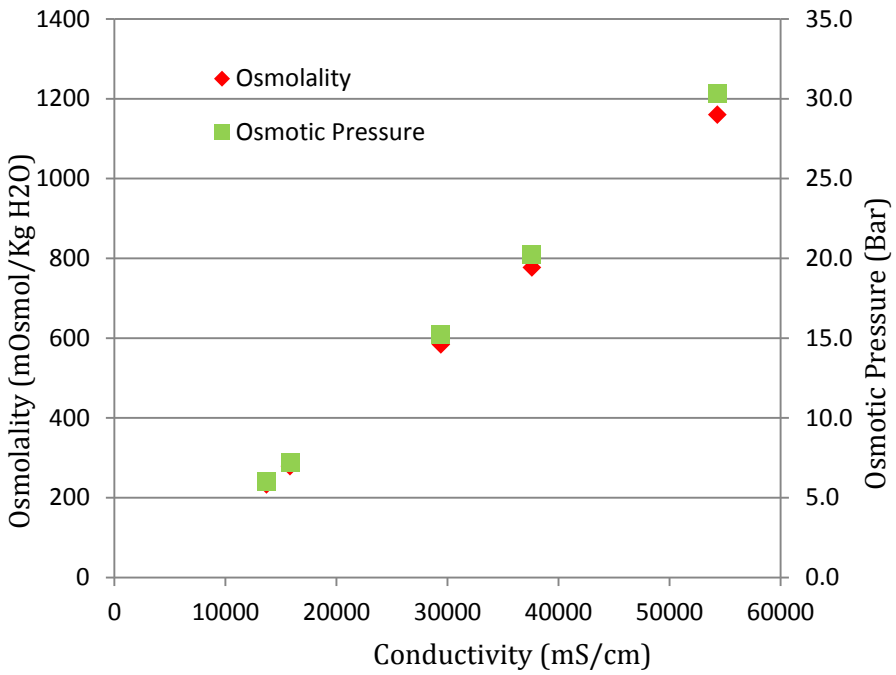
Table 7.2 – Limit of quantification for each individual compound and each sample, limits of detection usually are three-fold lower.

Sample	Unit	SWWE/SS collected	SWWE/SS spiked	DS diluted	Blank sample	Permeate LPRO
1,4-Dioxane	µg/L	0.5	0.5	0.5	0.5	0.5
17α-Ethynilestradiol	µg/L	0.005	0.005	0.001	0.001	0.001
Bisphenol A	µg/L	0.025	0.025	0.005	0.005	0.005
Carbamazepine	µg/L	0.05	0.05	0.01	0.01	0.01
Caffeine	µg/L	0.1	0.1	0.01	0.01	0.01
Fenoprofen	µg/L	0.05	0.05	0.01	0.01	0.01
Gemfibrozil	µg/L	0.05	0.05	0.01	0.01	0.01
Ketoprofen	µg/L	0.05	0.05	0.01	0.01	0.01
Metronidazole	µg/L	0.05	0.05	0.01	0.01	0.01
Naproxen	µg/L	0.05	0.05	0.01	0.01	0.01
Acetaminophen	µg/L	0.05	0.05	0.01	0.01	0.01
Phenazone	µg/L	0.05	0.05	0.01	0.01	0.01
Ibuprofen	µg/L	0.05	0.05	0.01	0.01	0.01

Table 7.3 – Concentration of MP in blank sample

Compound (MW in g/mol)	Unit	Blank sample
1,4-Dioxane (88)	µg/L	< 0.5
Acetaminophen (151)	µg/L	< 0.001
Metronidazole (171)	µg/L	< 0.005
Phenazone (188)	µg/L	< 0.01
Caffeine (194)	µg/L	< 0.01
Bisphenol A (228)	µg/L	< 0.01
Carbamazepine (236)	µg/L	< 0.01
EE2 (296)	µg/L	< 0.01
Ibuprofen (206)	µg/L	< 0.01
Naproxen (230)	µg/L	< 0.01
Fenoprofen (242)	µg/L	< 0.01
Gemfibrozil (250)	µg/L	< 0.01
Ketoprofen (254)	µg/L	< 0.01

Fig. 7.1 – Correlation among conductivity, osmolality and osmotic pressure of seawater



$$C = 0.032\theta - 0.1061 \qquad \text{Equation (7-1)}$$

Where C is the NaCl concentration in g/KgH_2O and θ is the osmolality in milliOsmol/ KgH_2O

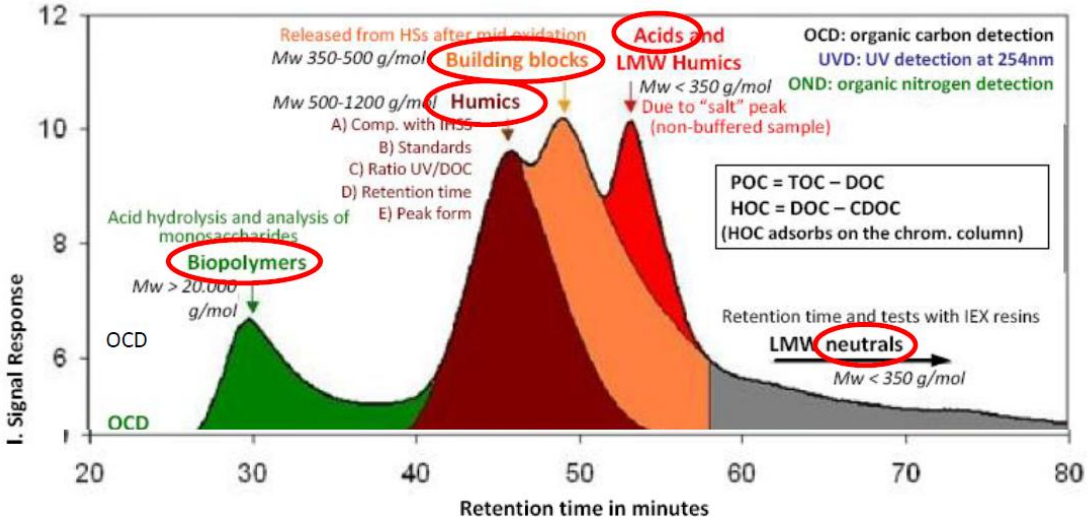
$$\pi = 0.8169C - 0.0037 \qquad \text{Equation (7-2)}$$

Where π is the osmotic pressure in Bar and C is the NaCl concentration in g/KgH_2O.

Table 7.4 – Zeta Potential results for the FO membrane in different conditions

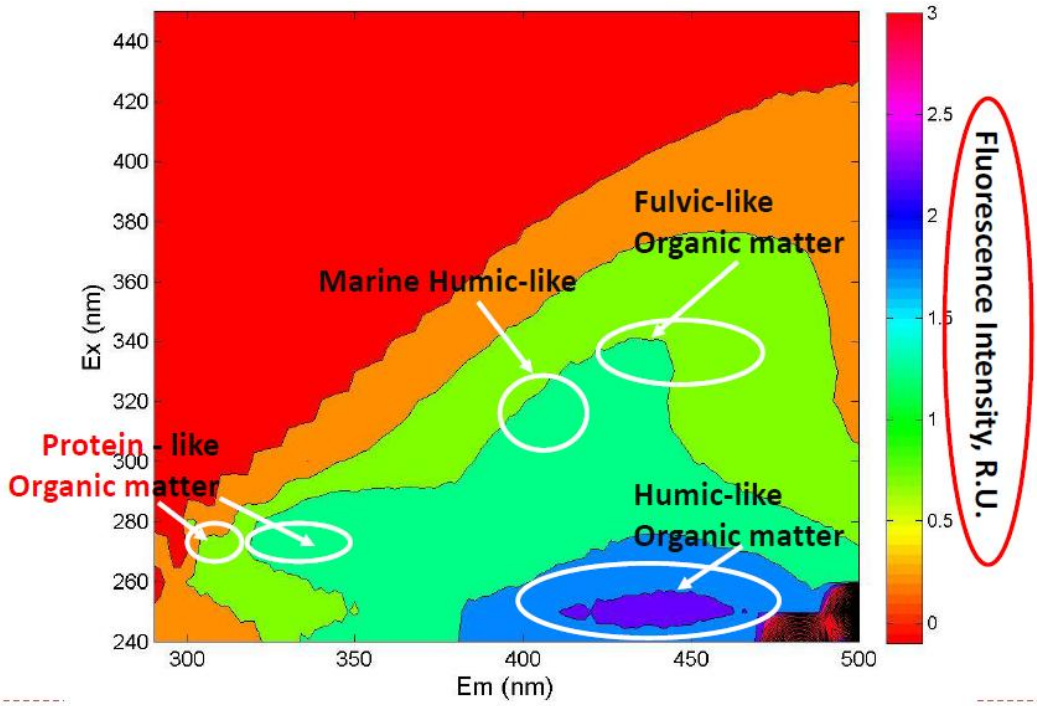
Electrolyte	Membrane	pH	ZP [mV]	ZP Std Dev [mV]
KCl	New	3.92	3.77	2.98
		4.75	-6.10	6.09
		5.72	-15.42	7.23
		7.24	-24.05	7.71
		7.66	-25.86	4.79
		8.31	-27.30	6.77
SWWE	New	7.48	-25.56	2.43
		7.44	-25.06	3.10
		6.68	-20.47	0.49
		6.30	-19.46	0.69
		6.15	-18.81	0.53
		5.91	-18.34	0.73
		5.51	-17.42	0.34
		5.09	-16.70	0.20
		4.67	-15.84	0.22
		4.24	-14.55	0.49
		3.75	-12.86	0.13
SWWE	Fouled	7.40	-30.64	4.49
		6.95	-30.34	4.77
		6.53	-28.22	1.74
		6.14	-25.84	2.64
		5.74	-23.17	2.92
		5.35	-21.22	0.47
		4.97	-20.98	0.58
		4.57	-19.20	1.34
		4.16	-15.62	0.89

Fig. 7.2 – Ideal LC-OCD Chromatogram



Source: DOC-LABOR, Germany (adapted from (Amy et al. 2010))

Fig. 7.3 – Typical spectra for 3-D FEEM



Source: Adapted from (Amy et al. 2010)

Table 7.5 – ATP calibration data

ATP (µg/L)	RLU
100	16,611,590
10	1,741,320
1	159,805
0.1	11,758

Fig 7.4 – ATP calibration curve