
# BIOFOULING CONTROL IN REVERSE OSMOSIS MEMBRANES FOR WATER TREATMENT

**Gerard Massons Gassol**

UNIVERSITAT ROVIRA i VIRGILI

# Biofouling control in reverse osmosis membranes for water treatment

Gerard Massons Gassol

**DOCTORAL THESIS**

**2017**

UNIVERSITAT ROVIRA I VIRGILI
BIOFOULING CONTROL IN REVERSE OSMOSIS MEMBRANES FOR WATER TREATMENT
Gerard Massons Gassol

UNIVERSITAT ROVIRA I VIRGILI
BIOFOULING CONTROL IN REVERSE OSMOSIS MEMBRANES FOR WATER TREATMENT
Gerard Massons Gassol

Gerard Massons Gassol

# Biofouling control in reverse osmosis membranes for water treatment

Doctoral Thesis

Supervised by Prof. Dr. Ricard Garcia-Valls
Co-supervised by Dr. Guillem Gilabert Oriol
Co-supervised by Dr. Tina Arrowood

Department of Chemical Engineering

UNIVERSITAT ROVIRA i VIRGILI

Tarragona

2017

UNIVERSITAT ROVIRA I VIRGILI
BIOFOULING CONTROL IN REVERSE OSMOSIS MEMBRANES FOR WATER TREATMENT
Gerard Massons Gassol

UNIVERSITAT ROVIRA i VIRGILI

I, Prof. Dr. Ricard Garcia-Valls, professor in Universitat Rovira i Virgili (URV), member of the Escola Tècnica Superior d'Enginyeria Química (ETSEQ), member of Centre Tecnològic de la Química de Catalunya (CTQC) and principle researcher of the Membrane and Process Engineering group (METEOR) of the URV,

I, Dr. Guillem Gilabert Oriol, Tarragona Leader of the Reverse Osmosis Antifouling Research and Development Platform by the Dow Chemical Company,

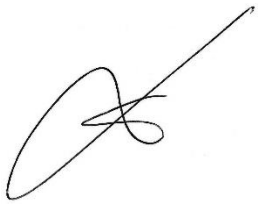
I, Dr. Tina Arrowood, Global Leader of the Reverse Osmosis Antifouling Research and Development Platform by the Dow Chemical Company,

CERTIFY:

That the present work entitled *"Biofouling control in reverse osmosis membranes for water treatment"*, presented by Gerard Massons Gassol to obtain the degree of doctor by the Universitat Rovira i Virgili, has been carried out under my supervision at the Chemical Engineering Department.

Tarragona, 4th September 2017

Prof. Dr. Ricard Garcia-Valls  Dr. Guillem Gilabert Oriol  Dr. Tina Arrowood



# Acknowledgments

Many people deserve gratitude for the successful completion of my PhD.

Foremost, I would like to express my sincere gratitude to my thesis supervisors, Prof. Dr. Ricard Garcia-Valls for his flexibility and support given. A special mention to my co-supervisors Dr. Guillem Gilabert for his understanding, fully committed support and guidance, and to Dr. Tina Arrowood for her trust, fruitful discussions, help and motivation given. It was a delightful experience to work with them on the different antifouling projects during the past years. They have been my coaches and from whom I adopted all knowledge for RO technology.

I would like to thank the thesis committee Dr. Josep Font, Dr. Wolfgang Gernjak and Dr. Markus Busch for accepting being the thesis tribunal examiners.

I thank Universitat Rovira i Virgili and The Dow Chemical Company, to allow me to do this doctorate in the Global Water Technology Center in Tarragona. I would like to acknowledge also the financial support received from Dow Chemical Ibérica, the Agency for Business Competitiveness (NEMOWATER RD14-1-003) and the Agency for Management of University and Research Grants (FI DGR).

My acknowledgments would not be complete without thanking my colleagues and coworkers. Enrique Avila, Javier de la Fuente, Javier Dewisme, David Puig and Nicolas Corgnet for sharing with me their experience in operating and troubleshooting pilot plants. Patricia Carmona, Mireia Font and Carolina Martinez for their analytical advice and support. Also to Jasna, David, Claudia, Elbir, Gerard, Yolanda, Jordi, Sonia, Supriyo, Justyna, Petra, Isa, Miquel, Angels, Lorena, Hector, Laís, Estefania, Diana, among many more, for all the time shared together.

I would also like to specially thank Veronica Gomez for her full support and encouragement, as well as Fernando Gutierrez for his technical sponsorship and assistance.

Last, but not least, I would like to make a special recognition to my parents and brother. Last words are for Ana, for her endless love and for always cheering me up.

# Abstract

Reverse osmosis (RO) filtration is one of the most competitive water purification technologies. RO systems have evolved significantly in the last years to provide real and sustainable solutions to water-related problems. They offer one of the highest levels of salts and pollutants removal, more than 99%. Its application opens new possibilities for advance water reuse strategies to reduce the stress on current potable water resources. The treatment of wastewater or seawater using RO produces high quality permeate water. One of the main hurdles that hinders RO expansion in water reuse is the loss of performance that RO elements suffer when dealing with contaminated waters. This phenomenon known as fouling has been studied over the last years, but still little progress has been made in the field. Fouling with a biological or organic origins, remains to be one of the biggest challenges for RO elements used in industrial or wastewater treatment plants.

Due to the complexity to study these problems in large scale systems, protocols need to be developed in order to mimic full-scale plants operation on a bench scale. Fouling problems are usually occurring after several months of operations. However, for a realistic time-scale research, the process needs to be accelerated in a controlled way and as similar as possible to what would be occurring naturally. Most of the biofouling testing experiments performed during this thesis have been carried out using flat cell units. The effect of different operating variables on biofouling development was studied. The role of RO module construction was also evaluated, testing different membranes and feed spacers side-by-side, to guide the improvements on the design of fouling resistant elements. To evaluate the amount of fouling generated under different conditions, an analytical method to determine the impact of biofouling in fouled samples was developed. Specific and reliable methods for biofouling quantification are critical for studying samples obtained using natural waters, where usually different types of fouling can be found.

The results from the trials performed clearly showed that different membrane chemistries can provide significant reduction in the levels of biofouling detected after operation. However, it was found that the main contributor to biofilm development was feed spacer. Large differences in the amount of biofouling generated could be associated with feed spacer presence. Feed spacer design was then studied in detail to achieve a balanced performance in spiral wound RO modules treating waters prone to biofouling. Feed spacers with various thickness, spacing and angle were tested. Some designs showed advantages in pressure drops, as well as in biologic and organic fouling accumulation.

It could be concluded that significant benefits in fouling accumulation could be obtained by optimizing module design. The scale-up of the results would result in more sustainable operation of RO element in water reuse pilot plants. Fouling resistant elements would provide a decrease in the footprint of the system by reducing energy consumption, chemical consumption and the complexity of the pretreatments.

# Resum

L'osmosi inversa (OI) és una de les tecnologies de purificació d'aigua més competitives. Els sistemes de OI han evolucionat significativament en els darrers anys per proporcionar solucions reals i sostenibles als problemes relacionats amb l'aigua. Ofereixen un dels nivells més alts d'eliminació de sals i contaminants, més del 99%. La seva aplicació obre noves possibilitats per implementar estratègies avançades de reutilització d'aigua, per tal de reduir l'estrès dels recursos hídrics potables actuals. El tractament de les aigües residuals o de mar mitjançant la OI produeix una aigua permeada d'alta qualitat. Un dels principals obstacles que dificulta l'expansió de l'ús de la OI en la reutilització aigües és la pèrdua de rendiment que pateixen els elements de OI quan tracten aigües contaminades. Els efectes que l'originen aquest fenomen, conegut com a embrutament o *fouling*, s'han estudiat intensament en els últims anys, però encara no hi ha solucions eficient. L'embrutament d'origen biològic (*biofouling*) o orgànic continua sent un dels reptes a superar en la optimització de moduls de OI per a plantes de tractament d'aigües residuals o industrials.

A causa de la complexitat d'estudiar aquests problemes en sistemes a gran escala, s'han de desenvolupar protocols per tal de reproduir l'operació de plantes a gran escala a plantes pilot escala de laboratori. Normalment, els efectes derivats de l'embrutament són només visibles després de diversos mesos d'operació. No obstant això, per a poder realizar una experimentació d'una duració realista, el procés d'embrutament ha d'accelerar-se d'una manera controlada i el més semblant possible al procés natural. La majoria dels experiments de *biofouling* realitzats durant aquesta tesi s'han realitzat mitjançant unitats de membrana plana. Es va estudiar l'efecte de diferents variables operatives en el desenvolupament del *biofouling*. També es va avaluar differencies en els resultats obtinguts provant diferents combinacions de membranes i espaiadors, per tal d'identificar les millors configuracions en el disseny d'elements resistents a l'embrutament. Per avaluar la quantitat i tipus de contaminants accumulats en diferents

condicions d'operació, es va desenvolupar un mètode analític per determinar l'impacte del *biofouling* en mostres d'elements de OI després de tractar aigua de depuradora. Els mètodes específics i fiables per a la quantificació de biofouling són crítics per estudiar mostres d'embrutament generat en aigües naturals, on generalment es poden trobar una matriu complexa de compostos.

Els resultats dels assaigs realitzats demostren clarament que algunes químiques de membrana poden proporcionar una reducció significativa en els nivells de *biofouling* detectats després de operació. No obstant això, es va trobar que el principal contribuent al desenvolupament de biopelicules era l'espaciador o *feed spacer*. Grans diferències en la quantitat de *biofouling* generat es van poder associar a la presència de l'espaciador. Es va estudiar detalladament el seu disseny per aconseguir una bona hidráulica en els mòduls de OI que tractaven les aigües contaminades. Es van provar *feed spacers* amb diversos espessors, separacions i angles entre filaments. Alguns dissenys van mostrar avantatges en la perdua de pressió que generaven, així com en acumulació d'embrutament biològic i orgànic.

Es pot concloure que es poden obtenir avantatges significatius en la resistencia dels elements de OI a l'embrutament mitjançant un disseny optimitzat del mòdul. L'escalat dels resultats resultaria en un operació més sostenible d'aquests l'elements en plantes pilot de reutilització d'aigua. Una operación més sostenible comporta una reducció en el consum d'electricitat, el consum de químics i en la complexitat dels pretractaments.

# Abbreviations

| | |
|---|---|
| AITASA | Aguas Industrials de Tarragona S.A. |
| AOC | Assimilable Organic Carbon |
| ASTM | American Society for Testing and Materials |
| ATP | Adenosine Triphosphate |
| BCA | Bicinchoninic Acid |
| BOD | Biological Oxygen Demand |
| BSA | Bovine Serum Albumin |
| BW | Brackish Water |
| C | Carbon |
| CAPEX | Capital Expenses |
| CC | Carbohydrates Carbon |
| CEB | Chemical Enhanced Backwash |
| CER | Cation Exchange Resin |
| CF | Cartridge Filter |
| CH | Carbohydrates |
| CIP | Cleaning In Place |
| COD | Chemical Oxygen Demand |
| DI | Deionized Water |
| DNA | Deoxyribonucleic Acid |
| DOC | Dissolved Organic Carbon |
| dP | Differential Pressure |
| dPI | Differential Pressure Indicator |
| DW&PS | Dow Water & Process Solutions |
| FI | Flow Indicator |
| FREPP | Fouling Resistant Elements Pilot Plant |
| LC-OCD | Liquid Chromatography Organic Carbon Detection |
| LDP | Lower Differential Pressure |
| LOD | Limit Of Detection |

| | |
|---|---|
| MBR | Membrane Bioreactor |
| MFS | Membrane Fouling Simulator |
| N | Nitrogen |
| ND | Not Detected |
| NN | Protein Nitrogen |
| ORP | Oxidation-Reduction Potential |
| Osmota | Flat Cell Experimental Plant |
| P | Phosphorous |
| PBS | Phosphate Buffer Saline |
| PE | Polyethylene |
| PI | Pressure Indicator |
| PN | Proteins |
| PP | Polypropylene |
| PV | Pressure Vessel |
| R&D | Research & Development |
| RO | Reverse Osmosis |
| RPM | Revolutions Per Minute |
| SMBS | Sodium Metabisulfite |
| SPI | Strands Per Inch |
| STD | Standard |
| TDS | Total Dissolved Solids |
| TEP | Transparent Exopolymeric Substances |
| TMP | Trans-Membrane Pressure |
| TN | Total Nitrogen |
| TOC | Total Organic Carbon |
| TSS | Total Suspended Solids |
| UF | Ultrafiltration |
| WW | Wastewater |
| WWTP | Waste Water Treatment Plant |

# Table of content

# List of figures

# List of tables

# 1 AIM OF THE THESIS

The aim of the thesis is to research on reverse osmosis design features and operating parameters that would improve its performance when treating waters prone to biological fouling.

# 2 THESIS OUTLINE

Water reuse strategies are a promising approach to reduce water scarcity problems. Thanks to advances in reverse osmosis (RO) membranes, this technology is being increasingly applied in the field of advanced water purification plants. Membranes systems have lower footprint and more robust operation than conventional treatments. However, RO systems dealing with challenging waters can suffer from a rapid loss of performance, a phenomenon known as fouling. Organic and biological fouling in particular, are one of the biggest concerns in water reuse pilot plants.

The main goal of this doctoral research is to obtain fundamental understanding on how biological fouling affects RO elements and what parameters influence the biofilm development. Understanding these correlations is of utmost importance since it will allow the optimization of pretreatments, reverse osmosis module designs and cleaning protocols. The ultimate goal of this research is to improve the performance of reverse osmosis membranes when used to purify contaminated waters. Chemical and energy consumption on RO plants would be reduced and water reuse strategies would become more cost-effective.

The thesis is first focused on the implementation of operational and analytical protocols to be used for biofouling research. These protocols will be used to understand the evolution of biofilm on the membrane surface and on the feed spacer within the feed-concentrate channel. Flat cell bench pilot units are useful tools for quick and reliable biofouling screening tests. Several factors can potentially impact biofilm development.

Operating conditions such as water temperature, cross-flow velocity or bio-assimilable nutrient levels, as well as RO module components, such as feed spacer and membrane surface, can be evaluated separately. The flat sheet testing allows a fundamental understanding of the evolution and triggers of biofouling development, with minimum resources and flexibility to precisely modify different parameters.

Analytical tools are also implemented. Specific quantification of EPS related compounds offers critical information regarding biofouling growth. The available analytical techniques used routinely for fouling study are not enough for an in-depth biofouling characterization. The new methods developed in this thesis will aid in screening and identifying different developments to provide higher fouling resistance to module designs.

Using the operational and analytical resources developed in this thesis, strategies for managing biofouling in reverse osmosis plants are also evaluated. Dominant effects influencing biofilm development are established and used to implement effective strategies to reduce or delay biofouling. These involve innovative solutions such as dosing strategies for non-oxidizing biocide formulations, novel RO configurations and new cleaning strategies. The result of this work can be translated into savings to customers, thanks to a higher reliability and more stable performance when treating challenging water than standard configurations.

This thesis is divided into different chapters, each one covering a particular research piece needed to reach the final goals previously defined. A brief summary of the main content of each chapter is provided in the following sections.

### 2.1 Chapter 1: Literature review

This chapter provides an overview in the membrane filtration technologies, being focused on reverse osmosis and its fundamentals. The impact of reverse osmosis

membranes in water purification systems is described and the factors that are limiting their full performance in certain challenging applications are discussed in detail.

### 2.2 Chapter 2: Method for distinguishing between abiotic organic and biological fouling of reverse osmosis elements used to treat wastewater

This chapter addresses a practical method to characterize foulants more specifically. The aim of the study is to distinguish between abiotic organic and biological fouling, which are challenging to discern analytically. This method offers an option to easily distinguish the dominant foulant substances as having either a biological or abiotic origin and can be easily applied in industrial water treatment plants. The method will serve to gain deeper knowledge of fouling formation and differentiate the impact of biological and organic fouling separately.

### 2.3 Chapter 3: Comparing biofouling development in membrane fouling simulators and spiral wound reverse osmosis elements using river water and municipal wastewater

This chapter shows the steps taken to reproduce the biofouling observed in industrial scale RO element pilot plants in small flat sheet units. The intention is to show the reliability and reproducibility of these units to study different feed spacer design using reverse osmosis coupons. A detailed comparison is performed using two different feed waters: river and wastewater. The flat sheet testing protocol reduces the resources needed for RO technology evaluation, including smaller samples size, multiple repetitions operated in parallel and more flexible operation than spiral wound elements.

### 2.4 Chapter 4: Development and application of an accelerated biofouling test in flat cell

This chapter discusses the steps followed to establish an accelerated reverse osmosis membrane biofouling test protocol. Bioassimable nutrients are dosed into water from the Ebro River, which was then fed into a membrane flat cell pilot plant. Using this approach, the biofouling trials can be drastically reduced from months to days, enabling rapid screening of different membrane configurations. Results are compared in terms of operational and analytical parameters to select the optimum dosing strategy.

### 2.5 Chapter 5: Effect of shear and permeation in biofouling development in different reverse osmosis membranes and feed spacers

The focus of this chapter is to study the impact of membrane chemistry and feed spacer designs in biofouling development. Several experimental tools are used including: a Center for Disease Control (CDC) reactor, a Membrane Fouling Simulator (MFS) and a membrane permeation Flat Cell (FC) unit. The methods and capabilities presented in this report provide a means to evaluate the biofouling resistance provided by the membrane chemistries and feed spacers tested.

### 2.6 Chapter 6: Conclusions

A final outlook of the main conclusions of this research are summarized in this chapter. Results interpretation and an overview of the previous chapters is included to effectively provide the key-takeaways learned during the development of the PhD thesis.

# 1 OBJECTIUS DE LA TESI

L'objectiu de la tesi és investigar les característiques del disseny d'osmosi inversa I els paràmetres operatius que millorin el seu funcionament quan es tracti d'aigües amb tendència a contaminació biològica.

# 2 DESCRIPCIÓ DE LA TESI

Les estratègies de reutilització d'aigües són una opció prometedora per reduir els problemes d'escassetat d'aigua. Gràcies als avenços en les membranes d'osmosi inversa (OI), aquesta tecnologia s'està aplicant cada vegada més en el camp de les plantes de depuració d'aigües residuals. Els sistemes de membranes tenen un menor impacte i un funcionament més robust que els tractaments convencionals. Tanmateix, els sistemes de RO que s'operen amb aigües complexes, poden patir una ràpida pèrdua de permeabilitat, un fenomen conegut com a embrutament o fouling. L'embrutament d'origen orgànic i biològic en particular són un dels majors reptes de les plantes pilot de reutilització d'aigua.

L'objectiu principal d'aquesta investigació doctoral és obtenir una comprensió fonamental sobre com l'embrutament biològic afecta els elements OI i quins paràmetres influeixen en el desenvolupament del biofilm o bio-pel·lícula. Aquestes correlacions és de gran importància ja que permetrà optimitzar els pretractaments, els dissenys dels mòduls d'osmosi inversa i els protocols de neteja. L'objectiu final d'aquesta investigació és millorar el funcionament de les membranes d'osmosi inversa quan s'utilitzin per tractar aigües contaminades. Es reduiria el consum energètic i de productes químics de les plantes RO i les estratègies d'aprofitament de l'aigua serien més factibles d'implementar.

La tesi s'ha centrat inicialment en el desenvolupament de protocols operatius i analítics que s'utilitzaran per a la recerca sobre el *biofouling*. Aquests protocols permetran entendre

l'evolució del biofilm a la superfície de la membrana i en l'espaciador o *feed spacer*. Les plantes pilot de membrana plana són eines útils per realitzar proves de detecció de *biofouling* ràpides i fiables. Diversos factors poden tenir un impacte potencial en el desenvolupament del biofilm. Les condicions d'operació, com ara la temperatura de l'aigua, el caudal d'alimentació o els nivells de nutrients biodegradables que conté l'aigua, així com els components del mòdul de OI, com ara el *feed spacer* i la superfície de la membrana, es poden avaluar separadament. Els tests de membrana plana obtenir un coneixement fonamental de l'evolució i els desencadenants del desenvolupament de *biofouling*, amb recursos mínims i flexibilitat per modificar amb precisió diferents paràmetres durant l'experimentació.

També s'han desenvolupat noves eines analítiques. La quantificació específica dels compostos relacionats amb els polímers excretats per el biofilm ofereix informació crítica sobre el creixement del *biofouling*. Les tècniques analítiques disponibles utilitzades rutinàriament pel seu estudi no són suficients per a una caracterització en profunditat de *biofouling*. Els nous mètodes desenvolupats en aquesta tesi ajudaran a la detecció i identificació de diferents estratègies per proporcionar una major resistència als dissenys de mòduls de OI.

Mitjançant els protocols analítics i d'operació desenvolupats en aquesta tesi, també s'avaluen estratègies per a la gestió del *biofouling* en plantes d'osmosi inversa. Els efectes dominants que influeixen en el desenvolupament del biofilm s'estableixen i s'utilitzen per implementar estratègies efectives per reduir o retardar el *biofouling*. Aquests inclouen solucions innovadores, com ara estratègies de dosificació per a formulacions de biocides no oxidants, noves configuracions de OI i noves estratègies de neteja. El resultat d'aquest treball es pot traduir en estalvis per als consumidors finals, gràcies a una major fiabilitat i un rendiment més estable que les configuracions estàndards quan tracten aigües complexes.

Aquesta tesi es divideix en diferents capítols, cadascun dels quals cobreix una determinada peça de recerca necessària per assolir els objectius finals definits prèviament. En les següents seccions es proporciona un breu resum del contingut principal de cada capítol.

### 2.1 Capítol 1: Revisió de literatura

Aquest capítol ofereix una visió general de les tecnologies de filtració mitjançant membranes, especialment sobre l'osmosi inversa i els seus fonaments. Es descriu tant l'impacte de les membranes d'osmosi inversa en els sistemes de purificació d'aigua com els factors que limiten el seu rendiment en determinades aplicacions d'aigües contaminades.

### 2.2 Capítol 2: Mètode per a distingir entre la contaminació abiòtica orgànica i biològica dels elements d'osmosi inversa utilitzats per tractar les aigües residuals

En aquest capítol s'aborda un mètode pràctic per a caracteritzar més específicament els compostos que causen embrutament en els sistemes de filtració. L'objectiu de l'estudi és diferenciar analíticament els contaminants orgànics d'origen abiòtic orgànica dels d'origen biològic. Aquest mètode es basa en un protocol simple per classificar els compostos orgànics que causen embrutament i es pot aplicar fàcilment en plantes de tractament d'aigües industrials. El mètode servirà per obtenir un coneixement més profund en la formació de l'embrutament i diferenciar l'impacte causat per la contaminació biològica i orgànica per separat.

## 2.3 Capítol 3: Comparació del desenvolupament de biofouling en els membrane fouling simulators i en elements d'osmosi inversa en espiral, utilitzant aigua de riu i aigua residual

En aquest capítol es mostren els passos necessaris per reproduir en petites unitats de membrana plana el *biofouling* observat en plantes d'elements industrial osmosi inversa (OI). La intenció és mostrar la fiabilitat i reproductibilitat d'aquestes unitats per estudiar diferents dissenys d'espaiadors mitjançant petits cupons. Es realitza una comparació detallada utilitzant dues aigües diferents: de riu i residual. Realitzar els tests amb membrana plana redueix els recursos necessaris per avaluar les estratègies d'optimització de la OI, incloent mostres més petites, múltiples repeticions operades en paral·lel i un funcionament més flexible que els elements industrials en espiral.

## 2.4 Capítol 4: Desenvolupament i aplicació d'un test accelerat de biofouling en membrana plana

En aquest capítol es detallen els passos a seguir per establir un protocol de formació accelerada de *biofouling* en membranes planes d'osmosi inversa. Es dosifiquen nutrients bioassimables en l'aigua del riu Ebre, que s'utilitza com alimentació a la planta pilot. Mitjançant aquesta metodologia, la duració dels assaigs de *biofouling* es poden reduir dràsticament de mesos a dies, cosa que permet testejar diferents configuracions de membrana de manera ràpida. Els resultats es comparen en termes dels paràmetres operació i analítics per a seleccionar l'estratègia de dosificació òptima.

## 2.5 Capítol 5: Efecte de la turbulència i permeabilitat en el desenvolupament de biofouling en diferents membranes i espaiadors

L'enfoc d'aquest capítol és estudiar l'impacte de la química de la membrana i els dissenys d'espaiador en el desenvolupament del *biofouling*. S'han utilitzat diverses eines

experimentals que inclouen: un reactor del Center for Disease Control (CDC), un Membrane Fouling Simulator (MFS) i una unitat de membrana plana (FC). Els mètodes i unitats que es presenten en aquest capítol proporcionen un mitjà per quantificar la resistència al embrutament biològic proporcionat per les química de membrana i els espaiadors provats.

## 2.6 Capítol 6: Conclusions

Una revisió final de les principals conclusions estan resumides en aquest capítol. La interpretació dels resultats i conclusions del capítols anteriors permeten obtenir una visió general detallada dels factors crítics identificats i els passos seguits durant el desenvolupament de la tesi.

UNIVERSITAT ROVIRA I VIRGILI
BIOFOULING CONTROL IN REVERSE OSMOSIS MEMBRANES FOR WATER TREATMENT
Gerard Massons Gassol

# Chapter 1

## Literature review

**This chapter is pending to be submitted**

# 1 INTRODUCTION

Due to the exponentially growing world population, water scarcity is being recognized as one of the main threats that humanity is facing globally. Water is an essential resource, but only 1% of water on Earth is drinkable and accessible. Since 1990, 2.6 billion people gained access to improved sources of potable water thanks to the coverage of the use of improved drinking water sources [1]. However, one out of eight people are still lacking access to safe water and 2 million deaths annually are related with contaminated water consumption [2]. Large amounts of freshwater are required to meet the rising food and energy demand. Therefore, freshwater shortage and declining feed water quality are important issues affecting the economic and social progress in many countries. In fact, Richard Smalley, Nobel Prize in 1996, identified water scarcity as one of the most pressing needs for humanity in the 21st century [3].

In order to reduce the stress on current potable water resources, the use of alternative water sources is promoted. Water purification systems have evolved significantly in the last years to provide affordable and sustainable solutions to water-related problems. Membrane technology based water treatment systems are an economically competitive solution, contributing to the availability of safe freshwater for personal and industrial use [4]. Membranes are a physical barrier capable of efficiently remove contaminants from feed water. The main advantage is that the quality and safety of the water produced is always ensured regardless of any variability on the influent water quality.

**Table 1-1. Rejection of pressure driven membrane filtration technologies**

| | Suspended solids | Bacteria | Viruses | Multivalent ions | Monovalent ions | Water |
|---|---|---|---|---|---|---|
| Microfiltration | ✓ | ✓ | | | | |
| Ultrafiltration | ✓ | ✓ | ✓ | | | |
| Nanofiltration | ✓ | ✓ | ✓ | ✓ | | |
| Reverse Osmosis | ✓ | ✓ | ✓ | ✓ | ✓ | |

For pressure driven membrane processes, the driving force is a pressure gradient difference across the membrane. Microfiltration, ultrafiltration, nanofiltration and reverse osmosis (RO) are ranked by a decreasing membrane pore size and an increasing rejection ability of smaller species [5], resulting in higher pressure required to operate (Table 1-1). The rapid growth of membrane separation technologies is attributed to the increasing health awareness and increasing regulatory controls.

Cross-flow membrane filtration is the most competitive technology for removing dissolved salts and pollutants, and RO is the most commonly used today. Reverse osmosis membranes offer the finest level of filtration available, able to remove even dissolved compounds, to obtain safe and clean water. RO systems have a high effectiveness in removing bacteria, viruses and common chemical contaminants like heavy metals, micro pollutants, chromium or nitrates. RO technology offers the possibility to produce freshwater from alternative sources such as seawater and wastewater for municipal and industrial water applications. RO has replaced other water purification technologies such as Multi-Stage Flash distillation, as a more energy efficient alternative [6]. Nowadays, the capacity of more than 15,000 reverse osmosis plants

worldwide is 86 million cubic meters per day [7], being Dow Water and Process Solutions the leading supplier of commercial RO elements.

## 2 REVERSE OSMOSIS TECHNOLOGY

Reverse osmosis systems are based on a semipermeable membrane in which the natural process of osmosis is reversed. This is achieved by applying a pressure greater than the osmotic pressure of the solution to be filtered, so the pure water flows through the membrane while leaving the contaminants behind. RO membranes can remove more than 99% of the dissolved solids contained in the feed water.

### 2.1 Reverse osmosis fundamentals

Semipermeable membranes have the ability to be permeable to pure water, but dissolved ions are rejected by the membrane. Osmosis is a natural phenomenon that occurs when two solutions with different concentrations of solutes are separated by a semipermeable membrane. Water will naturally flow through the semipermeable membrane from the diluted solution to the concentrated solution. The flow of water is driven by the osmotic pressure difference on the two sides of the membrane. Osmotic pressure is described by the Van't Hoff equation (1) for dilute solutions:

$$\pi = \Phi \cdot C_i \cdot R \cdot T \tag{1}$$

$\pi$ - Osmotic pressure [pis]
$\Phi$ - Osmotic pressure coefficient
$C_i$ - Concentration of the solute [lb/gal]
$R$ - Gas constant
$T$ - Absolute temperature [K]

If a hydrostatic pressure greater than the osmotic pressure is applied on the concentrated side of the membrane, the natural flow of water due to osmosis can be reversed. The flow of water from a concentrated solution to a diluted solution is a process called reverse osmosis.

The convective water flux across a semipermeable membrane at a given pressure is defined by the Darcy's law [8] as detailed in equation 2. Solute flux in pressure-driven membranes is described by the Fick's diffusion law [9] shown in equation 3:

$$Fw = A \cdot ((P_f - P_p) - (\pi_f - \pi_p)) \quad (2)$$

$$Fs = B \cdot (C_f - C_p) \quad (3)$$

$F_w$ - Water flux [gfd]
$A$ - Water permeability constant [gfd/psi]
$P_f$ - Feed pressure [psi]
$P_p$ - Permeate pressure [psi]
$\pi_f$ - Feed osmotic pressure [psi]
$\pi_p$ - Permeate osmotic pressure [psi]
$F_s$ - Salt flux [lbfd]
$B$ - Solute permeability constant [gfd]
$C_f$ - Concentration of solute on feed [lb/gal]
$C_p$ - Concentration of solute on permeate [lb/gal]

## 2.2 Commercial modules construction

The development of reverse osmosis membrane began in 1963, when Loeb and Sourirajan produced the asymmetric cellulose acetate (CA) membranes, which exhibited a relatively high flux and good salt rejection [10]. The structure was consisting of a dense selective layer on top of a porous layer that holds the mechanical strength of the membrane.

Cellulose acetate membrane chemistry was the first employed to build modules to purify water and a major advance in RO technology. However, other synthetic polymer materials with better mechanical, chemical and biological tolerance, started to be used for membrane synthesis. Soon, thin film composite (TFC) polyamide membranes started to dominate the market. The fluxes and rejections achieved by the TFC membrane exceeded those of CA. These membranes, as shown in Figure 1-1, consist of three layers: a polyester support to provide mechanical strength and stability, a microporous polysulfone and a thin polyamide layer, also known as active layer. One of the main drawbacks of TFC membranes is the sensitivity of the polyamide layer to oxidizing compounds. Polyamide molecular structure can be quickly attacked and even degraded by chlorine, causing a drastic reduction in salt rejection.

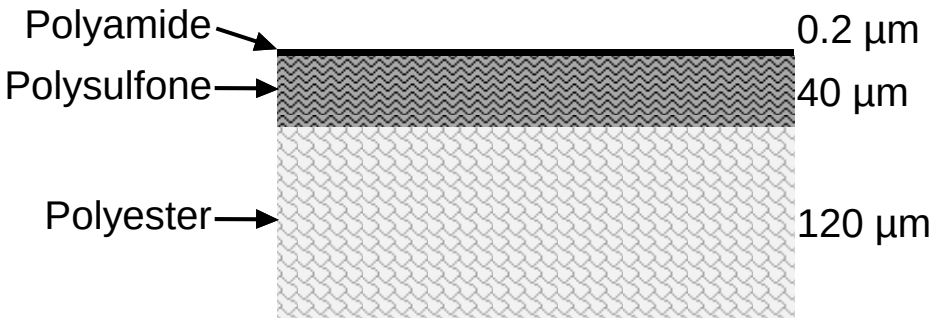



**Figure 1-1. Reverse osmosis operating principle**

Reverse osmosis membranes are typically operated in cross-flow mode, generating a concentrate and a permeate stream. Cross-flow filtration provides several advantages: it sweeps away foulants, minimize the precipitation of concentrated salts and the build-up of filter cake.

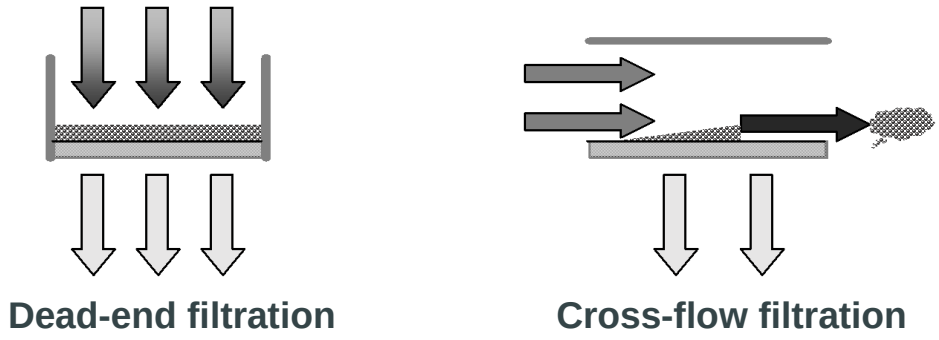



**Figure 1-2. Flow types on reverse osmosis filtration**

In the 1970s, John Cadotte developed a spiral wound reverse osmosis membrane that reduced the cost of RO by two-thirds. Spiral wound RO elements have become the industry standard. Modules are typically manufactured with one to more than 30 membrane envelopes and rolled around a central permeate collection pipe as shown in Figure 1-3. Each membrane leaf is made of two membrane sheets glued together by their polyester side. The standard commercial RO module is 8'' in diameter (20 cm) and 40'' long (~ 1 m). This design creates a large surface area of up to 41 m², maximizing productivity in a compact size. Typically, 10-20% of the water fed to each module permeates through the membrane to the permeate water tube. In membrane systems, several spiral wound elements are placed in series inside of a pressure vessel. The concentrate stream of the first element is the feed of the second element, while the permeate tubes of each individual module are connected.

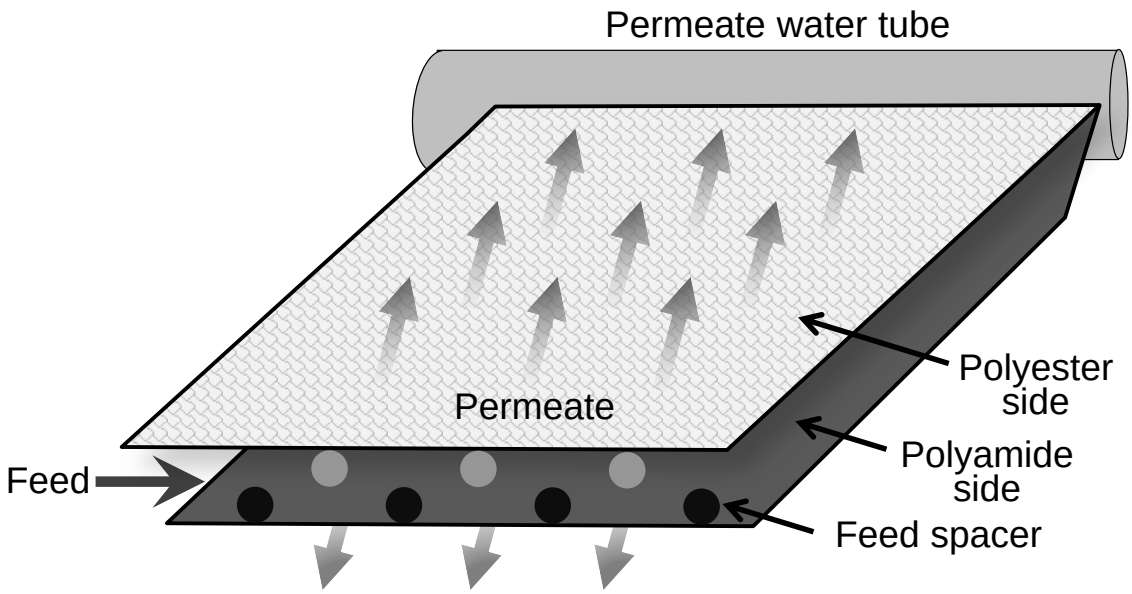



**Figure 1-3. Spiral wound reverse osmosis element construction**

A plastic net known as feed spacer is placed between membrane envelopes to provide a feed-concentrate open channel for water to flow along the element. Feed spacers are placed on the active side of the membrane to promote mixing and reduce the concentration polarization (osmotic pressure near the membrane surface) of ions and foulants.

The spacers used are defined by their stands per inch, thickness, and angle and are made out of polypropylene and/or polyethylene. Feed spacers are oriented so the feed flow intersects the angle formed by the strands knot as displayed in Figure 1-4. The typical feed spacer thicknesses are very thin, between 0.7 mm (28 mil) and 0.9 mm (34 mil) [8]. The thickness of the spacer used will inversely affect the amount of membrane surface that can be fitted in a spiral wound element of a set diameter. Using a thicker feed spacer will reduce the amount of membrane active area that will fit in the element, and thus, will lower the element productivity.

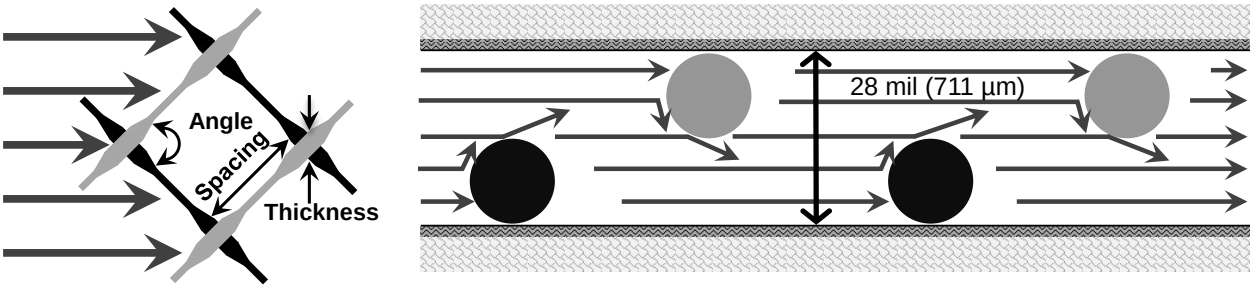



**Figure 1-4. Top view (left) and cross-section (right) of feed spacer mixing effect**

## 3 FOULING ON MEMBRANE TREATMENT PROCESSES

The reuse of water is becoming a more and more recognized option to solve water scarcity problems. Thanks to the great advances in membrane technology, reverse osmosis membranes are increasingly applied in the field of drinking water production and advanced water reuse treatments. Membranes can efficiently remove a large variety of pollutants, with more reliability and lower footprint than conventional technologies, such as coagulation, flocculation and sedimentation. However, a major challenge facing the widespread application of reverse osmosis technology is membrane fouling. The term fouling includes the accumulation of compounds found in the feed water in the membrane surface and/or feed spacer.

Membrane fouling is one of the most difficult operational concerns faced by the reverse osmosis (RO) end users. Fouling can be categorized as inorganic, organic or biological. Inorganic fouling occurs through the precipitation and build-up of inorganic salts layer, or scale, onto the membrane. In organic fouling, substances such as proteins, oils or humic substances deposits on the membrane surface. Colloidal fouling is often included as a separate category and can include clay, silt, silica, and other particulate matter. Biological fouling, also known as biofouling, is characterized by the adhesion of micro-organisms to the membrane and their subsequent growth and accumulation. Both organic and inorganic fouling can occur directly on the surface of a polyamide RO membrane. End

users will typically first notice these forms of fouling as a loss in membrane permeability, or productivity, in their system. Biofouling develops on the membrane surface as well as on the feed spacer. Biofouling is associated with an increase in the pressure drop, from the inlet or feed of an element to the outlet or concentrate. Among the main types of fouling, biofouling is characterized as one of the most challenging to prevent and control [3].

Although pretreatment options are often preventative measures for the different fouling types as shown in Table 1-2, in practice, organic and biological fouling cannot be fully controlled by any pretreatment method. Better performances can be obtained by optimizing RO module with more fouling resistant feed spacer design and membrane chemistry than the ones commonly used.

**Table 1-2. Main types of fouling in reverse osmosis systems**

| Fouling | Description | Prevention |
|---|---|---|
| Particulate | Particles block the membrane | Improved pretreatments |
| Scaling | Inorganic salts precipitate on the membrane | Controlled dosing of antiscalant |
| Organic | Organic molecules adsorb on the membrane | Optimized membrane chemistry<br>Pretreatment (e.g. bioreactor) |
| Biologic | Bacteria grow on the membrane and in the feed spacer forming biofilm | Pretreatment (e.g. biocide)<br>Optimized Feed Spacer |

### 3.1 Biofouling

Among the various fouling types, biofouling is the most difficult to manage in RO systems. The sensitivity of polyamide-based membranes to oxidizing agents, such as chlorine, greatly limits the use of chemicals to prevent bacterial growth in the feed water. Additionally, traditional pretreatments such as coagulation, flocculation, ultrafiltration

or cartridge filters, are not effective in removing the biofouling potential of the feed water. Commercial plants are not sterile environments and any microorganism that enters into the system, will rapidly multiply. Some bacteria are able to duplicate their population in only 30 minutes, showing an exponential growth.

A number of microorganisms use water as a means of transport and create their living space within the large surface of the reverse osmosis elements. The convective water flow through the reverse osmosis feed channel and the abundance of dissolved bio-assimilable nutrients constitute an optimal environment for bacteria proliferation.

It has been shown by several authors that microorganisms tend to attach and generate a biofilm on the feed spacer and, to a lesser extent, on the membrane surface. The formation of bacterial biofilms is initiated with the attachment of planktonic, free-swimming bacteria on the surface. Biofilm matrix is a sticky polymeric structure used by microorganisms to attach themselves and grow on a surface. The main component of the matrix is a strongly hydrated [11] mixture of carbohydrates and proteins, known as Extracellular Polymeric Substances (EPS) [12][13].

Biofilms can significantly impair the performance of reverse osmosis element, by plugging the feed-concentrate channel and restricting water flow, a phenomenon also known as the 'hair-in sink effect'. As it can be observed in Figure 1-5, strong biofilm growth can be typically found on the feed spacer strands.

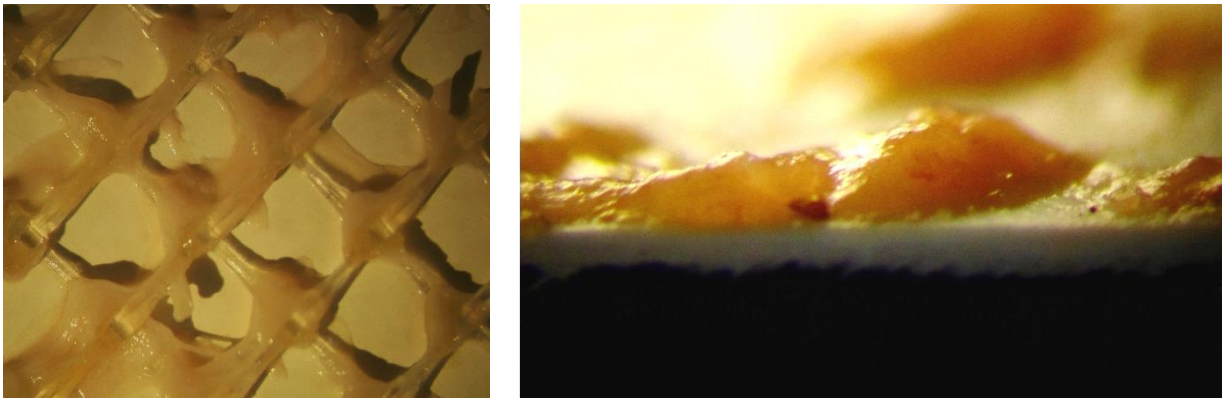


**Figure 1-5. Biofouling in reverse osmosis sample (left: top view, right: cross-section)**

EPS stabilize biofilms by holding the microbial cells together and attaching the growing biofilm on the membrane and the feed spacer surface, creating structures that fill the available volume [14]. Thus, the void space of feed-concentrate channel is reduced and the resistance of water to flow increases. This effect is associated with an exponential pressure drop increase [15]. Additionally, biofilms are challenging to clean due to the sticky nature of EPS, which provides a high mechanical and chemical stability to bacteria [16].

The research interest around biofouling is clearly reflected in the increasing number of publications per year as summarized in Figure 1-6. The motivation for a better understanding of the biofilm formation fundamentals is not only from academia, but also for industries around the world, where biofouling causes significant problems [17]. Biofilms reduce the efficiency and increase the energy consumption in, for example, heat exchangers, ship hulls or drinking water systems. In membrane applications alone, biofouling is estimated to account for 30% of the operating costs, which in plants like Water Factory 21 (Orange County, USA) is about $750,000 per year [18][19]. The understanding of the concepts will enable novel and cost-effective strategies for biofouling control.

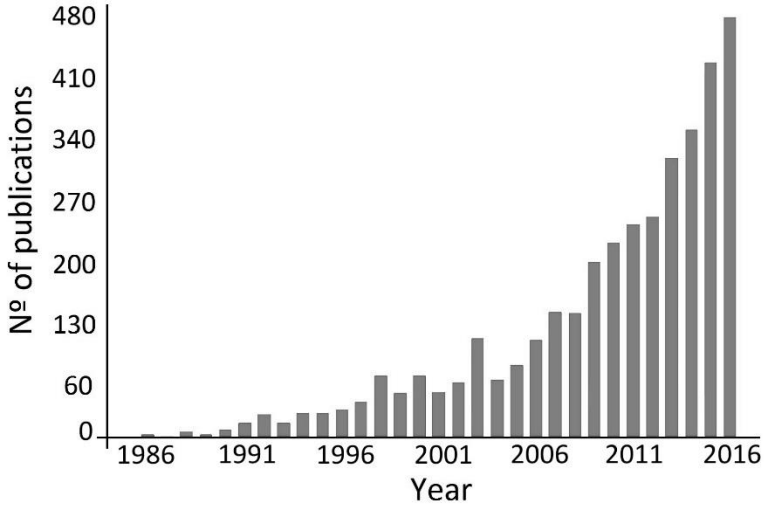



**Figure 1-6. Publishing items in each year for biofouling research [20]**

## 4 ANTIFOULING TECHNOLOGIES

The reuse of water implies operating with waters having high fouling potential. Therefore, an effective fouling resistant RO element has to offer both high and reliable rejection towards contaminants and resistance against fouling. The current strategies to deal with biofouling problems at industrial scale are not effective [21]. The lack of information, unfriendly product design to operate under biofouling conditions and ineffective pretreatments/cleanings, are creating a vicious circle that compromises the RO system leading to uncontrolled fouling.

To overcome these deficiencies, an integrated strategy, focused in three key areas: module design, pretreatment and system cleaning, is needed. Product design has been explored through membrane chemistry modification to mitigate fouling attachment, as well as improved feed spacers to reduce pressure drop increase [22]. Pretreatments and cleaning are also areas of focus, to inactivate and remove the microorganisms from the feed water, to reduce its biofouling potential.

Each method has its own specific advantages, but the optimal strategy is typically a combination of the different approaches [23]. The ultimate goal is to avoid the negative interferences of biofilms in the water treatment facilities in the most efficient way.

### 4.1 Pretreatment

One strategy to avoid biofouling is to minimize the number of bacteria entering the RO system with an efficient pretreatment. Most common approaches are the physically removal bacteria, using filtration (e.g. sand filtration or ultrafiltration), or the metabolic inactivation of bacteria present in the feed water, to prevent the contact of living microorganisms with the membrane surface [24].

Some of the disadvantages that filtration based pretreatments have is the need of a buffer tank before the RO unit for the regular backwashes required and the poor removal of biodegradable compounds from the feed water [25]. Buffer tanks have high residence time and can act as a source of contamination, even more if biodegradable compounds from the feed water are not efficiently removed upstream. Thus, RO system with a pretreatment based on filtration are still vulnerable to biofouling, despite the high bacterial removal efficiency of these pretreatments [26]. The metabolic inactivation of bacteria, however, can be applied in-line just before water reaches the RO modules, minimizing the risk of bacteria regrowth [27]. The inactivation can be via physical (e.g. ultraviolet light) or chemical (e.g. biocides).

Biocides have been recognized as efficient compounds to prevent biofouling formation [28]. Unlike physical inactivation, biocides are dissolved in the feed water and are effective in the entire system, not only at the point where are applied. Many of the currently applied biocides are oxidizing in nature and these type of chemicals could damage the polyamide membrane over time (e.g. hypochlorite or chloramines) [29][30].

Only the non-oxidizing biocides provide control without adversely affecting thin-film composite RO membranes [31].

One of the most promising biocides which can be used to prevent biological fouling is 2,2-dibromo-3-nitrilo-proprionamide (DBNPA). DBNPA is non-oxidizing biocide, used in relatively low concentrations, from 1 to 20 mg/L, depending on the severity of the biological fouling), and is quickly degraded in aqueous environments [32]. The dosing strategy can be either as a continuous dosage of low biocide concentrations or as a discontinuous (intermittent) shock dosing of biocide at certain intervals.

The prevention of RO biofouling through the use of DBNPA is explored and evaluated under different scenarios and dosing strategies.

### 4.2 Module design

Module design plays an important role on improving the performance of RO elements under challenging water. The potential foulants present in the feed water are in direct contact with the feed spacer and the active layer of the membrane. Thus, the fouling resistance of an element depends largely on the interaction of the feed spacer and membrane surface with the foulants. Foulants can be gradually accumulated inside the RO module by either depositing (e.g. organic fouling) or growing (e.g. biological fouling). Fouling development (via deposition or growth) is initiated by the different velocity profiles found within the module. A fluid like water flowing over a static surface like the membrane surface or spacer, experiments a gradient of tangential velocity. In the region close to the membrane surface, known as the fluid boundary layer, the mass transport of dissolved species is regulated by diffusion. Under diffusion conditions, the main forces are weak electrostatic or Van der Waals interactions of small molecules (salts, surfactants or organics) with the membrane surface [33]. At the regions with higher fluid velocities,

mass transport occurs by convective forces. Convection is promoted by the feed spacer presence, causing mixing and shear on the compounds present in the bulk liquid.

The fluid velocity inside an RO element is defined by the feed flow, the leaf length and the spacer thickness, as shown in Figure 1-7 below.

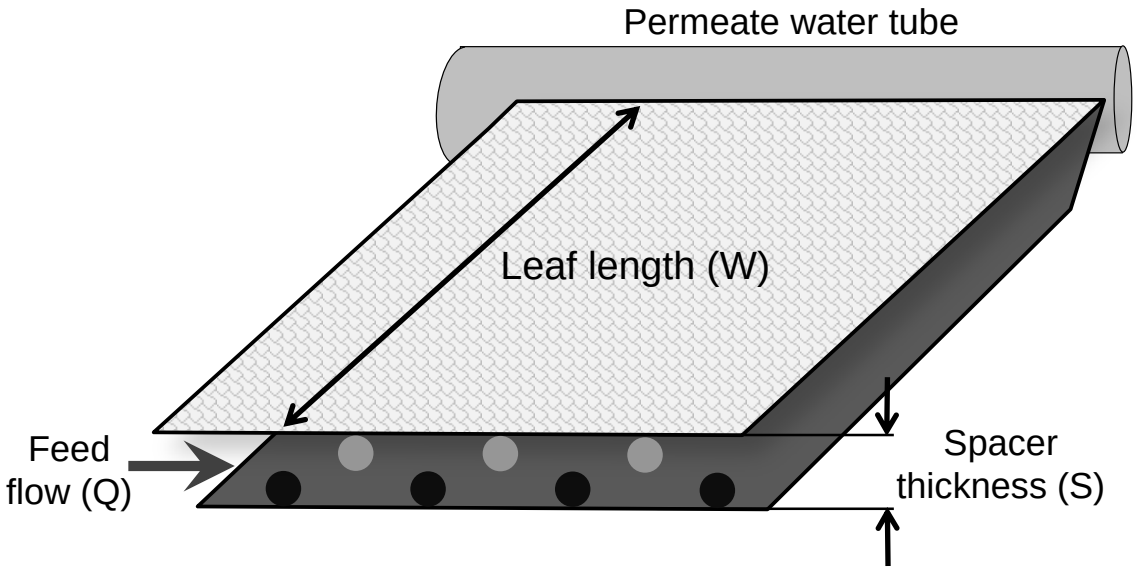



**Figure 1-7. Spiral wound reverse osmosis operation**

Cross-flow velocity (equation 4) is correlated with the pressure drop of the element by the Darcy-Weisbach formula [34] (equation 5). The pressure drop or differential pressure (dP), is a measure of the resistance of water to flow across the element. High pressure drops results in high energy consumptions and risk of damaging the elements. If the dP of a single fiberglassed element exceed 1 bar, it can suffer mechanical damage (i.e. cracks in the shell).

Cross-flow velocity (equation 4) is also correlated with pressure drop (equation 5) and the fluid mixing (equation 6). By increasing the feed spacer thickness, pressure drop is reduced. Nevertheless, thicker spacers are impacting the active area of the elements and thus, their productivity. All parameters should be smartly balanced when designing the module.

$$v = \frac{Q}{W \cdot S} \tag{4}$$

$$\Delta P = \lambda \cdot \frac{\rho}{2} \cdot \frac{v^2 \cdot L}{2 \cdot S} \tag{5}$$

$$\mathrm{Re} = \frac{2 \cdot v \cdot S \cdot \rho}{\mu} \tag{6}$$

$v$ - Cross-flow velocity [m/s]
$Q$ - Feed flow [m³/s]
$W$ - Leaf length [m]
$S$ - Spacer thickness [m]
$\Delta P$ - Pressure drop [Pa]
$\lambda$ - Friction factor
$\rho$ - Density [kg/m³]
$L$ - Element length [m]
$\mu$ - Dynamic viscosity [N-s/m²]
$\mathrm{Re}$ - Reynolds number

Different feed spacer configurations will be tested under challenging conditions to ensure a reliable performance. The optimal feed spacer design should have an equilibrium between hydrodynamics, ensuring good mixing to avoid fouling accumulation, and hydraulics, to reduce pressure drop. Similarly, modifications of the membrane chemistry, to avoid permeability decline due to fouling deposition, will be explored. The surface modifications should reduce foulant interactions with the membrane while ensuring high overall water permeability.

### 4.3 System cleaning

Fouling effects should be addressed at an early stage to restore the initial performance of RO elements. Otherwise, fouled elements could suffer from a permanent loss of productivity and mechanical damage [35]. Consequently, during operation, end users

periodically shut down their systems to remove the foulants accumulated. Cleanings that are performed directly on the pressure vessels with the elements loaded, are referred as a clean in place or CIP. A high CIPs frequency increases system downtime due to cleanings, decreases membranes durability (life time) and increases the cost of water produced (energy and chemicals) [9]. Membrane cleaning approaches can be divided into physical or chemical.

Physical cleanings use mechanical forces to extract and remove the foulants accumulated. However, the most effective methods, such as air bubbling, backwashing or reverse flushing, are usually not suitable for spiral wound RO modules. These methods are too aggressive and the integrity of the module can be compromised if applied regularly.

Chemical cleaning is the most common membrane cleaning method. Reverse osmosis membranes are stable over a wide pH range (1-12). Elements are generally cleaned at low and high pH conditions using a heated cleaning solution (30-35ºC) to increase the chemical activity. Cleaning processes are generally performed at low pressures and high cross-flow velocities to minimize re-deposition of the foulants removed. The choice of chemical agent is based on the type of foulant to be cleaned (Table 1-3). The recommendation is to start the CIP cycles with alkaline cleaning conditions (i.e. sodium hydroxide) to hydrolyze and remove biofilm and organic compounds. The last step of the CIP should be an acid solution (i.e. hydrochloric acid) to solubilize inorganic salts and metals.

**Table 1-3. Cleaning solutions according the type of foulant [36]**

| Type of fouling | Chemical agent |
|---|---|
| Metal oxides | Citric acid or HCl |
| Silica | NaOH |
| Carbonate scales ($CaCO_3$) | Citric acid or HCl |
| Sulphate scales ($CaSO_4$, $BaSO_4$) | HCl or sequestration agents (e.g. EDTA) |
| Colloidal | NaOH, chelating agents and surfactants |
| Organic | NaOH, chelating agents and surfactants |
| Biofilms | NaOH, chelating or sequestration agents, surfactants and disinfectants |

As described in section 3.1, the build-up of biofilm in RO systems is not only challenging to prevent, but also very complicated to remove once it has been formed. Caustic solutions can potentially hydrolyze the polysaccharides and proteins from the EPS matrix to disperse the fouling layer. However, literature review reveals that the current prevention and cleaning methods for biofouling are not efficient enough. The EPS matrix provides high mechanical and chemical stability for biofilms. Moreover, even harsh cleaning conditions cannot fully remove biofouling from RO modules, resulting in rapid re-growth after each CIP. In Figure 1-8, an example of the typical pressure drop profile observed in RO plants when dealing with biofouling problems is shown. Biofouling was not fully removed after the CIP cycles, resulting in a gradual increase of the baseline dP due to irreversible fouling. In the plot it could also be observed that the dP increase impact was much higher in the lead elements (1$^{st}$ to 3$^{rd}$ element in the pressure vessel), than the tail elements (4$^{th}$ to 6$^{th}$ element in the pressure vessel).

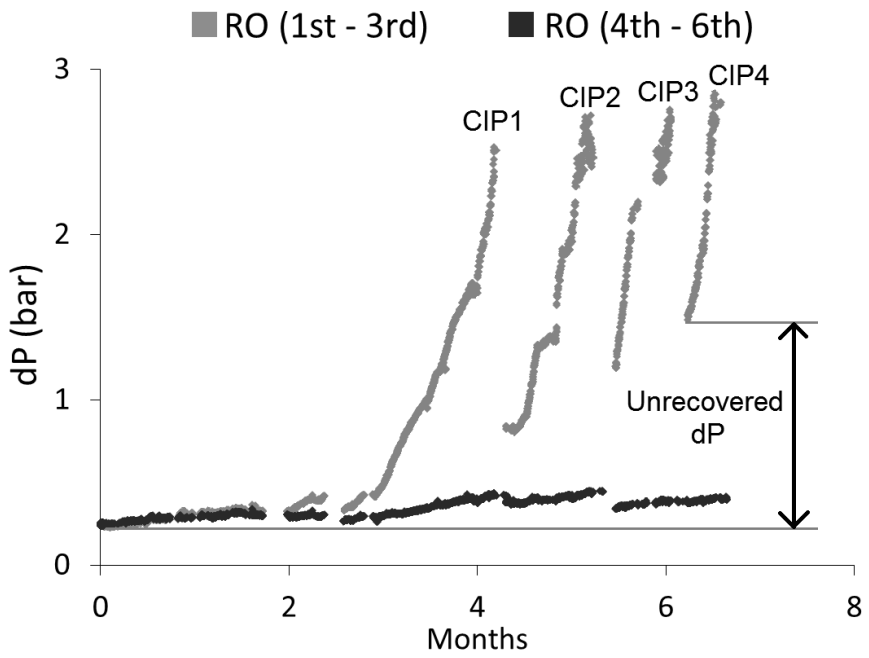



**Figure 1-8. Pressure drop evolution for RO elements over several cleaning cycles**

The factors that contribute to the poor cleaning efficiency of biofilm were evaluated in this thesis. The effect of module design, operating conditions and effective fouling removal has been studied to improve CIPs effectiveness. Sustained advantage through successive cleaning cycles is necessary to achieve a long term fouling performance and avoiding early element failure.

## 5 REFERENCES

[1] Gleick, P. H. (1993). Water and conflict: Fresh water resources and international security. International security, 18(1), 79-112

[2] Bartram, J., Cairncross, S. (2010). Hygiene, sanitation, and water: forgotten foundations of health. PLoS Med, 7(11), e1000367

[3] Smalley, R. E. (2003, May). Top ten problems of humanity for next 50 years. In Professor RE Smalley, Energy NanoTechnology Conference, Rice University

[4] Nicolaisen, B. (2003). Developments in membrane technology for water treatment. Desalination, 153(1-3), 355-360

[5] Fane, A. G., Tang, C., Wang, R. (2011). Membrane technology for water: microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. Treatise on Water Science

[6] Ghaffour, N., Missimer, T. M., Amy, G. L. (2013). Technical review and evaluation of the economics of water desalination: current and future challenges for better water supply sustainability. Desalination, 309, 197-207

[7] Burn, S., Hoang, M., Zarzo, D., Olewniak, F., Campos, E., Bolto, B., Barron, O. (2015). Desalination techniques—a review of the opportunities for desalination in agriculture. Desalination, 364, 2-16

[8] Hubbert, M. K. (1956). Darcy's law and the field equations of the flow of underground fluids (pp. 20-26). Shell Development Company, Exploration and Production Research Division

[9] Tyrrell, H. J. V. (1964). The origin and present status of Fick's diffusion law. J. Chem. Educ, 41(7), 397

[10] Loeb, S.; Sourirajan, S. "Seawater dimineralization by means of an osmotic membrane", Advances in Chemistry Series, 38 (1963) 117-132

[11] F. Beyer, B. M. Rietman, A. Zwijnenburg, P. van den Brink, J. S. Vrouwenvelder, M. Jarzembowska, J. Laurinonyte, A. J. M. Stams, C. M. Plugge, "Long-term performance and fouling analysis of full-scale direct nanofiltration (NF) installations treating anoxic groundwater", Journal of Membrane Science 468 (2014) 339–348

[12] J. S. Vrouwenvelder, D. Van der Kooij. "Diagnosis, prediction and prevention of biofouling of NF and RO membranes", Desalination 139(1) (2001) 65-71

[13] A. Magic-Knezev, D. Van Der Kooij. "Optimisation and significance of ATP analysis for measuring active biomass in granular activated carbon filters used in water treatment", Water Research 38(18) (2004) 3971-3979

[14] Q. Wei, L. Ma, "Biofilm Matrix and Its Regulation in Pseudomonas aeruginosa", International Journal of Molecular Sciences 14(10) (2013) 20983–21005

[15] R. J. Barnes, R. R. Bandi, F. Chua, J. H. Low, T. Aung, N. Barraud, A. G. Fane, S. Kjelleberg, S. A. Rice, "The roles of Pseudomonas aeruginosa extracellular polysaccharides in biofouling of reverse osmosis membranes and nitric oxide induced dispersal", Journal of Membrane Science 466 (2014) 161–172

[16] B. W. Peterson, Y. He, Y. Ren, A. Zerdoum, M. R. Libera, P. K. Sharma, A.-J. van Winkelhoff, D. Neut, P. Stoodley, H. C. van der Mei, H. J. Busscher, "Viscoelasticity of biofilms and their recalcitrance to mechanical and chemical challenges", FEMS Microbiology Reviews 39(2) (2015) 234–245

[17] Flemming, H. C. (2002). Biofouling of Industrial Systems. Encyclopedia of environmental microbiology

[18] Coetser, S. E., Cloete, T. E. (2005). Biofouling and biocorrosion in industrial water systems. Critical reviews in microbiology, 31(4), 213-232

[19] Flemming, H. C., Schaule, G., McDonogh, R., Ridgway, H. F. (1994). Effects and extent of biofilm accumulation in membrane systems. Biofouling and Biocorrosion in Industrial Water Systems. CRC Press, USA, 63-105

[20] Scientific, T. (2007). ISI Web of knowledge. Science Citation Index and Journal Citation Report

[21] Flemming, Hans-Curt. Microbial biofouling: unsolved problems, insufficient approaches, and possible solutions. En Biofilm highlights. Springer Berlin Heidelberg, 2011. p. 81-109

[22] Bucs, S. S., Radu, A. I., Lavric, V., Vrouwenvelder, J. S., Picioreanu, C. (2014). Effect of different commercial feed spacers on biofouling of reverse osmosis membrane systems: a numerical study. Desalination, 343, 26-37

[23] Majamaa, K., Johnson, J. E., Bertheas, U. (2012). Three steps to control biofouling in reverse osmosis systems. Desalination and Water Treatment, 42(1-3), 107-116

[24] Flemming, H. C. (1997). Reverse osmosis membrane biofouling. Experimental thermal and fluid science, 14(4), 382-391

[25] Schneider, R. P., Ferreira, L. M., Binder, P., Bejarano, E. M., Góes, K. P., Slongo, E., Rosa, G. M. Z. (2005). Dynamics of organic carbon and of bacterial populations in a conventional pretreatment train of a reverse osmosis unit experiencing severe biofouling. Journal of Membrane Science, 266(1), 18-29

[26] Volk, C. J., Lechevallier, M. W. (2002). Effects of conventional treatment on AOC and BDOC levels. Journal (American Water Works Association), 94(6), 112-123

[27] Baker, J. S., Dudley, L. Y. (1998). Biofouling in membrane systems—a review. Desalination, 118(1-3), 81-89

[28] Kim, D., Jung, S., Sohn, J., Kim, H., Lee, S. (2009). Biocide application for controlling biofouling of SWRO membranes—an overview. Desalination, 238(1-3), 43-52.

[29] Kang, G. D., Gao, C. J., Chen, W. D., Jie, X. M., Cao, Y. M., Yuan, Q. (2007). Study on hypochlorite degradation of aromatic polyamide reverse osmosis membrane. Journal of membrane science, 300(1), 165-171.

[30] da Silva, M. K., Tessaro, I. C., Wada, K. (2006). Investigation of oxidative degradation of polyamide reverse osmosis membranes by monochloramine solutions. Journal of Membrane Science, 282(1), 375-382.

[31] Majamaa, K., Bertheas, U., Finlayson, F., Levy, R. B. (2011). Preservation of reverse osmosis membranes with non-oxidizing biocides–comparison with SMBS. Water Science and Technology: Water Supply, 11(3), 342-351.

[32] Bertheas, U., Majamaa, K., Arzu, A., Pahnke, R. (2009). Use of DBNPA to control biofouling in RO systems. Desalination and Water treatment, 3(1-3), 175-178.

[33] Hughes, Z. E., Gale, J. D. (2012). Molecular dynamics simulations of the interactions of potential foulant molecules and a reverse osmosis membrane. Journal of Materials Chemistry, 22(1), 175-184.

[34] Charcosset, C., Falconet, C., Combe, M. (2009). Hydrostatic pressure plants for desalination via reverse osmosis. Renewable Energy, 34(12), 2878-2882.

[35] Hijnen, W. A. M.; Castillo, C.; Brouwer-Hanzens, A. H.; Harmsen, D. J. H.; Cornelissen, E. R.; van der Kooij, D. "Quantitative assessment of the efficacy of spiral-wound membrane cleaning procedures to remove biofilms." Water Research 2012, 46, 6369.

[36] Fritzmann, C., Löwenberg, J., Wintgens, T., Melin, T. (2007). State-of-the-art of reverse osmosis desalination. Desalination, 216(1-3), 1-76.

# Chapter 2

# Method for distinguishing between abiotic organic and biological fouling of reverse osmosis elements used to treat wastewater

**This chapter was accepted for publication on 07/2017 (I.F. 1.63):**

G. Massons-Gassol, G. Gilabert-Oriol, V. Gomez, R. Garcia-Valls, V. Garcia Molina, T. Arrowood, *Method for distinguishing between abiotic organic and biological fouling of reverse osmosis elements used to treat wastewater*, Desalin. Water Treat., 83 (2017) 1944-3986

**doi: 10.5004/dwt.2017.21266**

# 1 INTRODUCTION

## 1.1 Fouling in reverse osmosis

Reverse osmosis (RO) is often used as one of the most cost-effective strategies for producing high quality water for a variety of applications. However, fouling is still one of the major hurdles in membrane technology and especially in RO systems, because it increases the energy needed and requires frequent shutdowns for cleanings [1]. When designing a new system, it is very complex to predict the severity of fouling, which might result in a higher frequency of cleaning and reduced productivity. Therefore, improving the ability to predict, troubleshoot and reduce the fouling of reverse osmosis systems continues to be a topic of great interest.

There are different types of membrane fouling. The two most problematic types are biological and organic [2]. Biological fouling is usually associated with an increase in differential pressure in the first stage pressure vessel [3][4][5]. Organic fouling usually causes an increase in resistance to transport water through the membrane, which reduces permeate flow [6]. Both types of fouling usually occur together, so it is difficult to optimize systems, because steps to improve biological fouling may worsen organic fouling and vice versa. The characteristics and distribution of each type of fouling must be studied if membrane performance is to be more sustainable [7]. Determining whether biological or organic fouling is dominant is important for designing improvements in pretreatment. If biopolymers such as proteins or carbohydrates are identified as the primary type of fouling, biocide dosing or nutrients limitation using biological pretreatment would likely improve RO fouling problems [8]. However, if the source of the foulants is not determined and fouling was actually caused by abiotic organic compounds, these same pretreatments solutions might result in inefficient fouling control. Unfortunately, commonly used fouling quantification techniques do not reveal the source of the organic compounds present in fouling samples. Information about the

type of RO contamination is also needed so that cleaning recommendations can be adapted to the pilot unit systems [9].

## 1.2 Fouling characterization

System fouling is assessed by monitoring performance and analytically characterizing the foulants. Changes in permeate flow rate, feed pressure, salt passage and pressure drop over time are symptoms of the onset and severity of fouling. After operation elements are usually autospied. ATP (adenosine triphosphate), TOC (total organic carbon) and TN (total nitrogen) are the most common analytical characterization techniques used to study both organic and biological fouling [10]. In most cases, biological and organic fouling are found together [11][12]. Only system differential pressure and foulant ATP concentration can be correlated with biological fouling [13].

## 1.3 Biofouling vs. organic fouling: characteristics and composition

The main component of biofouling is a polymer matrix excreted by bacteria [14]. This matrix is a strongly hydrated mixture of polysaccharides, proteins, nucleic acids and lipids known as extracellular polymeric substances (EPS) [15][5]. Polysaccharides and proteins are, on a mass basis, the main components of the biofilm matrix [16]. The amount and type of proteins and carbohydrates found in EPS depends on the bacteria strain, environmental conditions and stress events [17][18]. Carbohydrates and proteins are rich in organic carbon, and peptides are also rich in nitrogen, so TOC and TN concentrations are high when biofilms are analyzed [19].

Organic fouling occurs when organic compounds found in the feed water are deposited on the membrane surface. These compounds usually contain carbon and nitrogen and, therefore, can be detected by a positive response for TOC and TN.

It has been suggested that comparing the ATP to TOC levels in a foulant as one way of determining whether organic foulants come from biofilm formation or abiotic compounds [1]. However, ATP degrades quickly and is highly sensitive to external factors [20] that can influence the bacterial metabolic state (chemical cleaning, biocides, etc.), so ATP levels can be unreliable. The ATP concentration does not correlate with the presence of EPS under certain conditions [21][22]. The presence of biomass rather than its metabolic activity is usually more directly correlated with the fouling problems in RO systems [23]. Nonetheless, TOC and TN levels alone did not differentiate the source of the foulants quantified (biological or abiotic).

Liquid chromatography-organic carbon and nitrogen detection (LC-OCD-OND) has emerged as a useful technique for identifying and quantifying the various fractions of the natural organic matter pool (protein and polysaccharide, humics, fulvics, building blocks and low-molecular-weight organics) [24]. This technique has been successfully used in some studies to calculate the fraction of organic carbon associated to biopolymer (proteins and polysaccharides) [25][26]. However, the results can be complex to interpret and the technique is generally not available for routine membrane fouling samples [27]. Other studies suggest that the proportion of biopolymer on a membrane foulant sample can be calculated using the area of the pyrochromatograms, obtained using pyrolysis gas chromatography−mass spectrometry [28]. However, and like the LC-OCD-OND method, analyzing samples is time consuming and technically challenging.

This paper reports a simplified approach for determining the relative extent of biofouling over organic fouling in RO samples. Carbohydrates and proteins are the main constituents of the biofilm matrix and whether they are present or not, can discern between biological and organic foulants [29]. The proportion of carbohydrates and proteins in the TOC and TN pool will be calculated to determine the fraction of biological carbon and nitrogen, respectively. To validate the viability of the approach, the protocol will be applied to determine the EPS fraction of various RO samples operated under two

different conditions. The protocol uses techniques that are available at most analytical laboratories. The proportions intend to provide information about the source and proportion of these compounds in complex fouling samples.

## 2 MATERIALS AND METHODS

Reverse osmosis elements were exposed to two different fouling conditions and autopsied to provide samples for analysis. The concentrations of the parameters quantified were compared to correlate the biopolymer levels according with the testing conditions.

### 2.1 Fouling field testing

Two separate RO element exposure tests were conducted, one with high and one with low biofouling tendency. Both tests used water from the secondary effluent collected from a municipal wastewater treatment plant (Vila-seca WWTP, Spain). The typical composition of the feed water is summarized in Table 2-1. The high chemical oxygen demand (COD) and TOC concentrations present an inherent organic fouling potential for the RO elements. Mainly associated with non-biodegradable organic compounds, according to the ratio of COD to the biological oxygen demand (BOD5) [1]. To promote high biofouling levels, an external dosing pump was used to dose nutrients in the feed stream and to stimulate bacteria present in the feed water (*trial with nutrients added*) [30]. In the experiment aiming for a low biofouling tendency, no dosing was used (*trial with no nutrients added*).

**Table 2-1. Characterization of feed wastewater**

| Feed water | Concentration |
|---|---|
| Total dissolved solids (mg/L) | 1,880 |
| Total suspended solids (mg/L) | 0.14 |
| COD (mg/L $O_2$) | 21.2 |
| BOD5 (mg/L $O_2$) | 2.1 |
| TOC (mg/L) | 6.0 |
| ATP (ng/L) | 38 |

In each trial, either six (*trial with nutrients added*) or eight (*trial with no nutrients added*) 1.8-inch-diameter by 12-inch-long reverse osmosis elements were operated in parallel and allowed to treat the wastewater without any recycling. Similar conditions were used in both trials (10 bar, 4.5% recovery and 25 L/m²h) and ran for approximately one week (temperature from 17-26ºC). To promote biofouling, nutrients were dosed in the feed water (*trial with nutrients added*). These include a source of carbon (0.1 mg/L C as acetate), nitrogen (0.02 mg/L N as nitrate) and phosphorous (0.01 mg/L P as phosphate). These compounds are readily bioavailable and promote rapid biofilm growth. After each test, exposed elements were autopsied and samples taken for analysis.

## 2.2 Membrane foulant extraction

After opening the elements lengthwise, a 4x4 cm (16 cm²) sample from the middle region of the membrane and spacer was placed in a glass vial. A 20 mL phosphate-buffered saline (PBS, VWR) solution was added to dissolve the foulant present [31]. Strong acid cation resin (DOWEX® MARATHON™ C Na+, Dow Chemical) was used (1 g) to improve EPS solubility [32][33]. The vial was sonicated using an ultrasonic cleaning bath (FB15061, Fisher Scientific) at room temperature for 2 min in triplicate [34][35]. After this treatment, all the foulant was fully dissolved. Samples were stored at -21ºC until analysis.

## 2.3 Adenosine triphosphate quantification

Adenosine triphosphate (ATP) concentration was used to estimate the amount of viable biomass present [17]. ATP content in the fouling extract was measured using a luminometer (Celsis Advance). The amount of light produced was converted to ATP concentration using the equipment calibration curve.

## 2.4 Total organic carbon and total nitrogen quantification

Both biological and organic foulants are rich in organic carbon and nitrogen. Thus, total organic carbon (TOC) and total nitrogen (TN) are good methods for capturing both types of fouling. TOC and TN were determined by catalytic combustion using a TOC/TN analyzer (TOC-L Shimadzu), calibrated using potassium hydrogen phthalate and urea-BSA (1:1), respectively.

TN is the sum of total inorganic nitrogen (TIN) and total organic nitrogen (TON) in a sample. Nevertheless, fouling analysis from previous studies, using the same wastewater, has shown that the total nitrogen present was over 92% organic [11]. Consequently, in this study it was assumed that the inorganic nitrogen portion ($NH_4$, $NO_3$ and $NO_2$), was negligible in comparison to the organic nitrogen. The TN analysis of the autopsied elements was considered equal than TON.

## 2.5 Carbohydrate quantification

The polysaccharides from EPS were measured using the Dubois method, also known as the phenol-sulfuric acid method [36]. The Dubois method has been widely reported for EPS polysaccharide quantification as a simple colorimetric method [37][38][39][40]. The

carbohydrate concentration of the fouling extract was detected colorimetrically using the Hach DR 5000 spectrophotometer (λ=490 nm).

Glucose (Sigma Aldrich) was used to calibrate the method. Glucose (180 g/mol) contains a significant amount of carbon (40 wt% C) [25]. This factor was used to convert glucose concentration to carbohydrate carbon units ($C_{carb.}$), so that it could be compared with the TOC measurements.

## 2.6 Protein quantification

The Bicinchoninic acid method (BCA) [41][42] was selected to quantify proteins in the membrane fouling extract. The BCA method can be readily used as a fast and simple colorimetric kit (Micro BCA™ Protein Assay Kit, Thermo Fisher). Absorbance was measured using the Hach DR 5000 spectrophotometer (λ=562 nm).

Bovine serum albumin (BSA, Sigma Aldrich) was used to calibrate the method. Albumin (66,463 g/mol) contains a significant amount of nitrogen (16 wt% N) [43]. This factor was used to convert the BSA concentration to protein nitrogen units ($N_{proteins}$) so that it could be compared with the TN measurements.

## 2.7 EPS fraction quantification

To compare the carbohydrate and protein results with the TOC and TN concentrations, the theoretical correlations for the calibration compounds used were checked.

For organic carbon, glucose TOC results were the same as the theoretical carbon percentage (40 wt% C). The TOC results for BSA showed that it contained a 2.5 wt% C, a factor that was later used to calculate the protein carbon ($C_{protein}$). Although this percentage was lower than the reported BSA elemental composition [43], it might be due to a low oxidation yield of the BSA carbon.

The sum of the protein and carbohydrate carbon divided by the TOC result gave the theoretical fraction of organic carbon associated with EPS, according to Equation 1.

$$EPS\ in\ TOC\ (\%) = \frac{C_{carb.} + C_{protein}}{TOC} \cdot 100 \qquad (1)$$

Likewise, the proportions of nitrogen in BSA and glucose solutions were determined using the TN method. As expected, glucose showed no nitrogen present. The measured nitrogen proportion for BSA was in agreement with its nitrogen composition (16 wt% N).

The percentage of protein nitrogen divided by the TN result expressed, the fraction of organic nitrogen associated with EPS, according to Equation 2.

$$EPS\ in\ TN\ (\%) = \frac{N_{protein}}{TN} \cdot 100 \qquad (2)$$

Potential interferences of BCA and Dubois method measurements were also discarded. The presence of glucose and BSA in the sample did not affect the quantification of proteins and carbohydrates, respectively.

## 3 RESULTS AND DISCUSSION

ATP, TOC, TN, $C_{carb.}$, $C_{protein}$ and $N_{protein}$ were measured in samples from the elements exposed to the *nutrients added* conditions or the *no nutrients added* environment.

### 3.1 Wastewater trial with nutrients added

The measured analytical parameters and the corresponding calculations of the composition of the foulants from the elements of the *trial with nutrients added* are summarized in Figure 2-1 and Figure 2-2. The biological fraction (C-carb., C-protein and N-protein) almost matches the overall organic carbon and nitrogen measured. The material balance was not perfect because of accumulative errors of the various quantification methods involved. However, the results leave little doubt that when

nutrients were dosed, most of the foulants present on the membrane were biopolymers (carbohydrates and proteins).

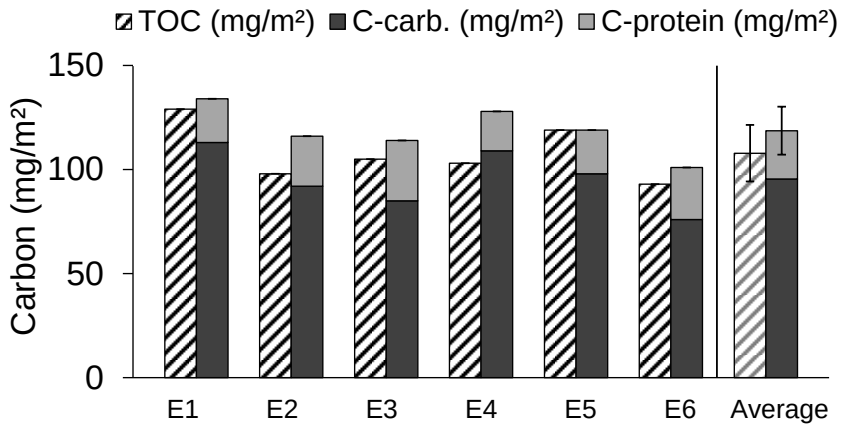



**Figure 2-1. TOC to carbon from carbohydrates and proteins measurements from elements, E1-E6, operated with nutrients added to the feed water**

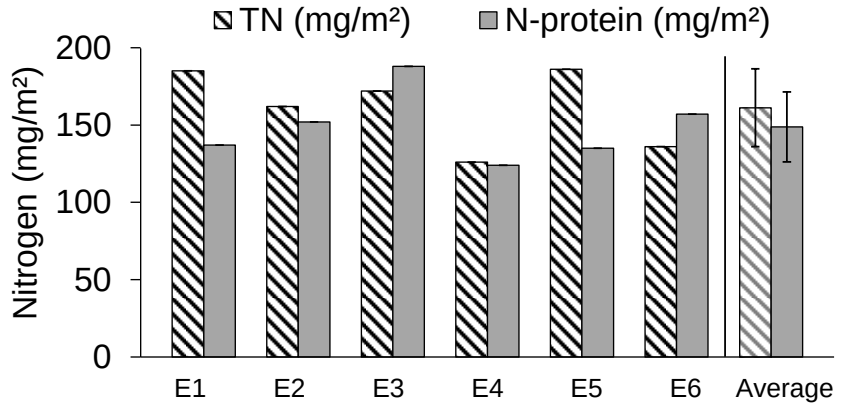



**Figure 2-2. TN to nitrogen from proteins measurements from elements, E1-E6, operated with nutrients added to the feed water**

### 3.2 Wastewater trial with no nutrients added

In the first trial, the carbohydrate and protein concentrations accounted for approximately all the TOC and TN present. However, when no nutrients were dosed, carbohydrates and proteins only account for approximately one fourth of the foulants on the surface (see Figure 2-3 and Figure 2-4). These differences could be explained by the high concentration of abiotic organic matter present in the feed water, as its high COD/BOD5 ratio (>10) suggests.

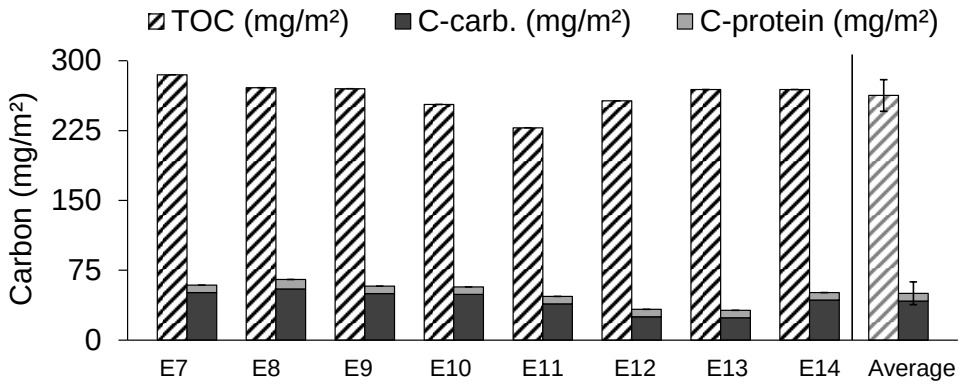



**Figure 2-3. TOC and carbon from carbohydrates and proteins measurements from samples of elements, E7-E14, operated without nutrients added to the feed water**

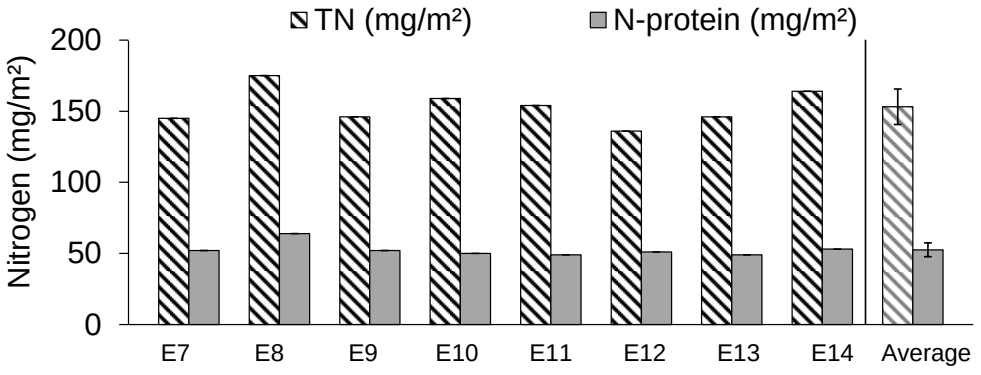



**Figure 2-4. TN and nitrogen from proteins measurements from elements, E7-E14, operated without nutrients added to the feed water**

### 3.3 Correlation between EPS fraction and membrane performance

Using the equations described in section 2.7, the EPS fraction was calculated for the elements from the test with and without nutrients (section 3.1 and 3.2, respectively).

The different EPS fractions (based on organic carbon and nitrogen distribution) are plotted in Figure 2-5. The same graph also shows the percent increase in the measured feed-concentrate pressure drop for each element at the end of the test. As expected, a clear correlation between the calculated EPS fraction and the dP increase can be observed. When nutrients were dosed (biofouling promoted), the pressure drop increased considerably and biopolymers accounted for almost all the organic nitrogen and carbon measured. However, in the samples from the *trial with no nutrients added*, the differential pressure increases and the EPS fractions were much lower. The method provided similar conclusions as other publications using LC-OCD-OND, where the biopolymer peak for samples containing biofouling was significantly larger than for samples containing organic fouling [44]. Nevertheless, a clear correlation between carbohydrates and proteins, detected by photometric methods, and performance decline, caused by biofouling, was not observed in other publications [45].

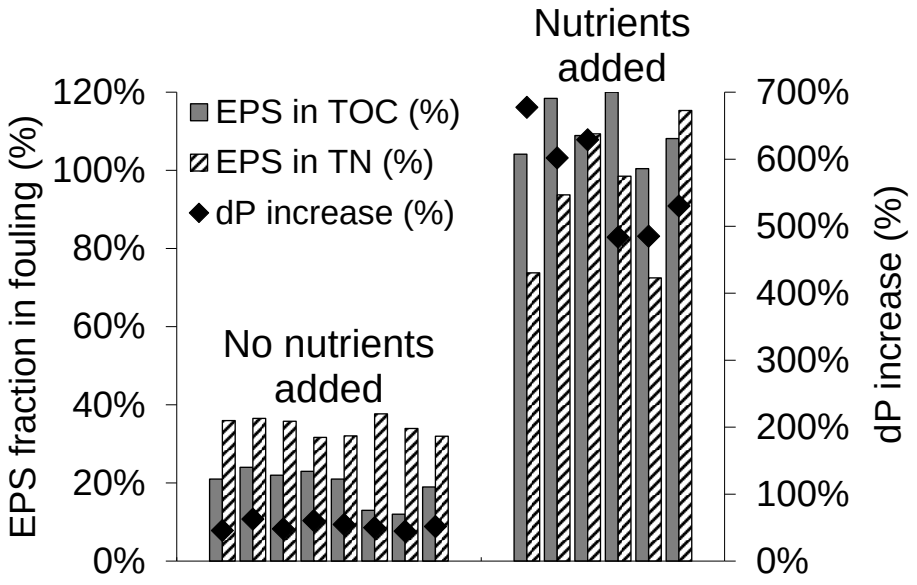



**Figure 2-5. Pressure drop increase and EPS fraction correlation**

A comparison of ATP results revealed good correlation with EPS percentages obtained in the two sets of samples (Table 2-2). The operational and analytical results both showed that when nutrients were used, fouling observed was mainly attributed to biofilm growth. Foulants found on the samples had higher concentrations of ATP as compared to foulants found on the elements operated without nutrients added. This highlights the importance of readily bioavailable nutrients to enhance bacteria colonization, reproduction and biofilm formation.

**Table 2-2. Average ATP, dP and EPS fraction summary for the two testing conditions**

| **Parameter** | ***No nutrients added test*** | ***Nutrients added test*** |
|---|---|---|
| EPS in TOC (%) | 19±4 | 111±9 |
| EPS in TN (%) | 34±2 | 94±18 |
| ATP (ng/cm²) | 1±0.1 | 40±10 |
| dP increase (%) | 51±5 | 568±80 |

## 4 CONCLUSIONS

The organic fouling found in RO elements that treat wastewater is usually a complex mixture of biological and abiotic organic compounds. The methods commonly used for membrane fouling quantification are non-specific and measure all organic compounds present as either total organic carbon or total nitrogen. The analysis of the contribution of carbohydrates and proteins in the measured TOC and TN values, can be linked with the proportion of EPS in the fouling. This allows a clearer understanding of whether the main source of the organic foulants is biologic or abiotic. Samples from elements taken from a *trial with nutrients added* and a *trial with no nutrients added* were used to validate that the new method can distinguish between the foulants produced in a high biofouling environment (nutrients dosed) or a low biofouling environment (no nutrients).

When nutrients were added, the percentage of TOC and TN accounted for by the carbohydrate and protein was nearly 100%. However, the percentages were much lower when no nutrients were dosed, indicating that a greater fraction of the fouling was caused by abiotic organic compounds. Additionally, the concentration of bacteria measured by ATP was found to be much higher than when the feed water was dosed with nutrients.

The ability to determine the proportion of EPS in the TOC and TN results has shown to be useful to determine the source of the compounds present as membrane foulants. The method described in this paper, will enable industrial water treatment plants to easily quantify the proportion of biological fouling present versus the proportion of non-biological organic fouling. Once assessed, pretreatments, operating conditions and cleaning protocols can be adjusted to tackle the primarily type of fouling occurring. Pretreatment optimization strategies, such as biocide dosage or nutrient limitation, could be implemented when biofouling is determined to be the main type fouling. Additionally, chemical cleanings protocols can be adapted for the predominant type of foulant present, such as the use of sanitizers or protease-based enzymatic cleaners for biofouling. Pre-concentration protocols for water samples will be explored in the future, to adapt the

method to characterize the feed water foulant composition. This will provide a method to monitor the removal of each particular foulant type after specific pretreatments steps.

## 5 REFERENCES

[1] F. Beyer, M. Rietman, A. Zwijnenburg, P. Van den Brink, J. S. Vrouwenvelder, M. Jarzembowska, J. Laurinonyte, Long-term performance and fouling analysis of full-scale direct nanofiltration (NF) installations treating anoxic groundwater, J. Membr. Sci., 468 (2014) 339–348

[2] J. S. Vrouwenvelder, D. Van der Kooij, Diagnosis, prediction and prevention of biofouling of NF and RO membranes, Desalin., 139 (2001) 65-71

[3] T. Nguyen, F. Roddick, L. Fan, Biofouling of water treatment membranes: a review of the underlying causes, monitoring techniques and control measures, Membr., 2 (2001) 804–840

[4] M. Al-Ahmad, F. A. Aleem, A. Mutiri, A. Ubaisy, Biofouling in RO membrane systems part 1: fundamentals and control, Desalin., 132 (2000) 173-179

[5] C. Dreszer, J. S. Vrouwenvelder, A. H. Paulitsch-Fuchs, A. Zwijnenburg, J. C. Kruithof, H. C. Flemming, Hydraulic resistance of biofilms, J. Membr. Sci., 429 (2013) 436-447

[6] J. S. Vrouwenvelder, D. Van der Kooij, Diagnosis of fouling problems of NF and RO membrane installations by a quick scan, Desalin., 153 (2000) 121-124

[7] A. Magic-Knezev, D. Van der Kooij, Optimisation and significance of ATP analysis for measuring active biomass in granular activated carbon filters used in water treatment, Water Res., 38 (2004) 3971-3979

[8] G. Naidu, S. Jeong, S. Vigneswaran, S. A. Rice, Microbial activity in biofilter used as a pretreatment for seawater desalination, Desalin., 309 (2013) 254-260

[9] K. Manish, S. Samer, W. R. Pearce., Investigation of seawater reverse osmosis fouling and its relationship to pretreatment type, Environ. Sci. Technol., 406 (2006) 2037-2044

[10] M. Filella, Understanding what we are measuring: Standards and quantification of natural organic matter, Water Res., 50 (2014) 287–293

[11] M. T. Khan, M. Busch, V. G. Molina, A. H. Emwas, C. Aubry, J. P. Croue, How different is the composition of the fouling layer of wastewater reuse and seawater desalination RO membranes?, Water Res., 59 (2014) 271–282

[12] J. S. Vrouwenvelder, J. W. N. M. Kappelhof, S. G. J. Heijman, J. C. Schippers, Tools for fouling diagnosis of NF and RO membranes and assessment of the fouling potential of feed water, Desalin., 157 (2003) 361-365

[13] R. J. Barnes, R. R. Bandi, F. Chua, J. H. Low, T. Aung, N. Barraud, A. G. Fane, The roles of Pseudomonas aeruginosa extracellular polysaccharides in biofouling of reverse osmosis membranes and nitric oxide induced dispersal, J. Membr. Sci., 466 (2014) 161–172

[14] C. Nuengjamnong, J. H. Kweon, J. Cho, C. Polprasert, K. H. Ahn, Membrane fouling caused by extracellular polymeric substances during microfiltration processes, Desalin., 179 (2005) 117-124

[15] S. S. Branda, F. Chu, D. B. Kearns, R. Losick, R. Kolter, A major protein component of the Bacillus subtilis biofilm matrix, Mol. Microbiol., 59 (2006) 1229–1238

[16] H. C. Flemming, J. Wingender, The biofilm matrix, Microbiol. Rev., 89 (2010) 623-633

[17] Q. Wei, L. Ma, Biofilm matrix and its regulation in Pseudomonas aeruginosa, J. Mol. Sci., 14 (2013) 20983–21005

[18] B. W. Peterson, Y. He, Y. Ren, A. Zerdoum, M. R. Libera, P. K. Sharma, A. J. Van Winkelhoff, Viscoelasticity of biofilms and their recalcitrance to mechanical and chemical challenges, FEMS Microbiol. Rev., 39 (2015) 234–245

[19] J. S. Vrouwenvelder, S. A. Manolarakis, J. P. Van der Hoek, J. A. M. Van Paassen, J. M. C. Van Agtmaal, M. C. M. Van Loosdrecht, Quantitative biofouling diagnosis in full scale nanofiltration and reverse osmosis installations, Water Res., 42 (2008) 4856-4868

[20] J. A. Novitsky, Degradation of dead microbial biomass in a marine sediment, Appl. Environ. Microb., 52 (1986) 504-509

[21] M. L. Yallop, D. M. Paterson, P. Wellsbury, Interrelationships between rates of microbial production, exopolymer production, microbial biomass, and sediment stability in biofilms of intertidal sediments, Microb. Ecol., 39 (2000) 116-127

[22] W. A. M. Hijnen, E. R. Cornelissen, D. Van der Kooij, Threshold concentrations of biomass and iron for pressure drop increase in spiral-wound membrane elements, Water Res., 45 (2011) 1607-1616

[23] M. Herzberg, S. Kang, M. Elimelech, Role of extracellular polymeric substances (EPS) in biofouling of reverse osmosis membranes, Environ. Sci. Technol., 4312 (2009) 4393-4398

[24] L. O. Villacorte, M. D. Kennedy, G. L. Amy, J. C. Schippers, The fate of transparent exopolymer particles (TEP) in integrated membrane systems: removal through pre-treatment processes and deposition on reverse osmosis membranes, Water Res., 43 (2009) 5039-5052

[25] T. J. Stewart, J. Traber, A. Kroll, R. Behra, L. Sigg, Characterization of extracellular polymeric substances (EPS) from periphyton using liquid chromatography-organic carbon detection–organic nitrogen detection (LC-OCD-OND), Environ. Sci. Pollut. R., 205 (2013) 3214-3223

[26] B. G. Choi, J. Cho, K. G. Song, Correlation between effluent organic matter characteristics and membrane fouling in a membrane bioreactor using advanced organic matter characterization tools, Desalin., 309 (2013) 74-83

[27] S. A. Huber, A. Balz, M. Abert, W. Pronk, Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography–organic carbon detection–organic nitrogen detection (LC-OCD-OND), Water Res., 45 (2011) 879-885

[28] M. T. Khan, C. L. de O. Manes, C. Aubry, L. Gutierrez, Kinetic study of seawater reverse osmosis membrane fouling, Environ. Sci. Technol., 47 (2013) 10884-10894

[29] S. E. Jensen, P. Hubrechts, B. M. Klein, K. R. Hasløv, Development and validation of an ATP method for rapid estimation of viable units in lyophilised BCG Danish 1331 vaccine, Biol., 36 (2008) 308–314

[30] G. Massons-Gassol, G. Gilabert-Oriol, R. Garcia-Valls, V. Gomez, T. Arrowood, Development and application of an accelerated biofouling test in flat cell, Desalin. Water Treat., 57 (2016) 23318-23325

[31] A. C. Fonseca, R. S. Summers, A. R. Greenberg, M. T. Hernandez, Extracellular polysaccharides, soluble microbial products, and natural organic matter impact on nanofiltration membranes flux decline, Environ. Sci. Technol., 41 (2007) 2491-2497

[32] J. Cho, S. W. Hermanowicz, J. Hur, Effects of experimental conditions on extraction yield of extracellular polymeric substances by cation exchange resin, The Sci. World J., 2012 (2001) 1-6

[33] A. Eldyasti, G. Nakhla, J. Zhu, Impact of calcium on biofilm morphology, structure, detachment and performance in denitrifying fluidized bed bioreactors (DFBBRs), Chem. Eng. J., 232 (2013) 183-195

[34] S. R. Suwarno, X. Chen, T. H. Chong, V. L. Puspitasari, D. McDougald, Y. Cohen, A. G. Fane, The impact of flux and spacers on biofilm development on reverse osmosis membranes, J. Mol. Sci., 405 (2001) 219-232

[35] E. Zuriaga-Agustí, A. Bes-Piá, A. Mendoza-Roca, Influence of extraction methods on proteins and carbohydrates analysis from MBR activated sludge flocs in view of improving EPS determination, Sep. Purif. Technol., 112 (2013) 1-10

[36] M. Dubois, K. A. Gilles, J. K. Hamilton, F. Rebers, Colorimetric method for determination of sugars and related substances, Anal. Chem., 28 (1956) 350-356

[37] T. Kawaguchi, A. Decho, A laboratory investigation of cyanobacterial extracellular polymeric secretions (EPS) in influencing $CaCO_3$ polymorphism, J. Cryst. Growth., 240 (2000) 230-235

[38] W. Hijnen, C. Castillo, A. Brouwer-Hanzens, Quantitative assessment of the efficacy of spiral-wound membrane cleaning procedures to remove biofilms, Water Res., 46 (2001) 6369-6381

[39] X. Pan, J. Liu, D. Zhang, Comparison of five extraction methods for extracellular polymeric substances (EPS) from biofilm by using three dimensional excitation-emission matrix (3DEEM) fluorescence spectroscopy, Water SA., 36 (2010) 111-116

[40] X. Zhang, P. Bishop, Biodegradability of biofilm extracellular polymeric substances, Chemosphere., 50 (2003) 63-69

[41] P. Smith, R. I. Krohn, G. T. Hermanson, A. K. Mallia, F. H. Gartner, M. Provenzano, D. C. Klenk, Measurement of protein using Bicinchoninic acid, Anal. Biochem., 150 (1985) 76-85

[42] C. Pellicer-Nàcher, C. Domingo-Félez, A. Mutlu, Critical assessment of extracellular polymeric substances extraction methods from mixed culture biomass, Water Res., 47 (2013) 5564-5574

[43] A. Bujacz, Structures of bovine, equine and leporine serum albumin, Acta Crystallogr., 86 (2001) 1278-1289

[44] W. Ying, N. Siebdrath, W. Uhl, V. Gitis, M. Herzberg, New insights on early stages of RO membranes fouling during tertiary wastewater desalination, J. Membr. Sci., 466 (2014) 26-35

[45] X: Zheng, R. Mehrez, M. Jekel, M. Ernst, Effect of slow sand filtration of treated wastewater as pre-treatment to UF, Desalin., 249 (2009) 591-595

# Chapter 3

# Validation of flat cell units to simulate spiral wound RO biofouling

**This chapter was accepted for publication on 09/2017 (I.F. 2.843):**

G. Massons-Gassol, G. Gilabert-Oriol, J. Johnson, T. Arrowood, *Comparing biofouling development in membrane fouling simulators and spiral wound reverse osmosis elements using river water and municipal wastewater*, Ind. Eng. Chem. Res., 56 (2017) 11628-11633

**doi: 10.1021/acs.iecr.7b03219**

# 1 INTRODUCTION

Water scarcity is recognized as one of the main threats that mankind is facing globally [1]. Reverse osmosis (RO) membrane technology has developed as a promising, cost effective technology to remove contaminants from nonpotable waters and provide fresh water supply to meet the growing demand [2]. RO elements, however, can suffer from progressive loss of performance when treating challenging waters due to fouling [3]. Among all fouling types, biofouling is one of the most complex to manage in RO water treatment systems [4]. It occurs when bacteria colonize and form biofilms in the feed channel of the RO elements, causing increased friction for water flow. This increases the differential pressure (dP) [5], leading to hydraulic imbalance and, if not controlled, can ultimately damage the element. Additionally, biofilms can affect membrane transport properties, as the polymeric film formed on the membrane surface decreases the overall water permeability [6]. Each of these effects increases the energy of operation and leads to frequent system shutdowns for chemical cleanings to recover membrane performance. The high pH conditions needed to remove biofilms during cleaning can result in membrane hydrolysis and shorten the useful life of the element. Therefore, in total, system productivity, chemical usage, membrane life, and energy each contribute to a higher cost of water production when biofouling occurs. Mechanisms to control biofouling are needed to enable long term performance when treating water with high contamination levels [7].

Studying biofouling in water treatment systems is complex due to the multiple variables that affect biofilm formation [5]. To accelerate research, screening tools which enable biofouling experiments to be conducted with different water types and capable to explore multiple parameters in parallel are needed.

Membrane fouling simulators (MFS) have been described as a cost-effective tool to predict biofouling evolution in full-scale RO systems [8]. Differential pressure in the MFS

models the increase of an RO system, since biofouling generally starts in the first centimeters of the feed-concentrate channel [9][10]. Thus, MFS units can be used to study biofilm formation and quickly screen new solutions without having to manufacture an entire RO element [11].

MFS units are especially suited for testing one of the key parameters influencing biofouling in spiral wound RO elements, the feed spacer [12]. The main role of the feed spacer is to promote turbulence and improve mass transfer by distorting the laminar profile of the axial flow when operated in cross-flow configuration [13]. However, low shear stress zones from flow stagnation are created by the feed spacer [14], and simulations suggest that these are the areas where biofilm develops more strongly [15]. Defining feed spacer design features (e.g., thickness, strand angle, spacing between filaments) to improve biofouling resistance and reduce the rate of element pressure drop increase has been a topic of recent interest [16][17][18].

The aim of this work is to demonstrate the ability of MFS units to model the biofouling that occurs in RO elements when treating water with high fouling potential. Additionally, the impact of feed spacer type on the rate of differential pressure increase is explored in a set of RO elements and MFS units. If results obtained are comparable, these will demonstrate the usefulness of the MFS units as a screening tool to predict module performance under biofouling environments.

## 2 MATERIALS AND METHODS

### 2.1 Membrane Fouling Simulators

The membrane fouling simulator (MFS) units are portable and can be installed in a feedwater side-stream as a stand-alone test unit or in parallel with full-scale RO systems (Figure 3-1). MFS are small units which simulate the feed channel of an RO element by

layering feed spacer on top of membrane, fitted in a rectangular flow cell. Water is directed through the feed spacer channel at a set flow rate, but does not permeate. The differential pressure across the MFS feed channel is monitored during the experiment. In the present study four MFS units (MFS1, MFS2, MFS3, and MFS4) were operated in parallel. The transparent cells were assembled with a feed spacer and membrane coupon (20 cm length and 4 cm width) in each. Manual readings from the pressure drop indicator were recorded daily during the course of each trial. The pressure drop as a function of time from the MFS units were compared to the respective full-scale RO systems that ran in parallel.

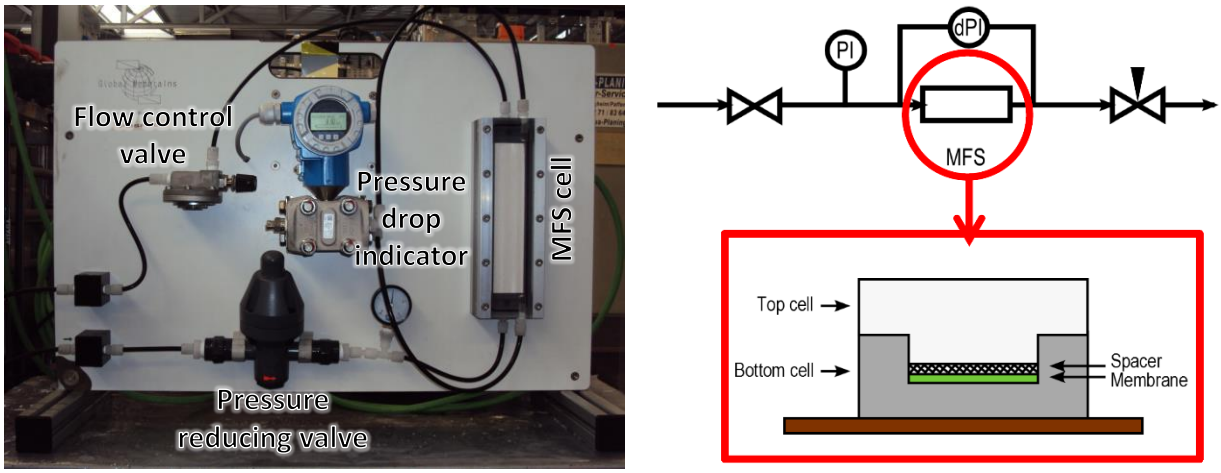



**Figure 3-1. MFS simulator picture and diagram**

## 2.2 RO Element Testing Units

### 2.2.1 The 2.5 in. Multielement RO Test

The pilot plant is configured with eight pressure vessels operated in parallel, each holding one 2.5 in. diameter by 14 in. long spiral-wound RO element (2514). A single feed pump provides the feed to all eight pressure vessels. This system has a sampling valve after the pump to use the side-stream as feedwater to operate the MFS units in parallel (Figure 3-2).

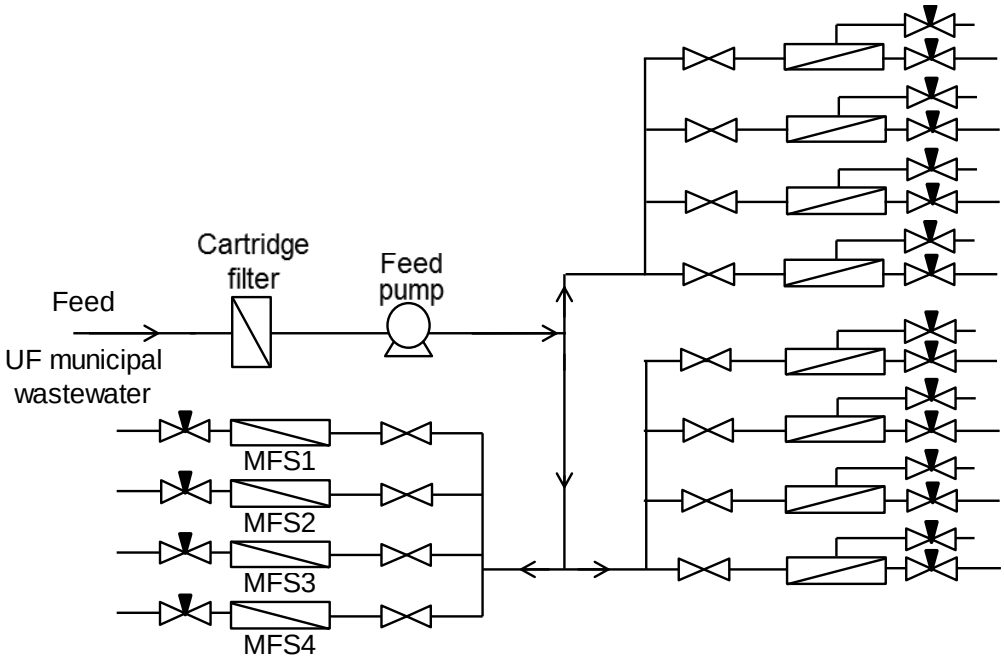



**Figure 3-2. Configuration of the 2.5 RO testing unit with MFS installed in parallel**

The 2514 elements used in each vessel had identical element designs (0.55 $m^2$ membrane area and 22 mil thick feed spacer) with the aim to provide seven replicate data points and measure vessel-to-vessel reproducibility. The elements were controlled and operated at the same feed flow and recovery and the feed-to-concentrate press drop of each vessel was monitored over the course of the experiment. Specific operating conditions for each 2.5 in. pressure vessel (PV) and MFS are provided in Table 3-1. Four MFS units were installed in parallel to the 2514 elements. Each transparent MFS cell was assembled with the same membrane and feed spacers type (34 mil thickness) in order to provide four replicates. The cross-flow velocity for each system was calculated [19] based on spacer thickness, dimensions of the 2514 element or MFS cell, and feed flow.

**Table 3-1. 2.5 test bench and MFS units conditions used during the wastewater test**

| | 2.5 test bench (7 PV) | MFS units (4 units) |
|---|---|---|
| Duration (days) | 46 | |
| Temperature (°C) | 23-27 | |
| Feed flow (L/h) | 340 | 16 |
| Flux (L/m²h) | 25 | - |
| Recovery (%) | 4 | - |
| Membrane area (m²) | 0.55 | 0.008 |
| Spacer type (mil) | 22 | 34 |
| Spacer thickness (mm) | 0.56 | 0.86 |
| Cross-flow velocity (m/s) | 0.09 | 0.13 |

At the end of the fouling period, the 2514 elements and the MFS cells were autopsied. Samples of feed spacer and membrane from each pilot plant were used to quantify and compare the ATP and TOC accumulated during the experiment.

### 2.2.2 The 8 in. Multielement RO Test System

The 8 in. RO element bench has three vessels operated in parallel. Each are equipped with three 8-inch diameter by 40 in. long elements (8040), as shown in Figure 3-3. The ultrafiltrated brackish water is fed to the RO vessels using a single feed pump. Sodium metabisulfite (SMBS, 3 mg/L) and antiscalant (AS, 1 mg/L) were dosed to avoid any chlorination risk and control scaling, respectively. The four MFS units were connected upstream of the feed pump but downstream of the chemical injection point.

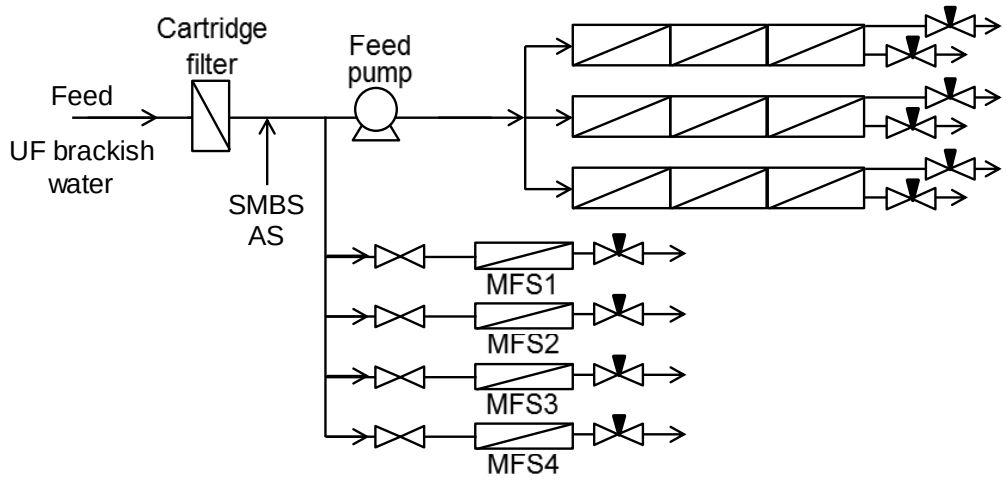



**Figure 3-3. The 8 in. multielement RO test system with MFS simulators in parallel**

Each pressure vessel and MFS unit were equipped with different feed spacer types as summarized in Table 3-2. The performance of the different feed spacer designs was tested under biofouling conditions. Three of the feed spacers were tested in both 8 in. elements and MFS cells, in order to confirm the reliability of the pressure drop results.

The two systems were adjusted so that the inlet cross-flow velocity for each feed spacer configuration was the same between the 8 in. test bench and the MFS unit. Despite the feedwater temperature being only 15 – 18$^{o}$C, biofouling developed very quickly and pressure drop increased after only 1 week of operation. Upon completion of the testing, only membrane and spacer samples from the MFS units were analyzed for biofilm quantification. The 8 in. elements were allowed to continue to operate for long-term performance testing.

**Table 3-2. Operating conditions 8-inch element vs. MFS comparison**

| | 8-inch element test bench | | | MFS units | | | |
|---|---|---|---|---|---|---|---|
| | PV1 | PV2 | PV3 | MFS1 | MFS2 | MFS3 | MFS4 |
| **Spacer type** | 28 STD | 34 STD | 34 T1 | 28 STD | 34 STD | 28 T1 | 34 T1 |
| **Spacer thickness (mm)** | 0.71 | 0.86 | 0.86 | 0.71 | 0.86 | 0.71 | 0.86 |
| **Membrane area ($m^2$)** | 111.4 | 111.4 | 111.4 | 0.008 | 0.008 | 0.008 | 0.008 |
| **Feed flow (L/h)** | 8,400 | 8,400 | 8,400 | 16 | 16 | 16 | 16 |
| **Cross-flow velocity (m/s)** | 0.16 | 0.13 | 0.13 | 0.16 | 0.13 | 0.16 | 0.13 |
| **Flux ($L/m^2h$)** | 24 | 24 | 24 | - | | | |
| **Recovery (%)** | 33 | 33 | 33 | - | | | |

## 2.3 Analytical Biofouling Characterization

After each trial was completed, the fouling distribution on the MFS was examined using a Leica MS5 stereoscope. Additionally, membrane and feed spacer samples were taken from the MFS coupons and the RO elements. Fouling was extracted using the protocol described in previous studies [19]. The extracted foulant was analyzed for total organic carbon (TOC) using a Shimadzu TOC-L analyzer and adenosine triphosphate (ATP) using a Celsis Advance Luminometer. Nitrate and phosphate concentration from feedwater were analyzed using kits and spectrophotometer (DR500) from Hach.

## 2.4 Water Sources

Water from the secondary effluent of the Vila-seca wastewater treatment plant and the Ebro River provide the feedwater to the 2.5 in. and the 8 in. RO element systems, respectively. Both waste and river waters are pretreated with Dow Ultrafiltration

modules prior to feeding to the downstream RO units. Table 3-3 summarizes the basic water composition of each water source.

**Table 3-3. Vila-seca wastewater and Ebro River water characterization**

| | **Vila-seca wastewater** (2.5-inch RO elements test) | **Ebro River water** (8-inch RO elements test) |
|---|---|---|
| TDS (mg/L) | 1,440 | 1,000 |
| TOC (mg/L) | 6.6 | 1.3 |
| ATP (ng/L) | 83 | 6 |
| Nitrate (mg/l) | 30 | 11 |
| Phosphate (mg/l) | 0.55 | 0.04 |

## 3 RESULTS AND DISCUSSION

### 3.1 MFS vs. 2.5 in. Element Test Bench

The MFS units were expected to show a similar biofouling characteristics as the elements, despite having less surface area to harbor bacteria. The ratio of membrane length between a MFS cell (4 cm x 20 cm) and a 2514 element (6.4 cm diameter x 35.5 cm long) was 1:1.8. Using municipal wastewater as feed, the rate of biofouling growth on the 2.5 in. elements and MFS cells was compared. Additionally, the reproducibility of each pilot unit was evaluated by comparing the average dP of seven elements and four MFS cells. As described in section 2.2.1, all the spiral-wound elements and MFS units were assembled with the same membrane and feed spacer and operated at the same conditions.

The biofouling rate of the Vila-seca wastewater was moderate. It took nearly 2 weeks before a measurable increase in the differential pressure was seen (Figure 3-4). The measurement variability between the 2.5 in. elements was about 8% while the MFS units have slightly higher variability (17%), due to manual operation and smaller sample size.

However, they provided excellent reproducibility of the stages of biofilm development on the spiral-wound elements.

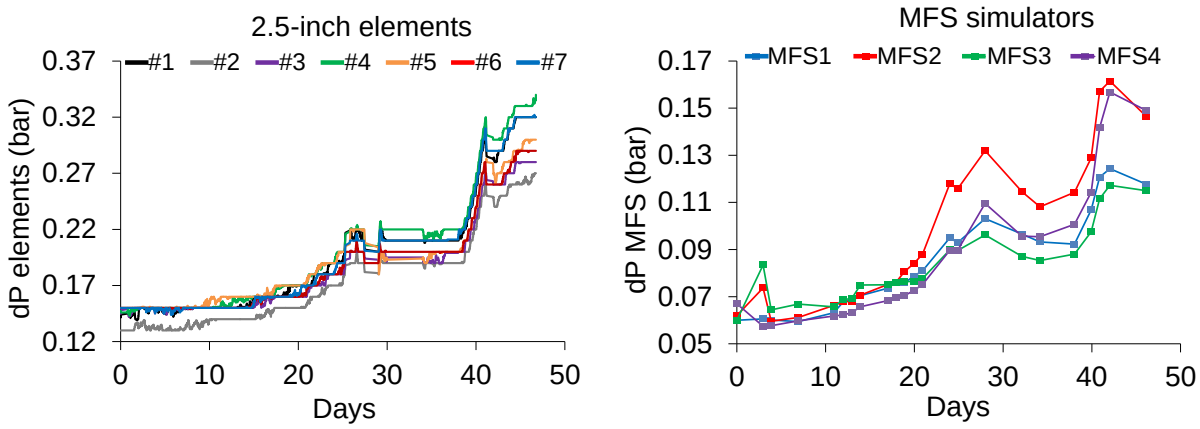



**Figure 3-4. Pressure drop of MFS and 2.5 in. elements**

The agreement between the 2.5 in. elements and the MFS cells performance is illustrated in Figure 3-5, where the daily average change in differential pressure is compared between the two units. The high correlation observed between the two sets of results was proved to be statistically significant using JMP Pro 12.2.0 with a calculated p-value lower than 0.0001. However, variability increases at higher degrees of biofouling. It can also be observed that the percentage dP increase in MFS was slightly higher than on 2.5 in. modules. The analytical results (Table 3-4) also showed the same trend. This could be explained by minor differences in the operating conditions like flux or cross-flow velocity (more details can be found in Table 3-1). Thus, the comparison was more reliable at early stages, where the results showed less scattering.

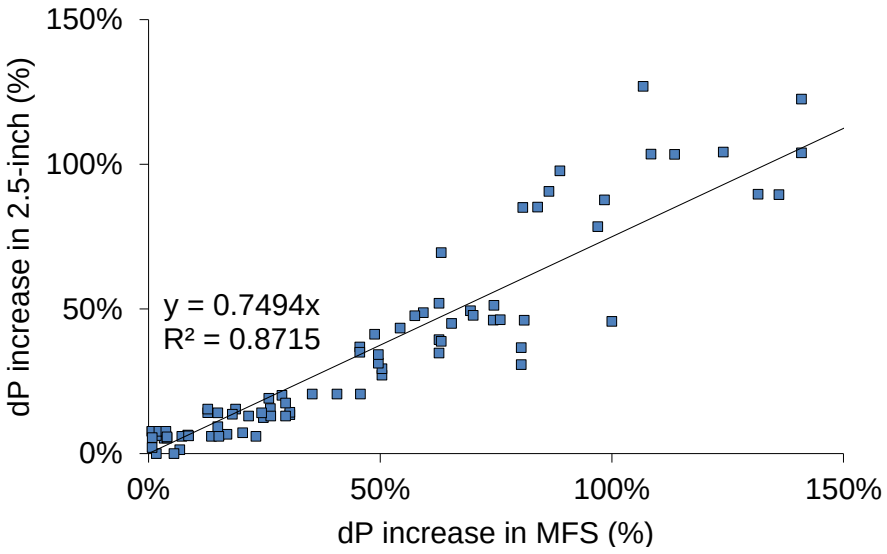



**Figure 3-5. Correlation in differential pressure increase of MFS and 2.5 in. elements**

The biofilm formed in the MFS unit was visually more concentrated on the feed spacer strands than the membrane surface (Figure 3-6), where flow was from left to right. This was similar to the observation of the biofilm distribution in the autopsied element, where the inlet part was showing more biofouling accumulation than the outlet areas.

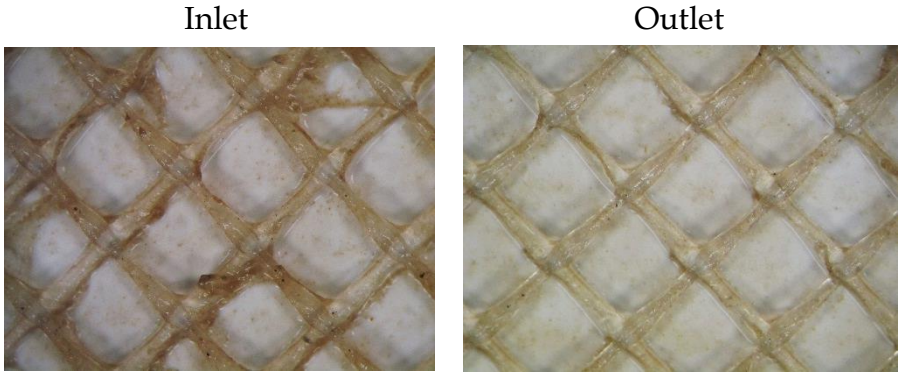



**Figure 3-6. Membrane and spacer assembly in the MFS after operation**

ATP and TOC analysis confirmed the presence of biofouling in both units (Table 3-4) and provided a useful measurement to compare the extent of biofouling in each system.

Among replicates, the standard deviation of the measurements was about 14%, which was in agreement with similar analyses found in the literature [20][21].

**Table 3-4. Biofouling Quantification in MFS Coupons Compared to Spiral-Wound Elements**

| ATP (ng/cm²) | | TOC (mg/m²) | |
|---|---|---|---|
| **MFS** | **2.5-inch** | **MFS** | **2.5-inch** |
| 8.7 | 7.9 | 19 | 32 |
| 8.3 | 13 | 18 | 37 |
| 8.9 | 12 | 21 | 47 |
| 5.8 | 8.2 | 20 | 38 |
| - | 9.2 | - | 45 |
| - | 11 | - | 49 |
| - | 11 | - | 34 |
| **Av.: 8±1** | **Av.: 10±2** | **Av.: 19±1** | **Av.: 40±6** |

### 3.2 MFS vs. 8-inch multi-element system

When comparing the MFS units to a three-elements 8 in. pressure vessel (20.3 cm diameter x 303 cm long), the ratio of total length, 1:15.2, is much greater than for the 2.5 in. single element, 1:1.8. The ability for the MFS to provide comparative relative pressure drop performance to full-scale system was examined. In this study, each pressure vessel was equipped with three 400 ft² active area elements containing different feed spacer types. Three of the MFS units were assembled with the same three types of spacers used in the elements, and the fourth MFS unit used a prototype 28 mil feed spacer. The feed spacers used in this study can be characterized based on the angle, spacing between strands, and thickness, as represented in Figure 3-7.

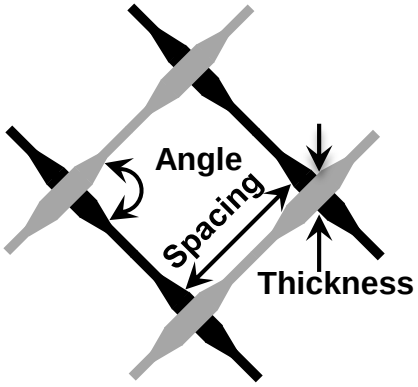



**Figure 3-7. Feed spacer geometry characterization**

Details of the different feed spacers used in each system are summarized in Table 3-5. Due to the proprietary nature of the prototype T1 feed spacer, directional arrows were used to show their relative measurement as compared to the standard version of the same thickness.

**Table 3-5. Details of the different feed spacers assessed**

| Spacer | Thickness | Spacing | Angle | MFS | 8-inch |
|---|---|---|---|---|---|
| 28 STD | 0.71 mm | 2.82 mm | 90° | ✓ | ✓ |
| 34 STD | 0.86 mm | 2.82 mm | 90° | ✓ | ✓ |
| 28 T1 | 0.71 mm | ↑ | ↓ | ✓ | - |
| 34 T1 | 0.86 mm | ↑ | ↓ | ✓ | ✓ |

This test began with the four parallel MFS units tied-in to the 8 in. element system feed line. Care was taken to ensure that MFS units were operated with the same cross-flow velocity as the RO modules (Table 3-2). Doing so provided the most comparable biofouling environment for evaluating the performance of the MFS units relative to the 8 in. elements. It also allowed a comparison of the feed spacer hydrodynamics, by

comparing their initial pressure drop. Figure 3-8 summarizes the differential pressure data collected during the experiment in both plants. The relative order of differential pressure measured in the 8 in. system was the same as that of the MFS units, from higher to lower: 28 STD, 34 STD, and 34 T1. The absolute differential pressure registered on the MFS for the 34 STD configuration was slightly lower than on the spiral-wound element. This could be caused by the inherent variability due to the manual assembly of the MFS units, as described in section 3.1. Also noteworthy in the MFS comparison, the differential pressure of the 28 T1 feed spacer was significantly lower than the two 34 mil feed spacers. This data shows that in addition to feed spacer thickness, spacer geometry can significantly impact the initial feed-concentrate differential pressure, as well as its increase due to biofouling.

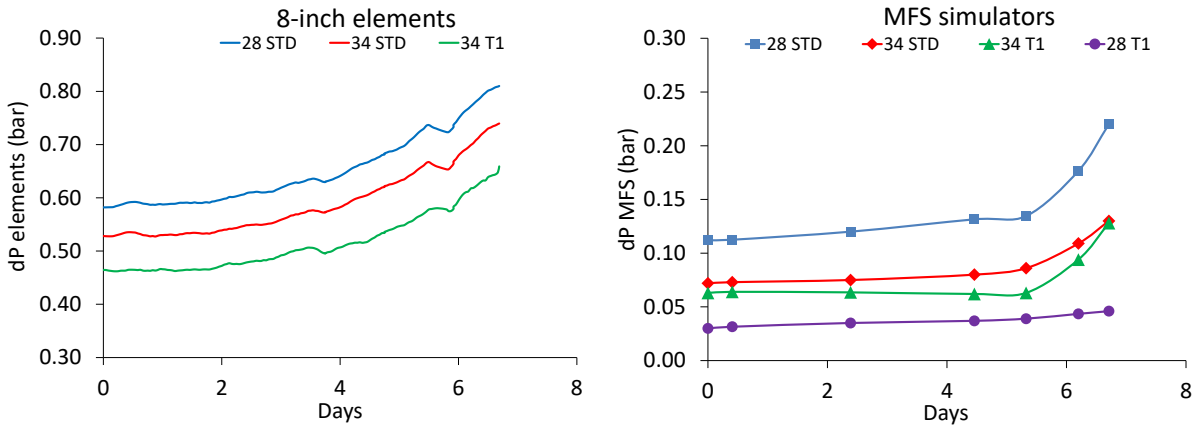



**Figure 3-8. Differential pressure rise in 8 in. element test bench and MFS units**

The Ebro River water caused high fouling potential in both the 8 in. and MFS systems as indicated by the rapid pressure drop increase within 7 days of operation (Figure 3-8). The performance of each spacer type gave similar relative differential pressure performance. The initial increase in pressure drop in the 8 in. element system was not captured in the MFS units, because the pressure readings were manual and the rise occurred over the weekend. However, on the last phase, the trends were very similar in both plants.

After operation, the MFS were disassembled and the foulant was extracted from membrane and feed spacer samples. ATP and TOC concentrations were measured and are summarized in Table 3-6. Significant TOC accumulated in each unit, and ATP levels confirmed high biological activity, in accordance with the operational results. The sample taken from the 28 T1 unit showed the lowest amount of fouling among all tested spacers. This agrees with the observed low differential pressure rise during the testing. Based on these promising results, a more thorough investigation to confirm the improved biofouling performance of the 28 T1 spacer will be explored in the future.

**Table 3-6. Biofouling Quantification in MFS Coupons**

| Feed spacer type | ATP (ng/cm²) | TOC (mg/m²) |
|---|---|---|
| 28 STD | 2.7 | 98 |
| 34 STD | 3.0 | 56 |
| 34 T1 | 5.2 | 103 |
| 28 T1 | 2.9 | 33 |

The biofouling distribution over the coupons was visually examined. In each unit, more biofouling was accumulated on the inlet side of the MFS than on the outlet side. Figure 3-9 shows the results from the 34 mil STD coupon. This observation is in agreement with other studies that show that most of the biofouling was accumulated on the feed side of the first element of an RO system [22]. The distribution of biofouling accumulation was similar to that observed on the fouled MFS coupons from the wastewater test (Figure 3-6), where feed flow was from left to right. The biofilm was a sticky yellowish slime, mostly attached on the feed spacer strands.

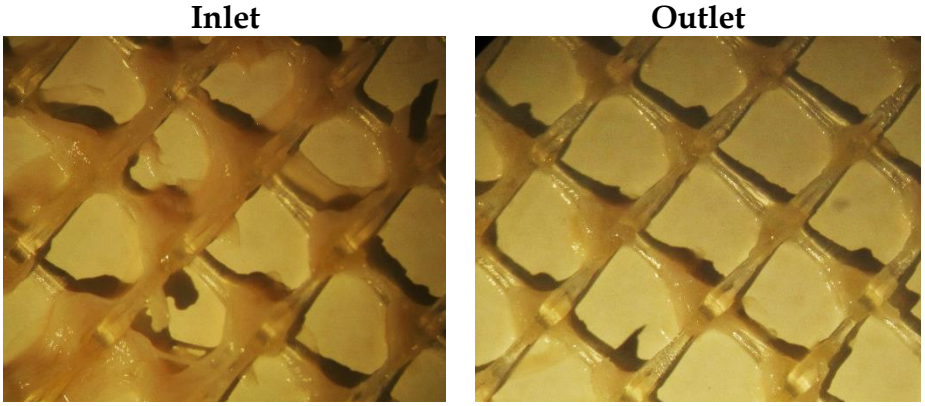



**Figure 3-9. Visual comparison of the inlet and outlet end of the 34 STD coupon**

## 4 CONCLUSIONS

The MFS units showed a similar biofouling trend as spiral-wound RO systems when exposed to river water and municipal wastewater. The MFS simulators can be useful screening tool to evaluate the pressure drop performance of large spiral-wound elements, as well as different module designs, such as feed spacer, during biofouling events.

The magnitude of the absolute differential pressure changes was not the same in the MFS than in the element systems due to the difference in scale. However, similar relative trends were observed and demonstrated the usefulness of the MFS units as a screening tool for biofouling in RO units.

This study also showed promising biofouling resistance for a feed spacer design labeled as 28 T1, with both lower relative pressure drop increase and lower biofouling accumulation compared to three other spacer tested. These qualities could enable savings in the energy required to operate the RO elements and extended performance when treating challenging water. Further examination of the biofouling resistance of this spacer type will be the subject of future studies.

## 5 REFERENCES

[1] C. Fritzmann, J. Löwenberg, T. Wintgens, T. Melin, State-of-the-art of reverse osmosis desalination, Desalin., 216 (2007) 1-76

[2] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: water sources, technology, and today's challenges, Water Res., 43 (2009) 2317–2348

[3] K. P. Lee, T. C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination—development to date and future potential, J. Membr. Sci., 370 (2011) 1-22

[4] H. C. Flemming, Biofouling in water systems–cases, causes and countermeasures, Appl. Microbiol. Biot., 59 (2002) 629-640

[5] C. Sun, L. Fiksdal, A. Hanssen-Bauer, M. B. T. Rye, T. Leiknes, Characterization of membrane biofouling at different operating conditions (flux) in drinking water treatment using confocal laser scanning microscopy (CLSM) and image analysis, J. Membr. Sci., 382 (2011) 194-201

[6] S. R. Suwarno, X. Chen, T.H. Chong, V.L. Puspitasari, D. McDougald, Y. Cohen, S.A. Rice, A.G. Fane, The impact of flux and spacers on biofilm development on reverse osmosis membranes, J. Membr. Sci., 405 (2012) 219–232

[7] A. Matina, Z. Khana, S.M.J. Zaidia, M.C. Boyceb, Biofouling in reverse osmosis membranes for seawater desalination: Phenomena and prevention, Desalin., 281 (2011) 1–16

[8] D. J. Miller, P. A. Araujo, P. B. Correia, M. M. Ramsey, J. C. Kruithof, M. C. Van Loosdrecht, J. S. Vrouwenvelder, Short-term adhesion and long-term biofouling testing

of polydopamine and poly (ethylene glycol) surface modifications of membranes and feed spacers for biofouling control, Water Res., 46 (2012) 3737-3753.

[9] J. S. Vrouwenvelder, S. A. Manolarakis, J. P. Van der Hoek, J. A. M. Van Paassen, W. G. J. Van der Meer, J. M. C. Van Agtmaal, M. C. M. Van Loosdrecht, Quantitative biofouling diagnosis in full scale nanofiltration and reverse osmosis installations, Water Res., 42 (2008) 4856-4868.

[10] J. S. Vrouwenvelder, M. C. M. Van Loosdrecht, J. C. Kruithof, Early warning of biofouling in spiral wound nanofiltration and reverse osmosis membranes, Desalin. 265 (2011) 206-212.

[11] J.S. Vrouwenvelder, J.A.M. van Paassen, L.P. Wessels, A.F. Van Dam, S.M. Bakker, The Membrane Fouling Simulator: A practical tool for fouling prediction and control, J. Membr. Sci., 281 (2006) 316–324

[12] J. S. Vrouwenvelder, D. G. Von Der Schulenburg, J. C. Kruithof, M. L. Johns, M. C. M. Van Loosdrecht, Biofouling of spiral-wound nanofiltration and reverse osmosis membranes: a feed spacer problem, Water Res., 43 (2009) 583-594.

[13] A. L. Ahmad, K. K. Lau, M. A. Bakar, Impact of different spacer filament geometries on concentration polarization control in narrow membrane channel, J. Membr. Sci., 262 (2005) 138-152.

[14] J. S. Vrouwenvelder, C. Picioreanu, J. C. Kruithof, M. C. M. Van Loosdrecht, Biofouling in spiral wound membrane systems: three-dimensional CFD model based evaluation of experimental data, J. Membr. Sci., 346 (2010) 71-85

[15] M. S. M. F. Shakaib, M. Hasani, M. Mahmood, CFD modeling for flow and mass transfer in spacer-obstructed membrane feed channels, J. Membr. Sci., 326 (2009) 270-284.

[16] S. S. Bucs, A. I. Radu, V. Lavric, J. S. Vrouwenvelder, C. Picioreanu, Effect of different commercial feed spacers on biofouling of reverse osmosis membrane systems: A numerical study, Desalin., 343 (2014) 26–37

[17] R. Valladares Linares, S. S. Bucs, Z. Li, M. AbuGhdeeb, G. Amy, J. S. Vrouwenvelder, Impact of spacer thickness on biofouling in forward osmosis, Water Res., 57 (2014) 223–233

[18] K. Majamaa, J. E. Johnson, U. Bertheas, Three steps to control biofouling in reverse osmosis systems, Desalin. Water Treat., 42 (2012): 107-116.

[19] G. Massons-Gassol, G. Gilabert-Oriol, R. Garcia-Valls, V. Gomez, T. Arrowood, Development and application of an accelerated biofouling test in flat cell, Desalin. Water Treat., 57 (2016) 23318-23325

[20] D. van der Kooij, H. R. Veenendaal, W. J. H. Scheffer, Biofilm formation and multiplication of Legionella in a model warm water system with pipes of copper, stainless steel and cross-linked polyethylene, Water Res., 39 (2005) 2789–2798

[21] N. Oulahal-Lagsir, A. Martial-Gros, M. Bonneau, L. J. Blum, Ultrasonic methodology coupled to ATP bioluminescence for the non-invasive detection of fouling in food processing equipment—validation and application to a dairy factory, J. Appl. Microb., 89 (2000) 433–441

[22] M. J. Boorsma, S. Dost, S. Klinkhamer, J. C. Schippers, Monitoring and controlling biofouling in an integrated membrane system. Desalin. Water Treat., 31(2011) 347-353.

# Chapter 4

# Development and application of an accelerated biofouling test in flat cell

**This chapter was accepted for publication on 03/2016 (I.F. 1.63):**

G. Massons-Gassol, G. Gilabert-Oriol, R. Garcia-Valls, V. Gomez, T. Arrowood, *Development and application of an accelerated biofouling test in flat cell*, Desalin. Water Treat., 57 (2016) 23318-23325

**doi: 10.1080/19443994.2016.1180476**

# 1 INTRODUCTION

Reverse osmosis membranes are prone to suffer from fouling due to the trace contaminants found in natural feed water [1]. The term fouling in reverse osmosis refers to the accumulation of material on the membrane surface and/or within the feed channel of the spiral wound element. If this phenomenon is not addressed, the element could suffer from a severe loss of performance [2]. There are four main types of fouling in the reverse osmosis membranes including colloidal/particle, biological, organic, and scaling (precipitated inorganic salts). Biological fouling is characterized to be especially challenging to prevent and control [7].

Laboratory experimental methods are needed to more rapidly and systematically optimize the reverse osmosis membrane chemistry to have a higher biofouling resistance. Current published methods for reproducing biofilm on reverse osmosis membranes are based on bacteria attachment determination [11][8]. The main protocols applied are the immersion test using the Center for Disease Control (CDC) biofilm reactor [20] and filtration with a high concentration of bacterial solutions [7][21][9].

Although these methods are commonly used, they are not realistic when simulating reverse osmosis operating conditions. Variables such as feed pressure, cross-flow velocity, feed spacer hydrodynamics and/or feed water composition are not measured or controlled. Therefore, the challenge remains to correlate the data obtained using these methods with observations in the field [7]. Moreover, these methods require sophisticated laboratory equipment and safety standards as they involve bacteria culturing.

The Tarragona Global Water Technology Center has access to natural water sources including the Ebro River water, wastewater, and seawater. These waters have natural sources of bacteria which can form biofilms.

The goal of this project is to utilize the continuous supply of the Ebro River water and a membrane flat cell unit to create an accelerated biofouling test protocol to study membrane biofouling. This membrane flat sheet testing capability can provide an efficient fouling performance screening without the need of extra investment to build an entire reverse osmosis module yet allow parameters such as membrane flux, feed velocity, and feed pressure to be adjusted for each test.

## 2 EXPERIMENTAL PROCEDURES

### 2.1 Flat cell description

The flat cell pilot unit used has three side-by-side flat cells. The system was manually operated in once-through mode without temperature control (Figure 4-1). Feed spacer and membrane coupons were cut to fit the cell using a template. The O-rings on the top and bottom flat cell plates ensure that the system is water tight when bolted together, as observed in Figure 4-2. Each cell provides an active membrane area of 84 $cm^2$. In the assembly, the membrane feed side has a void space which is 31 mil (31 thousandth of an inch) deep. A 28 mil feed spacer coupon is placed in this space to provide a representative shear environment at the membrane surface. There is a 3 mil difference in the void space and the feed spacer thickness which can create a potential for by-pass in the feed channel. However, feed spacer imprinting is observed on the membrane after each experiments, which indicates that the spacer is in contact with the membrane when mounted. Additionally, the feed spacer did not appear to deform during the experiment (i.e., shift to one end), suggesting that the fit in the channel is secure enough to maintain its position on the membrane surface when mounted. Since the focus for this test method was to study the impact of membrane chemistry on biofouling and not the impact of the feed spacer, further measures to eliminate the hypothetical by-pass were not implemented at this time.

A concentrated nutrient solution (labeled "Acetate" in Figure 4-1) was dosed to the Ebro River water in order to accelerate the fouling process. Feed pressure and feed flow were adjusted using a by-pass needle valve. Individual cell feed water flows and recoveries were set by adjusting the feed and concentrate valves. Feed flows were measured using individual flow-meters with interval range of 1 to 4 L/min.

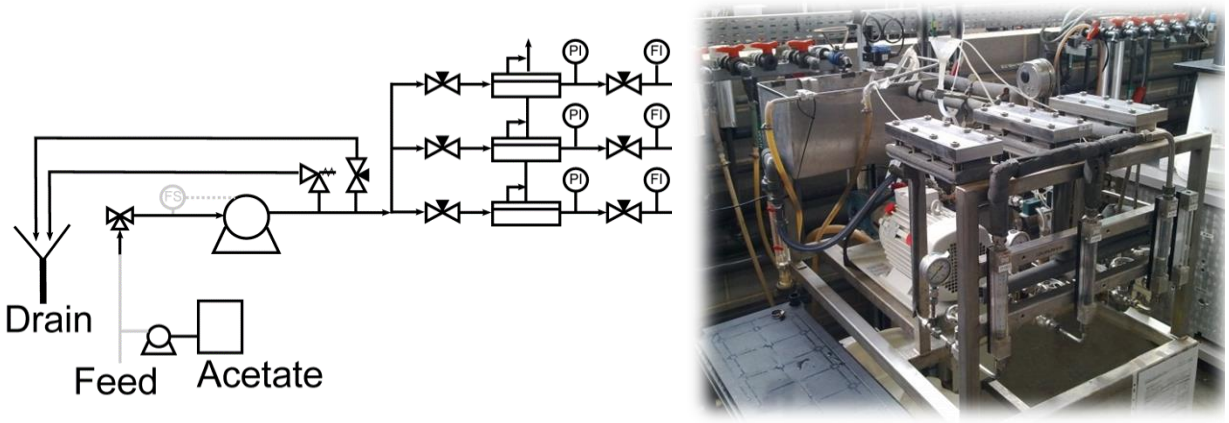



**Figure 4-1. Pilot unit for flat cell testing**

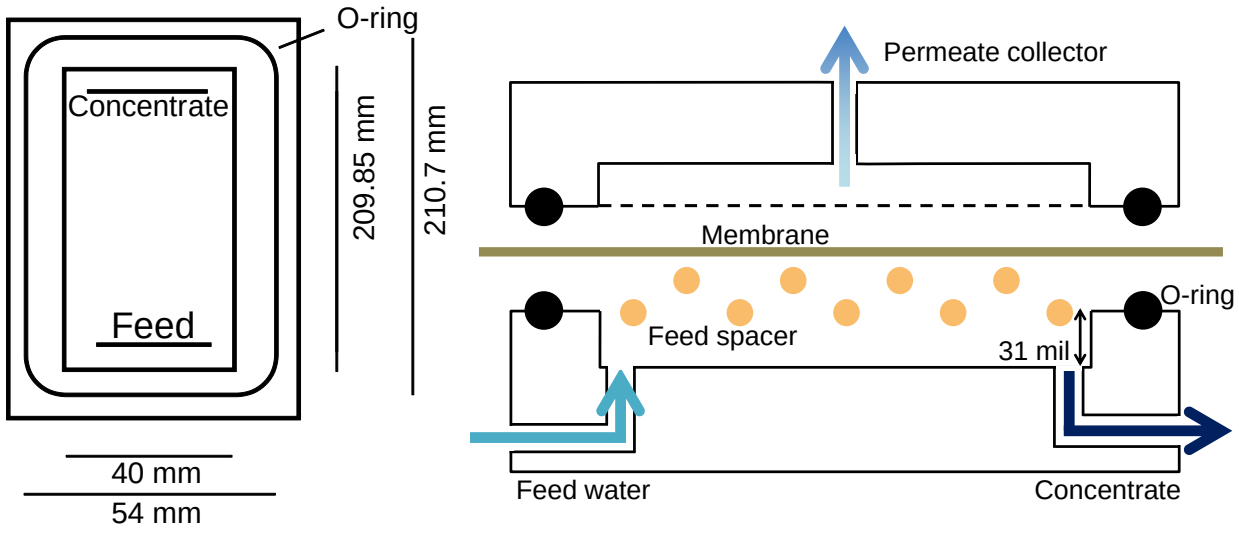



**Figure 4-2. Flat cell sketch and cross-section configuration**

## 2.2 Operating conditions

The system was operated with three flat cells in parallel in once-through water feed mode (versus recycling permeate and concentrate back to the feed and reusing). The same operational conditions were set for all 3 flat cells used in each experiment. The aim was to provide triplicate data points and measure the reproducibility in terms of amount of accumulated biomass on each flat cell operated in parallel under the same experimental conditions.

The permeate flow and feed flow were controlled within a range to most closely mimic typical commercial element operation (Table 4-1). However, due to equipment limitations, the lowest cross-flow velocity achievable for the flat cell unit is 0.6 m/s which is higher than a commercial element [10]. The concentrate flow of each cell was adjusted individually to ensure they were operating at the same flux.

**Table 4-1. Quick biofouling method for flat cell**

| Parameter | Flat cell operating range evaluated | Commercial element typical operating range |
|---|---|---|
| Flux (L/m²h) | 20 - 58 | 20 - 27 |
| Flow velocity (m/s) | 0.7 - 1.3 | 0.1 – 0.3 |
| Recovery (%) | 0.2 - 0.3 | 10 - 15 |

The feed flow was controlled to provide a set cross-flow velocity over the membrane surface. The cross-flow velocities were calculated by equation (1):

$$v = \frac{Q}{w \cdot h - \frac{m}{L \cdot \rho}} \qquad (1)$$

Where v is the cross-flow velocity (m/s), Q is the average feed flow ($m^3/s$), m is the mass of the spacer (gram) and ρ is the density of the water ($g/m^3$). The dimensions L, w, and h (meter) correspond to the length of the channel, width, and thickness of the feed spacer sample that is cut for weighing.

### 2.3 Flat sheet membranes

The reference membrane chemistry selected for the development of the biofouling test method was the one used in DOW FILMTEC™ BW30 RO elements. This membrane is well-known and extensively used across many different applications. With a stabilized salt rejection of 99.5% and a pH resistance from 1 to 13, this membrane offers reliable performance and robustness across a wide range of feed conditions.

### 2.4 Feed spacers

The 28 mil polypropylene feed spacers used are defined by their stands per inch, thickness and angle (Table 4-2). Feed spacer coupons were oriented in the flat cell so the feed flow intersects the angle formed by the strands knot. For example, in the picture in Table 4-2, the flow would be from right to left.

**Table 4-2. Details of the spacers used**

| Spacer | Thickness (mil) | Strands/in | Angle (º) |
|---|---|---|---|
| 28 mil | 28 | 9 | 90 |

## 2.5 Brackish water characterization

The feed water was taken from the Ebro River in L'Ampolla (Tarragona, Spain) after pretreatment with coagulation, flocculation, sand filtration and chlorination. Water is distributed through AITASA (Aguas Industrials de Tarragona SA) which applies a dechlorination step before supplying it to the Water Center. Table 4-3 provides a general summary of the water composition, highlighting especially those most commonly linked to biofouling, including phosphate ($PO_4$), nitrate ($NO_3$), total organic carbon (TOC), and adenosine triphosphate (ATP). The concentration of each of these contaminants in addition to total dissolved solids (TDS) was monitored over the course of the flat cell trials (July – November 2013). Sodium metabisulfite was injected prior to use in the flat cell unit as an additional measure to ensure that chlorine concentration is lower than 0.02 mg/L.

**Table 4-3. Feed water composition**

| Feed water characteristics | Average±σ (n=13) |
|---|---|
| Total Dissolved Solids (mg/L) | 800 ± 190 |
| Conductivity (µS/cm) | 1028 ± 210 |
| Total Organic Carbon (mg/L) | 1.3 ± 0.2 |
| Adenosine Triphosphate (ng/L) | 11 ± 5 |
| Nitrate (mg/L) | 8 ± 2 |
| Phosphate (µg/L) | 25 ± 22 |
| Chlorine (mg/L) | <0.02 |

The water composition remains reasonably constant during the year and shows a relatively low biofouling potential, compared to the ATP concentration found in tap water ranging from 5 to 20 ng/L [11].

## 2.6 Nutrients dosing strategy

Carbon, nitrogen and phosphate are needed by bacteria to grow, reproduce and eventually build a biofilm [12]. Since these values are relatively low in the Ebro River water supply, in order to promote biological fouling and reduce the duration of each experiment, readily bioassimable nutrients were continuously dosed to the feed water of the flat cell unit. A nutrient stock solution was prepared in an external tank using sodium acetate (VWR, USA), sodium nitrate (Sigma-Aldrich, USA) and sodium dihydrogen orthophosphate hydrate (Sigma-Aldrich, USA) to achieve a C:N:P ratio of 100:20:10. Sodium hydroxide (VWR, USA) was used to adjust the tank solution to pH 12 to avoid contamination, before being injected to the feed water using a peristaltic pump.

The nutrient ratio was chosen based on typical C, N, P compositions found in biomass and ensured that there was enough of each constituent to avoid limiting biofouling development [13]. Since these inorganic salts can be directly used by bacteria, the concentration needed for accelerating biofouling development is very low, less than 1 mg/L. The calculation to determine the injection rate was based on the feed water flow rate, the dosing pump frequency and the nutrient stock tank concentration. An example calculation for an experiment needing 0.2 mg/L of carbon in the feed water is provided in Table 4-4. Nutrient dosing rate is typically expressed as the concentration of carbon (mg/L of C) required in the feed water, assuming C:N:P ratio to be always constant at 100:20:10.

**Table 4-4. Example for a nutrient loading of 0.2 mg/L carbon in feed water**

| Parameter | Value |
|---|---|
| Feed flow (L/h) | 700 |
| Nutrient Pump stroke (%) | 80 |
| Nutrients Dosing Pump (L/h) | 0.8 |
| Dosing tank volume (L) | 60 |
| $CH_3COONa$ in tank (g) | 36.3 |
| $NaNO_3$ in tank (g) | 12.9 |
| $NaH_2PO_4 \cdot H_2O$ in tank (g) | 5.3 |

## 2.7 ATP analysis

Adenosine triphosphate (ATP) is the nucleoside triphosphate found in all living cells, including bacteria. This molecule is involved as a quick energy transfer unit in many endothermic biochemical reactions. This characteristic is the reason for its correlation with active biomass [14]. ATP acts as a phosphate group donor, releasing energy when the phosphodiester bond is hydrolyzed to adenosine diphosphate (ADP) or adenosine monophosphate (AMP) [15].

ATP content in liquid samples was measured using a Celsis Advance Luminometer, with luciferin as a reagent. This equipment has a detection limit of 2 ng/L, and the sampling volume is 100 µL. Biofouled samples of the membrane and feed spacer (4 cm x 4 cm) were submerged in 20 mL of ultrapure water to extract and dissolve the biofilm. A physical removal of the attached biofilm was achieved by applying a 6 minute sonication in an ultrasonic bath (Fisher Scientific FB15061) at room temperature. The liquid sample was transferred into a sterile Eppendorf, where it was immediately analyzed or stored at -20 $^oC$ for no longer than 7 days to avoid any potential degradation. The samples were analyzed by adding luciferin reagent, which reacts with ATP emitting light that is

detected by the instrument and converted to an ATP concentration using a calibration curve (bioluminescence). ATP results are expressed as ng/cm² according to equation (2).

$$0.8\frac{\mu g}{L}\ ATP \cdot \frac{100}{1}(Dilution\ factor) \cdot \frac{0.02\ l\ extraction\ volume}{16\ cm^2\ membrane\ surface}\frac{1000\ ng}{1\ \mu g} = \frac{100\ ng}{cm^2}\ ATP \qquad (2)$$

## 2.8 TOC analysis

Total organic carbon (TOC) content in liquid samples was measured using TOC-L Shimadzu using UNE EN-1484:1998 method. The sample is oxidized via high temperature catalytic combustion and quantified using an infrared detector. The equipment has a detection limit of 0.01 mg/L and the sampling volume is 50 µL.

Fouled (4 cm x 4 cm) membrane and feed spacer samples were extracted using the same procedure described for the ATP analysis (section 2.7). The liquid extraction sample was either analyzed immediately or was stored at 5 ºC after sample acidification, for no longer than 7 days. This is done to prevent degradation of the organic compounds present in the sample.

Samples were measured and expressed as TOC concentration using the equipment internal calibration curve. Taking into account the size of the surface and the extraction volume, TOC results are expressed as mg/m². The calculation steps are done using TOC concentrations and equation (2).

# 3 RESULTS AND DISCUSSION

In general, it is recognized that biofilms are formed as a defense mechanism by bacteria to protect from their surroundings [8]. The biofilm also serves as a mechanism to capture nutrients from the water and provide an environment to colonize and thrive [16][17]. If

the nutrients in the feed water are reduced, bacteria will survive by switching to a dormant state or consume the polysaccharides in their biofilm.

With this basic understanding, the development of an accelerated flat cell biofouling screening test was focused on three main variables shear forces, membrane flux, and nutrient concentration. Shear force is expected to impose stress on the bacteria and promote biofilm formation. The shear is related to the velocity of the water flowing through the feed channel and the resistance of the feed spacer. Membrane flux provides a means to draw organic contaminants to the membrane surface to develop a conditioning layer for biofilm initiation. It also provides a high concentration of nutrients to feed the bacteria at the surface of the membrane. The higher the membrane flux is, the greater the concentration polarization and the accumulation of nutrients on the membranes surface. This in combination with the concentration of nutrients in the feed water and water temperature are expected to affect the rate of biofilm formation [17].

### 3.1 Initial biofouling protocol set-up

Initial probing experiments identified the following conditions for obtaining a thick biofilm within 3 days: cross-flow velocity of 1.2 m/s, operating flux of 34 L/m²h, and nutrient addition to provide 0.4 mg/L carbon. The flux or salt rejection of the membranes showed little change over the course of the experiment (Figure 4-3). The ATP and TOC values from the extracted membrane and spacer collected at the end of the experiment were 205±166 ng/m² and 122±16 mg/m², respectively. These values are well above the detection threshold of the measurement methods and appear to correlate well with the visual observation of high levels of biofilm growth (Table 4-5, 1-1). Thus, further optimization using these measurements was conducted to develop the method. The ATP and TOC values are the average for the three individual cells operated in parallel. To

achieve good reproducibility, the objective is to reduce the variation of the results to less than 20% relative standard deviation.

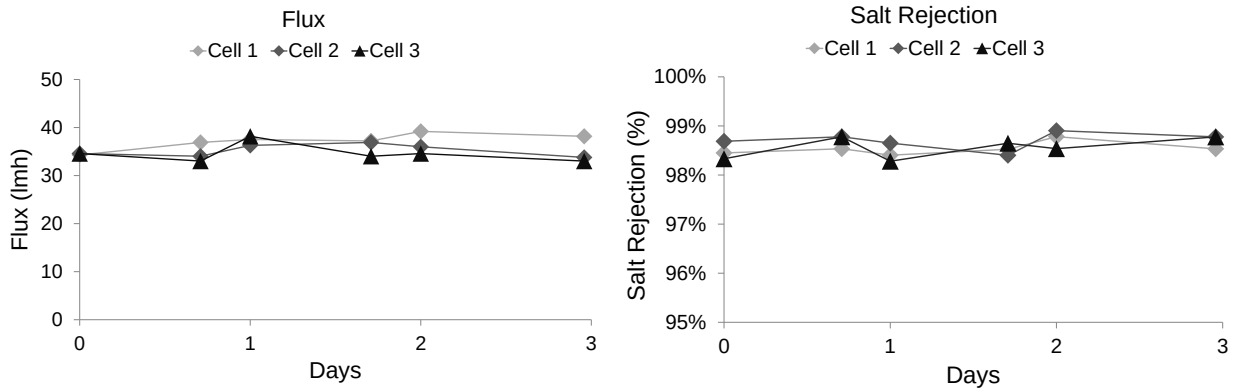



**Figure 4-3. Operating results example for flux and salt rejection**

The same operating conditions were repeated in a second experiment (Table 4-5, 1-2). However, the standard deviations of the ATP and TOC measurements between each flat cell within an experiment were still unacceptably high. In addition, poor reproducibility between experiments was observed. Further optimization to adjust the cross flow velocity, flux and nutrient loading was pursued to reduce the standard deviation.

**Table 4-5. Initial probing experiment results**

| Experiment | 1-1 | 1-2 |
|---|---|---|
| C (mg/L) | 0.4 | 0.4 |
| N (mg/L) | 0.08 | 0.08 |
| P (mg/L) | 0.04 | 0.04 |
| Flux (L/m²h) | 34 | 34 |
| Velocity (m/s) | 1.2 | 1.2 |
| ATP (ng/cm² ± 1σ) | 205 ± 166 | 132 ± 51 |
| TOC (mg/m² ± 1σ) | 122 ± 15 | 233 ± 112 |
| Flux loss (% ± 1σ) | 3 ± 15 | 15 ± 4 |

### 3.2 Cross-flow velocity optimization

Since the cross-flow velocity in the first set of experiments was much higher than typically observed in an element, the effect of reducing the feed flow was explored. High cross-flow velocity is expected to impose a high shear stress on the bacteria, but it may also be very disruptive to the growing biofilm and cause sloughing, which may create measurement variability. Keeping all other conditions the same, but reducing the cross-flow velocity from 1.2 to 0.6 m/s, provided a reduction in the variability. The results of two experiments are summarized in Table 4-6. Further optimization of the nutrient loading was pursued in an attempt to reduce the measurement variability.

**Table 4-6. Results at lower cross-flow velocity**

| Experiment | 2-1 | 2-2 |
|---|---|---|
| C (mg/L) | 0.4 | 0.4 |
| N (mg/L) | 0.08 | 0.08 |
| P (mg/L) | 0.04 | 0.04 |
| Flux (L/m²h) | 33 | 32 |
| Velocity (m/s) | 0.6 | 0.6 |
| ATP (ng/cm² ± 1σ) | 139 ± 3 | 200 ± 38 |
| TOC (mg/m² ± 1σ) | 132 ± 8 | 105 ± 15 |
| Flux loss (% ± 1σ) | 5 ± 4 | 6 ± 6 |

### 3.3 Nutrient loading optimization

Since mature biofilms slough over time, the formation of a less mature biofilms during the 3-day test was targeted by lower nutrient concentrations. The operating flux was also lowered to further slow the rate of the biofilm. Both were expected to reduce the differences in the ATP and TOC measurements between cells at the end of the test. The results are summarized in Table 4-7. When comparing the ATP and TOC results of

experiment 3-1 (Table 4-7) to 2-1 and 2-2 (Table 4-6), the reduced flux did not appear to significantly lower the amount of biofilm formed. Lowering the nutrient level, however, lowered the ATP and TOC values, but they were still well above the detection limit of the methods. The relative standard deviations were similar to those in Table 4-6; however, test conditions with lower levels of nutrients were chosen for the final test validation since there is less risk of reaching a too mature of biofilms, prone to sloughing.

**Table 4-7. Nutrient loading effect on lower flux experiments**

| Experiment | 3-1 | 3-2 | 3-3 |
|---|---|---|---|
| C (mg/L) | 0.4 | 0.2 | 0.1 |
| N (mg/L) | 0.08 | 0.04 | 0.02 |
| P (mg/L) | 0.04 | 0.02 | 0.01 |
| Flux (L/m²h) | 20 | 20 | 20 |
| Velocity (m/s) | 0.6 | 0.6 | 0.6 |
| ATP (ng/cm² ± 1σ) | 280 ± 50 | 76 ± 26 | 21 ± 5 |
| TOC (mg/m² ± 1σ) | 91 ± 11 | 59 ± 3 | 17 ± 5 |
| Flux loss (% ± 1σ) | 3 ± 3 | 3 ± 2 | 3 ± 2 |

### 3.4 Testing method validation

Operating at lower flux and nutrient loading levels of 0.1 and 0.2 mg/L carbon provided acceptable results on the three flat cells operated in parallel. Final validation of each of these conditions was completed by conducting three replicate experiments (Table 4-8 and Table 4-9).

Good reproducibility and acceptable standard deviations were observed within each run. The standard deviation and amount of fouling are in accordance with other biological fouling test found in the literature [1][19][20]. Nevertheless, variability between runs still exists, which may be due to uncontrolled changes in the natural water composition [17]. The results are summarized in Table 4-8. With these optimized conditions, only a very

small change in flux was noticed but the standard deviation of the measurement was low enough to be used to compare biofouling formation.

**Table 4-8. Validation of the quick biofouling test at 0.2 ppm C**

| Experiment | 4-1 | 4-2 | 4-3 |
|---|---|---|---|
| C (mg/L) | 0.2 | 0.2 | 0.2 |
| N (mg/L) | 0.04 | 0.04 | 0.04 |
| P (mg/L) | 0.02 | 0.02 | 0.02 |
| Flux (L/m²h) | 20 | 20 | 20 |
| Velocity (m/s) | 0.6 | 0.6 | 0.6 |
| ATP (ng/cm² ± 1σ) | 59 ± 8 | 98 ± 9 | 52 ± 3 |
| TOC (mg/m² ± 1σ) | 28 ± 2 | 47 ± 2 | 56 ± 4 |
| Flux loss (% ± 1σ) | 0 ± 1 | 5 ± 3 | 2 ± 1 |

Using only 0.1 ppm C as nutrients, in general, provided less biofouling than 0.2 ppm C, as can be observed in Table 4-9. Experiment 4-6 had especially low levels of biofouling, which is getting closer to the detection limit of the measurements, so the relative error in the measurement of ATP and TOC is more pronounced. Because of this, the nutrient loading of 0.2 ppm C was chosen in the final test protocol.

**Table 4-9. Validation of the quick biofouling test at 0.1 ppm C**

| Experiment | 4-4 | 4-5 | 4-6 |
|---|---|---|---|
| C (mg/L) | 0.1 | 0.1 | 0.1 |
| N (mg/L) | 0.02 | 0.02 | 0.02 |
| P (mg/L) | 0.01 | 0.01 | 0.01 |
| Flux (L/m²h) | 20 | 20 | 20 |
| Velocity (m/s) | 0.6 | 0.6 | 0.6 |
| ATP (ng/cm² ± 1σ) | 34 ± 11 | 18 ± 7 | 8 ± 4 |
| TOC (mg/m² ± 1σ) | 96 ± 35 | 15 ± 2 | 14 ± 3 |
| Flux loss (% ± 1σ) | 2 ± 1 | 2 ± 2 | 0.7 ± 0.5 |

## 4 CONCLUSIONS

An accelerated, 3-day biofouling test protocol to compare biofilm formation on reverse osmosis membranes coupons has been developed using a membrane flat cell unit. Measuring the ATP and TOC extracted from coupons of membrane and feed spacer after the prescribed method presented in this report was an effective means to quantify biofouling. Good reproducibility between the three parallel operated flat cells is obtained. The feed velocity, permeate flux and nutrient dosing levels were each evaluated and optimized. Of these three variables, nutrient dosing level had the biggest impact on improving the measurement variability within a test. The method development work completed in this study provides the foundation to enable rapid screening of the biofouling resistance of new reverse osmosis membranes.

## 5 REFERENCES

[1] H. C. Flemming, Reverse osmosis membrane biofouling, Experimental Thermal and Fluid Science 14 (1997) 382-391

[2] S. R. Suwarno, X. Chen, T. H. Chong, V. L. Puspitasari, D. McDougald, Y. Cohen, S. A. Rice and A. G. Fane, The impact of flux and spacers on biofilm development on reverse osmosis membranes, Journal of Membrane Science 405 (2012) 219–232

[3] J. S. Vrouwenvelder, J. A. M. Van Paassen, L. P. Wessels, A. F. Van Dam and S. M. Bakker, The Membrane Fouling Simulator: A practical tool for fouling prediction and control, Journal of Membrane Science 281 (2006) 316–324

[4] L. Vanysacker, P. Declerck and I. Vankelecom, Development of a high throughput cross-flow filtration system for detailed investigation of fouling processes, Journal of Membrane Science 442 (2013) 168–176

[5] C. M. Pang, P. Hong and H. Guo, Biofilm formation characteristics of bacterial isolates retrieved from a reverse osmosis membrane, Environmental Science & Technology 39 (2005) 7541-7550

[6] W. Lee, C. H. Ahn and S. Kim, Evaluation of surface properties of reverse osmosis membranes on the initial biofouling stages under no filtration condition, Journal of Membrane Science 351 (2010) 112-122

[7] D. J. Miller, P. A. Aráujo and P. B. Correia, Short-term adhesion and long-term biofouling testing of polydopamine and poly(ethylene glycol) surface modifications of membranes and feed spacers for biofouling control, Water Research 46 (2012) 3737-3753

[8] T. H. Chong, F. S. Wong and A. Fane, The effect of imposed flux on biofouling in reverse osmosis: Role of concentration polarization and biofilm enhanced osmotic pressure phenomena, Journal of Membrane Science 325 (2008) 840-850

[9] K. J. Varin, N. H. Lin and Y. Cohen, Biofouling and cleaning effectiveness of surface nanostructured reverse osmosis membranes, Journal of Membrane Science 446 (2013) 472–481

[10] A. I. Radu, J. S. Vrouwenvelder, M. C. M. van Loosdrecht and C. Picioreanu, Effect of flow velocity, substrate concentration and hydraulic cleaning on biofouling of reverse osmosis feed channels, Chemical Engineering Journal 188 (2012) 30–39

[11] K. Ochromowicz and E. J. Hoekstra, ATP as an indicator of microbiological activity in tap water, European Commission Directorate, General Joint Research Centre (2005)

[12] J. D. Jacobson, M. D. Kennedy, G. Amy and J. C. Schippers, Phosphate limitation in reverse osmosis: An option to control biofouling?, Desalination and Water Treatment 5 (2009) 198–206

[13] J. S. Vrouwenvelder and M. C. M. Van Loosdrecht, Phosphate limitation to control biofouling, Water Research 44 (2010) 3454-3466

[14 N. Oulahal-Lagsir, A. Martial-Gros, M. Bonneau and L. J. Blum, The development of an ultrasonic apparatus for the non-invasive and repeatable removal of fouling in food processing equipment, Letters in Applied Microbiology 30 (2000) 47–52

[15] C. A. Reddy, T. J. Beveridge, J. A. Breznak, G. A. Marzluf, T. M. Schmidt and L. R. Snyder, Methods for General and Molecular Microbiology (3rd Edition), American Society for Microbiology, ASM Press, Washington 2007, pp. 869-878

[16] H. C. Flemming, J. Wingender and U. Szewzyk, Biofilm Highlights, Springer Series on Biofilms 5, Springer Berlin Heidelberg 2011, pp. 81-109

[17] V. D. Villanueva, J. Font, T. Schwartz and A. M. Romaní, Biofilm formation at warming temperature: acceleration of microbial colonization and microbial interactive effects, Biofouling 27 (2011) 59–71

[18] D. Van der Kooij and H. R. Veenendaal, Biofilm formation and multiplication of Legionella in a model warm water system with pipes of copper, stainless steel and cross-linked polyethylene, Water Research 39 (2005) 2789–2798

[19] N. Oulahal-Lagsir, A. Martial-Gros, M. Bonneau and L. J. Blum, Ultrasonic methodology coupled to ATP bioluminescence for the non-invasive detection of fouling in food processing equipment-validation and application to a dairy factory, Journal of Applied Microbiology 89 (2000) 433–441

[20] J. S. Vrouwenvelder, C. Hinrichs, W. G. J. Van der Meer and M. C. M. Van Loosdrecht, Pressure drop increase by biofilm accumulation in spiral wound RO and NF membrane

systems: role of substrate concentration, flow velocity, substrate load and flow direction, Biofouling 25 (2009) 543–555

# Chapter 5

# Biofouling development in different membranes and feed spacers

**This chapter was submitted for publication on 10/2017 (I.F. 2.36):**

G. Gilabert-Oriol, G. Massons-Gassol, J. Shu, J. Curtis-Fisk, M. Woodward, T. Arrowood, *Effect of shear and permeation in biofouling development in different reverse osmosis membranes and feed spacers*, Biofouling

## 1 INTRODUCTION

Biofouling in reverse osmosis (RO) water treatment occurs when the feed channel in the RO element is partially or fully blocked by bacteria-produced biofilm. This can cause the pressure drop (dP) across the RO element to increase, leading to a hydraulic imbalance and possibly a permanent damage of the element. Additionally, biofilms can affect membrane transport properties and create a drop in trans-membrane pressure which lowers the flux and increases the energy consumption. To regain performance and avoid element damage, the systems typically undergo a clean-in-place (CIP) using strong basic followed by strong acidic cleaning solutions. Frequent exposure of the RO membrane polyamide to these harsh cleaning chemicals can lead to the deterioration of the membrane performance over time. Summarizing, biofouling affects the energy consumption of the system, the water productivity, the membrane lifetime, the chemical consumption and ultimately the cost to produce clean water [1].

The surface biofouling mechanism described in the literature follows three main sequential phases [2][3]. The first is the deposition of organic matter to condition the surface; the second is the attachment of functional microbial communities, and the third is the growth of a complex biofilm network composed of extracellular polysaccharides, proteins and bacteria. In RO systems, this mechanism is affected by the hydrodynamics of an operating RO element. Three main effects influence the described mechanism. The first one is the water cross-flow that impacts the average shear at the membrane surface. The second refers to water mixing from the feed spacer that creates localized regions of high and low shear. The third one is related with water permeation through the membrane that drives contaminants to the membrane surface.

The aim of this work was to develop testing capabilities to evaluate the design features of an RO element which impacts biofilm formation. These capabilities can be used to screen new technologies and develop advanced biofouling resistant RO elements.

## 2 METHODS

The laboratory biofouling test equipment employed were a Center for Disease Control (CDC) reactor [4], Membrane Fouling Simulators (MFS) [5] and a membrane permeation Flat Cell (FC) unit [6]. The CDC reactor was used to compare biofilm formation on different membrane surfaces in a low shear environment. The MFS and Flat Cells were used to evaluate biofouling under cross-flow velocities similar to an RO element and also to explore operation with and without a feed spacer. The FC units, however, operate with permeation whereas the MFS units do not. The capabilities of each of these test methods relative to a typical RO element are summarized in Table 5-1.

**Table 5-1. Comparison of laboratory equipment used for studying biofouling**

| Parameter | CDC | MFS | Flat Cell | Element |
|---|---|---|---|---|
| Cross-flow velocity | No | 0–0.5 m/s | 0.3–1.3 m/s | 0–0.3 m/s |
| Membrane surface | Yes | Yes | Yes | Yes |
| Feed Spacer | No | Yes / No | Yes / No | Yes |
| Permeation | No | No | Yes | Yes |
| Feed channel pressure drop | No | Yes | No | Yes |

### 2.1 CDC reactor

The method used with the experiments undertaken in the Center for Disease Control (CDC) reactor is based on the ASTM method E2562-07. This approach involves securing membrane samples to eight rods that are placed in the CDC reactor vessel (Figure 5-1). Membranes are placed in the reactor and exposed to a solution containing bacteria to allow for biofilm formation. A 1 mL of *Pseudomonas aeruginosa* culture grown overnight to a $10^{+8}$ CFU/mL is added to 350 mL of M9 media with 0.9% glucose (Sigma Aldrich). The solution is incubated at room temperature and refreshed during the experiment by flowing fresh M9 media with 0.9% glucose solution into the reactor at a rate of about 1

mL/min for about 12 hours each day and collecting the overflow in a waste container. The continuous flow of fresh solution aids in maintaining a consistent level of bacteria in the reactor. The solution is stirred at 300 rpm to create a gentle shear.

Samples are removed from the CDC reactor at the targeted time points. The amount of bacterial adhesion is quantified by removing samples from each membrane coupon, vortexing in cell culture media and using agar plate count to determine cell count. The shear over the membrane in the CDC reactor is significantly lower than in RO elements; however, the CDC reactor provides a means to screen up to 24 membrane chemistries at one time for high throughput exploration.

**Figure 5-1. CDC Reactor diagram**

## 2.2 Membrane Fouling Simulator

The Membrane Fouling Simulator (MFS) (Figure 5-2) is a portable assembly that can be installed as a stand-alone test unit or in parallel with an RO system. These units have been described in the literature as a cost-effective way to monitor biofouling in reverse osmosis systems, to determine the biofouling potential of various feed waters, and to compare the fouling performance of membranes and spacers [7]. The assembly includes a pressure limitation valve set at 1 bar, a flow meter, a transparent cell, a high precision pressure drop indicator and a flow control valve. The transparent cell is assembled with a membrane and feed spacer as shown in the cross-sectional image in Figure 5-2. The MFS unit has a cross-flow velocity range that can match the feed channel velocity of a commercially operated 8-inch RO element, but the MFS does not allow water permeation through the membrane. With the cross-flow velocity controlled at approximately 0.12 m/s, MFS units installed in a feed water side stream in parallel to an industrial 8-inch RO system has shown to give similar relative differential pressure rise due to biofouling as the 8-inch systems [8]. To accelerate biofouling and enable faster screening of conditions, the feed water to the MFS can be optionally dosed with bio-assimilable nutrients (Section 2.4).

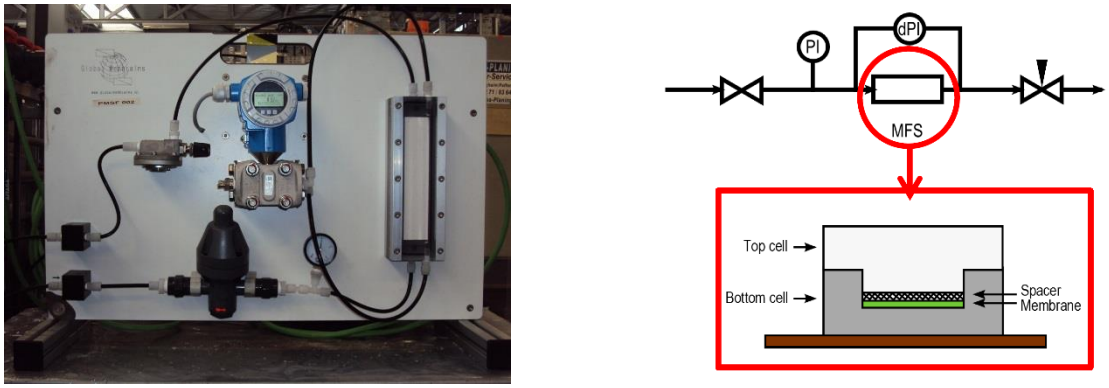



**Figure 5-2. MFS Simulator picture and diagram**

## 2.3 Flat Cells

The membrane permeation Flat Cell units are used to closely mimic the conditions found in a spiral wound element [9]. The system used for this study has three parallel Flat Cells (Figure 5-3). These cells are assembled with a membrane and can also optionally host a feed spacer. The feed water is surface water taken from Ebro River in L'Ampolla (Spain) after conventional pretreatment (Table 5-2). The water was fed in once-through mode and can be dosed with nutrients to promote biofouling [6]. Each cell has a manual feed and concentrate flow control valve to provide equal operating fluxes (30 L/m²h) for the three parallel cell assemblies. The cross-flow velocity was controlled to approximately 0.5 m/s. This is slightly higher than in an element, but is not expected to significantly impact the observations since biofouling will still develop at this higher flow rate [10]. Each test was stopped after 4 days, and the amount of biofouling was quantified by collecting a sample of the membrane and spacer and analyzing the concentration of adenosine triphosphate (ATP) and total organic content (TOC) present (Section 2.5).

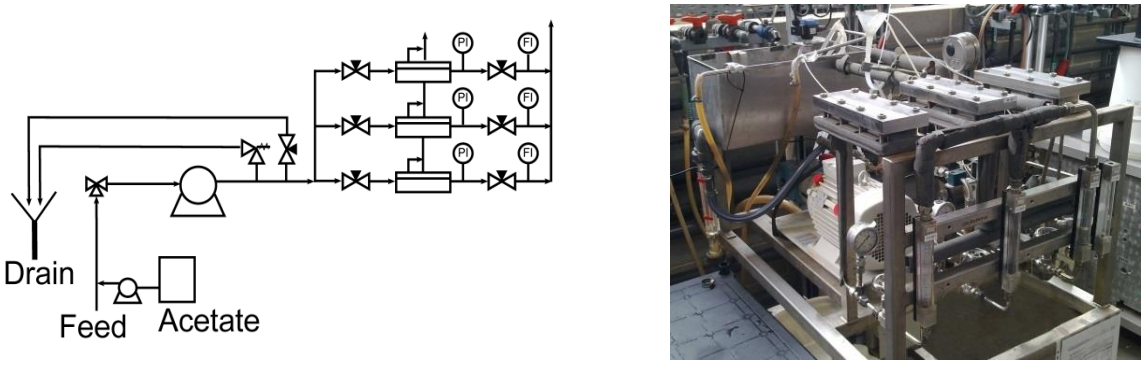



**Figure 5-3. Flat Cell pilot unit for flat cell testing**

## 2.4 Natural River and wastewater

Surface water pretreated with coagulation, flocculation, sand filtration from the Ebro River in L'Ampolla, Spain was used in the flat cell experiments and was one of the two water sources used in the MFS experiments. The main composition of this water is summarized in Table 5-2.

**Table 5-2. UF pretreated Ebro River water composition**

| Parameter | Concentration |
|---|---|
| TDS | 1,000 mg/L |
| TOC | 1.3 mg/L |
| ATP | 6 ng/L |
| Nitrate | 11 mg/L |
| Phosphate | 0.040 mg/L |

The other water type used was secondary aerobic treated wastewater from Vila-Seca Wastewater Treatment Plant (WWTP) in Spain. The water was filtered through a Membrane Bioreactor (MBR) and cartridge filters before feeding the MFS unit. The composition of the water to the MFS is summarized in Table 5-3.

**Table 5-3. MBR pretreated Vila-Seca wastewater characteristics**

| Parameter | Concentration |
|---|---|
| TDS | 1,440 mg/L |
| TOC | 6.6 mg/L |
| ATP | 83 ng/L |
| Nitrate | 30 mg/L |
| Phosphate | 0.55 mg/L |

When experiments required accelerated biofouling, bioassimilable nutrients, in the form of acetate, nitrate, and orthophosphate sodium salts, were dosed. The carbon, nitrogen and phosphorous ratios used were leveraged from that described in the literature [11][12]. Three different nutrient concentrations were employed to study the effect on biofilm development rate. The highest concentration provided 0.40 mg/L carbon, 0.08 mg/L nitrogen and 0.04 mg/L phosphate, the intermediate concentration provided 0.20 mg/L carbon, 0.04 mg/L nitrogen and 0.02 mg/L phosphate, and the lowest provided 0.10 mg/L carbon, 0.02 mg/L nitrogen and 0.01 mg/L phosphate additional nutrients to the feed water.

## 2.5 ATP and TOC analytical methods to quantify biofouling

Samples of the membrane and spacer was analyzed after the MFS or flatcell experiments to quantify the level of ATP and TOC present. These analyses provide a measure of the bacteria and biofilm present in the feed channel. ATP and TOC were used as the exclusive measure for biofouling in the flat cells where no dP measurements were available.

The membrane and feed spacer sample materials were analyzed by cutting a 4 x 4 cm square sample of membrane and spacer from the center of the exposed area. The sample was then placed into 20 mL of ultrapure water and sonicated at room temperature for three intervals of 2 minutes each.

The ATP content of the water was analyzed using a Celsis Advance Luminometer. The response is based on luciferin bioluminescent reaction with ATP which provides a light signal. This light signal was analyzed with a photo-detector, and it is later converted to ATP concentration. This parameter is proportional to the amount of living microorganisms present in the sample and can be directly correlated to colony forming units (CFU) [13].

Additionally, TOC analyses were also performed using the same fouling extract method described above. TOC content in liquid samples was analyzed using a TOC-L Shimadzu based on the UNE EN-1484:1998 method. The sample was oxidized via high temperature catalytic combustion and quantified using an infrared detector. The conversion was performed using a calibration curve obtained from a TOC standard solution. The organic carbon concentration is proportional to the amount of organic material present in the sample like extracellular polymeric substances (EPS) [14].

### 2.6 Membranes and feed spacers tested

Smoother, more hydrophilic, and lower surface-charged membranes are described in the literature as being more fouling resistant [2][15][16]17]. Therefore, two membranes, A and B, were chosen in this study to represent examples of a low and high fouling resistance membrane surface, respectively. The properties of the two membranes are summarized in Table 5-4. Membranes A and B have similar degrees of roughness, but Membrane A is more hydrophobic and more negatively charged, than Membrane B and is expected to be fouled more rapidly.

**Table 5-4. Membrane characteristics**

| Parameter | Membrane A | Membrane B |
|---|---|---|
| AFM Average Roughness | 61 nm | 61 nm |
| Contact Angle | 72º | 43º |
| Zeta Potential (pH 8) | -25 mV | -5 mV |

Standard polypropylene extruded feed spacers were used in the MFS and Flat cell experiments. The material had 9 strands/inch and was either 28 or 34 mil thick (1 mil = 0.001 inch).

## 3 RESULTS AND DISCUSSION

The biofouling testing equipment described above provides the flexibility to evaluate the effect of several parameters on membrane chemistry to resist biofilm formation. The variables studied were the impact of shear, membrane flux, presence of a feed spacer, and concentration of bioassimilable nutrients. This fundamental understanding not only provides direction for designing fouling resistant elements in the future, but also provides effective laboratory screening tools to evaluate new designs/prototypes. Table 5-5 summarizes the experimental design employed in this study and the results of each are discussed herein.

**Table 5-5. Summary of the experiments performed**

| Section | Asset | Throughput | Cross-flow | Flux | Spacer | Water type | Bioassimiliable nutrients |
|---|---|---|---|---|---|---|---|
| 3.1 | CDC | x24 | - | No | No | Synthetic | Yes |
| 3.2 | CDC | x24 | - | No | No | Synthetic | Yes |
| 3.3 | MFS | x4 | 16 cm/s | No | Yes | River water | No |
| 3.4 | MFS | x4 | 16 cm/s | No | Yes/No | Wastewater | Yes |
| 3.5 | FC | x3 | 30 cm/s | Yes | Yes/No | River water | Yes |

### 3.1 No shear and high nutrient dosage without spacer or permeation (CDC)

The CDC Reactor is an especially attractive technique for exploring biofilms since it provides the potential to screen multiple surface chemistries within a short period of time. In this work, however, the aim was to first demonstrate that this method could easily differentiate two different membrane surface types, A and B, on the basis of biofouling accumulation.

Figure 5-4 shows the evolution of the colony forming units on the surface of Membrane A and Membrane B during a two hour study using a high bacteria concentration in the

CDC reactor. In this study, the fouling solution was prepared by adding 1 mL of a high cell density cell culture to the 350 mL CDC Reactor fouling unit. The goal was to achieve a bacteria concentration of approximately $10^6$ CFU/mL. Membrane samples were then taken and analyzed after 30, 60, 90 and 120 minutes with the expectation that the colony forming units on the membrane would gradually increase over this time period. The results, however, showed that bacteria initially attached very quickly and did not increase over the course of the 120 minutes, as can be observed in Figure 5-4. Additionally, both membranes, despite the different surface properties, gave similar results.

The results raise the question if the high bacteria concentration in the CDC reactor provides fouling conditions which were too accelerated. After just 30 minutes there was substantial adhesion of bacteria on both membrane surfaces, while reaching these levels of bacteria in typical RO applications occurs over the course of weeks to months [18].

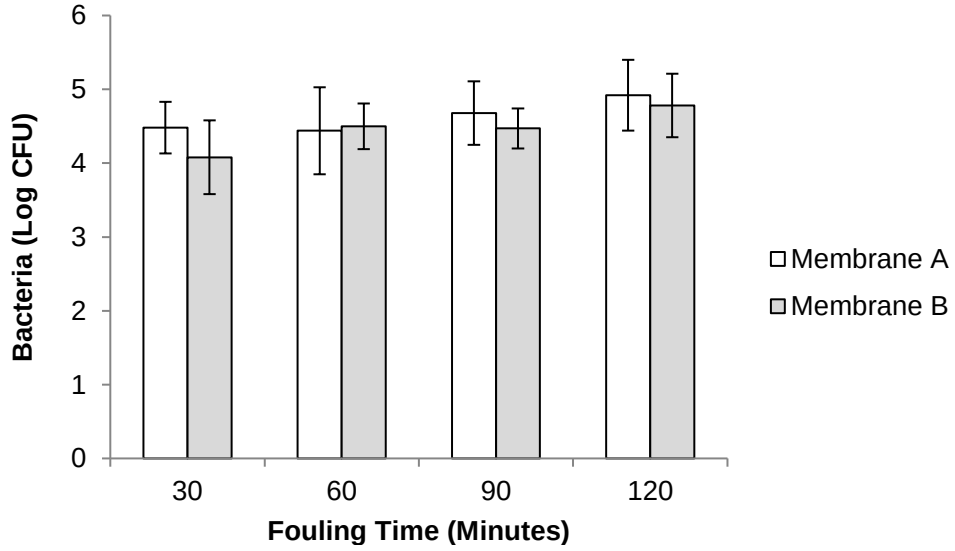



**Figure 5-4. CFU evolution of different membranes in an accelerated trial on CDC**

### 3.2 No shear and low nutrient dosage without spacer and permeation (CDC)

To evaluate the effect of slower evolution of biofouling in the CDC reactor the experiment in section 3.1 was repeated using a lower bacteria concentration. The amount of bacteria was reduced to approximately $10^4$ CFU/mL. The fouling process was also slowed by limiting the concentration of bacteria in the CDC reactor by flowing sterile nutrient media into the reactor. The goal was to displace the established cell culture with the addition of fresh solution at a rate of about 1 mL/min for about 12 hours each day. Membrane samples were removed and analyzed after 2, 7, 9 and 14 days. Results are shown in Figure 5-5. This data shows a more gradual development of biofilm on the surface of the membrane over the course of the experiment, but no significant differences observed between Membranes A and B.

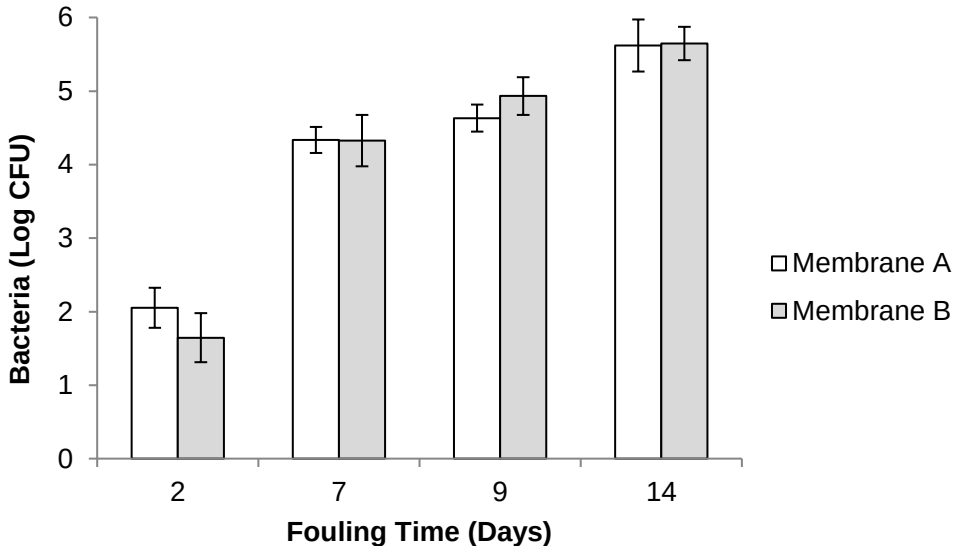



**Figure 5-5. CFU evolution of different membranes in a slower trial on CDC**

The CDC reactor provides a high throughput means to evaluate various membrane surfaces, but under the test conditions no differentiation of the two membranes was observed. Based on these results, membrane chemistry might not be enough to provide a

strong biofouling resistance. The CDC reactor does not capture the dynamic biofouling environment of a reverse osmosis element, thus additional methods were explored.

### 3.3 Typical shear and spacer without permeation (MFS)

Bacteria are known to express differently under high and low shear environments [10]. The water cross-flow within an RO element feed channel provides much higher shear environment than the CDC reactor. Additionally, the feed spacer in the feed channel provides water mixing which creates regions of high and low shear. The MFS test unit provides a means to evaluate membrane under the typical water cross-flow environments of an RO element. Four portable MFS units were assembled in parallel and connected to the brackish water source characterized in Table 5-2. Each MFS unit had a membrane and a 34 mil feed spacer. Two units were assembled with Membrane A and two with Membrane B to provide replicates for each membrane type.

After 5 days of operation the pressure drop of the MFSs increased from 0.05 bar to 0.14 bar. The units were removed from service, disassembled and membrane and spacer samples were analyzed for ATP and TOC. The results summarized in Table 5-6 show that the two membrane types could not be distinguished with statistical relevance. However, the average data suggests that Membrane B had slightly less biofilm accumulation than Membrane A.

**Table 5-6. Analytical results for typical shear with 34 mil spacer on MFS**

| ATP (ng/cm²) | | TOC (mg/m²) | |
|---|---|---|---|
| **Membrane A** | **Membrane B** | **Membrane A** | **Membrane B** |
| 4.1 ± 2.1 | 2.7 ± 0.6 | 47.2 ± 11.6 | 40.3 ± 3.3 |

The transparent window of the MFS cells allowed addition visual observations. Figure 5-6 includes a series of photographs of the cells where the flow direction in each photo was from left to right, and where the inlet position and center positions of the coupons were magnified. Two important observations could be extracted from these pictures. Firstly, more biofilm appeared close to the feed inlet side of the cell than the center. This was in line with what is reported in the literature, that biofilm mainly develops in the lead elements when RO elements are installed inside a pressure vessel [19][20][21][22]. Secondly, the biofilm in the form of bulk slime appeared to be more localized on the feed spacer than on the membrane. In particular, the biofilm was located at the spacer strand intersections where zones of low shear are present. It should be noted that the observations shown in Figure 5-6 were also observed in the replicate set of cells.

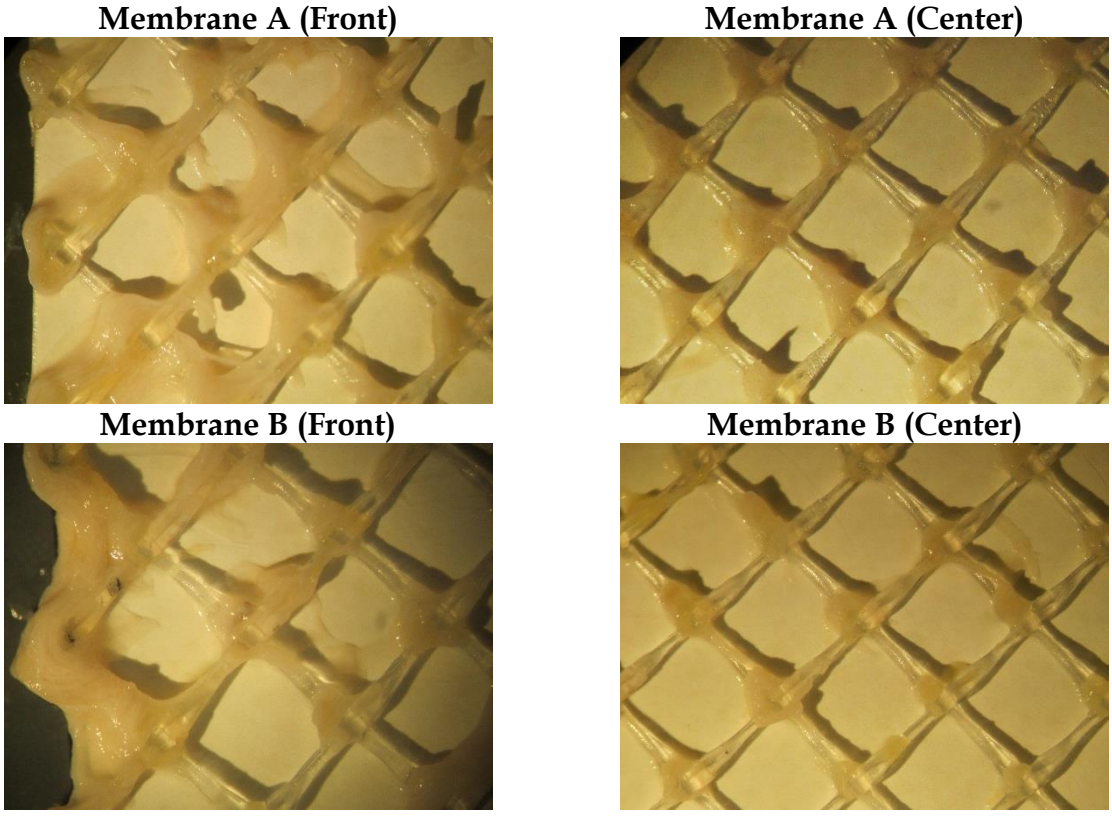



**Figure 5-6. Biofilm distribution on the membrane surface (34 mil spacer)**

Biofilm is highly hydrated and can be difficult to be observed on the white membrane background. Therefore, in order to visually examine the biofilm on top of the membrane surface, each MFS cell was opened at the end of the experiment.

The regions were feed spacer was present, where biofilm appear to be thicker. These were regions of water flow around the feed spacer where there is less turbulence, and could serve as regions for bacteria to settle and colonize to form the biofilm. When comparing feed spacer with the membrane surface (Figure 5-6), it could be seen that visually less biofilm developed on the membrane surface than in the feed spacer. This highlights the important role that feed spacers have in biofouling formation.

### 3.4 Typical shear with and without spacer and without permeation (MFS)

The results in the previous experiment show the dominant effect that the feed spacer has on accumulating biofilm, and it masks the effect of the different membrane types. Conducting the cross-flow experiment in the absence of the feed spacer was evaluated in an attempt to observe only the membrane effect. Four MFS units were used in this experiment, two contained Membrane A and two contained Membrane B. One of each pair was equipped with a 34 mil feed spacer and the other had a modified 34 mil feed spacer where the feed spacer in the center of the cell was removed but the inlet and outlets had small pieces of feed spacer used as shims to maintain the feed channel height of the MFS. The experiment was concluded after 7 days at which time the pressure drop of the vessels hosting the standard 34 mil feed spacer increased from 0.10 bar to 0.43 bar.

Samples of the membrane and feed spacer (if present) were cut from the center portion of the coupon were analyzed for ATP and TOC. Results are summarized in Table 5-7. The two cells fitted with the 34 mil spacer gave similar results to the previous experiment. Membrane A and B were difficult to distinguish, especially since there were no replicates in this experiment. However, the two cells that did not have a feed spacer in the center of

the MFS, showed slightly lower values for Membrane B than Membrane A. The most relevant observation was that, despite all four MFS units operating with the same feed flow rates, those with the modified feed spacer have significantly less biofilm in the center of the MFS unit than those with the standard 34 mil spacer. This might be due to the presence of low shear zones that feed spacer creates across the feed-concentrate channel which may facilitate biofilm attachment. In the absence of a feed spacer; the low shear (dead) zones were eliminated.

**Table 5-7. Analytical results with and without 34 mil spacer on MFS**

| ATP (ng/cm²) | | | | TOC (mg/m²) | | | |
|---|---|---|---|---|---|---|---|
| Membrane A | | Membrane B | | Membrane A | | Membrane B | |
| 34 mil | No spacer | 34 mil | No spacer | 34 mil | No spacer | 34 mil | No spacer |
| 19.3 | 2.2 | 21.4 | 1.2 | 56.3 | 14.3 | 44.8 | 10.5 |

In addition to the analytical results shown in Table 5-7, photos of the MFS cells with and without 34 mil spacer were taken (Figure 5-7). Both photos show that with the feed spacer present, more biofilm can be observed in the MFS cell. As with the previous experiment, more biofilm was seen at the feed side (left) of the MFS cell than the center. This was also observed in the experiments with the modified feed spacer where brown biofilm was present in the short section of feed spacer at the inlet, but the center of the cell appears very clean.

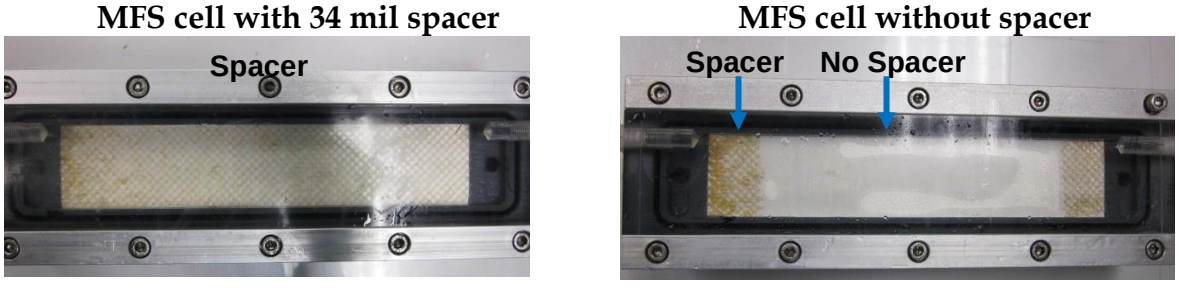



**Figure 5-7. Biofilm distribution with and without 34 mil spacer in the MFS cells**

### 3.5 High shear with and without spacer and permeation (Flat Cell)

The CDC and MFS results show little differentiation of Membrane A and Membrane B in terms of biofilm development. However, the MFS results indicated a slight advantage for Membrane B. One explanation for the lack of differentiation may be the absence of permeation in the cross-flow experiments. Permeation draws water contaminants to the membrane surface, thus membranes that are more organic fouling resistant will have a slower rate of forming the organic conditioning layer, which is the first step in biofouling [23]. Flat cell units provide the ability to evaluate the impact of water permeation in addition to feed channel hydrodynamics on the fouling performance of different membrane surfaces.

The flat cell unit available for this study was limited to three cells operating in parallel. These three cells were fed with a common feed that was either dosed with 0.1, 0.2 or 0.4 mg/L carbon nutrients. Membrane A was installed in two of the cells and Membrane B in the third. The cell with Membrane B and one with Membrane A was also equipped with a feed spacer. The second Membrane A cell was operated without a feed spacer. The first four sets of experiments evaluating different nutrient dosing concentrations were conducted with 28 mil feed spacer and the last two sets of experiments with 34 mil feed spacers. Each test was stopped after 4 days and samples of the membrane and the spacer (if present) of each flat cell unit were analyzed for ATP and TOC concentrations (Table 5-8 and Table 5-9).

Comparing the ATP and TOC results of Membrane A and B operated in the presence of a feed spacer shows Membrane B to accumulate less biofouling regardless of the nutrient dosing level (Table 5-8). The exception being Experiment 3 where the ATP value was slightly higher for Membrane B (this may be an outlier). The differentiation between the membrane types was more pronounced in Experiments 1 and 2 when more biofilm was formed due to the higher nutrient addition. These results suggest that the membrane

surface properties have more influence on the evolution of the biofilm on its way to maturation than the initial colonization step.

Regardless of the level of nutrients added to the water, the results show the important role the feed spacer has on biofouling development. The ATP and TOC values were always much higher when feed spacer was present. These results were in agreement with previous experiment performed in MFS.

As expected, the ATP levels on the membrane surface were correlated with the level of nutrients added. There was a direct correlation when the feed spacer was present. However, in the absence of the feed spacer there appears to be a critical threshold between 0.2 to 0.4 mg/L C nutrient dosing levels which trigger the bacteria begin to colonize and multiply).

**Table 5-8. Analytical results with and without 28 mil spacer on Flat Cells**

| | | ATP (ng/cm²) | | | TOC (mg/m²) | | |
|---|---|---|---|---|---|---|---|
| | | Membrane A | | Membrane B | Membrane A | | Membrane B |
| Test | C (mg/l) | 28 mil | No spacer | 28 mil | 28 mil | No spacer | 28 mil |
| 1 | 0.4 | 239.4 | 48.4 | 170.1 | 199.4 | 20.2 | 166.8 |
| 2 | 0.2 | 109.3 | 4.0 | 42.7 | 64.6 | 22.8 | 51.5 |
| 3 | 0.1 | 23.9 | 2.4 | 26.6 | 37.5 | 11.9 | 31.4 |
| 4 | 0.1 | 8.6 | 0.4 | 6.9 | 53.9 | 9.3 | 41.0 |

Figure 5-8 shows a comparison of biofilm on Membrane A and Membrane B exposed with a 28 mil spacer (right and left pictures) to Membrane A exposed without a spacer present (center). The brown coloration of the biofilm slime produced was evident only on the membranes exposed with a feed spacer present. This photo was obtained in Experiment 1, but was representative of all the other experiments performed.

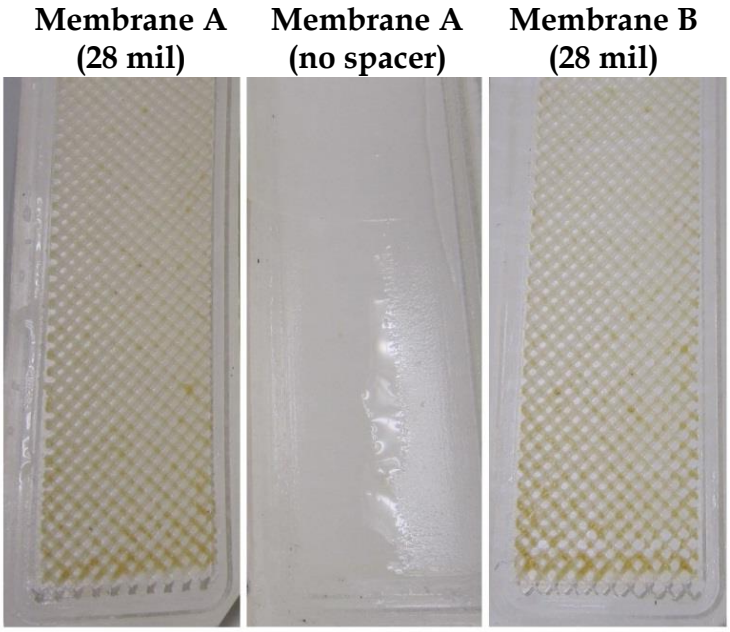



**Figure 5-8. Biofouling developed on membrane surface and feed spacer**

### 3.6 Experiment with 34 mil spacer

The results from the two flat cell experiments conducted with 34 mil spacers instead of the 28 mil spacers supported the same conclusions. Very little fouling occurred in the absence of the feed spacer, but significantly high amount of fouling was obtained when the feed spacer was present.

**Table 5-9. Analytical results with and without 34 mil spacer on Flat Cells**

| | | ATP (ng/cm²) | | | TOC (mg/m²) | | |
|---|---|---|---|---|---|---|---|
| | | Membrane A | | Membrane B | Membrane A | | Membrane B |
| Test | C (mg/l) | 34 mil | No spacer | 34 mil | 34 mil | No spacer | 34 mil |
| 5 | 0.2 | 6.7 | 1.6 | 3.8 | 88.3 | 26.3 | 49.0 |
| 6 | 0.2 | 9.8 | 3.0 | 4.2 | 33.6 | 10.5 | 15.8 |

## 4 CONCLUSIONS

In this study, two membranes expected to have low (Membrane A) and high (Membrane B) fouling resistance were examined under various biofouling conditions. Biofouling developed in both membranes. However, Membrane B showed slightly improved biofouling resistance but only when exposed to moderate to high biologically active water, with cross-flow over the membrane surface and in the presence of a feed spacer. The feed spacer was shown to have the biggest impact on promoting biofouling compared to the membrane surface, as when the spacer was not present, biofouling hardly developed in cross-flow systems. Under these conditions, both Membrane A and B exhibited very little biofouling. The MFS and Flat cell methods described in this report were found to be the most reliable and will be used to screen improved feed spacer designs and fouling resistant membrane chemistries for advancing the DOW FILMTEC™ BW element fouling resistant product line.

## 5 REFERENCES

[1] A. Matina, Z. Khana, S.M.J. Zaidia, M.C. Boyceb, Biofouling in reverse osmosis membranes for seawater desalination: Phenomena and prevention, Desalination 281 (2011) 1–16

[2] M. Herzberg, M. Elimelech, Biofouling of reverse osmosis membranes: Role of biofilm enhanced osmotic pressure, J. of Membrane Sci. 295 (2007) 11–20

[3] E. Bar-Zev, I. Berman-Frank, O. Girshevitz, T. Berman, Revised paradigm of aquatic biofilm formation facilitated by microgel transparent exopolymer particles, Proc. of the Natl. Acad. of Sci. 109 (2012) 9119-9124

[4] ASTM E2562-12, Standard Test Method for Quantification of Pseudomonas aeruginosa Biofilm Grown with High Shear and Continuous Flow using CDC Biofilm Reactor, ASTM International, West Conshohocken, Pennsylvania, 2012

[5] J.S. Vrouwenvelder, J.A.M. van Paassen, L.P. Wessels, A.F. van Dam, S.M. Bakker, The membrane fouling simulator: a practical tool for fouling prediction and control, J. of Membrane Sci. 281 (2006) 316-324

[6] G. Massons-Gassol, G. Gilabert-Oriol, R. Garcia-Valls, V. Gomez, T. Arrowood, Development and application of an accelerated biofouling test in flat cell, Desalination and Water Treat., 57 (2016) 23318-23325

[7] C. Dreszer, J. S. Vrouwenvelder, A. H. Paulitsch-Fuchs, A. Zwijnenburg, J. C. Kruithof, H.-C. Flemming, Hydraulic resistance of biofilms, J. of Membrane Sci. 429 (2013) 436–447

[8] G. Gilabert-Oriol, G. Massons, D. Dubert, J. Johnson, T. Arrowood, Feed spacers biofouling comparison for small simulators and industrial systems, AMK 2014 Conference, Aachen, Germany, 2014

[9] L. Vanysacker, P. Declerck, I. Vankelecom, Development of a high throughput cross-flow filtration system for detailed investigation of fouling processes, J. of Membrane Sci. 442 (2013) 168–176

[10] J. S. Vrouwenvelder, C. Hinrichs, W. G. J. Van der Meer, M. C. M. Van Loosdrecht, J. C. Kruithof, Pressure drop increase by biofilm accumulation in spiral wound RO and NF membrane systems: role of substrate concentration, flow velocity, substrate load and flow direction, Biofouling 25 (2009) 543–555

[11] J. D. Jacobson, M. D Kennedy, G. Amy, J. C. Schippers, Phosphate limitation in reverse osmosis: An option to control biofouling?, Desalination and Water Treat. 5 (2009) 198–206

[12] J. S. Vrouwenvelder, M. C. M. Van Loosdrecht, Phosphate limitation to control biofouling, Water Res. 44 (2010) 3454-3466

[13] S. E. Jensen, P. Hubrechts, B. M. Klein, K. R. Hasløv, Development and validation of an ATP method for rapid estimation of viable units in lyophilised BCG Danish 1331 vaccine, Biologicals 36 (2008) 308–314

[14] R. J. Barnes, R. R. Bandi, F. Chua, J. H. Low, T. Aung, N. Barraud, A. G. Fane, S. Kjelleberg, S. A. Rice, The roles of Pseudomonas aeruginosa extracellular polysaccharides in biofouling of reverse osmosis membranes and nitric oxide induced dispersal, J. of Membrane Sci. 466 (2014) 161–172

[15] M. Herzberg, S. Kang, M. Elimelech, Role of extracellular polymeric substances (EPS) in biofouling of reverse osmosis membranes. Environ. Sci. & Technol. 43 (2009) 4393-4398

[16] E. M. Van Wagner, A. C. Sagle, M. M. Sharma, Y. H. La, B. D. Freeman, Surface modification of commercial polyamide desalination membranes using poly (ethylene glycol) diglycidyl ether to enhance membrane fouling resistance. J. of Membrane Sci., 367 (2011) 273-287

[17] E. Matthiasson, The role of macromolecular adsorption in fouling of ultrafiltration membrane, J. of Membrane Sci. 16 (1983) 23–36

[18] L. A. Bereschenko, H. Prummel, G. J. W. Euverink, A. J. M. Stams, M. C. M. van Loosdrecht, Effect of conventional chemical treatment on the microbial population in a biofouling layer of reverse osmosis systems, Water Res., vol. 45 (2011) 405–416

[19] J. S. Vrouwenvelder, M. C. M. Van Loosdrecht, J. C. Kruithof, Early warning of biofouling in spiral wound nanofiltration and reverse osmosis membranes, Desalination 265.1 (2011) 206-212

[20] M. B. Dixon, S. Lasslett, C. Pelekani, Destructive and non-destructive methods for biofouling analysis investigated at the Adelaide Desalination Pilot Plant, Desalination 296 (2012) 61–68

[21] J. S. Vrouwenvelder, J. C. Kruithof, M. C. M. Van Loosdrecht, Integrated approach for biofouling control, Water Sci. & Technol. 62 (2010) 2477-2490

[22] J. S. Vrouwenvelder, S. A. Manolarakis, J. P. van der Hoek, J. A. M. van Paassen, W. G. J. van der Meer, J. M. C. van Agtmaal, H. D. M. Prummel, J. C. Kruithof, M. C. M. van Loosdrecht, Quantitative biofouling diagnosis in full scale nanofiltration and reverse osmosis installations, Water Res. 42 (2008) 4856–4868

[23] S. R. Suwarno, X. Chen, T. H. Chong, V. L. Puspitasari, D. McDougald, Y. Cohen, S. A. Rice, A. G. Fane, The impact of flux and spacers on biofilm development on reverse osmosis membranes, J. of Membrane Sci. 405 (2012) 219–232

# Chapter 6

## Summary and outlook

## 1 THESIS CONCLUSIONS

The research presented in this thesis was focused on improving the operation of reverse osmosis (RO) elements treating waters prone to biological fouling. It was demonstrated the need of accelerated and controlled testing protocols for screening novel concepts.

Flat sheet testing was the preferred testing approach for its high throughput. Biofouling development on flat sheet coupons was compared to full-scale spiral-wound RO elements and results were equivalent. This conclusion provided the foundation for adapting the operating conditions of flat sheet pilot plants to control the rate of biofouling development. The optimization included adjusting the concentration of bioassimilable nutrients dosed, the cross-flow velocity and the exposure time, among other parameters. Once conditions were adjusted, the amount of biofouling quantified analytically on coupons operated in parallel, showed good reproducibility. It was proved that the rate of biofouling development could be accelerated without creating variability on the results.

Additional solutions to measure analytically the fouling present in the membrane and feed spacer after operation were reviewed. Biofouling and organic fouling are difficult to quantify specifically and one can potentially mask the effect of the other. The comparison of carbohydrates and proteins in the measured total organic carbon and nitrogen (TOC and TN) values, was found to be reliable and specific. Nevertheless, determining the contribution of extracellular polymeric substances (EPS) in the fouling measured proved to provide clear differentiation of biologic and organic fouling.

Once determined the best operating conditions and analytical method for a reliable fouling testing, different configurations of membrane and feed spacers were evaluated. It was confirmed that different membrane chemistries can provide significant reduction in the levels of biofouling detected after operation. However, the major contributor to biofilm growth was, by far, feed spacer. Large differences in the amount of biofouling developed were observed on membrane coupons during operation if feed spacer was

present or not. Thus, it was concluded that the role of feed spacer design should be studied in detail to achieve a balanced performance in spiral wound RO modules when treating challenging water. Feed spacer designs with various thickness, spacing and angle were evaluated to study the correlation of each parameter with element productivity as well as with its biofouling resistance. A feed spacer designed coded as T1 showed a lower pressure drop increase, but also a lower biofouling and organic fouling accumulation, without impacting element productivity.

Overall, it can be concluded that significant benefits in fouling accumulation could be obtained with optimized module design. The scale-up of the results would result in more sustainable operation of RO element in water reuse pilot plants. The advantage in fouling resistance decreases the footprint of treatment, reducing energy consumption, chemical consumption and the complexity of the pretreatments.

### 1.1 Chapter 1

This chapter provides an overview on the membrane filtration technologies and the current state of the art research related with fouling management. The most promising strategies to improve the performance of RO elements treating challenging waters are provided. The research plan is based on the current limitations identified, with the objective of designing better reverse osmosis elements and optimized filtration and cleaning processes.

### 1.2 Chapter 2

This chapter covers the development and validation of a novel approach to normalize and compare analytical results to characterize more specifically the source of the foulants detected. The analysis of the contribution of carbohydrates and proteins in the measured

total organic carbon and nitrogen (TOC and TN) values can be linked with the proportion of extracellular polymeric substances (EPS) in the fouling. This allows a clearer understanding of whether the main source of the organic foulants is biologic or abiotic. Using this approach, real RO samples exposed at different fouling scenarios could be easily differentiated. When biofouling was promoted (bioassimilable nutrients dosed in the feed water), the percentage of TOC and TN accounted for by the carbohydrate and protein was nearly 100%. However, the percentages were much lower in samples from elements operated without nutrients, indicating that a greater fraction of the fouling was caused by abiotic organic compounds. Operating parameters such as feed-concentrate pressure or bacteria concentration in terms of adenosine triphosphate were also aligned with the fraction EPS results. The advantages of this method is that is much easier to implement and robust to conditions that RO elements might be exposed, such as cleanings or biocides. Once the main source of fouling is assessed, pretreatments, operating conditions and cleaning protocols can be adjusted effectively to tackle the primarily type of fouling occurring.

### 1.3 Chapter 3

This chapter shows the cross-validation of a flat cell units (MFS) with spiral wound RO systems, to be used a screening capability for biofouling research. These flat cell units are more convenient to test different membranes and feed spacers than large size RO modules. The results of both systems running in parallel showed that the performance of coupons and spiral wound elements was comparable. The magnitude of the differential pressures measured were not the same in the MFS and element systems due to the difference in scale. Nevertheless, the relative trends were very similar, and demonstrated the usefulness of the MFS units as a screening tool for biofouling in RO units.

Furthermore, a new feed spacer design was also evaluated using the MFS pilot plant. The novel spacer showed promising results with both lower pressure drop increase during operation and lower biofouling accumulation, compared to three other spacer designs that were also tested.

### 1.4 Chapter 4

This chapter discusses the steps followed to adapt an accelerated, 3-day biofouling test protocol, to compare biofilm formation in reverse osmosis membranes coupons. The amount of biofouling analytically quantified in the coupons operated in parallel, showed good reproducibility. On average, the standard deviations in the repetitions were around 15%. The effect of feed velocity, permeate flux and nutrient dosing levels was carefully evaluated and each parameter was optimized to reduce the deviation in the repetitions.

Operating at a flux of 20 L/m²h and at a cross-flow velocity of 0.6 m/s provided good reproducibility. Bioassimilable nutrients were dosed in the range of 0.2-0.1 mg/L of carbon as acetate form for more controlled biofilm growth. This protocol enables rapid screening of the biofouling resistance of new reverse osmosis membranes and spacers.

### 1.5 Chapter 5

In this chapter, a membrane chemistry expected to have an improved biofouling resistance, Membrane B, was compared to a control membrane with poor biofouling resistance, Membrane A. The comparison was performed using three different experimental tools for flat cell biofouling testing. After side-by-side testing, membrane B showed slightly improved biofouling resistance. However, the results were only significant when exposed to biologically active water, with cross-flow over the membrane surface and in the presence of a feed spacer. It could be concluded that feed spacer was

key in promoting biofouling development. If feed spacer was not present, little biofouling growth was observed and differentiation between Membrane A and B became less obvious. The testing performed in the Center for Disease Control (CDC) reactor, Membrane Fouling Simulator (MFS) and membrane permeation Flat Cell (FC) unit provide similar results. However, the MFS and Flat cell methods described in this report were found to be the most reliable to screen improved feed spacer designs and fouling resistant membrane chemistries.

UNIVERSITAT ROVIRA I VIRGILI
BIOFOULING CONTROL IN REVERSE OSMOSIS MEMBRANES FOR WATER TREATMENT
Gerard Massons Gassol

## 6 CONCLUSIONS DE LA TESI

La investigació presentada en aquesta tesi s'ha centrat en la millora del funcionament dels elements d'osmosi inversa (RO) que tracten aigües propenses a l'embrutament biològic. S'ha demostrat la necessitat de protocols de prova accelerats i controlats per a l'avaluació de nous conceptes i dissenys.

El tipus de testeig mitjançant membrana plana ha sigut l'enfocament preferit degut a la flexibilitat i rapidesa que permet assolit. El desenvolupament del *biofouling* en cupons de membrana plana es va comparar amb el que succeïa en elements industrials de RO i els resultats van ser equivalents. També es van adaptar les condicions d'operació per a poder controlar la velocitat del desenvolupament de *biofouling*. Es van ajustar la dosificació de nutrients bioassimilables, la velocitat de circulació d'aigua i el temps de contacte, entre altres paràmetres. Un cop ajustades aquestes condicions, la quantitat de *biofouling*, mesurada analíticament en cupons operats en paral·lel, mostrava una bona reproductibilitat. Es va demostrar que la velocitat de desenvolupament de *biofouling* es pot accelerar sense augmentar la variabilitat en els resultats.

S'han desenvolupat també noves eines analítiques per poder determinar analíticament l'origen dels contaminants presents en la membrana i l'espaciador després de operació. El *biofouling* i els compostos orgànics solen trobar-se combinats i són difícils de quantificar específicament, el que pot emmascarar l'efecte de l'altre. La comparació de glúcids i proteïnes en els valors totals de carboni orgànic i nitrogen (TOC i TN) es va trobar que aportava un paràmetre fiable i específic. La determinació del percentatge de substàncies polimèriques extracel·lulars (EPS) en els contaminants mesurats permet una diferenciació clara entre la contaminació biològica i orgànica.

Un cop determinades les millors condicions d'operació per a un assaig fiable de la resistència a l'embrutament, es van avaluar diferents configuracions de membranes i espaciadors. Es va confirmar que diferents químiques de membrana poden proporcionar

una reducció significativa en els nivells de *biofouling* que es produeixen durant l'operació. No obstant això, el principal component responsable del creixement del biofilm és, amb diferència, l'espaiador. Es va observar grans diferències en la quantitat de biofouling desenvolupat en cupons de membrana depenent de si el espaiador estava present o no durant l'operació. D'aquesta manera, es va concloure que el disseny del *feed spacer* havia de ser estudiat en detall per aconseguir un rendiment equilibrat en els mòduls RO per millorar la seva resistència a l'embrutament. Es van avaluar diversos dissenys d'espaiadors amb diferents espessors, espaiats i angles per estudiar la correlació de cada paràmetre amb la hidràulica final de l'element, així com amb la seva resistència a la *biofouling*. Un dissenyat espaiador codificat com T1 va mostrar un menor augment de la pressió diferencial, així com una menor acumulació de *biofouling* i *fouling* orgànic.

En general, es pot concloure que es poden obtenir importants beneficis en l'acumulació de compostos present en l'aigua d'alimentació, mitjançant un disseny optimitzat del mòdul. L'extrapolació dels resultats obtinguts a plantes industrials resultaria en un funcionament més sostenible dels elements de RO, amb una disminució de la petjada del la instal·lació, una reducció en el consum d'energia i de químics, així com una menor complexitat dels pretractaments.

## 6.1 Capítol 1

Aquest capítol ofereix una visió general sobre les tecnologies de filtració de membranes i l'estat de l'art actual sobre la investigació relacionada amb el seu embrutament. S'enumeren les estratègies més prometedores per millorar el rendiment dels elements RO que tracten aigües complexes. El pla de recerca es va basar en les limitacions actuals identificades, amb l'objectiu de dissenyar millors elements d'osmosi inversa i optimitzar els processos de filtració i neteja.

## 6.2 Capítol 2

Aquest capítol cobreix el desenvolupament i la validació d'un nou mètode per normalitzar i comparar els resultats analítics per poder caracteritzar més específicament la font dels compostos detectats en la superfície de la membrana i el *feed spacer*. L'anàlisi de la contribució dels carbohidrats i les proteïnes en els valors mesurats de carboni orgànic i nitrogen (TOC i TN), es pot vincular amb la proporció de *extracellular polymeric substances* (EPS) presents. Això permet identificar més clarament si la font principal del contaminació és biològica o abiòtica. Utilitzant aquest enfocament, es poden diferenciar fàcilment entre mostres de contaminants obtinguts al exposar els elements a diferents condicions. Quan es va promoure el *biofouling* (es van dosificar nutrients bioassimilables en l'aigua d'alimentació), el percentatge de TOC i TN degut als carbohidrats i proteïnes era gairebé del 100%. No obstant això, els percentatges van ser molt més baixos en mostres d'elements operats sense nutrients, la qual cosa indica que una major fracció de la contaminació va ser provocada per compostos abiòtics orgànics. Els paràmetres d'operació, com ara els diferencials de pressió o la concentració de bacteris en termes de trifosfat d'adenosina (ATP), també es estaven alineats amb els resultats de la fracció EPS. Els avantatges d'aquest mètode són que és molt més fàcils d'implementar i robust envers diferents químics que els elements RO poden exposats, com ara neteges o biocides. Els pretractaments, les condicions de funcionament i els protocols de neteja es poden ajustar de manera efectiva un cop determinat els compostos principals que causen l'embrutament.

## 6.3 Capítol 3

Aquest capítol mostra la validació de les unitats de cel·la plana (MFS) amb els sistemes osmosis inversa industrials, per a ser utilitzades per a la recerca de *biofouling*. Aquestes unitats de cel·la plana són més convenients per provar diferents prototips de membranes

i *spacers* amb mostres més reduïdes. Els resultats d'aquestes dos plantes pilot quan van operar en paral·lel van permetre veure que el desenvolupament de biofilm en els cupons de membrana plana i els elements industrials és comparable. El valor absolut de les diferents pressions diferencials mesurades no va ser el mateixa en els sistemes MFS i elements a causa de la diferència d'escala entre ells. No obstant això, les tendències relatives van ser molt similars, i es va demostrar la utilitat de les unitats MFS com a eina de avaluació a escala de laboratori per a la recerca de *biofouling*.

A més, es va avaluar una nova geometria de *feed spacer* utilitzant el MFS. El nou disseny va mostrar resultats prometedors amb un menor augment de la pressió diferencial durant l'operació i una menor acumulació de *biofouling*, en comparació amb altres tres dissenys d'espaiadors que també es van provar.

### 6.4 Capítol 4

En aquest capítol es detallen els passos seguits per adaptar un protocol d'assaig accelerat de *biofouling* en 3 dies, per tal de comparar la formació de biofilms en cupons de membranes d'osmosi inversa. La quantitat de biofilm quantificat analíticament en els tres cupons operats en paral·lel, va mostrar una bona reproductibilitat. De mitjana, les desviacions estàndard en les repeticions van ser al voltant del 15%. Es va avaluar l'efecte que la velocitat de l'alimentació, el flux de permeat i els nivells de dosificació de nutrients tenien sobre el desenvolupament del biofilm i es va optimitzar cada paràmetre per reduir la variabilitat en les concentracions de cada repetició.

Operant a un flux de 20 L/m²h i amb una velocitat de alimentació de 0,6 m/s, es va trobar una bona reproductibilitat. La concentració òptima de nutrients bioassimilables dosificats va ser en el rang dels 0,2-0,1 mg/L de carboni en forma d'acetat, per tal d'obtenir un creixement controlat del biofilm. Aquest protocol permet una avaluació ràpida de la resistència al *biofouling* de noves membranes i espaiadors d'osmosi inversa.

## 6.5 Capítol 5

En aquest capítol, es va comparar una química de membrana amb una resistència al *biofouling* millorada, anomenada Membrana B, amb una membrana de control amb una menor resistència teòrica al *biofouling*, anomenada Membrana A. La comparació es va realitzar mitjançant tres mètodes experimentals diferents per a avaluar el creixement de biofilm en superfícies de materials. Comparant els resultats obtinguts usant aquests mètodes, la membrana B va mostrar una resistència al *biofouling* lleugerament superior. No obstant això, els resultats només van ser significatius quan es van exposar a aigua amb un nivell biològic alt i amb la presència de l'espaiador. Es va concloure que la presencia del *feed spacer* és clau per promoure el desenvolupament del biofilm. Quan l'espaiador no estava present, es va observar poc creixement de *biofouling* i la diferenciació entre membranes A i B va ser menys evident. Les proves realitzades en el reactor del *Center for Disease Control* (CDC), MFS i la unitat de membrana plana van proporcionar resultats comparables. Tot i així, els mètodes de MFS i membrana plana descrits en aquest informe es van trobar com els més fiables per avaluar els dissenys d'espaiadors i les químiques de membrana.

UNIVERSITAT ROVIRA I VIRGILI
BIOFOULING CONTROL IN REVERSE OSMOSIS MEMBRANES FOR WATER TREATMENT
Gerard Massons Gassol

UNIVERSITAT
ROVIRA i VIRGILI