OPTIMIZATION OF ULTRAFILTRATION MEMBRANE CLEANING PROCESSES. PRETREATMENT FOR REVERSE OSMOSIS IN SEAWATER DESALINATION PLANTS

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Optimization of ultrafiltration membrane cleaning processes

Pretreatment for reverse osmosis in seawater desalination plants

Guillem Gilabert Oriol

Doctoral Thesis

Universitat Rovira i Virgili

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Doctoral Thesis

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I, Dr. Markus Busch, Application Development Leader, Application Development Leader Europe, Middle East & Africa by the Dow Chemical Company,

CERTIFY:

That the present work entitled "Optimization of ultrafiltration membrane cleaning processes. Pretreatment for reverse osmosis in seawater desalination plants", presented by Guillem Gilabert Oriol 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, 21st January 2013

Prof. Dr. Ricard Garcia-Valls Dr. Veronica Garcia Molina Dr. Markus Busch

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Abstract

The use of pressurized ultrafiltration as a pretreatment for the reverse osmosis membranes in seawater desalination has experimented an impressive increase as a result of the continuous search for cost-effective technologies which enable a sustainable production of water. Key benefits associated to the ultrafiltration technology versus conventional pretreatment are a low footprint, the ability to remove virus and bacteria and to significantly reduce colloids, suspended particles, turbidity and some total organic carbon. Even more importantly, the ability to reliably provide good quality filtrate water to the downstream reverse osmosis are the most remarkable benefits associated with this technology. Backwash is identified as the most important cleaning process to be improved in order to increase the efficiency of the ultrafiltration process. Compared to the Chemical Enhanced Backwash (CEB) and the Clean in Place (CIP), the backwash consumes a huge amount of time, because it takes place more often.

This thesis researches how to improve the effectiveness of the cleanings done in the ultrafiltration in order to improve the process efficiency. Thanks to this research, ultrafiltration efficiency is increased from its original value of 88% to 98% in desalination plants. This represents filtrating 96 minutes extra per day and a reduction of 100% in the filtrated water used during backwashes. This represents a cost decrease in the ultrafiltration process of 7.1%, and a cost decrease of 1.2% in the whole desalination process. Moreover, sodium hypochlorite chemical equivalent concentration is reduced from 0.28 mg/l to 0.06 mg/l. Backwash sequence is also simplified from five cleaning steps to only two cleaning steps. These are the backwash top with air scour and the forward flush. The steps eliminated are the air scour, the draining and the backwash bottom. Backwash frequency is optimized from 30 minutes to 90 minutes. Backwashing with reverse osmosis brine is also proven feasible in an ultrafiltration and reverse osmosis integrated process. Chemical Enhanced Backwashes frequency is decreased from one CEB per day to one CEB every five days. All the findings of the ultrafiltration cleaning research are integrated together and validated. A methodology to predict the trans-membrane pressure evolution over time is proposed. This technique is also useful to analyze the effectiveness of a filtration cycle, a backwash or a CEB. Polyvinylidene difluoride (PVDF) fibers are assessed against Polyethersulfone (PES) fibers. It has been observed that PES fibers show initially higher permeability, but are less fouling resistant. Therefore, they need 2.5 more CEBs to sustain the same operating flux. Moreover, if these CEBs are not done, PVDF membranes show 55% higher permeability. If the smaller active filtration area of PES modules is taken into account, savings of 18% in the ultrafiltration step and of 2% in the desalination plant are achieved. A process to prevent reverse osmosis chlorination due to sodium hypochlorite used during CEBs in the upstream ultrafiltration process is also explained.

Abbreviations

ANOVA	Analysis of Variance
AS	Air Scour
BW	Backwash
BWB	Backwash Bottom
BWT	Backwash Top
CAPEX	Capital Expenses
CEB	Chemical Enhanced Backwash
CEC	Chemical Equivalent Concentration
CFS	Coagulation/ Flocculation/ Sedimentation step
CIP	Cleaning in Place
cUSD	United States dollar cent
D	Draining
DOE	Design of Experiments
FF	Forward Flush
H_0	Null hypothesis
H_1	Alternate hypothesis
JMP	Statistical Analysis Software
NOM	Natural Organic Matter
OPEX	Operational Expenses

P	Pressure
PES	Polyethersulfone
PIM	Polymers with Intrinsic Microporosity
PVDF	Polyvinylidene difluoride
RO	Reverse Osmosis
SEM	Scanning electron microscope
T	Temperature
TB	Turbidity
TCF	Temperature Correction Factor
TDS	Total Dissolved Solids
TMP	Trans-membrane Pressure
TOC	Total Organic Carbon
TSS	Total Suspended Solids
UF	Ultrafiltration
USD	United States dollar

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1. Aim of this thesis

1.1 Thesis hypothesis

The hypothesis of this thesis is that the efficiency of the ultrafiltration process can be drastically increased by improving its cleaning steps performance.

1.2 Thesis outline

This thesis focuses in gaining a better understanding of the different cleaning protocols and mechanisms of the pressurized ultrafiltration as a pretreatment for the reverse osmosis desalination in industrial plants. This thesis suggests different optimization protocols for the backwash cleanings, the chemical enhanced backwash (CEB) cleanings and the clean in place (CIP). This is achieved through the optimization of the different backwash steps, the backwash length, the backwash frequency, the backwash flow, the chemicals used during the CEB, the CEB frequency, the CEB time, the chemicals used during the CIP and its frequency. The improvement in these cleaning variables ultimately leads to an increase in the ultrafiltration process yield, which eventually increases the total net flux obtained from the ultrafiltration process. The increase of the net flux has a tremendous impact in lowering the total water cost in terms of capital expenses (CAPEX) costs, which translates to less modules used, and the operational expenses (OPEX), which ultimately translates to a reduction of the chemicals used and low energy to sustain the same filtration process. The advances made are also described and argued following a lean six sigma waste elimination process. This thesis is divided into different chapters, each one researching a different parameter that deals with the ultrafiltration cleaning process. Each chapter gives a better insight of the general overview of this research. Figure 1 visually depicts the structure of this work. On the left side the state of the art is schematically defined, while on the right side, an overview of the optimized conditions is presented together with the relationships that link all the chapters.

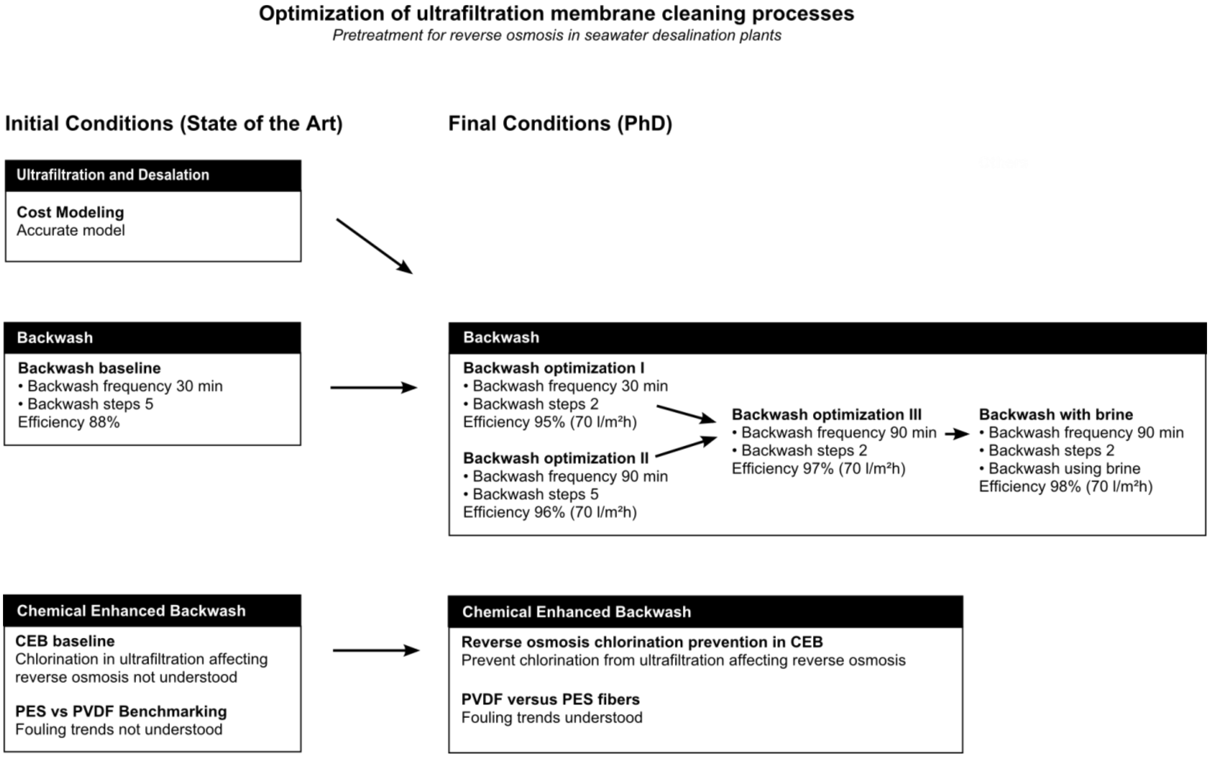

Figure 1. Thesis outline

1.2.1 Chapter 1 – Aim of the thesis

This chapter exposes the aim of the thesis together with the main thesis hypothesis, which is that the ultrafiltration cleanings can be improved thus increasing the ultrafiltration process efficiency, and how each chapter helps in validating the hypothesis through the validation of different sub hypothesis developed in each chapter.

1.2.2 Chapter 2 – Introduction

This chapter gives an overview of the different membrane technologies available and their classification according to its pore size and according to their mass transport model. It describes the basis to understand what the ultrafiltration technology is about, the transport equations, the normalization equations, the efficiency equations together with the recovery and availability equations. It also compares the ultrafiltration pretreatment for the reverse osmosis seawater desalination with the conventional pretreatment. Finally, it gives an overview of the different types of cleanings in order to address fouling efficiently.

1.2.3 Chapter 3 – Backwash optimization I

This chapter presents an overview of the backwash cleaning process, with a particular focus on reducing the total number of the backwash steps done during a conventional backwash cleaning. Special attention is put in the identification of the steps that contributes the less to the fouling reduction. To validate this hypothesis, a Lean Six Sigma methodology has been used to reduce waste. This is accomplished by applying a fractional design of experiments and analyzing the results through an analysis of variance and then building a statistical model to support the conclusions extracted.

1.2.4 Chapter 4 – Backwash optimization II

This chapter assesses the benefits of different cleaning configurations and their impact in the ultrafiltration efficiency and the chemical equivalent consumption. Their impact in the ultrafiltration water treatment cost is also assessed for each different scenario. The reduction in the backwashes done per day is selected as the most relevant configuration.

1.2.5 Chapter 5 – Backwash optimization III

This chapter combines the two benefits associated with operating the ultrafiltration doing longer filtration cycles, which means doing less cleanings, and the benefit obtained through the reduction of the backwash cleaning steps. Through this novel combination, a very high efficiency is achieved. The data is analyzed assessing the correlations between the trans-membrane starting and finishing value during the filtration cycle, the backwash cycle and the chemical enhanced backwash cycle. This enables ultimately to build a trans-membrane predictive model over time which is able to predict the fouling evolution over time.

1.2.6 Chapter 6 – Backwash using brine

This chapter researches the operation of ultrafiltration using reverse osmosis brine in order to clean the membranes during the backwash sequence. These results are integrated with the previous cleaning research findings. The advantage of using this reverse osmosis waste when cleaning the ultrafiltration membranes translate to a 100% of product recovery in the ultrafiltration process, since no filtrated water is used during the backwashes and in CEBs. The result of this process integration of ultrafiltration and reverse osmosis leads to high efficiency values in ultrafiltration. This operation is validated through 15 days of real plant operation. A cost analysis of each one of the different pressurized ultrafiltration cleaning research phases is also presented. This overview allows a better understanding of the real impact of the present research in the industry. This work may be published into a confidentiality agreement due to future patenting opportunities.

1.2.7 Chapter 7 – PVDF versus PES fibers

This chapter is included through a confidentially agreement and it assesses the two predominant technologies in the current pressurized Ultrafiltration market. These are the Polyvinylidene difluoride (PVDF) membranes using an outside-in flux technology and the Polyethersulfone (PES) membranes using an inside-out flux technology. This allows establishing a comparison of the number of CEBs both technologies need to sustain the flux, as well as their fouling resistance under different operating conditions. A cost comparison between both fiber types and both elements taking into account each filtration area is also performed.

1.2.8 Chapter 8 – Reverse osmosis chlorination prevention in CEB

This chapter is included in this thesis through a confidentially agreement and it analyses the root causes that leads to chlorinate the reverse osmosis membranes with chlorine coming from chemical enhanced backwashes done upstream in the ultrafiltration pretreatment. The research indicates how to prevent this halogenation suggesting control mechanisms and reverse osmosis chlorine risk free designs. This is achieved by providing additional cleaning steps and cleaning protocols for the chemical enhance backwash. The aim of this research is to be kept as a trade secret by the Dow™ Chemical Company.

1.2.9 Chapter 9 – Conclusions

This chapter gives a final outlook to the dissertation, presenting the conclusions reached during this research. It also gives a short outline about the author's biography, and presents his research curriculum build during the realization of this thesis.

2. Introduction

Membranes popularity is increasing drastically in a broad range of industrial processes thanks to its ability to control the permeation rate of species through the membrane. This allows the design of different separation processes where the goal is to allow one component of a mixture to permeate freely through the membrane, while the other elements have difficulties to permeate. This is achieved through different driving forces which drive each different mass transfer across the membrane. These are represented by any combination of a concentration, a pressure, a temperature or an electric potential gradient.

One of the key aspects of membranes is to effectively control the membrane fouling, which decreases the permeability of the membrane. If fouling is not properly controlled, the membrane can irreversibly lose flow.

Ultrafiltration, in particular, is a separation membrane technology based on particle size exclusion. This is achieved thanks to the different small micropores which act as a sieve and prevent the particles which are bigger than the pore diameters to flow freely through the membrane. The use of ultrafiltration as a pretreatment of the reverse osmosis in the seawater desalination application has gained special popularity in recent years. Ultrafiltration is a key factor in reducing fouling to the reverse osmosis. Among its key benefits against the conventional pretreatment is a lower footprint and a better filtrate water quality.

2.1 Membrane filtration

Membranes are classified according to their pore diameter. An overview of each membrane technology regarding its pore diameter is given in the next paragraph. In addition, Figure 2 provides a graphical scheme summary [1]. Figure 3 details the intersection region between both mass transport models [1]. The pore flow model, represented by ultrafiltration, and the solution diffusion model represented, by reverse osmosis. In the intermediate section, nanofiltration combines both models to describe its behavior. Finally, Table 1 illustrates some examples of typical species that are filtrated using one of the described membrane technologies, together with their typical size [1]. Therefore, using Figure 2 and Figure 3, it is possible to assess which filtration technology will be more suitable to filtrate or concentrate one of the species shown in the table.

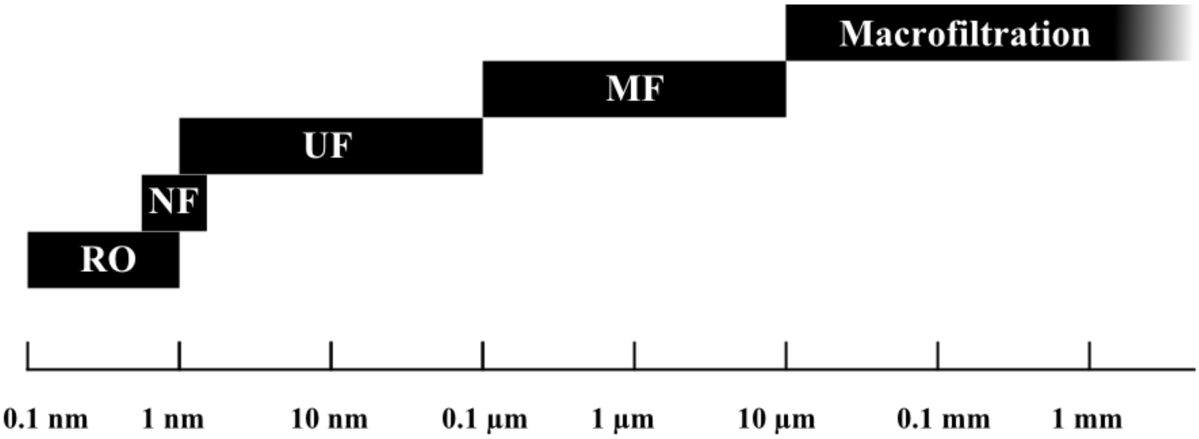

Figure 2. Membranes classified by their pore diameter

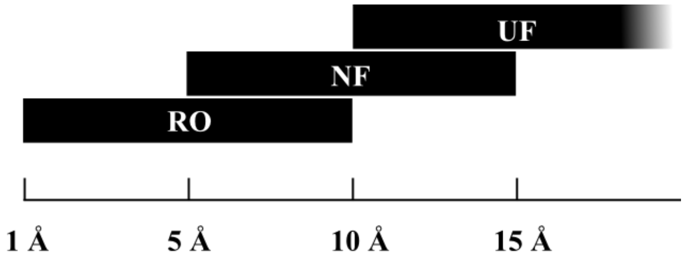

Figure 3. Reverse osmosis, nanofiltration and ultrafiltration membranes classified by their pore diameter

Table 1. Species with their size

Species	**Size**
H_2O	0.2 nm
Na^+	0.37 nm
Sucrose	1 nm
Hemoglobin	7 nm
Influenza virus	0.1 µm
Pseudomonas diminuta	0.28 µm
Staphylococcus bacteria	1 µm
Starch	10 µm

Reverse osmosis membranes have pore diameters that range from 0.1 nm to 1 nm [1]. These pores have the particularity that they are so small, that discrete pores do not exist. Instead, the pores are formed through unstable spaces between polymer chains, which are created and faded as a result of their molecular thermal motion. These fluctuating pores represent the diffusion of species throughout the dense membranes. In contraposition, the bigger and stable pores observed in the ultrafiltration porous membranes represent the mass flux through convection described by the pore flow model. The solution diffusion model, which is not covered in this thesis, makes two assumptions. The first is that the solvents dissolve inside the membrane, and thereafter they diffuse through the dense film according to the present concentration gradient. In the reverse osmosis, separation occurs because of the different solubility and mobility of each specie throughout the membrane.

Nanofiltration membranes have pore diameters that range from 0.5 nm to 1.5 nm [1]. These pores have the particularity of being between truly microporus membranes and clearly dense films. Therefore, mass transfer through nanofiltration membranes is described using both pore flow and solution diffusion models. This happens because if membrane polymer chains are very stiff, the molecular motion of the polymer is restricted, and semi-permanent microcavities are formed which are interconnected. These membranes are also called polymers with intrinsic microporosity (PIM) [2].

Ultrafiltration membranes have pore diameters that range from 1 nm to 0.1 µm [3]. These pores have the property of being bigger and stable micropores which do not vary over time and do not appear and disappear because of molecular thermal motion like reverse osmosis membranes do. The filtration principle that produces separation is the sieving mechanism practiced by the pores, which result into a convective flux across the membrane.

Microfiltration membranes have pore diameters that range from 0.1 µm to 10 µm [4]. These pores are similar to the pores used by the ultrafiltration membranes but with a much bigger size. Its filtration mechanism is also described by the pore flow model as it achieves separation using the same sieving mechanism principle.

Macrofiltration, also known as conventional filtration, presents pore diameters above 10 µm [5]. The pore sizes are normally visible by a human eye and they use the same sieving separation mechanism as the ultrafiltration and the microfiltration. Therefore, its flow across the membrane is also achieved by the pore flow model.

2.2 Ultrafiltration

Ultrafiltration membranes are characterized by being asymmetric porous membranes with a pore size between 1 nm to 100 nm and a membrane wall thickness around 150 µm [1]. The driving force is typically a pressure gradient between the filtrate and the feed membrane side, with a trans-membrane pressure (TMP) typically between 1 bar to 10 bar [1]. The separation principle is the sieving mechanism and it is described by the pore flow filtration model. The ultrafiltration membranes technology most widely used is the pressurized technology. It uses a pressure vessel to store the hollow fibers. This enables the system to work at a higher pressure and therefore at higher filtration fluxes. Two main configurations are the most predominant. These are the outside-in technology, where the flux enters the membrane from the outside part of the fiber to the inside part of the fiber, and the inside-out technology, where the membrane filters from inside the hollow fiber to the outside part. Typically, outside-in technology fibers are made of Polyvinylidene difluoride(PVDF) and uses air scour during cleanings, while inside-out technology fibers are made of Polyethersulfone (PES) [6]. The most common way to operate an ultrafiltration module is through the dead-end disposition. This means the concentrate pipe is closed, so everything that enters the ultrafiltration pressure vessel and that does not exit remains in the membrane. Therefore, it remains a key factor to clean effectively the ultrafiltration membrane. The other possible configuration is the cross-flow disposition, where the concentrate pipe opens to some extent. This process is less used since the net process yield is lower in last case as in addition to the concentrate flow loss, the membrane must also be cleaned frequently.

Main Ultrafiltraiton materials types are polymeric and ceramic membranes. Among the polymeric membranes, typical materials are polysulfone (PS), poly(ether sulfone) (PES), sulfonated polysulfone, poly(vinylidene fluoride (PVDF), polyacryloíntrile , cellulosics like cellulose acetate, polyimide, poly(ether imide), aliphatic polyamides and polyetheretherketone. Among the inorganic ceramics membranes, the main materials used are aluminia (Al_2O_3 and zirconia (ZrO_2) [1].

Main applications include water treatment, dairy industry (milk, whey, cheese making), food (potato starch and proteins), metallurgy (oil-water emulsions, electropaint recovery), textile (indigo), pharmaceutical (enzymes, antibiotics, pyrogens) and automotive (electro paint). Ultrafiltration has been mainly used in aqueous solutions, but now new non-aqueous solutions applications are also emerging.

An example of a typical pressurized ultrafiltration membrane is shown in Figure 4. There, it is shown a rack of DOW™ Ultrafiltration 2880 membranes which are used as a pretreatment for the reverse osmosis desalination. The first picture shows the rack operating in the Water Technology Application Development Global Center in Tarragona. The second picture shows a DOW™ Ultrafiltration 2660 membrane with its air inlet connection (bottom), its feed entry connection (bottom right), its concentrate output connection (top) and its filtrate water exit connection (top right). Figure 5 shows some PVDF hollow fibers and its section viewed using a Scanning electron microscope (SEM). Finally Figure 6 shows the membrane section, the outer membrane surface and the inner membrane surface as observed in the SEM.

Figure 4. Outside-in pressurized ultrafiltration membranes installed in a rack and its module

Figure 5. PVDF hollow fibers and its section

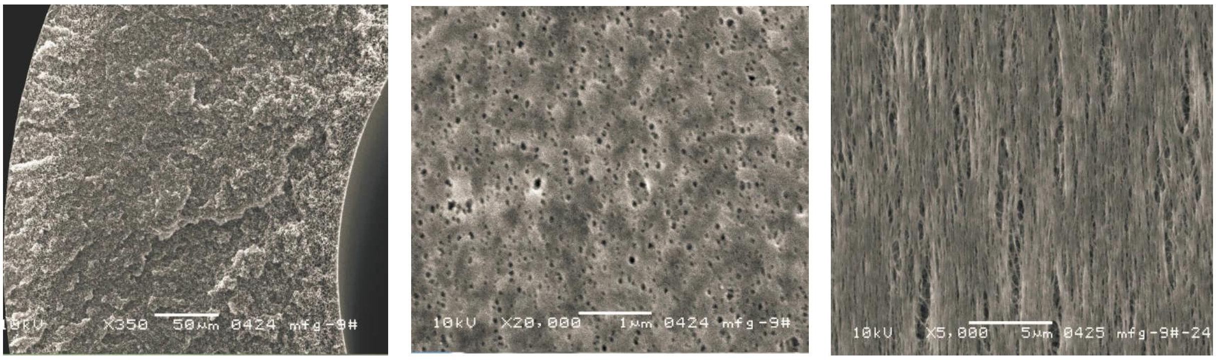

Figure 6. Section, outer surface and inner surface morphology

2.2.1 Transport equations

The transport equations of the pore flow model are presented in order to gain a better understanding of the filtration mechanisms that describe the mass transport across the ultrafiltration membrane. This is useful in determining with a more solid background, the permeability equation used in this thesis.

The starting point for the mass transfer inside a membrane is the statement, based on thermodynamics, that the driving forces such as the pressure, temperature, concentration and electrical potential are interrelated. So, the overall driving force that procures the movement of a specie (J_i in g/ cm^{2}s) through the membrane (dx) is represented by a gradient in the chemical potential ($d\mu_i$), where $\frac{d\mu_i}{dx}$ is the chemical potential gradient of the component and L_i is a proportionality coefficient not necessarily constant. The net flux across a membrane is given by Equation 1 [1].

$$J_i = -L_i \frac{d\mu_i}{dx}$$ **Equation 1**

Driving forces such as concentration, pressure and electric potential can be expressed as gradients in chemical potential ($d\mu_i$). This relationship is expressed by Equation 2 [7]. There, the concentration gradient ($d\ln(a_i)$) is expressed in terms of activity ($a_i = \gamma_i n_i$), where γ_i is the activity coefficient and n_i is the mole fraction, and it is related with temperature (T) and the gas constant (R). The pressure gradient (dP) is related with the molar volume of the component (v_i in m^3/ mol). The electrical potential (dE) is related with the Faraday constant (F) and the valence number of the ion (z_i).

$$d\mu_i = RTd\ln(a_i) + v_i dP + z_i FdE$$ **Equation 2**

In the pore flow model, it is assumed that the mass transfer across the membrane occurs driven by a favorable gradient in the chemical potential, which goes from a region with a higher value at the feed side of the membrane, to a region with a lower value at the filtrate side of the membrane. This favorable chemical potential occurs because of a favorable pressure gradient across the membrane. In ultrafiltration, however, the concentration of the specie that passes through the membrane remains constant as, because of the membrane sieving effect done by the pores, a component either pass through it or is rejected. This model is illustrated by Figure 7 [1].

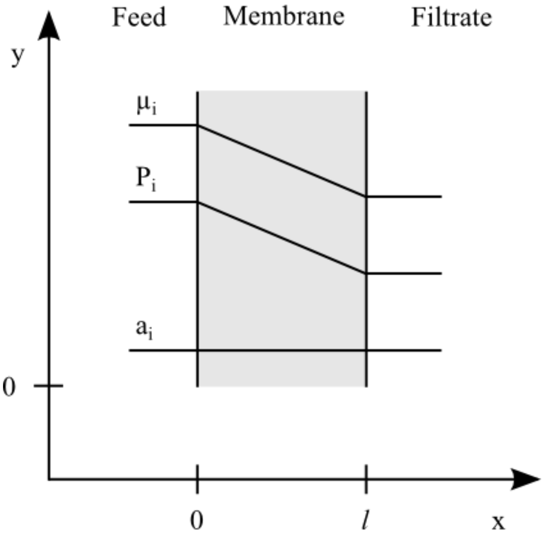

Figure 7. Pore flow model assumptions

After applying the assumptions made for the pore flow model in ultrafiltration membranes, Equation 1 and Equation 2 can be combined in order to obtain a model to predict the mass flux across the membrane. Equation 3 shows both equations combined.

$$J_i = -L_i \frac{RT \int_{a_i}^{a_i} \frac{da_i}{a_i} + v_i \int_{P_0}^{P_l} dP + z_i F \int_{E}^{E} dE}{\int_{x_0}^{x_l} dx}$$ **Equation 3**

As there is no concentration and electrical potential gradients across the membrane, Equation 3 can be simplified to obtain Equation 4, which describes the mass flux across an ultrafiltration membrane based on the pore flow model.

$$J_i = -L_i v_i \frac{dP}{dx}$$ **Equation 4**

Equation 5 shows Darcy's law after integrating Equation 3 and defining the Darcy's law coefficient constant (K) defined as $K = L_i v_i$ [8].

$$J_i = -K \frac{P_{perm} - P_{feed}}{l}$$ **Equation 5**

Equation 5 can be adapted to the general equation used in ultrafiltration modules in order to monitor its permeability value over time. This leads to Equation 6, where Flux (F) is expressed in terms of l/ m²h, Permeability (P) is expressed in terms of l/ m²·h·bar and Trans-membrane pressure (TMP) in bar. It must be noticed that due to fouling, the permeability value would vary over time as a result of a TMP increase if the membrane operates at a constant flux, or as a result of a flux decrease if the membrane operates at a constant TMP.

$$F = P \cdot TMP$$ **Equation 6**

2.2.2 TMP normalization equations

The normalized (TMP^*) is calculated multiplying the measured TMP by the temperature correction factor (TCF) as described by Equation 7.

$$TMP^* = TCF \cdot TMP$$ **Equation 7**

The purpose of the temperature correction factor is to take into consideration the effect of the Temperature (T) in Celsius degrees and its influence on the viscosity of water, as described by Equation 8 [9]. Therefore, different TMP values obtained at different temperatures can be compared and transported to the same reference temperature of 25 ºC.

$$TCF = \frac{10^{\left(\frac{247.8}{25+273.16-140}\right)}}{10^{\left(\frac{247.8}{T+273.16-140}\right)}}$$ **Equation 8**

2.2.3 Efficiency equations

Efficiency is defined as the net yield of the ultrafiltration process. It is obtained multiplying the product water recovery yield by the availability yield. Efficiency is used to make a fair comparison between these two parameters, making sure both time and water produced are taken into consideration to calculate the overall process yield. This yield is calculated using Equation 9.

$$Efficiency = Availability \cdot Recovery$$ **Equation 9**

Availability measures the time the ultrafiltration module is producing water. Therefore, the time when the unit is not filtrating is discounted. This yield is calculated using Equation 10.

$$Availability = \frac{t_{filtrating}}{t_{total}}$$ **Equation 10**

Water product recovery measures net water produced. Filtrated water consumed during backwashes and CEBs is discounted. This yield is calculated using Equation 11.

$$\mathrm{R}ecovery = \frac{V_{water\ produced} - V_{\ CEB} - V_{BW}}{V_{water\ produced}}$$ **Equation 11**

Chemical equivalent concentration (CEC) represents the concentration of pure chemicals per volume of feed water if the system was operated continuously. It is calculated dividing the total amount of pure chemicals between the water fed into an ultrafiltration system for a certain amount of time. This concentration is calculated using Equation 12.

$$\text{CEC}= \frac{M_{chemicals}}{V_{water\ fed}} \qquad \textbf{Equation 12}$$

2.2.4 Pretreatment to reverse osmosis

Conventional pretreatment for reverse osmosis seawater desalination uses a coagulation step followed by a flocculation step and a sedimentation steps in order to remove colloids and natural organic matter (NOM) particles. Afterwards, a deep media sand filtration step is added in order to reduce the turbidity of water. This pretreatment has different drawbacks. Firstly, a high footprint is needed to install this process. This raises the cost of the plant as more land must be paid. Secondly, this technology makes difficult to control the output water quality. This happens because there is no absolute barrier acting as a sieve and sand filters only reduce turbidity proportionally to its feed composition. Therefore, when the feed water quality changes as a result of a turbidity increase, the treated water turbidity also increases. Another key benefit is the chemical consumption, as the flocculation step needs a continual dosage of chemicals, which can highly increase the treatment costs.

On the other hand, ultrafiltration technology presents several benefits compared to the conventional pretreatment. The first benefit is a low footprint thanks to the compaction of thousands of fibers inside a pressure vessel. This benefit can be crucial when dealing with places where land costs are extremely expensive such as off-shore oil platforms. Another key benefit is the outstanding water quality of the treated water regardless the feed water quality. As an example, when dealing with high turbidity river water of 1,000 NTU, the filtrated water has only 0.050 NTU.

Therefore, it is very important to operate the ultrafiltration in the recommended ranges in order not to affect the fiber integrity. This happens since ultrafiltration has pores with defined diameters which ensure that all the particles bigger than the pores such as colloids, bacteria and viruses cannot pass the membrane. This also has the additional advantage to protect downstream reverse osmosis from biofouling since bacteria is retained in the ultrafiltration membrane. This factor can increase the reverse osmosis hydraulic performance by increasing its operating flux. However, the bacteria nutrients such as the total organic carbon (TOC) are typically very poorly rejected in ultrafiltration [10]. This factor can eventually cause biofouling in reverse osmosis. Special consideration must be taken with the sieving advantage shown by ultrafiltration as this can turn to a problem if fouling is not treated correctly, since if the membrane is completely blocked, it stops filtering water. Another advantages deals with a low chemical consumption as no coagulation, flocculation and sedimentation steps are needed when using PVDF fibers with an outside-in technology [6].

2.2.5 Fouling

Ultrafiltration membranes typically show pure water permeability fluxes greater than 500 l/ m^{2}h [1]. However, when it deals with real seawater containing colloids, macromolecules, microalgae and bacteria, its flux falls to 50 l/ m^{2}h [1]. This happens because all the foulants are retained on the membrane surface forming a gel layer [11]. This gel layer is an additional barrier to the one created by the pores themselves, which hinders the clean water flux across the membrane [11]. Figure 8 illustrates the gel layer formed above the membrane surface, together with the internal fouling formed when the particles block the internal membrane pores [12]. Typically, surface fouling is reversible and can be easily addressed than inside pore blocking fouling which tends to be irreversible fouling.

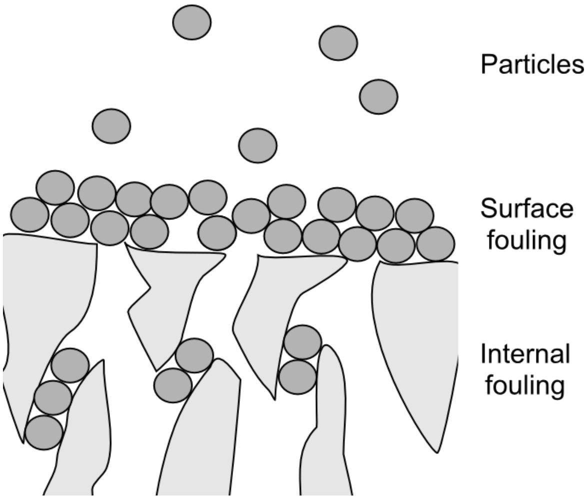

Figure 8. Fouling in an ultrafiltration membrane

Several techniques exist in order to control fouling depending on the addressable type of fouling. As ultrafiltration works in dead-end mode, everything that comes inside a pressure vessel and that does not pass through the membrane is retained on its surface. Table 2 summarizes the different cleaning protocols strategies, together with its frequency, the fouling type they do address and the chemicals used during the cleanings. Moreover, Figure 9 schematically depicts a typical ultrafiltration plant [13]. In this diagram, it can be easily assessed the different paths each backwash step must take in order to clean the membrane.

The more common observed type of fouling is the one caused by particles as shown previously in Figure 8 [12]. To address particle fouling a backwash cleaning sequences performed [14]. A backwash takes place repeatedly from every 10 to 120 minutes depending on the fouling the membrane is suffering. A backwash usually consists of an aeration step, which shakes the fibers through the bubbles, which also create a tensile strength above the fouling layer. Afterwards, there is the draining step which empties the pressure vessel. Then a backwash top that uses filtrated water and that removes the waste through the top concentrate vale with aeration can be done. In addition, a backwash bottom that uses filtrated water is also performed, which removes the waste through the bottom concentrate valve. Finally, a forward flush that uses feed water is done in order to create a tensile strength above the membrane surface and remove any remaining foulant [15]. Addressing particle fouling through backwashes is one of the most important parameters in order to attain good process efficiency because the backwash is the cleaning process that it is repeated more frequently every day.

Backwash cleanings deal with particle fouling, but not with bacteria. Therefore, after a certain amount of time, the effect of biogrowth starts to be appreciated. So, a backwash with some biocide must be done in order to remove all the bacteria attached to the membrane pores and surface. This is called a chemical enhanced backwash (CEB) [16]. This process uses several steps. The first one is a backwash top with biocide dosing. The second one is a backwash bottom with biocide dosage. Afterwards, a soaking period is performed so the fibers are soaked with the biocide and it has enough time to be effective. Finally, a backwash is done in order to remove the dosed biocide and the waste from the system. Typically, sodium hypochlorite (NaClO) is used as biocide because it is cheap and effective [16]. However, it can oxidize reverse osmosis membranes located downstream if the process gets uncontrolled. Therefore, other commercial non-oxidizing biocides can be used if the process reliability must be increased.

Finally, organic matter such as humic acids and inorganic matter such as iron and aluminum gets slowly sedimented above the membrane material. This narrows the pore size, which ultimately leads to fouling. To remove organic and inorganic matter, a clean in place is performed every one to three months. To eliminate organic fouling, a basic substance such as caustic (NaOH) is normally used [17]. To dissolve again precipitated organic matter, an acid substance like oxalic acid or citric acid is used [18].

Table 2. Cleaning strategies

Cleaning	Foulant	Chemicals	Time	Frequency
Backwash (BW)	Particle	-	1 min – 5 min	10 min – 120 min
Chemical Enhanced Backwash (CEB)	Biological	Oxidant	5 min – 45 min	12 h – 36 h
Cleaning in Place (CIP)	Organic	Basic	30 min – 240 min	1 m – 3 m
Cleaning in Place (CIP)	Inorganic	Acid	30 min – 240 min	1 m – 3 m

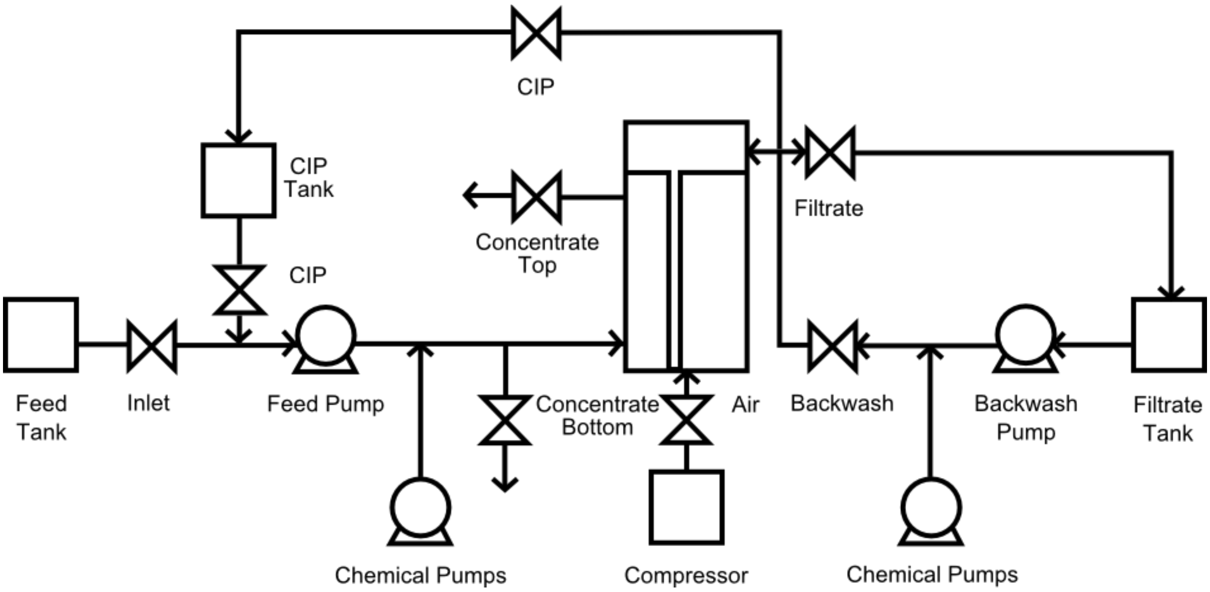

Figure 9. Typical ultrafiltration plant

Fouling is typically monitored assessing the trans-membrane pressure evolution over time when the flux is constant. The TMP increases because as the pores diameters get smaller because of fouling, more pump power is needed to sustain the same operating flux. If fouling is very severe, the pump might not be able to deliver the targeted flux and the filtrate flux starts to decrease over time.

During a filtration cycle, TMP increases over time as the overall porous surface of the membrane gets smaller due to particles blocking it. However, when a backwash is done, the TMP is slightly recovered. This cleaning methodology enables a sustainable operation that keeps the TMP stable and controlled into the operating limits. However, after a certain amount of time, TMP starts to show a high value. This happens because biofouling starts to be important. When a chemical enhanced backwash is performed, TMP lowers its value and the filtration and backwash cleaning cycles can start again in a controlled and sustainable TMP range. Figure 10 shows the TMP increase due to the various filtration cycles, together with the TMP decrease due to the various backwash cycles. Finally, the TMP reduction achieved thanks to a CEB can be assessed. Figure 11 shows the overall performance of an ultrafiltration membrane when a larger time period is assessed. In this figure, it can be assessed the constant effect of each CEB. However, it is very difficult to assess the individual contribution of every backwash performed [19].

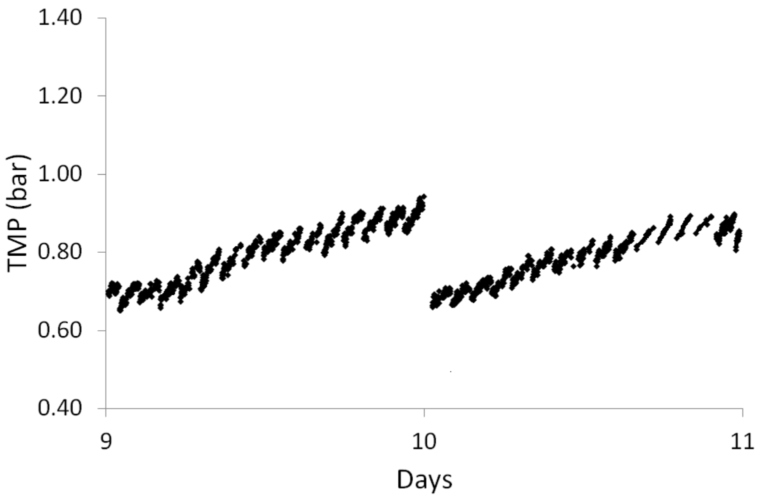

Figure 10. Effect of filtration, backwash cycles and a CEB in an ultrafiltration membrane

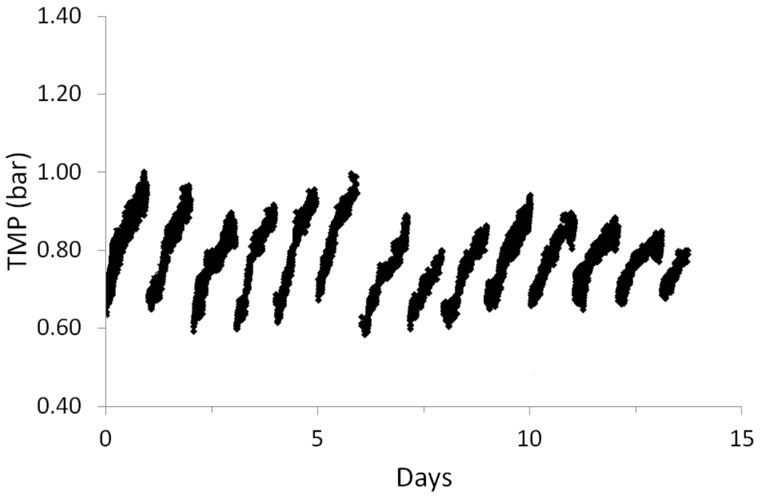

Figure 11. Long term performance of an ultrafiltration membrane

2.3 References

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3. Optimizing seawater operating protocols for pressurized ultrafiltration based on advanced cleaning research

Backwash optimization I

This chapter is part of a global research project conducted by Dow Water & Process Solutions to optimize the efficiency of ultrafiltration processes. After an initial identification of the backwash as the key opportunity to increase the efficiency of the process, a study based on its optimization is developed. Main emphasis is given to the sequence and subsequent number of steps involved in the backwash. The ultimate goal is thus to increase the availability and recovery of the process while still attaining a high cleaning effect during the backwash. This optimization is done through the realization of various experiments using DOW™ Ultrafiltration SFP-2660 outside-in polyvinylidene difluoride (PVDF) membranes following an exhaustively planned factorial design of experiments. The factors being assessed are the steps normally performed during a backwash. These are the Air Scour, the Draining, the Backwash Top with or without Air Scour, the Backwash Bottom and the Forward Flush. The responses analyzed are the calculated efficiency of the process and the experimentally obtained transmembrane pressure (TMP), which represents the fouling rate of the membrane. The results are analyzed through a formal statistical study of the analysis of the variance (ANOVA) and are validated through 25 days of stable operation. The results show that the backwash can be simplified from an original sequence of five steps to only two steps, which are the

Backwash Top with Air Scour and the Forward Flush without impairing the effectiveness of the cleanings. This leads to an increase in efficiency higher than 5%, which represents a decrease of 50% in the filtration inefficiency. This is achieved thanks to the reduction of the time invested for the cleanings and the decrease in the amount of water consumed.

3.1 Introduction

The ultrafiltration process is characterized, unlike Reverse Osmosis, by having relatively short filtration cycles given the need of higher cleaning frequency. The duration of the filtration cycle strongly depends on the type of raw water leading to a filtration cycle between 10 to 100 minutes. Between two filtration cycles a Backwash (BW) will occur to enable the cleaning of the fibers and consequently, a reduction in the transmembrane pressure (TMP) accumulated during the filtration. A second type of cleaning, which takes place with a lower frequency compared to the Backwash is the Chemically Enhanced Backwash (CEB). Often, the CEB occurs once or twice per day and is characterized by a longer duration compared to the Backwash and also by the use of chemicals. The last type of cleanings, the Cleaning in Place (CIP) occurs once every couple of months and is characterized by its longer duration (few hours typically) and higher chemical concentration used compared to a CEB.

Short term cleanings such as the backwash (BW) are carried out every 10 to 80 minutes, with a median of 30 min. The median duration of all steps in the sequence is approximately 3 min, where the backwash takes about 1 min. The backwash flux varies between 70 and 300 L/m²h (10/90% percentiles) and typically reflects double the operating flux. Occasionally chemicals such as hydrogen peroxide (H_2O_2) and Sodium Metabisulfite (SMBS) are used as backwash chemicals, but were judged as less effective than chlorine. As an example, backwash chemistry is evaluated comparing 25 mg/l H_2O_2 and 10 mg/l NaClO, and the NaClO chemistry seemed to be far more effective [1]. NaClO has recently been the most widely used and has emerged as the standard for backwash schemes with chemicals. Its typical range is 3 to 20 mg/l with a median of 10 mg/l. Occasionally, especially in outside-in modules, air scouring is used in the range of 3 to 20 Nm^3/h every 1 to 8 backwash cycles.

There are two types of Chemical Enhanced Backwash (CEB) type operations used for medium term cleanings, an oxidizing CEB, and an acidic CEB. The predominant oxidizing agent in CEB operations is NaClO at 20 to 500 mg/l (10 and 90% percentile), with a median of 150 mg/l. Lower concentrations in the 50 mg/l range are used more frequently in every 2 to 8 hours [2], while higher concentrations are applied less frequently with a range of 12 and more hours. NaOH was tried in few occasions with and without NaClO but was quickly dismissed due to its scaling nature [3]. In fact, precipitations have already been discovered with NaClO, which is also a weak base [4]. In the acid CEB: most frequently, H_2SO_4 and HCl are used, occasionally also citric acid. The frequency of the chlorine CEB is in the range of every 6 to every 92 hours (10 and 90% percentile) with a median of 24 hours. Acid CEB is carried out at a frequency of 1:1 to 1:3 compared to chlorine CEBs. The chemical dosing duration in CEB steps is typically 30 s, hence shorter than the BW duration in a normal backwash. Information about CEB flux is very scarce – and as a rule of thumb it is safe to assume the CEB flux is equivalent to the backwash flux. In order to extend the chemical exposure duration, often extended soak times are provided after the chemical dosing – these are in the range of 2 to 36 min (10 and 90% percentile) and the median is 15 min.

Medium term cleanings (which in the framework of this work are termed “Chemical Enhanced Backwash”) are the most diverse among all cleaning conditions and many different variations are described. A protocol which combined chemical dosing for only a very short time period with air bubbling has also been proposed [5]. With outside-in technology, it has also been frequently described to automatically dose chemicals to the feed, instead of the product, and recirculate [6]. Finally, the addition of chemicals to Reverse Osmosis permeate is described as well. A special backwash protocol, involving the use of heated cleaning solution, not only in the CIP, but also in the CEB is proposed as well [7] [8]. This advanced method has also been described for medium term cleanings, called "HEFM - Heated Enhanced Flux Maintenance": at the Buzzer platform and the Brownsville pilot: "this method is used daily - each MF rack is taken offline and heated chlorine solution (at about 250 – 400 mg/ l chlorine at 30-35 ºC) is automatically circulated through the MF membrane rack for about 30 minutes" [8] [9]. Some CEB type medium term cleanings may carry character of a CIP operation, e.g. involving multiple hours soak duration and higher concentration.

Clean in place operations are carried out every 21 days to every 14 months, with a median of every 1.5 months. CIP operations are often composed of two steps, one which nowadays often uses NaClO at elevated concentrations (up to 4,000 mg/ L with PVDF fibers) and optional NaOH (often pH ~12), and a second one with acid (often organic acid at very high concentrations in the low percent range). Often, multiple hours of recirculation and soak time are used. Often heating is used to enhance the effect. A wide variety of special chemicals is reported, e.g. formulated cleaners, EDTA or enzymes.

This chapter is a part of a general research project focused on maximizing the efficiency of DOW™ Ultrafiltration processes by optimizing the operating sequence, including the filtration conditions and its cleaning strategy taken into account the different backwashes, chemical enhanced backwashes and cleanings in place. Among these various processes, the backwash is identified as a key parameter that influences the overall efficiency of the process. Despite the relatively short duration of the backwash, it can occur up to 48 times per day when done every 30 minutes. This involves a large amount of time out of operation. Moreover, the backwash has a double negative effect from the point of view of the water produced because during the backwash, water is not produced and in addition previously produced water is consumed.

The impact of the backwash in the overall efficiency of the process is depicted in Figure 12, where a reduction of 50% in the number of backwashes per day leads to an increase in efficiency from 90% up to 95%. This plot is obtained using the efficiency equations described in the Introduction section. The same applies if the time needed by a backwash to clean the ultrafiltration fibers is reduced by a half.

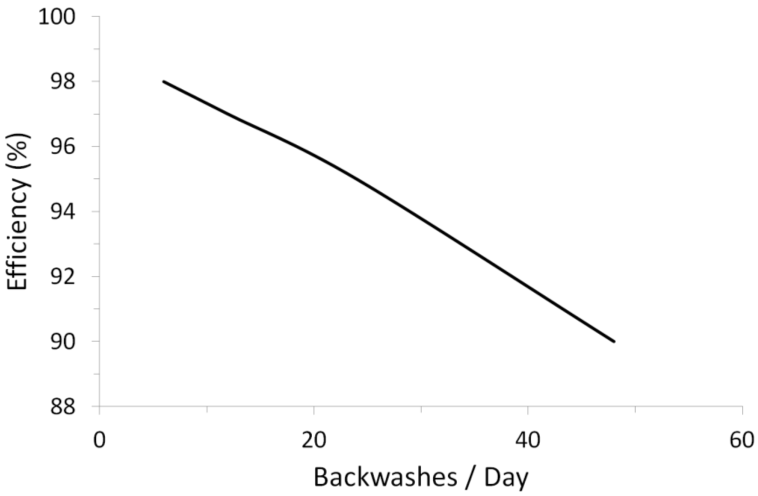

Figure 12. Importance of backwash in overall efficiency

Therefore, this chapter is focusing on reducing the time invested for the backwash sequence, while still maintaining the same cleaning effectiveness.

The steps typically included in the backwash sequence are the Air Scour, with a duration between 30 to 60 s; the Draining, with a duration between 10 to 15 s; the Backwash Top with Air Scour, with a duration between 30 to 40 s; the Backwash Bottom, with a duration between 30 to 40 s; and the Forward Flush, with a duration between 10 to 60 seconds.

This research is focused in the identification of those steps inside the backwash sequence that have a lesser contribution to the overall cleaning efficiency of the backwash. The elimination of those steps will certainly enable higher efficiencies, which ultimately can be translated into savings in operational expenses (OPEX) and capital expenses (CAPEX).

3.2 Materials and methods

3.2.1 Unit description

This research is done in the experimental containerized seawater desalination plant Dow Water & Process Solutions has in Tarragona (Spain) and is fed with Mediterranean seawater. Figure 13 shows the scheme of the plant, which consists of two independent lines both containing ultrafiltration as a pretreatment for reverse osmosis. This unit represents one of the pilot plants currently operated with various water sources in the Dow Tarragona Global Water Technological Center. The intake of the seawater supplied into this particular unit is located at the industrial harbor of the city. The pretreatment before the ultrafiltration unit includes an Amiad® Arkal disk filter of 250 µm. The ultrafiltration modules used are DOW™ UF SFP-2660 and FILMTEC™ SW30XLE-4040 are used in the reverse osmosis section.

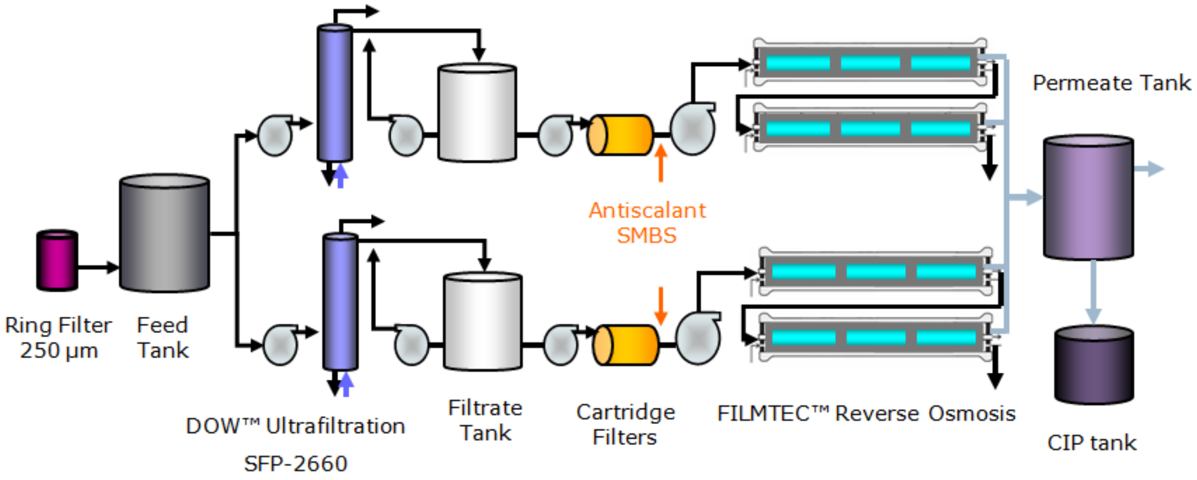

Figure 13. Ultrafiltration and seawater reverse osmosis desalination installation scheme

3.2.2 Ultrafiltration membranes

In order to validate the hypothesis of this research, only one of two parallel ultrafiltration lines is used. The membrane used is a DOW™ Ultrafiltration SFP-2660 module, with a diameter of 165 mm (6.5 inches) and a length of 1500 mm (59.1 inches) are used. This type of module uses polyvinylidene difluoride (PVDF) fibers with a pore size of 30 nm, 0.7 mm inner diameter and an outside fiber diameter of 1.3 mm and comprises a total active surface area of 33 m² (355 ft²). DOW™ Ultrafiltration modules operate following an outside-in configuration given the advantages associated with this modus operandi such as better cleanability, lower fouling trends, the benefit of using air scour and higher mechanical and chemical resistance.

3.2.3 Design of experiments

Before starting each experiment, there is a need to ensure the membranes were not fouled. Therefore, a complete backwash and chemical enhanced backwash sequence is needed at the beginning of each experiment to ensure the transmembrane pressure is reduced to the initial levels to establish a baseline. This complete sequence includes an Air Scour of 30 s, a Draining of 10 s, a Backwash Top combined with an Air Scour of 20 s, a Backwash Bottom of 20 s and a Forward Flush of 15 s. After this initial backwash, a CEB that does 350 mg/l of NaClO through a Backwash Top and has a Soaking time of 6 minutes is needed. After this sequence, another complete backwash is needed to remove residual chlorine.

Each experiment consists of 5 filtration cycles of 30 minutes each. Approximately, each experiment lasts between 2:30 h and 3:00 h. The filtration flux of the ultrafiltration module is set up to 90 l/m^{2}h (3 m^3/h). Between each filtration cycle, a backwash at each specific given condition is done. The operating conditions of each experiment and their set points are summarized in Table 3 and are kept constant for the whole research. In order to properly calculate the efficiency, it must be taken into account the automated valves need 2 seconds time to change their position.

To make sure any change in the feed water quality does not influence the response variable, the feed turbidity is monitored with a Hach Lange 1720E Turbidimeter Low Range. Filtrate turbidity is also monitored with a Hach Lange FilterTrakTM 660sc Laser Nephelometer, which is able to measure low ranges of turbidity values. The turbidity measurements are compared with samples analyzed in the Tarragona Dow

Water & Process Solutions Analytical Laboratory. The temperature is also controlled in order to assess any possible influence in the response variable.

Table 3. Backwash steps conditions

Step	Order	Time (s)	Flux (l/ m^{2}h)	Flow (m^3/ h)	Flow Air (m^3/ h)
Air Scour (AS)	1	30	-	-	20
Draining (D)	2	10	-	-	-
Backwash Top (BWT)	3	20	135	4.5	20
Backwash Bottom (BWB)	4	20	135	4.5	-
Forward Flush (FF)	5	15	90	3	-

3.2.4 Variable coding

Each experiment has its own unique backwash cleaning sequence. To determine the contribution of each cleaning step within the backwash sequence to the final TMP reduction and its relationship to the overall efficiency of the ultrafiltration process, a Yes/ No strategy is proposed as part of the design of experiments (DOE). Therefore, each factor is coded according to Table 4.

Table 4. Design of experiments coding

Step	Coding	Meaning
Air Scour (AS/ D)	0	No Air Scour
	1	Air Scour (30 s)
	2	Air Scour (30 s) + Draining (10 s)
Backwash Top (BWT)	0	No Backwash Top
	1	Backwash Top without Air Scour (20 s)
	2	Backwash with Air Scour (20 s)
Backwash Bottom (BWB)	0	No Backwash Bottom
	1	Backwash Bottom (20 s)
Forward Flush (FF)	0	No Forward Flush
	1	Forward Flush (15 s)

The variables assessed in the DOE are the different backwash steps. Thus, as Table 4 shows, these factors are the Air Scour with and without a Draining afterwards, which is coded as 0, 1, 2; the Backwash Top with and without Air Scour, which is coded as 0, 1, 2; the Backwash Bottom, which is coded as 0, 1; and the Forward Flush which is coded as 0, 1. It is important to notice that all the variables are coded as discrete categorical variables.

Once these factors are coded, different experiments are statistically designed and executed according to the coding described in Table 4. The full list of experiments is summarized in Table 5. The experiment number reflects the order in which the experiment is done as randomization is applied in order to eliminate the influence of secondary factors and time dependent events. Moreover, three center points (1 1 1 1) are done in order to assess the accuracy and the precision of the results obtained and to keep the DOE balanced.

To illustrate this coding some examples are given. The experiment number 1 (0 0 0 0) consists of no backwash cleanings between filtration cycles. Another example is experiment number 15 (0 0 1 1) where each backwash cleaning consist only of a Backwash Bottom and a Forward Flush. One last example is experiment number 17 (2 2 1 1), which reflects the current state of the art where all the possible cleaning steps are done during the backwash sequence. These steps are the Air Scour, the Draining, the Backwash Top with an Air Scour, the Backwash Bottom and the Forward Flush.

Table 5. Design of Experiments planned

Experiment Number	AS/ D	BWT	BWB	FF
1	0	0	0	0
15	0	0	1	1
4	0	1	0	1
18	0	1	1	1
24	0	2	0	0
25	0	2	0	0
22	0	2	0	1
12	0	2	1	0
28	1	0	0	1
9	1	0	0	1
23	1	0	1	0
13	1	0	1	0
21	1	1	0	0
2	1	1	0	0
16	1	1	1	1
5	1	1	1	1
10	1	1	1	1
19	1	2	1	1
7	2	0	0	1
26	2	0	0	1
20	2	0	1	1
11	2	1	0	1
14	2	1	1	0
3	2	2	0	0
17	2	2	1	1

3.2.5 TMP normalization

TMP is normalized according to the equations described in Section 2.2.2 [10].

3.2.6 Efficiency calculation

Efficiency is calculated according to the equations described in Section 2.2.3.

3.2.7 Variance comparison

The results obtained from the design of experiments are statistically evaluated through the different hypotheses testing using the analysis of variance (ANOVA) methodology. Therefore, each categorical variable representing the status of each different backwash step is tested for statistical significance in each hypothesis test against the defined confidence level set to 0.95 and the significance level set to 0.05. This confidence level indicates a 95% of probability of being right with the conclusions extracted. This hypotheses contrast is performed using JMP® Pro 9.0.3 (SAS Institute Inc.) software.

The variance measures how far the data is spread out, thus measuring the average distance between each set of data points and their mean value, equal to the sum of the squares of the deviation from the mean value. Therefore, before checking the statistical significance of each backwash step, a contrast of hypotheses against a significance level of 0.05 is done in order to check if the variances are the same for each categorical variable. Table 6 summarizes the different null and alternate hypothesis to be validated according to the Brown-Forsythe Test [11]. If the variances are the same, a conventional ANOVA test will be done in order to compare means, while if they are not the same, a Welch ANOVA test would be needed.

Table 6. Hypothesis statements to contrast variances

Backwash Step	Hypothesis type	Hypothesis statement
Air Scour (AS/ D)	H_0	The variance of each level of the AS/ D variable remains constant
	H_1	The variance of each level of the AS/ D variable is different
Backwash Top (BWT)	H_0	The variance of each level of the BWT variable remains constant
	H_1	The variance of each level of the BWT variable is different
Backwash Bottom (BWB)	H_0	The variance of each level of the BWB variable remains constant
	H_1	The variance of each level of the BWB variable is different
Forward Flush (FF)	H_0	The variance of each level of the FF variable remains constant
	H_1	The variance of each level of the FF variable is different

3.2.8 Mean comparison

The null (H_0) and alternate (H_1) hypotheses statements established for their evaluation are included in Table 7, which assess the contribution of each backwash step to the TMP reduction. A conventional analysis of variance is done in order to do a means comparison against a significance level of 0.05. To illustrate these tests, the first null hypothesis indicates the first step, which is the Air Scour with or without Draining does not statistically influence in cleaning the membranes. On the contrary, the alternate hypothesis indicates that the Air Scour with or without Draining does statistically influence in cleaning the membranes

Table 7. Hypothesis statements to contrast means

Backwash Step	Hypothesis	Hypothesis statement
Air Scour (AS/D)	H_0	The AS/D step does not influence significantly the fouling decrease
	H_1	The AS/D step does influence significantly the fouling decrease
Backwash Top (BWT)	H_0	The BWT step does not influence significantly the fouling decrease
	H_1	The BWT step does influence significantly the fouling decrease
Backwash Bottom (BWB)	H_0	The BWB step does not influence significantly the fouling decrease
	H_1	The BWB step does influence significantly the fouling decrease
Forward Flush (FF)	H_0	The FF step does not influence significantly the fouling decrease
	H_1	The FF step does influence significantly the fouling decrease

3.2.9 Validation

Once all the hypotheses are contrasted against their confidence interval to assess their statistical significance, an optimum is achieved which reflects the new ideal operating conditions. The last step before implementing the new optimum as a standard is to validate this optimum in a real installation. For this purpose, two ultrafiltration lines are operated in parallel. The first one operates with the standard conditions and the second one operates with the optimum conditions.

This validation is done by using brand new DOW™ Ultrafiltration SFP-2660 membranes operating at fluxes more similar to real operating conditions, this means operating at a constant flux of 70 l/ m^{2}h, with a backwash every 30 min, a CEB every 24 hours consisting of 6 minutes of soaking with 350 ppm of NaClO.

Before doing this validation, a first 7 days period operating both lines at the same baseline conditions depicted in Table 8 is performed in order to assess if there are differences between both brand new modules or if there are differences between both ultrafiltration lines.

Table 8. Baseline conditions

Parameter	AS	D	BWT+AS	BWB	FF
Time (s)	30	30	30	30	30
Flux (l/ m^{2}h)	-	-	80	80	80
Flow air (m^3/ h)	12	-	12	-	-

After assessing there are no differences in both ultrafiltration modules and both lines, a second 25 days period is performed. Therefore, the first line operates at the baseline conditions depicted in Table 8, while the second line operates at the optimum conditions depicted in Table 9. The optimum is validated if during this period both lines do not show major differences and show the same sustainable operating trend.

Table 9. Optimum conditions

Parameter	AS	D	BWT+AS	BWB	FF
Time (s)	-	-	30	-	30
Flux (l/ m^{2}h)	-	-	80	-	80
Flow air (m^3/ h)	-	-	12	-	-

3.3 Results and discussion

3.3.1 TMP increase and efficiency

To illustrate the assessment and calculation of the experimentally obtained TMP increase, Figure 14 depicts the TMP evolution over time of two experiments. The first experiment (0 0 0 0) where no cleanings are done show a straight line representing the constant TMP increase, while the second experiment (1 1 0 0) where only an Air Scour and a Backwash Top are done show a straight line that every 30 minutes is being interrupted by a cleaning which reduces the TMP when performed.

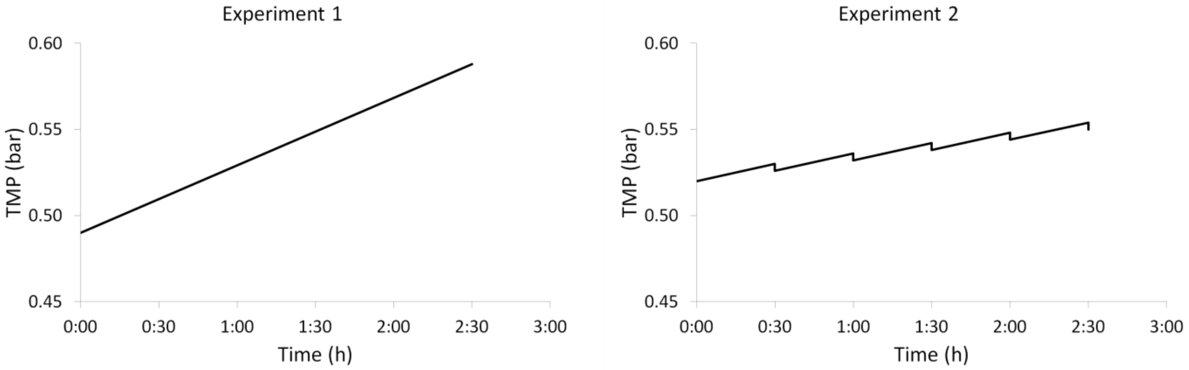

Figure 14. Evolution of normalized TMP with and without Backwashes

All these results are summarized in Table 10, where the results are stored putting the experiments showing a higher efficiency first. The ultimate goal is to minimize the TMP increase while maximizing the efficiency.

Table 10. Efficiency and TMP increase of each experiment. Results ordered by Efficiency

Exp	AS/ D	BWT	BWB	FF	Efficiency (%)	TMP increase (%)
1	0	0	0	0	100.00	20.72
24	0	2	0	0	97.04	8.03
25	0	2	0	0	97.04	9.68
28	1	0	0	1	96.04	7.02
9	1	0	0	1	96.04	7.73
7	2	0	0	1	95.53	5.07
26	2	0	0	1	95.53	5.67
21	1	1	0	0	95.37	3.91
2	1	1	0	0	95.37	4.65
23	1	0	1	0	95.37	13.50
13	1	0	1	0	95.37	24.15
3	2	2	0	0	94.86	4.49
22	0	2	0	1	94.85	2.78
15	0	0	1	1	94.85	7.48
4	0	1	0	1	94.85	13.01
12	0	2	1	0	94.16	10.63
20	2	0	1	1	92.74	2.20
11	2	1	0	1	92.74	7.32
14	2	1	1	0	92.06	6.44
18	0	1	1	1	92.05	1.89
19	1	2	1	1	90.50	1.57
16	1	1	1	1	90.50	6.76
5	1	1	1	1	90.50	6.83
10	1	1	1	1	90.50	10.04
17	2	2	1	1	90.02	2.31

These points are plotted in Figure 15 where the TMP increase is a function of the efficiency. Therefore, the optimum point is the one allocated at the bottom right part of the plot and seeks a compromise between the starting point, represented by experiment 17 (2 2 1 1) where all the backwash steps are performed and has the lowest TMP increase but lowest efficiency, and the most unfavorable point, represented by experiment 1 (0 0 0 0), where no cleanings are done and hast the highest efficiency but the highest TMP increase.

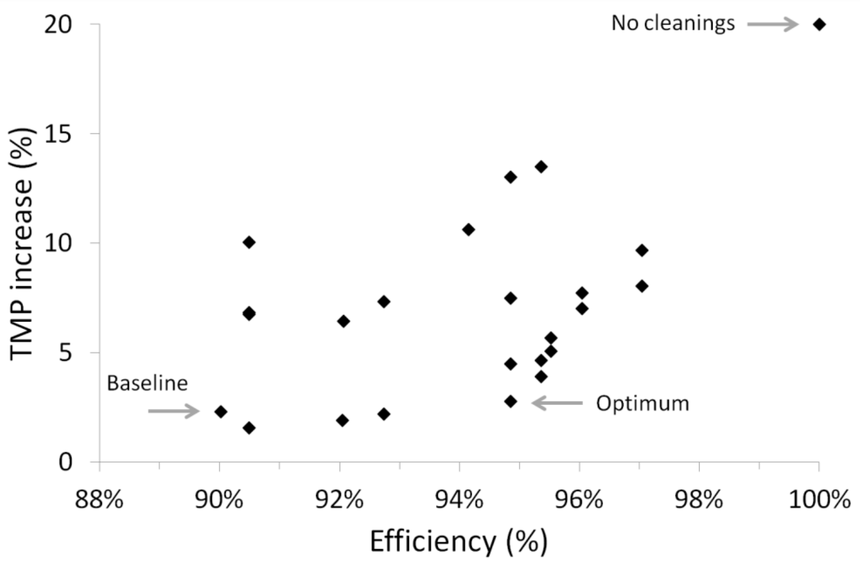

Figure 15. TMP increase versus efficiency of each experiment

Figure 15 suggest experiment 22 (0 2 0 1), where a backwash consist only the two steps sequence of a Backwash Top with an Air Scour and a Forward Flush as the optimum experiment which maximizes the efficiency while keeps the TMP increase at the same level as the starting point. Table 11 summarize the efficiency and TMP increase achieved for the starting point, the no cleanings point and the optimal point, which shows a TMP increase from 2.31% to 2.78% and efficiency increase from 90.02% to 94.85%.

Table 11. Comparison between the starting conditions and the optimal conditions

Experiment	AS/ D	BWT	BWB	FF	Efficiency (%)	TMP increase (%)	Description
1	0	0	0	0	100.00	20.72	No Cleanings Point
22	0	2	0	1	94.85	2.78	Optimal Point
17	2	2	1	1	90.02	2.31	Starting Point

3.3.2 Variance comparison

To validate the optimum backwash sequence identified, a formal statistical hypotheses contrast analysis is done. The null hypothesis states the specific backwash step does not statistically contribute the TMP reduction, while the alternate hypothesis states the specific backwash step does statistically contribute the TMP reduction. This allows to determine which backwash steps are statistical significant and therefore, contribute the less to the TMP increase.

Table 12 summarizes the results obtained from each hypothesis contrast. As the p-values obtained are bigger than the significance level of 0.05, the null hypothesis cannot be rejected, which means there are no differences between variances.

Table 12. Results of variances comparison

Backwash Step	P-value	Hypothesis validated	
Air Scour (AS/ D)	0.3390	H_0	The variance of each level of the AS/ D discrete variable remains constant
Backwash Top (BWT)	0.3158	H_0	The variance of each level of the BWT discrete variable remains constant
Backwash Bottom (BWB)	0.4794	H_0	The variance of each level of the BWB discrete variable remains constant
Forward Flush (FF)	0.0791	H_0	The variance of each level of the FF discrete variable remains constant

3.3.3 Mean comparison

Table 13 summarizes the results obtained from the hypotheses comparison. It can be observed that the Backwash Bottom step is not statistically significant at all. The Air Scour, the Draining and the Backwash Top step are also not statistically significant, although the Backwash Top step shows a slightly statistical significance. Finally, the Forward Flush step is statistically significant. These hypotheses contrast can be visually assessed in Figure 16.

Table 13. Results of means comparison

Backwash Step	P-value	Hypothesis validated	
Air Scour (AS/ D)	0.2416	H_0	The AS/ D step does not influence significantly the fouling decrease
Backwash Top (BWT)	0.1852	H_0	The BWT step does not influence significantly the fouling decrease
Backwash Bottom (BWB)	0.9593	H_0	The BWB step does not influence significantly the fouling decrease
Forward Flush (FF)	0.0299	H_1	The FF step does influence significantly the fouling decrease

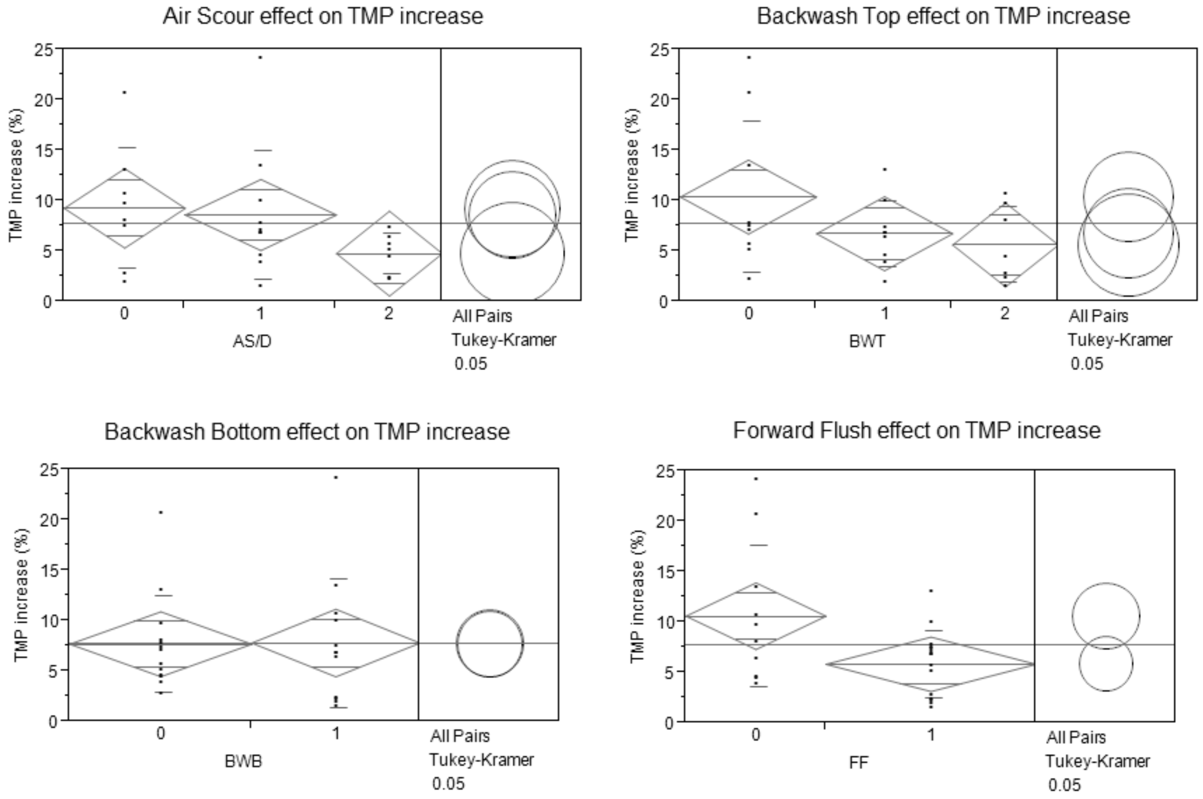

Figure 16. Backwash steps effect on TMP increase. a) Air Scour effect, b) Backwash Top effect, c) Backwash Bottom effect, d) Forward Flush effect

3.3.4 Model fit

In order to determine if the Air Scour and the Backwash Top steps have some statistical influence in reducing the TMP, a model is constructed. This model only takes into account the primary factors as the data is obtained from a fractional design of experiments. The model is based on a first grade polynomial fit as it follows the Taylor series approach that states that for a given range, any complex equation can be fit within an "n" grade polynomial.

Figure 17 shows the experimentally obtained TMP increases versus the model predicted TMP increases of each experiment and it presents a determination coefficient (r^2) of 0.5094, an adjusted coefficient (r^2 adjusted) of 0.3459. The model is statistically significant as the p-value obtained is 0.0284 and there is no statistically lack of fit as the p-value obtained is 0.0909.

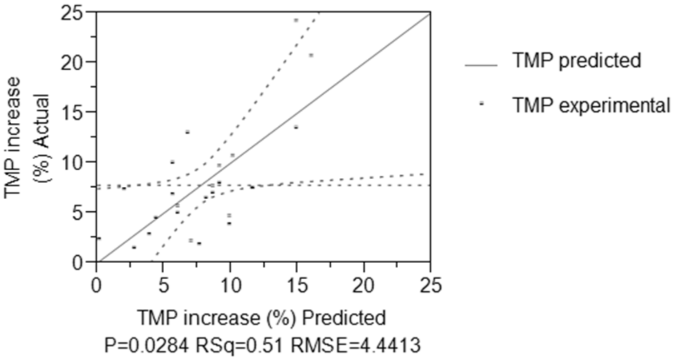

Figure 17. Experimentally obtained TMP increases versus predicted TMP increases

Table 14 summarizes the backwash steps that are statistically significant according to the model prediction. Therefore, it can be assessed the Air Scour and the Backwash Bottom steps are not statistically significant, while the Backwash Top and the Forward Flush steps are statistically significant since the p-value is smaller than the confidence level of 0.05.

Table 14. Main effects analysis

Backwash Step	P-value	Hypothesis validated	
Air Scour (AS/D)	0.1619	H_0	The AS/D step does not influence significantly the fouling decrease
Backwash Top (BWT)	0.0288	H_0	The BWT step does influence significantly the fouling decrease
Backwash Bottom (BWB)	0.6082	H_0	The BWB step does not influence significantly the fouling decrease
Forward Flush (FF)	0.0129	H_1	The FF step does influence significantly the fouling decrease

Table 15 summarizes the statistically significance of each value each backwash step can have. Therefore, it can be seen not doing the Backwash Top (BWT[0]) step is statistically negatively significant while doing it with an Air Scour (BWT[2]) is statistically positively significant. Moreover, not doing the Forward Flush (FF[0]) is statistically negatively significant while doing it (FF[1]) is statistically positively significant since the p-value is smaller than the confidence value of 0.05.

Table 15. Backwash steps statistically significance

Term	Coefficient	P-value	Result
Intercept	7.92694	<.0001	Statistically significant
AS/D[0]	2.273701	0.1124	Not statistically significant
AS/D[1]	0.194669	0.8838	Not statistically significant
AS/D[2]	-2.46837	0.0834	Not statistically significant
BWT[0]	3.62437	0.0106	Statistically significant
BWT[1]	-0.41149	0.7546	Not statistically significant
BWT[2]	-3.21289	0.0405	Statistically significant
BWB[0]	-0.47923	0.6082	Not statistically significant
BWB[1]	0.479229	0.6082	Not statistically significant
FF[0]	2.61731	0.0129	Statistically Significant
FF[1]	-2.61731	0.0129	Statistically significant

3.3.5 Model boundaries

To determine when these conclusions extracted are valid, the model boundaries are determined. Therefore, a hypotheses contrast against a significance level of 0.05 is made in order to determine if the average feed turbidity, the average feed temperature and the feed pressure statistically influences the TMP increase. Table 16 shows the fittings of these three variables. From the evaluation of the determination coefficients and the analyses of variance it can be seen the three models fit poorly and they are not statistically significant. Therefore, the conclusions extracted from this research are valid at least for seawater with a feed turbidity between 0 and 3 NTU, for a temperature ranging from 20 up to 30 ºC and for a feed pressure ranging from 0.6 to 1.0 bar. Figure 18 shows the different plots for the TMP increase versus the average turbidity, the average temperature and feed pressure of each experiment with their correlations.

Table 16. Fittings of the average turbidity, average temperature and initial feed pressure

Variable	Abbreviation	R^2	P-value	Result
Turbidity (NTU)	TB	0.000544	0.9119	Not statistically significant
Temperature (ºC)	T	0.021228	0.4871	Not statistically significant
Pressure feed (bar)	P0	0.045779	0.3044	Not statistically significant

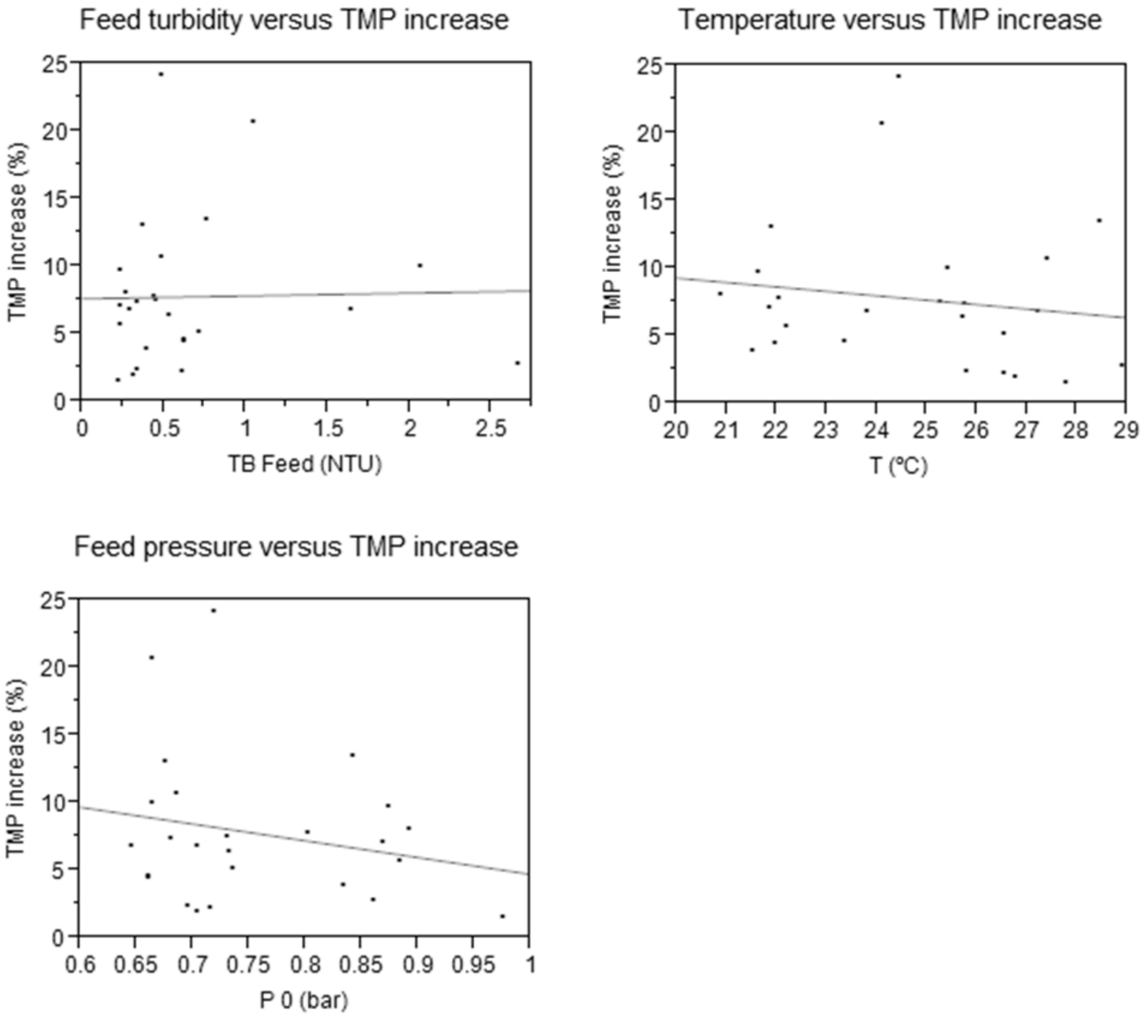

Figure 18. Effect of feed turbidity (top left), temperature (top right) and feed pressure (bottom) on TMP increase

3.3.6 Validation

Figure 19 shows the first operating period where both lines run at the exact same operating conditions with brand new modules. From this graph, it can be seen there are no major differences between both modules and both lines, as they show the same fouling trend and the same stable operation.

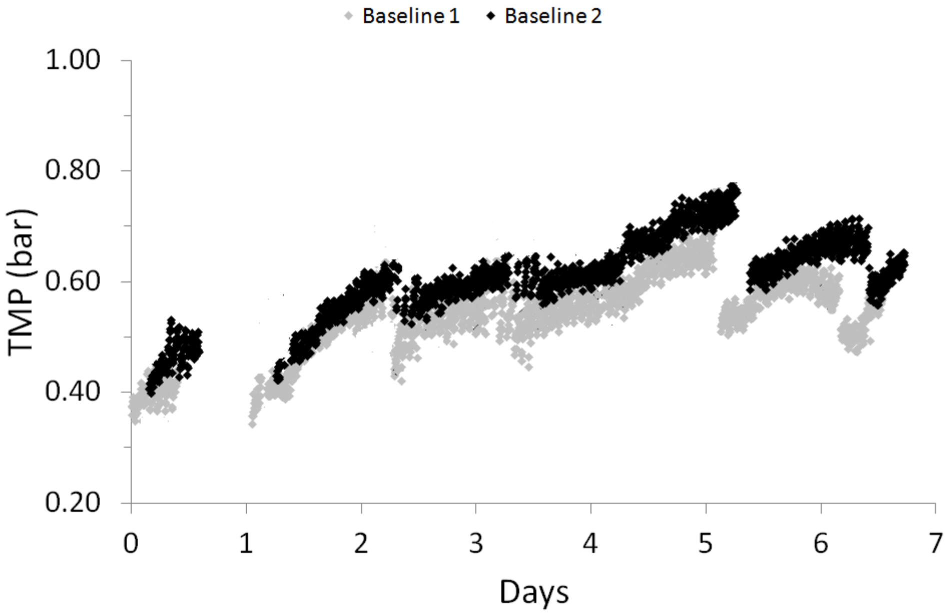

Figure 19. Baseline conditions in both ultrafiltration lines

Figure 20 shows the baseline conditions maintained during the first seven days of operation against the new optimum conditions extracted from the DOE experiments. From this plot, it can be seen that both lines show the same fouling trend for these 25 days of operation. Therefore, it can be concluded the optimum conditions are validated.

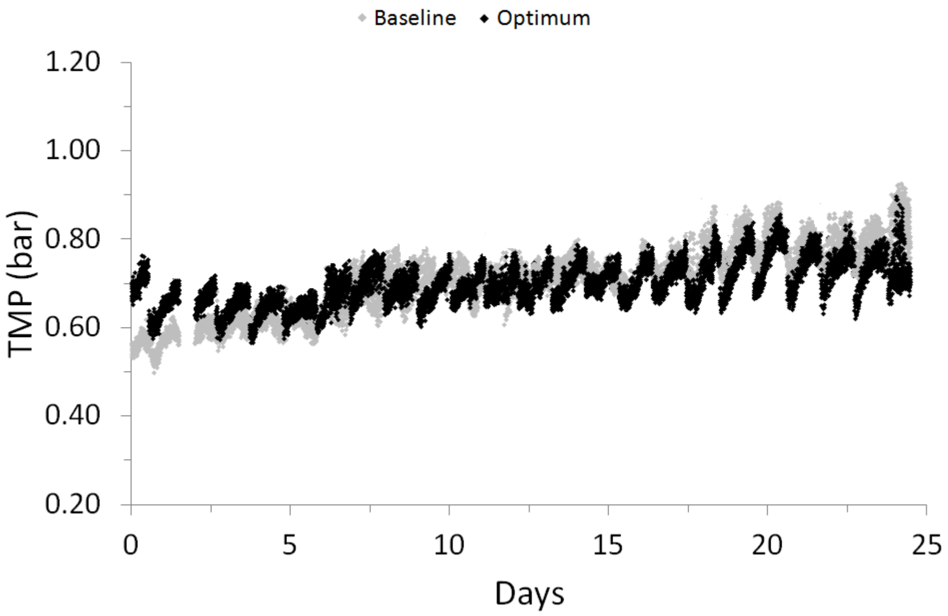

Figure 20. Baseline conditions against optimum conditions

3.4 Conclusions

The backwash cleaning process is simplified from 5 to 2 steps showing a reduction of 60% in the number of steps and this improvement is validated through statistics using different hypotheses statements contrast. This is achieved by eliminating the redundant steps involved, the time the valves take to change their states, the time needed for the backwash pump to ramp up and down to their set point in each step. These conclusions are proven statistically valid for seawater with a turbidity ranging from 0 to 3 NTU, from a temperature ranging from 20 to 30 ºC and from a feed pressure ranging from 0.6 to 1.0 bar and are validated through 25 days of stable operation.

In the past, DOW™ Ultrafiltration membranes were used in Qingdao 2009 with an efficiency of 80% as some other commercially available ultrafiltration systems show nowadays [12]. After the first improvement phase done in Barcelona, the efficiency of DOW™ Ultrafiltration was increased up to 90% [12]. Nowadays, and thanks to this research, DOW™ Ultrafiltration technology has experienced an efficiency increase up to 95%. This means an increase of efficiency of 20% and a decrease in inefficiency of 75% to some market available solutions.

A better understanding of the ultrafiltration process is also achieved as some duplicities are identified. Therefore, the aeration effect done by the Air Scour step is already included in the Backwash Top with Air Scour step. The function of the Draining step is to empty the module which contains dirty water coming out from the cleaning of the previous step. However, the Forward Flush step already achieves this effect because it fills the module with fresh water that displaces dirty water and it does in addition a shearing effect above the fibers that prevents the dirty water to adhere to the fibers while the module is being emptying. The function of the Backwash Bottom step is to do a backwash using the already filtrated water do unblock the fiber blocks. However, the Backwash Top with Air Scour steps already achieves this effect as it is not deemed important if the dirty water coming out from the fibers goes out from the module by the top concentrate valve or the bottom feed valve. Figure 21 describes this logic using a path diagram and following a Lean Six Sigma waste reduction approach [13].

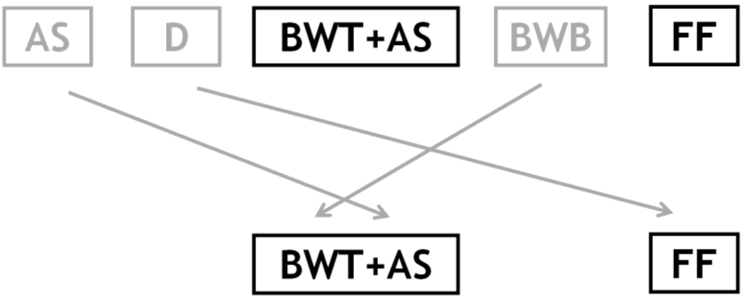

Figure 21. Lean Six Sigma waste reduction approach used to understand the improvement process

3.5 Acknowledgments

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4. Ultrafiltration advanced cleaning research and modeling applied to seawater

Backwash optimization II

The well documented technical advantages of Pressurized Ultrafiltration (P-UF), compared to alternative conventional pretreatments, have positioned P-UF as the preferred, most efficient technology in a wide variety of water treatment applications. Continuing advancements in hollow fiber membrane performance, module design, and operating protocols furthers the differentiated cost effectiveness of P-UF. In this chapter, special focus is given to the optimization of the various processes included in the operation of any Ultrafiltration system, in order to attain the maximum efficiency and ultimately the lowest cost of water. A seawater desalination installation with a DOW™ Ultrafiltration system as pretreatment has been used first to optimize its efficiency and secondly to develop a model to enable the prediction of Trans-membrane pressure (TMP) increase with time depending on the cleaning strategy followed. The results of the modeling suggest that the lowest cost of water is achieved through operational schemes based on low frequency of Clean in Place (CIP) and Backwash. The results of this work lead to increases in efficiency of the ultrafiltration process from 88% to 96%, which results in a reduction in the cost of water of 5%.

4.1 Introduction

A major difference between Reverse Osmosis and Ultrafiltration, a part from the different filtration mechanism which dominates each one of the processes (solution-diffusion vs size exclusion filtration) is the duration of the filtration cycle. More specifically, Reverse Osmosis units can be operated continuously for months and are typically stopped for an off-line cleaning (CIP, Clean-in-Place) when the normalized permeate flow loss accounts for 10% to 15% of the initial flow or a higher than expected differential pressure and/or normalized salt passage is observed. On the other hand, an Ultrafiltration unit has typically filtration cycles between 15 to 90 minutes depending on the raw water quality and process design. This different operational philosophy is mainly related to the fact that Ultrafiltration deals with raw water or water which has been slightly pre-treated with a strainer or disc filter. The water treated by a Reverse Osmosis installation has however been previously pretreated with a membrane system (Ultrafiltration or Microfiltration) or with a conventional pretreatment (such as media sand filtration).

In addition to CIP type of cleanings, which are done in both technologies (Ultrafiltration and Reverse Osmosis) in Ultrafiltration processes, Backwash (BW) and Chemical Enhanced Backwash (CEB) are also part of the cleaning strategy.

Short term cleanings, often simply called backwash but also backpulse or Simultaneous Air Scrub Reverse Flush are named by the key element in the sequence. They usually occur every 15 to 90 minutes, with a total protocol duration of 1 to 5 min. Backwash cleanings use an automatic protocol of multiple steps which can vary in terms of order, duration, hydrodynamics and chemistry, typically triggered by time, and sometimes by increases in Transmembrane Pressure (TMP). The Backwash often includes the following steps: draining, air scouring, backwash (reverse flow) and flushing. Occasionally small amounts (2-30 mg/l) of chemicals (especially chlorine) are dosed in the regular backwash. The use H_2O_2 (about 25 mg/l) and NaClO (about 10 mg/l) have been studied in the past concluding that chlorine was far more effective [1].

Medium term cleanings occur in the range of multiple hours to days (typically in the range of 4 hours to 2 days) and are applied with an increased concentration of chemicals (especially chlorine, typically 30-500 mg/ l). Lower concentrations, i.e., in the 50 mg/ l range, are used when cleanings take place more frequently (approx. every 2 to 8 hours) [2], while higher concentrations are applied less frequently with a range of 12 and more hours. This type of cleaning, which is carried out for extended time period of 10 to 30 minutes has been termed “Chemical Enhanced Backwash”, “Maintenance Clean” or “(Heated) Enhanced Flux Maintenance”. The main differences between a Backwash (BW) and a Chemical Enhanced Backwash (CEB) are on one hand the use of higher concentrations of chemicals in the CEB and secondly, the soaking time, which is a step that takes place only in the CEB to enable sufficient contact time between the chemicals and the fibers for better cleaning efficiencies. CEB can be classified into acidic or basic CEB depending on the chemical used. Experiences with NaOH (with or without NaClO) can be found in the literature, but should be used carefully, especially in seawater applications, due to its scaling nature [3]. In fact, precipitations have already been discovered with NaClO, which is also a weak base [4]. For acidic CEB, typically H_2SO_4 and HCl are used, and occasionally, also citric acid.

CEB are the most diverse among all cleaning conditions and many different variations have been described. A protocol which combined chemical dose for only a very short time period with air scour has also been proposed [5]. With outside-in technology, it has also been frequently described to automatically dose chemicals to the feed, instead of the product, and re-circulate the solution [6]. A special backwash protocol, involving the use of heated cleaning solution, not only in the CIP, but already in the CEB has also been proposed [7] [8]. This advanced method has also been described for medium term cleanings, called “HEFM - Heated Enhanced Flux Maintenance”: at the Buzzer platform and the Brownsville pilot: “this method is used daily - each MF (Microfiltration) rack is taken offline and heated chlorine solution (at about 250 – 400 mg/ l chlorine at 30-35 ºC) is automatically circulated through the MF membrane rack for about 30 minutes” [8] [9]. Some CEB type medium term cleanings may carry character of a CIP operation, e.g. involving multiple hours soak duration and higher concentration.

CIP or long term cleanings typically occur in the range of several to many (3-12) months and involve very intense cleaning sequences with high chemical concentrations, high temperature and use of Reverse Osmosis permeate (if available) to prepare the cleaning solution. It is important to emphasize that Backwash and Chemical Enhance Backwash typically use Ultrafiltration filtrated water to perform the cleaning.

The discontinuity associated with the Ultrafiltration process offers a wide variety of possibilities to improve the overall process in order to optimize the recovery, availability, efficiency and chemical consumption. The optimization of an Ultrafiltration system can become even more challenging and interesting if all the steps included in each cleaning sequence (air scour, backwash top, backwash bottom, forward flush, chemical enhanced backwash, clean in place) and all the potential factors to be optimized (flux, chemical concentration, duration and frequency) are taking into consideration.

In this chapter, an optimization of the cleaning strategy of an ultrafiltration system treating seawater is described based on real operating data and on a model which enables the prediction of the fouling trends and thus the need for cleanings. The ultimate goal is certainly to achieve the minimum cost of water through optimized operating sequences.

4.2 Materials and methods

This optimization work is on one hand based on modeling and simulation of various scenarios with a further evaluation of the operating sequence in the overall sustainability of the process (in terms of fouling increase with time). On the other hand, the operating sequences, mainly cleaning strategies, are tested in two real ultrafiltration systems, both operated with the same feed seawater. The units used for this experimentation together with the feed water description are described in this chapter.

4.2.1 Feed water characterization

The two desalination systems, consisting of Ultrafiltration and Reverse Osmosis, used for this work are located and operated in Tarragona (Spain), within the facilities of Dow Water & Process Solutions. The feed water comes from the Tarragona Industrial Harbor (Mediterranean Sea), where an intake supplies seawater to various industries or companies of the area, including Dow Chemical Ibérica. The intake has a capacity of 10,000 m^3/h but the flow used by the units is limited to 90 m^3/h of capacity. Out of these 90 m^3/h of seawater, Unit A consumes approximately 5 m^3/h whereas the second installation, Unit B, can treat up to 80 m^3/h depending on the operating regime selected (Figure 22).

Figure 22. Aerial view and location Seawater desalination facilities

The location of the intake, inside the harbor of Tarragona, makes the feed water quality arriving in the units rather fluctuating. On one side, leakages of oil and petrol from ships and the various industrial activities can occur and on the other hand, there is a small river, called Francolí, ending in the harbor, which only brings water during heavy rainy days. Sudden increases in the total suspended solids content have been monitored in the feed water from the Francolí River in the days following rain events.

Historical values of TOC (Total Organic Carbon) and TSS (Total Suspended Solids) of the feed water indicate that most of the time the TOC is below 5 mg/l while some measurements between 5 and 10 mg/l have been reported as well. 100% of the water analyzed during second half of 2011 and first month of 2012 indicate TOC values below 5 mg/l. Regarding measurements of Suspended Solids, the historical data shows an important fluctuation or variability, being the lowest values close to 0 and the highest close to 50 mg/l. More recent data shows TSS content below 3 mg/l (January-February 2012) but peaks up to 20 mg/l during march 2012 as a result of the heavy rains which occurred in the region at that time.

Regarding turbidity measurements, on-line turbidity meters is Hach Lange 1720E Turbidity meter Low Range and Hach Lange FilterTrakTM 660sc Laser Nephelometer are used to monitor feed and filtrate quality respectively. Measurements of the feedwater indicate that turbidity is below 3 NTU 95% of the time and below 15 NTU 100% of the time.

4.2.2 Installations overview

An installation consisting of an Ultrafiltration and a Reverse Osmosis system containing two parallel and independent lines have been used for this work. The unit consists of a pretreatment of an Amiad® self-cleaning filter and two identical UF+RO lines, each one composed by: Ultrafiltration, filtrate tank, cartridge filter and Reverse Osmosis with six 4-inch FILMTEC™ Reverse Osmosis elements in series. The unit also has a CIP system which can be used either for the Ultrafiltration or for the Reverse Osmosis. Figure 23 shows a scheme of the installation. Further detailed information regarding the pilot unit itself can be found in existing literature [11].

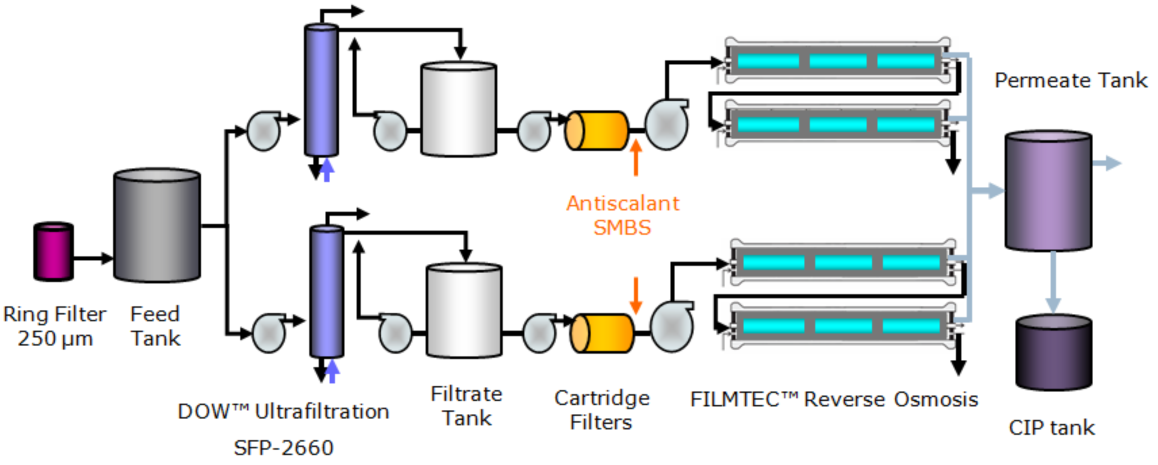

Figure 23. Installation overview

4.3 Results and discussion

In this section, the different operating sequences and cleaning protocols suggested and tested in order to minimize the cost of water are described and discussed. Operational data indicating the fouling trends corresponding to each set of operating conditions will be shown in terms of TMP increase. On the other hand, the economical evaluation of each operating strategy will be evaluated by directly calculating the cost of water in some cases or by the estimation of those parameters directly impacting the cost of water, namely the chemicals consumption and the availability/ recovery/ efficiency of the system. The first parameter to be considered is the availability, which gives an idea of the time invested in the production of water with respect to the overall time (i.e., filtration time + time invested in cleanings). The second important parameter is the recovery, which gives an estimation of the water produced versus the feed water consumed. The efficiency is described as the multiplication of the availability and the recovery and gives an idea of how efficient the process is taking into consideration time and production. Finally, in order to be able to make a fair comparison between various operating sequences with different cleaning protocols, the "continuous chemical concentration" concept is used. This parameter is defined as the amount (in weight units) of chemicals used per unit of volume (feed water). This parameter could be used as well using flow of feed water instead of volume. These equations are described in Section 2.2.3

The baseline operating conditions used for this work are 70 L/m^{2}h of operating flux and filtration cycles of 30 minutes. The backwash sequence consists of an initial air scour (30s) followed by a draining (10s), then 10 seconds of backwash top (130 L/m^{2}h) with air scour and 15 second of backwash bottom (130 L/m^{2}h) and finally a forward flush with a duration of 15 seconds. Chemical Enhanced Backwash takes place once per day and a concentration of 350 mg/l of NaClO is used. The sequence of the CEB consists of an initial Air scour and backwash as previously described, then a backwash with chemical dosing for 30 seconds, then a soaking period of 15 minutes and finally another backwash to ensure all the chemicals are removed from the unit before filtration is started again. These operating conditions, considered as baseline case are summarized in Table 17. Time consumed by the valves to change position as well as time consumed by the pumps to achieve the set points are not included in the times mentioned above but they are definitely considered in the calculations which are shown later in this chapter.

Table 17. Operating conditions baseline scenario

Parameter	Conditions
Operating Flux	70 l/m^{2}h
Filtration cycles	30 min
BW sequence	Air scour (30s) + Draining (10s) + Backwash top with air scour (10 s) + Backwash bottom (15 s) + Forward flush (15 s)
BW Flux	130 l/m^{2}h
CEB frequency	24 h
CEB chemical	350 mg/l NaClO
CEB sequence	Air scour + Backwash sequence + Backwash chemical dosing (30 s) + Soaking (15 min) + Backwash sequence

According to these operating conditions, the recovery of the system is 96.33%, the availability is 91.1%, efficiency is 88.46% and finally, the equivalent continuous chemical concentration is 0.48 mg/l. This is considered as the starting point of this optimization work.

More than nine months of Ultrafiltration operational data using DOW™ Ultrafiltration technology treating Seawater has been evaluated and used to develop the "UF Operation Model". This model is aimed at predicting the fouling behavior of an installation, or in order words, the Trans-membrane Pressure evolution with time. The model is composed by three major segments:

- Segment A: Model of TMP increase with time
- Segment B: Model of TMP decrease as a result of a Backwash
- Segment C: Model of TMP decrease as a result of a Chemical Enhanced Backwash

Equations for each one of these segments have been developed empirically in order to be able to predict the Trans-membrane Pressure with time depending on the operating strategy followed. For example, the model should predict different TMP increase trends depending on the frequency of Backwash and/or Chemical Enhanced Backwash.

The methodology followed consisted of selecting a certain backwash and CEB frequency and then let the model calculate how often a CIP should be applied. The criterion established for this particular exercise is that a CIP should be done every time the model predicts a TMP above 1.7 bar. According to this, the inputs for the model are the backwash and CEB frequency, taking into account the maximum allowed TMP. The model output is the number of CIPs. The results of the modeling applied to the various cases evaluated are shown in Table 18.

Table 18. Summary BW, CEB and CIP cases studied

Case	Baseline	I	II	III	IV	V	VI	VII	VIII	IX
Backwashes per day	48	48	48	12	12	12	12	0	0	0
CEBs per week	7	0	1	0	1	2	7	0	7	14
CIPs per 90 days	1	1	0	11	9	7	0	30	18	0

The next step in the evaluation is to compare each one of the nine operating schemes previously modeled. For this purpose, the efficiency (recovery and availability) together with the continuous equivalent chemical concentration (CEC) is calculated. Cost of water is calculated for a desalination plant with a production of 20,000 m^3/day and a cost of energy of 0.10 USD/kWh. The results of these calculations are shown in Table 19 and the efficiency and chemical concentration of each case are plotted in Figure 24.

Table 19. Efficiency, continuous equivalent chemical consumption and cost of water

Case	Baseline	I	II	III	IV	V	VI	VII	VIII	IX
CEC (mg/l)	0.48	0.28	0.04	2.29	1.91	1.54	0.25	6.37	4.02	0.49
Efficiency (%)	88.46	89.40	89.47	95.37	95.58	95.72	96.24	94.44	95.49	97.65
Cost of Water (cUSD/m^3)	4.64	4.61	4.60	4.57	4.56	4.54	4.49	4.71	4.62	4.47

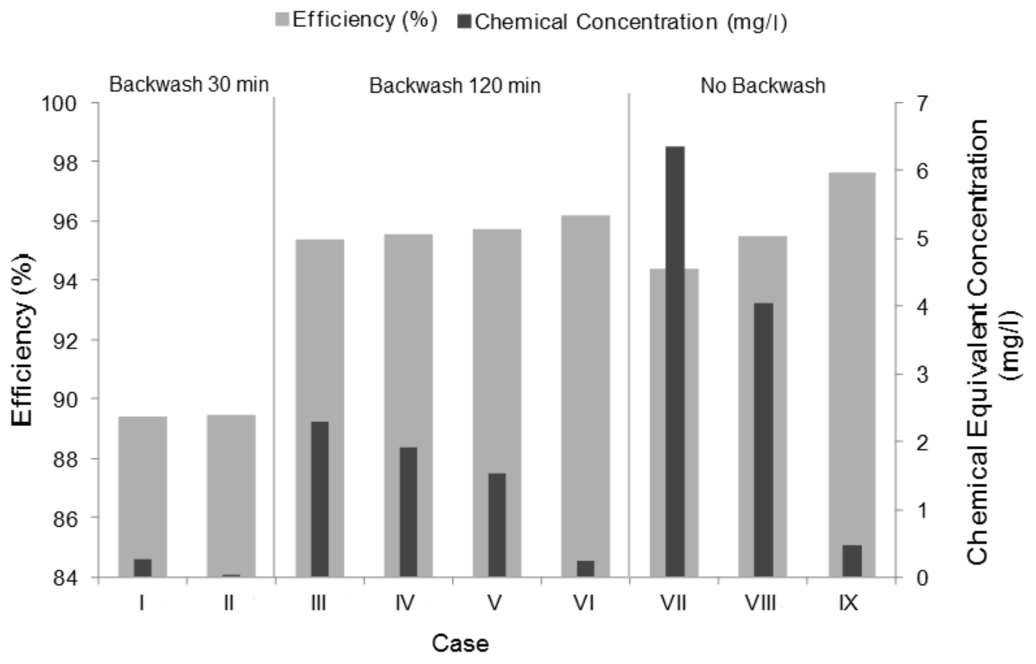

Figure 24. Efficiency and Chemical Equivalent Concentration

The first important conclusion from the various operating strategies evaluated is that as soon as the frequency of the Backwash decreases the efficiency of the process increases significantly. Three different group of cases have been studied, first one (cases I and II) with BW every 30 minutes, the second one comprising cases III to VI with BW every 2 hours and the third one, including the last three cases, without BW. At this point, it should be emphasized that all the cases are based on a sustainable operation, meaning that the TMP will be always maintained below the targeted value. According to the calculations, if the BW takes place every 30 minutes, the efficiency of the process will be in the range of 88% (baseline scenario) whereas the chemical concentration will be rather low (below 0.5 mg/ l). If the frequency is reduced to once every two hours (cases III to VI), the efficiency increases up to 96%. In these cases, more frequent chemical cleanings will be required to maintain a low TMP. Case III is based on frequent CIP and no CEB but this strategy leads to relatively high chemical consumption. Cases IV and V are also based on frequent CIP but they also implement CEB. The comparison of these two cases (IV and V) results of interests, since by decreasing the number of CIP (from 9 to 7 in three months) and slightly increasing the number of CEB (from 1 to 2 per week) an increase in efficiency from 95.6% to 95.7% and a reduction in the chemical concentration from 1.9 to 1.5 mg/l are attained. Following this trend, a further reduction in the number of CIP leads to case VI, which has CEB every day but no CIP in 90 days. These conditions lead to high efficiencies (96.24%) and very low chemical concentrations (0.24 mg/l).

In case no BW is done (cases VII to IX) very frequent CEB and/or CIP will be required. A strategy based on too frequent CIP might lead to very high chemical consumption, such as in case VII. On the other hand, a strategy based on frequent CEB leads to lower chemical consumption but still quite high efficiency, case IX.

According to the previous discussion and to the data presented in Table 19 and Figure 24, the two optimum cases are VI and IX. The baseline operating strategy consisted in Backwash being done every 30 minutes and one CEB per day. This set up leads to an efficiency of 88% and an equivalent continuous chemical concentration of 0.48 mg/l. Case VI, based on a backwash taking place every 2 hours represents an efficiency of 96% and lower chemical consumption compared to the baseline case. On the other hand, case IX, which is based on the elimination of Backwash has an efficiency of 97.65% but the chemical consumption is comparable to the one of the baseline case. The calculation of the theoretical cost of water for each one of the cases modeled indicates that the lowest cost of water is achieved by these two scenarios (case VI and IX). Common feature is that frequency of BW and CIP is minimal and sustainable operation is however attained through relative higher CEB frequencies.

4.4 Conclusions

The operational data collected from nine months of operation of a system with DOW™ Ultrafiltration treating Mediterranean Seawater has been utilized to empirically develop a mathematical model to be able to predict operational trends. More specifically, the model is capable to predict trans-membrane pressure (TMP) evolution with time depending on the process strategy selected. Once the model was validated, it was used to predict the TMP with time according to various operating protocols with different frequencies of Backwash and Chemical Enhanced Backwash. When the maximum TMP allowed selected by the user is predicted by the model, then a CIP needs to be done. According to this, the output of the model is on one hand the TMP evolution and on the other hand the number of CIP to sustain operation. A baseline and nine alternative scenarios or cases have been studied in the framework of this project. The results of the model for each case are used to calculate the efficiency and chemical consumption. The cost of the water produced is then calculated according to these parameters.

The modeling of each case and the later calculation of the cost of water suggest that the lowest cost in the Ultrafiltration process of Seawater is attained when the frequency of the Backwash and the Clean in Place is reduced to it minimum while the frequency of the Chemical Enhanced Backwash needs to be adjusted accordingly in order to avoid exceeding the maximum allowable Transmembrane Pressure. The results of this project indicate that this optimized operating sequence results in cost of water reductions of 5% and process recovery increases of 8%.

4.5 Acknowledgements

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5. High efficiency operation of pressurized ultrafiltration based on seawater advanced cleaning research

Backwash optimization III

This chapter discusses a method to operate polyvinylidene difluoride (PVDF) fibers based on outside-in pressurized Ultrafiltration (pUF) membranes at very high efficiency. The backwash (BW) sequence was initially identified as the key contributor to the process efficiency yield. Special efforts are done to optimize this key parameter. Based on experimental design, the backwash duration is reduced from 170 seconds to 100 seconds eliminating three redundant cleaning steps from an original sequence of five steps. The backwash frequency is decreased from once every 30 min to once every 90 min in order to do fewer backwashes per day. These two modifications together result in an efficiency increase of 10% (from 88% to 97%). Thanks to this higher efficiency operation, it is possible to save 1.4 m^3 of ultrafiltrated water per day and filtering 96 extra minutes per day. A side by side validation is performed for 14 days in order to validate the new optimum conditions identified versus the reference conditions. In addition, the data is analyzed in order to prove that both backwashes have the same cleaning strength in reducing the trans-membrane pressure (TMP). Moreover, a model to predict the TMP evolution over time, based on the TMP increase during the filtration cycle, the TMP recovered during the backwash cleaning and the TMP recovered during the chemical enhanced backwash (CEB) is presented and validated against the real plant performance during the validation period.

5.1 Introduction

The use of pressurized Ultrafiltration as a pretreatment for the Reverse Osmosis membranes in seawater desalination has experimented an impressive increase as a result of the continuous search for cost-effective technologies which enable a sustainable production of water [1]. Key benefits associated to the Ultrafiltration technology versus conventional pretreatment are a low footprint, the ability to remove virus and bacteria and to significantly reduce colloids, suspended particles, turbidity and some total organic carbon. Even more importantly, the ability to reliably provide good quality filtrate water to the downstream Reverse Osmosis are the most remarkable benefits associated with this technology [2].

5.1.1 Ultrafiltration cleanings

The ultrafiltration process is characterized, unlike Reverse Osmosis, by having relatively short filtration cycles given the need for higher cleaning frequency. The duration of the filtration cycle strongly depends on the type of raw water leading to a filtration cycle between 10 to 100 minutes. Between two filtration cycles a Backwash (BW) will occur to enable the cleaning of the fibers and consequently, a reduction in the trans-membrane pressure (TMP) accumulated during the filtration. A second type of cleaning, which takes place with a lower frequency compared to the Backwash is the Chemically Enhanced Backwash (CEB). Often, the CEB occurs once or twice per day and is characterized by a longer duration compared to the Backwash and also by the use of chemicals. The last type of cleanings, the Cleaning in Place (CIP) occurs once every couple of months and is characterized by its longer duration (few hours typically) and higher chemical concentrations used compared to a CEB.

Short term cleanings such as the backwash (BW) are typically carried out every 10 to 80 minutes, with a median of 30 min. The median duration of all steps in the sequence is approximately 3 min, where the backwash takes about 1 min. The backwash flux varies between 70 and 300 L/m²h (10/90% percentiles) and typically reflects double the operating flux. Occasionally chemicals such as hydrogen peroxide (H_2O_2) and Sodium Metabisulfite (SMBS) are used as backwash chemicals, but were judged as less effective than chlorine, which is frequently used. As an example, backwash chemistry is evaluated comparing 25 mg/l H_2O_2 and 10 mg/l NaClO, and the NaClO chemistry seemed to be far more effective [3]. NaClO has recently been the most widely used and has emerged as the standard for backwash schemes with chemicals. Its typical range is 3 to 20 mg/l with a median of 10 mg/l. Occasionally, especially in outside-in modules, air scouring is used in the range of 3 to 20 Nm³/h every 1 to 8 backwash cycles. The steps typically included in the backwash sequence are the Air Scour, with a duration between 30 to 60 s; the Draining, with a duration between 10 to 30 s; the Backwash Top with or without Air Scour, with a duration between 30 to 40 s; the Backwash Bottom, with a duration between 30 to 40 s; and the Forward Flush, with a duration between 10 to 60 seconds as it can be seen in Chapter 3 [4].

There are two types of Chemical Enhanced Backwash (CEB) type operations used for medium term cleanings, an oxidizing CEB and an acidic CEB. The predominant oxidizing agent in CEB operations is NaClO at 20 to 500 mg/l (10 and 90% percentile), with a median of 150 mg/l. Lower concentrations in the 50 mg/l range are used more frequently in every 2 to 8 hours [5], while higher concentrations are applied less frequently with a range of 12 and more hours. NaOH was tried in few occasions with and without NaClO but was quickly dismissed due to its scaling nature [6]. In fact, precipitations have already been discovered with NaClO, which is also a weak base [2]. In the acid CEB: most frequently, H_2SO_4 and HCl are used, occasionally also citric acid. The frequency of the chlorine CEB is in the range of every 6 to every 92 hours (10 and 90% percentile) with a median of 24 hours. Acid CEB is carried out at a frequency of 1:1 to 1:3 compared to chlorine CEBs. The chemical dosing duration in CEB steps is typically 30 s, hence shorter than the BW duration in a normal backwash. Information about CEB flux is very scarce – and as a rule of thumb it is safe to assume the CEB flux is equivalent to the backwash flux. In order to extend the chemical exposure duration, often extended soak times are provided after the chemical dosing – these are in the range of 2 to 36 min (10 and 90% percentile) and the median is 15 min.

Medium term cleanings (which in the framework of this work are termed "Chemical Enhanced Backwash") are the most diverse among all cleaning conditions and many different variations are described. A protocol which combined chemical dosing for only a very short time period with air bubbling has also been proposed [7]. With outside-in technology, it has also been frequently described to automatically dose chemicals to the feed, instead of the product, and recirculate [8]. Finally, the addition of chemicals to Reverse Osmosis permeate is described as well. A special backwash protocol, involving the use of heated cleaning solution, not only in the CIP, but also in the CEB is proposed as well [9] [10]. This advanced method has also been described for medium term cleanings, called "HEFM - Heated Enhanced Flux Maintenance": at the Buzzer platform and the Brownsville pilot: "this method is used daily - each MF rack is taken offline and heated chlorine solution (at about 250 – 400 mg/l chlorine at 30-35 ºC) is automatically circulated through the MF membrane rack for about 30 minutes" [10] [11]. Some CEB type medium term cleanings may carry character of a CIP operation, e.g. involving multiple hours soak duration and higher concentration.

Clean in place operations are carried out every 21 days to every 14 months, with a median of every 1.5 months. CIP operations are often composed of two steps, one which nowadays often uses NaClO at elevated concentrations (up to 4000 mg/L with PVDF fibers) and optional NaOH (often pH ~12), and a second one with acid (often organic acid at very high concentrations in the low percent range). Often, multiple hours of recirculation and soak time are used. Often heating is used to enhance the effect. A wide variety of special chemicals is reported, e.g. formulated cleaners, EDTA or enzymes [12].

5.1.2 Advanced Cleaning Research

In the past, and in the seawater desalination space, DOW™ Ultrafiltration membranes were used in Qingdao 2009 with an efficiency of 80% as some other commercially available ultrafiltration systems show nowadays [12]. After the first improvement phase done in Barcelona, the efficiency of DOW™ Ultrafiltration was increased to 88% [12].

Previous investigations have focused in reducing the number of backwash steps, so that the steps that contribute the less can be omitted. This reduction from five steps (Air Scour, Draining, Backwash Top with Air Scour, Backwash Bottom and Forward Flush) to two steps (Backwash Top with Air Scour and Forward Flush) at a constant backwash frequency of 30 min increased the efficiency to 95%. This investigation was done planning a fractional Design of Experiments and then analyzing the TMP as a response variable throughout an analysis of Variance as it can be seen in Chapter 3 [4].

Simultaneously, previous investigations focused on reducing the backwash frequency in order to raise the ultrafiltration efficiency to 95%. The experiments were done keeping the 5 main backwash steps but reducing the backwash frequency from 30 min to 90 min. Therefore, it was possible to operate the ultrafiltration system doing fewer backwashes per day as it can be seen in Chapter 4 [13].

The aim of this work is to integrate the different pressurized ultrafiltration advance cleaning researches described in Chapter 3 [4] and in Chapter 4 [13], integrating in a same operation protocol the reduction in the number of backwash steps from five steps to two steps, and reducing the backwash frequency from 30 minutes to 90 minutes. So, combining both approaches, the efficiency representing the total ultrafiltration process yield can be increased to a very high level. Therefore, the hypothesis of this investigation is that the ultrafiltration can be operated in a stable way and sustainably by operating with a backwash frequency of 90 min and only using the two main backwash steps previously identified as being the most effective in cleaning the ultrafiltration membrane. Doing this, the efficiency can be increased even higher, which ultimately can be translated into cost savings in operational expenses (OPEX) and capital expenses (CAPEX).

Backwash is identified as the most important cleaning process to be improved in order to increase the efficiency of the ultrafiltration process. Compared to the CEB and the CIP, the backwash consumes a huge amount of time, because it takes place more often. Figure 25 shows the linear relationship between the backwash duration per day and the availability of the ultrafiltration unit. This plot is obtained using the efficiency equations described in the Introduction section. As an example, it can be seen that just reducing by halving the backwash duration per day (min/ day), the availability (%) of the filtration process is doubled. Another drawback is the consumption of ultrafiltrated water to clean the fibers.

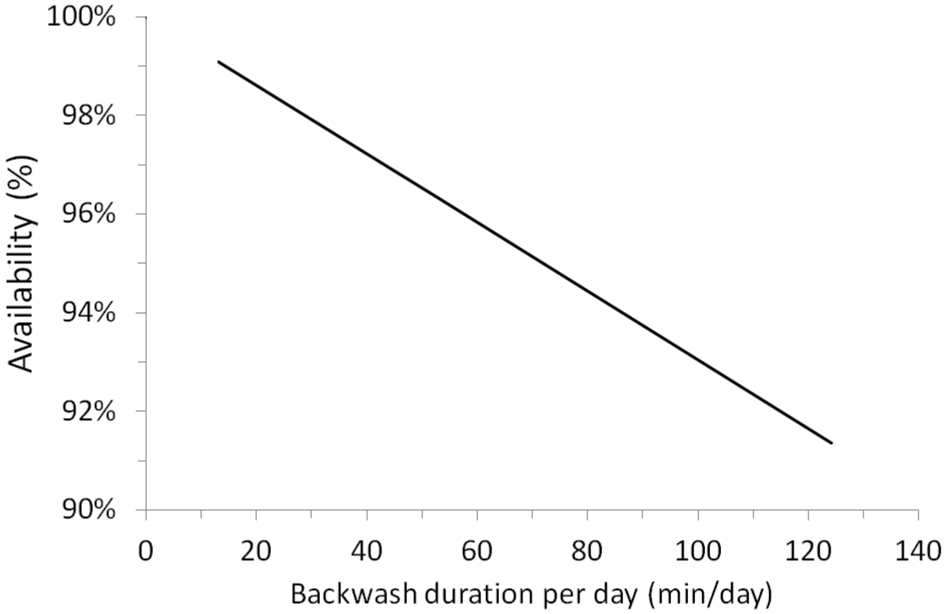

Figure 25. Effect of backwash in the total filtering time

5.2 Materials and methods

5.2.1 Unit description

This research is done in an experimental containerized seawater desalination plant. This unit represents one of the twenty experimental units that Dow Water & Process Solutions has in its Global Water Technology Development Center in Tarragona, Spain. Figure 26 shows the scheme of the installation, which consists of two independent and parallel lines, both containing ultrafiltration membranes pretreatment to the reverse osmosis train. The pretreatment before the ultrafiltration unit includes an Amiad® Arkal disk filter of 250 µm. The ultrafiltration modules used are DOW™ Ultrafiltration SFP-2660 modules, and the reverse osmosis used are DOW™ FILMTEC SW30XLE-4040 membranes.

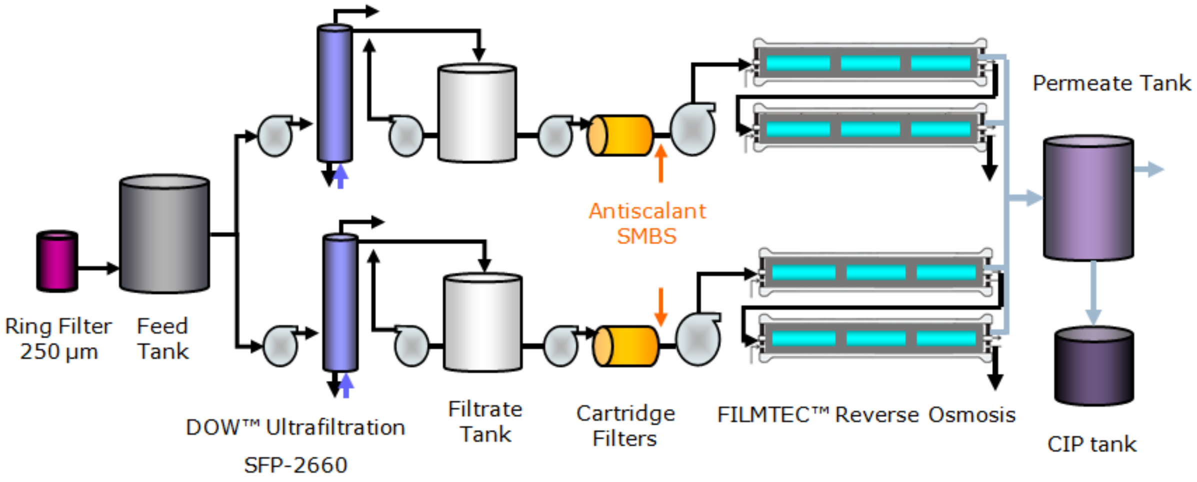

Figure 26. Ultrafiltration and seawater reverse osmosis desalination plant

5.2.2 Ultrafiltration membranes

The membranes used to validate the hypothesis of this research are two DOW™ Ultrafiltration SFP-2660 modules. These are characterized by having a diameter of 165 mm (6.5 inches) and a length of 1500 mm (59.1 inches). The fibers are made of polyvinylidene difluoride (PVDF) with a special treatment to make the material more hydrophilic. With this technology, it is possible to increase the fiber permeability and make it more fouling resistant. These fibers have a nominal pore size of 30 nm with a 0.7 mm inner diameter and an outside diameter of 1.3 mm. The module has a total active area of 33 m^2 (355 ft^2). DOW™ Ultrafiltration modules operate following an outside-in configuration given the advantages associated with this modus operandi such as better cleanability, lower fouling trends, the benefit of using air scour and higher mechanical and chemical resistance.

5.2.3 Seawater characterization

Seawater from the Mediterranean Sea taken from Tarragona Harbor is used for this research. Water has a Total Dissolved Solids (TDS) salt content of 39,252 mg/l.

Table 20 depicts the total ionic seawater characterization. Total Organic Carbon (TOC) has an average value of 1.15 mg/l, Total Suspended Solids (TSS) has an average value of 8.29 mg/l and Turbidity (TB) has an average value of 3.11 NTU. This analysis is done in the Water Analytical Laboratory that Dow Water & Process Solutions has in Water Technology Application Development Global Center.

Table 20. Seawater ion characterization

Ions	Concentration (mg/ l)
Potassium (K)	446
Sodium (Na)	11,941
Magnesium (Mg)	1,483
Calcium (Ca)	465
Strontium (Sr)	10
Carbonate (CO_3)	4
Bicarbonate (HCO_3)	138
Chloride (Cl)	21,640
Fluoride (F)	1
Sulfate ($SO_{4)}$	3,045
Boron (B)	5
Bromide (Br)	74

5.2.4 Normalization equations

TMP is normalized according to the equations described in Section 2.2.2 [14].

5.2.5 Efficiency equations

Efficiency is calculated according to the equations described in Section 2.2.3.

5.2.6 Validation

The hypothesis of this research is that a high efficiency operation of the ultrafiltration process can be achieved through further optimizing the backwash sequence. This is achieved combining the reduction of the backwash steps from five to two as it can be seen in Chapter 3 [4], and the optimization of its frequency from 30 to 90 min as it is described in Chapter 4 [13]. This is achieved by assessing the total backwash time per day the membrane needs to be cleaned effectively. Reducing the backwash duration and its frequency contributes in adjusting the backwash duration per day.

In order to validate the hypothesis of this research, new UF modules are installed. The first phase is verifying these two modules that will be used later are actually performing in a similar way under the same operating conditions. For this purpose both ultrafiltration lines are identically operated for seven days according to the conditions depicted in Table 21. Moreover, this trial would also validate the conditions where the ultrafiltration is operated with a backwash every 90 min and with the five main backwash steps (Air Scour, Draining, Backwash Top with Air, Backwash Bottom and Forward Flush), as stated in the literature by Garcia-Molina described in Chapter 4 [13]. In order to prevent biofouling, a CEB is done on a daily basis.

Table 21. Baseline and optimum conditions

Parameter	Baseline	Optimum
Flux	70 l/ m²h	70 l/ m²h
Backwash frequency	90 min	90 min
Backwash flux	80 l/ m²h	80 l/ m²h
Air flow	12 Nm³/ h	12 Nm³/ h
Air Scour duration	30 s	-
Draining duration	30 s	-
Backwash Top with Air Scour duration	30 s	60 s
Backwash Bottom duration	30 s	-
Forward Flush duration	30 s	30s
Valve changing time	2 s	2 s
CEB frequency	24 h	24 h
NaClO Concentration	350 mg/ l	350 mg/ l
Soaking time	6 min	6 min

After the initial validation, the first ultrafiltration line is operated according to the optimized alternative conditions, while the second ultrafiltration line is operated with the reference conditions as depicted in Table 21. The optimum is designed keep the total effective backwash time per day. This represents keeping the product recovery constant while optimizing the filtration process availability. This is achieved keeping 60 s of effective backwash represented only by the backwash top plus air scour step in the optimized line, while in the baseline line this time is distributed between the backwash top plus air scour and the backwash bottom. However, the optimized line does use neither the air scour nor the draining. This happens because the air scour step is already performed during the backwash top plus air scour step. The draining effect is already achieved during the forward flush step. The logic applied is described in a previous published work also described in Chapter 3 [4]. The forward flush step is operated so that the volume of the entire module is renewed with 2.6 times of raw water.

Using the optimized conditions against the baseline conditions, the same effective backwash time per day is achieved. This represents operating at the same product recovery in both conditions, but increasing the availability thanks to a decrease in the time each backwash cycle invests in cleaning the membrane. In the reference conditions there are 5 steps that take 30 s each to be completed, and that represents investing at least 2 min 30 s in each backwash cycle. On the other hand, in the optimized conditions there are 2 steps that take one 60 s and the other 30 s to be completed, and that represents investing at least 1 min 30 s in each backwash cycle. These shorter backwash cycles represent a reduction in the time needed by each backwash to be completed of at least 40%. This value could be even higher if the time each pump takes to ramp and each valve takes to go from one cleaning step to the other are taken into account.

5.2.7 TMP modeling

The TMP evolution over time is modeled to predict the fouling trend in the long term operation. This is achieved analyzing the TMP at the starting and ending of each filtration cycle, each backwash cycle and each CEB cycle. These three cases are the TMP increase during filtration, the TMP reduction during backwash and the TMP reduction during CEB. These three datasets allow the obtaining of three different mathematical functions. These are used to predict the TMP increase over time. Analyzing the mathematically obtained coefficients, it is possible to assess the effectiveness of each cleaning. The ultimate goal of the modeling is to build a robust set of equations which enable the prediction of the long term TMP evolution. Thanks to the model, the operator will be able to decide which operating conditions are more adequate to its installation depending on each type of cost like the cost of chemicals, the cost of electricity and the cost of manpower.

5.3 Results and discussion

5.3.1 Validation

Figure 27 shows the validation of both lines operated at the same conditions. No major differences between both ultrafiltration lines and modules are seen, although the second ultrafiltration line presents a slightly higher TMP. This also proves that operating at the base line conditions is sustainable.

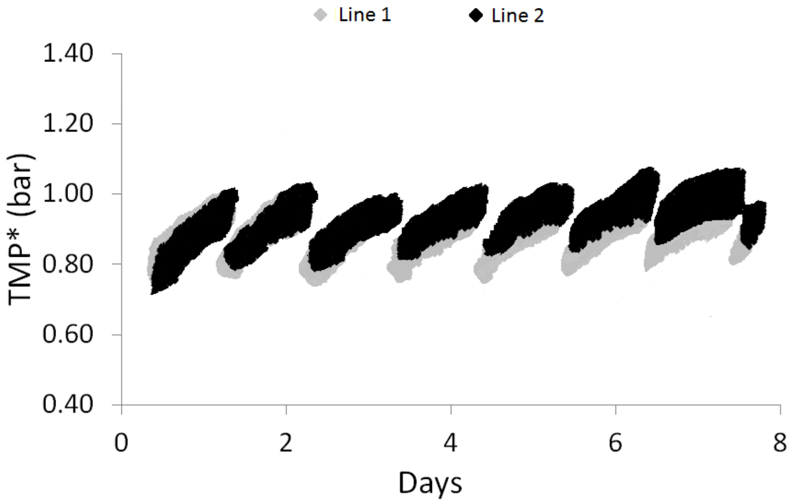

Figure 27. Baseline conditions

In order to test if the hypothesis stated in this research is correct and the optimum conditions are sustainable, a validation period of 14 days is completed. Figure 28 depicts the TMP evolution over time, where it can be seen that both lines follow the same fouling trend. According to this, the optimum conditions are thus validated. These results show the same fouling trend observed in the literature by Gilabert

Oriol in Chapter 3 [4]. Combining both researches it can be assessed that the TMP increases with a rate of 0.25 bar per day. Moreover, thanks to the CEB, the TMP is fully recovered to its initial value. As the TMP is controlled kept constant below 1 bar, the operation is considered sustainable. The benefit associated with a high efficient and optimized backwash, enables the operation of the modules at a high efficiency, maximizing the total net flux produced.

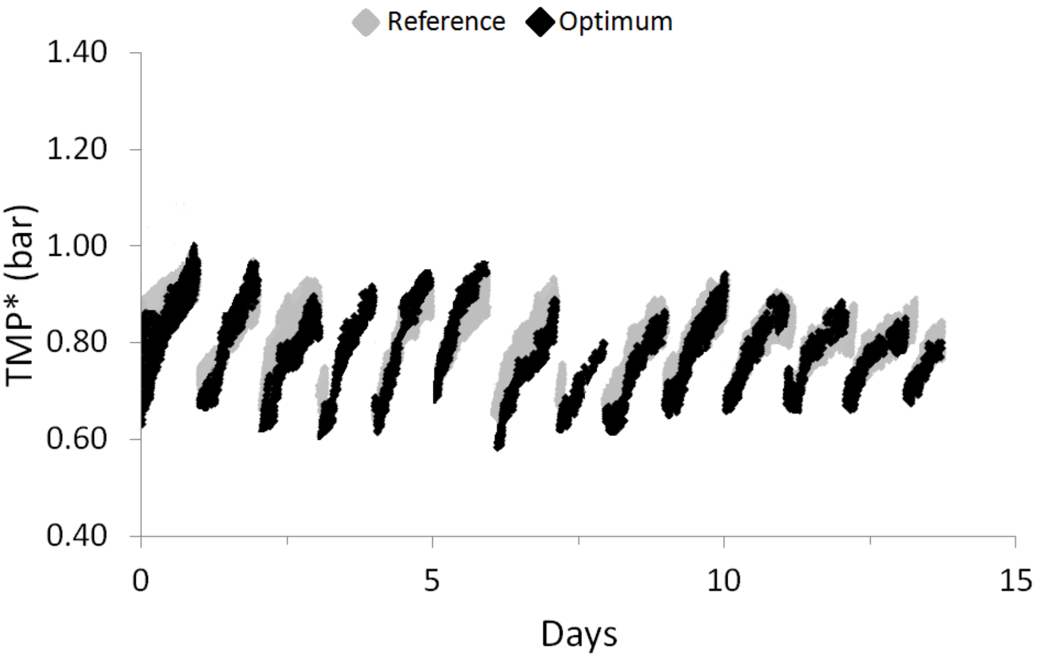

Figure 28. Validation period

5.3.2 TMP modeling

Once the hypothesis of this work is validated, a model is proposed to predict the TMP within boundaries and conditions in which the unit is operating. In order to build the model, the TMP values at the beginning and at the end of the filtration cycle are plotted in order to assess if any correlation exist between these values. The same is done for the TMP before a backwash and after the backwash, as well as for the CEB cleaning protocol. Figure 29 depicts these correlations. This model is built in order to analyze the data through the study of the different batch cycles that occur during the operation of the ultrafiltration. Analyzing the data in this way helps obtaining a general picture of the process, since the backwash efficiency is separated from the filtration TMP increase and from the CEB cleaning efficiency.

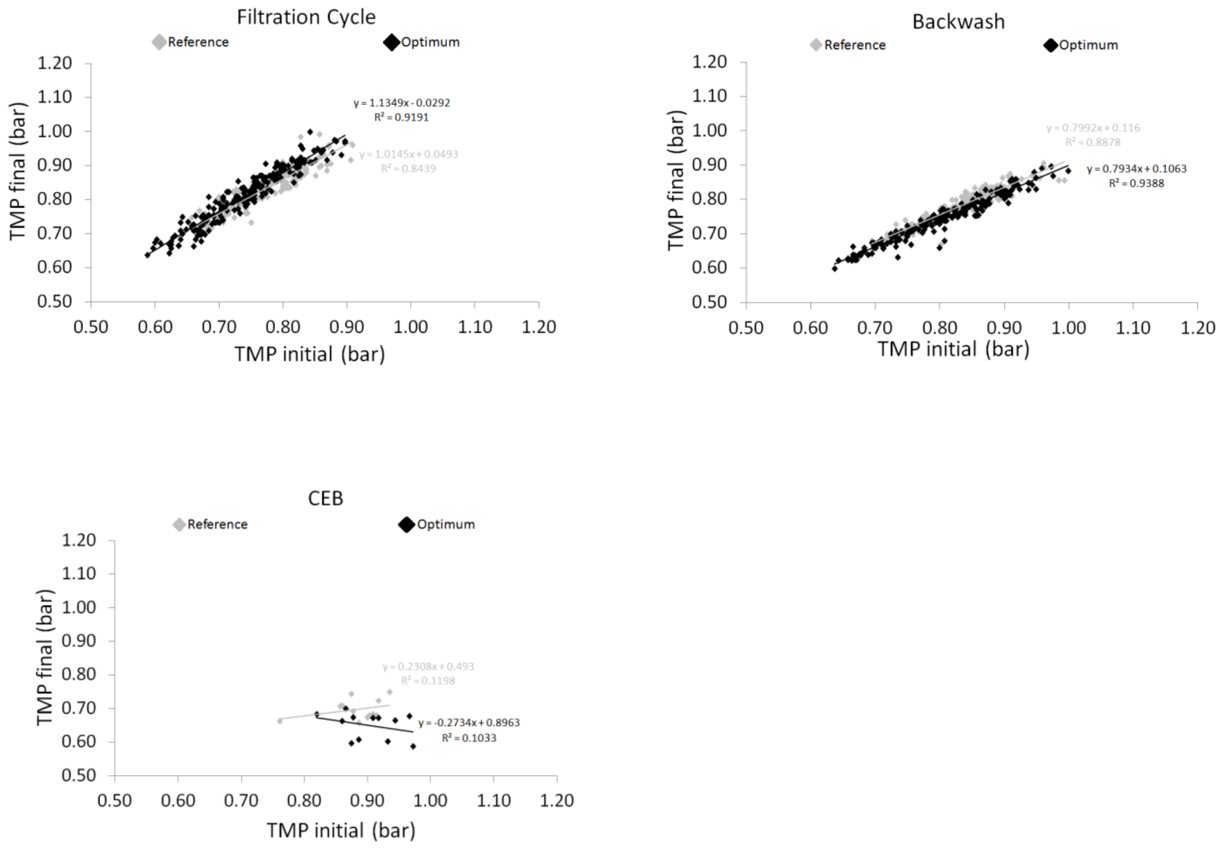

Figure 29. Correlation between the initial and final TMP in a filtration cycle (top left), backwash cycle (top right) and CEB cycle (bottom)

The correlations obtained are summarized in Table 22, where TMP_0 represents the TMP at the beginning of each cycle, and the TMP_f represents the TMP at the end of each cycle. It must be noticed that the TMP at the end of the filtration cycle corresponds to the TMP at the beginning to the TMP at the end of the previous backwash cycle.

Table 22. TMP correlations in filtration, backwash and CEB cycles

	Filtration	**Backwash**	**CEB**
Optimum	$TMP_{F_f} = 1.135\, TMP_{F_0} - 0.029$	$TMP_{BW_f} = 0.793\, TMP_{BW_0} + 0.106$	$TMP_{CEB_f} = -0.273\, TMP_{CEB_0} + 0.896$
Reference	$TMP_{F_f} = 1.015\, TMP_{F_0} + 0.049$	$TMP_{BW_f} = 0.799\, TMP_{BW_0} + 0.116$	$TMP_{CEB_f} = -0.231\, TMP_{CEB_0} + 0.493$
Average	$TMP_{F_f} = 1.075\, TMP_{F_0} + 0.010$	$TMP_{BW_f} = 0.796\, TMP_{BW_0} + 0.111$	$TMP_{CEB_f} = -0.021\, TMP_{CEB_0} + 0.695$
r^2	0.89	0.91	0.11

Using the equations shown in Table 22, a model is built in order to predict the TMP over time. As it can be seen when analyzing the data, both filtration cycles are almost identical. So, taking into account the two extreme scenarios where the TMP is at is lower value (0.60 bar) and the TMP is at its higher value (1.00 bar) among the experimental data collected, the difference in terms of percentage TMP is only -0.9% and 3.8% respectively. In addition, similar performance is observed when line 1 and line 2 operate at the same conditions (Figure 27). Moreover, observing the backwash TMP equations, it can be assessed that the baseline backwash and the optimized backwash are almost identically. These two analyses might suggest the improvement made in the backwash sequence is effective as both types of backwash have the same cleaning power. Since both equations have the same cleaning strength, it is more economically viable to use the optimum conditions since the same cleaning effect is achieved with a shorter amount of time. This represents a time reduction during the backwash cleaning cycle of 42%, since the backwash time is reduced form 2 min 50 s to 1 min 38 s.

However, it can be observed that the CEB presents a low regression coefficient (r^2) value. This means that regardless the final TMP value of the filtration cycle, the TMP will always be restored to its initial value. The equation to predict the TMP reduction during the CEB cycle is therefore calculated averaging all the TMP final points, and has a value of 0.68 bar. This might suggest that the dosage concentration of 350 ppm of NaClO can be minimized to a lower value as the chemical concentration is possibly overdosed, or the CEB frequency can be reduced.

After analyzing all data obtained, Table 23 summaries the equations obtained to predict the TMP evolution over time at the conditions the unit has been operating.

Table 23. Model equations for the filtration, the backwash and the CEB cycle

	Filtration	Backwash	CEB
Equation	$TMP_{F_f} = 1.075\, TMP_{F_0} + 0.010$	$TMP_{BW_f} = 0.796\, TMP_{BW_0} + 0.111$	$TMP_{CEB_f} = 0.68$

5.3.3 Model validation

Once the modeling equations are obtained, the model is validated with the experimental data obtained during the validation period. As the reference and the optimized conditions show the same performance, the improved conditions are chosen to validate the model. Figure 30 depicts a detail of the model validation where the effect of the backwash can be assessed. This plot is presented in order to do a fair comparison between the filtration cycles and the backwash cycles predicted by the model and the ones obtained from the real operation of the ultrafiltration unit. Figure 31 depicts a detail of the model validation for the whole two weeks validation period, where the effects of the CEBs can be assessed. From these plots, it can be observed that the model fits accurately the real operation.

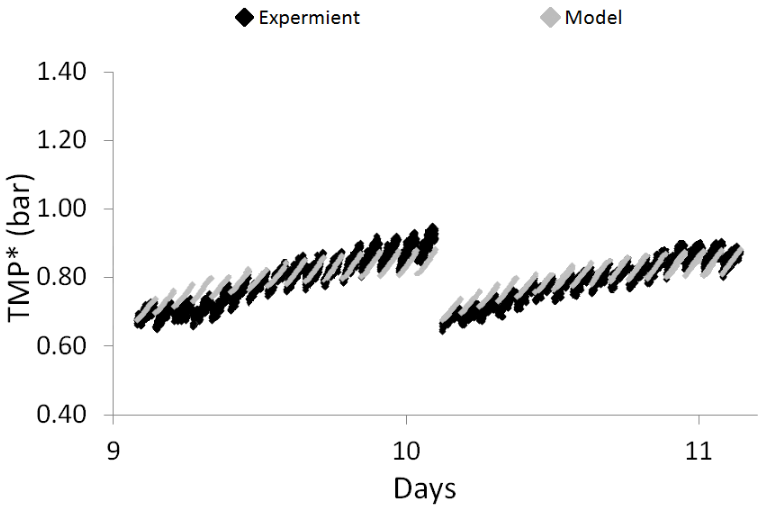

Figure 30. Backwash model validation

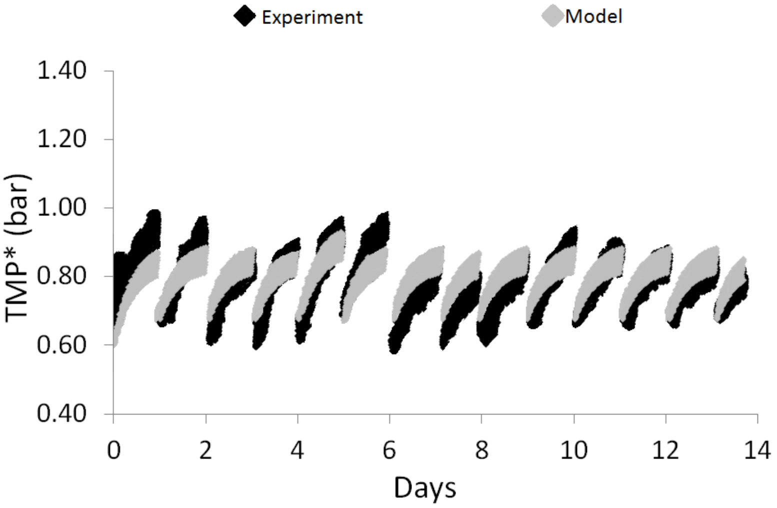

Figure 31. Model validation

The present model used to evaluate the backwash and the fouling associated with it, is only valid for the given set of operating conditions. These are a filtration flux of 70 l/m²h, a backwash flux of 80 l/m²h, a CEB done every 24 hours with a chlorine concentration of 350 mg/l, an air flow of 12 Nm³/h, a seawater feed turbidity below

5 NTU and a TMP between 0.6 and 1.0 bar. Extrapolating this model out of this range could induce misleading results. However, the filtration cycle duration could be reduced since the backwash is independent from it.

5.3.4 Efficiency determination

Table 24 depicts the different phases done during the pressurized Ultrafiltration cleaning research. Phase 1 was the baseline established thanks to the research done in Qingdao during 2009 [12], Phase 2 was the result of the research done in Tarragona during 2012 done in Chapter 3 [4], while Phase 3 was the baseline parallel established in Tarragona during 2012 done in Chapter 4 [13], and finally, Phase 4 is the result of this present research also done in Tarragona during the year 2012. It must be noticed that AS refers to the Air Scour step, D refers to Draining step, BWT+AS refers to Backwash Top with Air Scour step, BWB refers to Backwash Bottom and FF refers to Forward Flush.

Table 24. Different cleaning research phases

Phase	Filtration (min)	BW steps	AS (s)	D (s)	BWT+AS(s)	BWB (s)	FF (s)
1	30	5	30	30	30	30	30
2	30	2	-	-	30	-	30
3	90	5	30	30	30	30	30
4	90	2	-	-	60		30

Table 25 shows the availability, the product recovery and efficiency yields according to each different phase of the pressurized ultrafiltration advanced cleaning research for a filtration flux of 70 l/ m²h, a backwash flux of 80 l/ m²h and 2 seconds of valve changing time.

Table 25. Availability, Recovery and Efficiency yields

Phase	Freq	Steps	Availability (%)	Recovery (%)	Efficiency (%)
1	30	5	91.4	96.2	87.9
2	30	2	96.4	98.1	94.5
3	90	5	96.9	98.7	95.7
4	90	2	98.2	98.7	97.0

Table 26 shows for each phases of the pressurized ultrafiltration advanced cleaning research, the evolution of different parameters. These are the number of backwashes done per day, the total filtrating time per day, the total backwash time per day, the water produced per day and the ultrafiltrated water consumed during backwashes every day. From this table, it can be assessed the direct correlation between the reduction of the number of backwashes done per day and the reduction of the backwash time per day, with the efficiency increase.

Table 26. Water saved and water produced balances

Phase	Freq	Steps	BW cycles (#/ day)	Filtration time (min/ d)	BW time (min/ d)	Water produced (m3/ d)	Filtrated water consumed (m^3/ d)
1	30	5	43.9	1,316	124	50.7	2.11
2	30	2	46.2	1,388	52	53.4	1.06
3	90	5	15.5	1,396	44	53.7	0.70
4	90	2	15.7	1,414	26	54.4	0.70

5.4 Conclusions

This chapter discloses a method to operate DOW™ Ultrafiltration membranes at high efficiency providing a good water quality of 44 mNTU to feed DOW FILMTEC™ Reverse Osmosis membranes for seawater desalination. The use of pressurized Ultrafiltration as a pretreatment has grown impressively as it is a good cost effective solution which enables a reliable production of water with an excellent water quality [1]. The key benefits associated with the use this technology is a low footprint, the ability to remove virus and bacteria, as well as to significantly reduce colloids, suspended particles, turbidity and some total organic carbon [2].

The backwash cleaning process is further optimized thanks to the fusion of two concepts. The first one refers to the reduction of redundant backwash step from 5 to 2 steps. The steps eliminated are the initial Air Scour, as an Air Scour is already done during the Backwash Top with Air Scour. The elimination of the Draining step, since the draining effect is achieved when the Forward Flush step introduces new water inside the ultrafiltration module, being the water introduced at least two times the module free volume. The last step eliminated is the Backwash Bottom, since the backwash cleaning effect is already done in the Backwash Top with Air Scour. The second step optimized, is the reduction of the backwash frequency from 30 minutes to 90 minutes.

Thanks to this process optimization, the efficiency is ultimately increased from 88% to 97%. This is achieved thanks to the availability increasing from 91% to 98% and to the product recovery increase from 96% to 99%. This 10% of efficiency increase represents reducing the total backwash time from 124 minutes per day to 26 minutes per day, which represents having the unit operating 96 minutes extra per day. Moreover, this improvement represents savings in the water produced used for the backwash, therefore, instead of using 2.1 m^3/d, only 0.7 m^3/d are used, which represents a saving of 1.4 m^3/d.

This achievement is finally validated with a side by side operation of two ultrafiltration modules, one having a reference point with all the five backwash steps but only does a backwash every 90 minutes, and the other having the optimum conditions. The backwash cleaning efficiency of both conditions is assessed analyzing all the operational data. So, the TMP reductions achieved in each backwash for each condition are compared, obtaining the same backwash cleaning time per day for both conditions, but, as the optimum condition uses a shorter backwash, it is concluded that the backwash efficiency of the optimum condition is higher.

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9. Summary and outlook

9.1 Thesis conclusion

The hypothesis of this thesis is validated, because the ultrafiltration efficiency is increased from its original value of 88% to 98% in desalination plants. This represents filtrating 96 minutes extra per day and a reduction of 100% in the filtrated water used during backwashes. This represents a cost decrease in the ultrafiltration process of 7.1%, and a cost decrease of 1.2% in the whole desalination process. Moreover, sodium hypochlorite chemical equivalent concentration is reduced from 0.28 mg/l to 0.06 mg/l. Backwash sequence is also simplified from five cleaning steps to only two cleaning steps. These are the backwash top with air scour and the forward flush. The steps eliminated are the air scour, the draining and the backwash bottom. Backwash frequency is optimized from 30 minutes to 90 minutes. Backwashing with reverse osmosis brine is also proven feasible in an ultrafiltration and reverse osmosis integrated process. CEBs frequency is decreased from one CEB per day to one CEB every five days. All these findings are integrated together to improve the ultrafiltration operation. A methodology to predict the trans-membrane pressure evolution over time is proposed. This technique is also useful to analyze the effectiveness of a filtration cycle, a backwash or a CEB. PVDF fibers are assessed against PES fibers. It has been observed that PES fibers show initially higher permeability, but are less fouling resistant. A process to prevent reverse osmosis chlorination due to sodium hypochlorite used during CEBs in the upstream ultrafiltration process is also explained.

9.2 Chapters conclusions

9.2.1 Chapter 1 – Aim of the thesis

This chapter presents the thesis as a whole and explains how all chapters link with the others. The realization of this thesis allowed having a better understanding of the whole ultrafiltration pretreatment process, as well as the downstream reverse osmosis process in the seawater desalination space. The backwash is identified as the main contributor to the low efficiency operation of the ultrafiltration water treatment process, as it is the cleaning step that repeats the most every day. Therefore, its contribution to the overall process yield is high. The main achievement of this thesis is to operate ultrafiltration in the seawater desalination space at a high efficiency rates. This is achieved through different strategies. Firstly, the number of backwash steps is reduced, which allows for shorter backwashes. Secondly, the backwash filtration cycles are longer and thus fewer backwashes per day are done. Thirdly, reverse osmosis concentrate is used to backwash the ultrafiltration, which eliminates the need of consuming filtrated water to backwash the ultrafiltration membranes. These techniques are validated through weeks of real plant operation in Mediterranean seawater and in Red Sea water. Moreover, a model to predict the long term fouling evolution of ultrafiltration membranes is proposed, upon fixing several operating and chemical parameters. Outside-in flux technology using PVDF membranes is also tested against Inside-out flux technology using PES membranes. Their different behavior is assessed, showing PVDF membranes to be initially less permeable but to resist better the fouling stress. Therefore, it demonstrated that PVDF membranes need less cleanings to sustain the same operating flux. The chemical enhanced backwash is also optimized in order to prevent sodium hypochlorite injected in this cleaning step and to reach and oxidize reverse osmosis membranes. A new methodology called RO-Norm and used to assess fouling rate of the reverse osmosis membranes is created. Moreover, a cost model to calculate the total cost of water in a desalination plant is proposed and validated with real plant data. Finally, new alternative membrane chemistries to the reverse osmosis polyamide active layer are proposed using a biomimetic approach.

9.2.2 Chapter 2 – Introduction

This chapter explains the basis to understand the different membranes technologies based on the size of its pore diameter size. Ultrafiltration is shown as a clear example of the pore flow model. This model describes the mass transfer of each species through the solid and stable pores present in an ultrafiltration membrane. On the other hand, reverse osmosis is the classical example of the solution diffusion model. This model describes the mass transfer of each species across the solid and dense membrane layer. The membrane presents a dense layer with no visible pores. However, the pores which facilitate the transfer of the smaller species are the free volumes spontaneously created and spontaneously dismantled between the membrane polymer chains. This effect occurs due to the normal thermal motion of the polymers macromolecules. The mass transport equation to obtain the water flux across and ultrafiltration membrane is explained through a theoretically mathematical deduction. The equation to obtain this flux is the permeability coefficient multiplied by the trans-membrane pressure. Fouling in ultrafiltration membrane is identified to be caused by a gel layer above the membrane surface and to internal blockages of the membrane pores. Gel layer fouling is typically reversible, while pore blockage is more difficult to be unblocked and it is thus called irreversible fouling. Fouling is controlled following different approaches. In order to remove the fouling associated with particles, a backwash with aeration is required, to remove biological fouling a chemical enhanced backwash with sodium hypochlorite is needed, to remove inorganic fouling a clean in place with oxalic acid or citric acid is required and to remove organic fouling a caustic clean in place is the most appropriate solution. Finally, the advantages of using ultrafiltration pretreatment are highlighted. These are a low footprint, which leads to lower land costs; a better water quality regardless the feed water quality, which translate in low fouling to the downstream reverse osmosis process and a lower chemical consumption.

9.2.3 Chapter 3 – Backwash optimization I

This chapter proposes a design of experiments and allows the reduction from five backwash cleaning steps to two backwash cleanings steps. This is achieved analyzing the design of experiments obtained data and contesting the hypothesis through the analysis of variance methodology. The starting point is the five backwash cleaning steps. These steps are air scour, the draining, the backwash top with air scour, the backwash bottom and the forward flush. The steps identified as the optimum steps are the backwash top with air scour and the forward flush. This conclusion is obtained because the initial air scour step is not needed as the air scour already takes place in the backwash top with air scour step. The draining step is also not needed since a forward flush already renews the water inside an ultrafiltration pressure vessel. The backwash bottom step is not needed because the backwash effect is already achieved during the backwash top with air scour step. Finally, these new optimum conditions are validated through two weeks of real operation. This enables an efficiency increase from 88% to 95%.

9.2.4 Chapter 4 – Backwash optimization II

This chapter discusses the reduction of the number of backlashes done per day in order to increase the efficiency and reduce the chemical but keeping the five backwash steps. Operating data is collected when operating at 70 l/ m²h and doing a backwash every 120 min and having each backwash step a short duration. These are 30 seconds for the initial air scour, 10 seconds for the draining, 10 seconds for the backwash top with air scour, 15 seconds for the backwash bottom and 15 seconds for the forward flush. Different scenarios considered and modeled according to different backwash, CEBs and CIPs settings. This has been achieved obtaining an empirical model through the analysis of the TMP at the beginning and at the end of each filtration cycle, the TMP at the beginning and at the end of a backwash cycle, and the TMP at the beginning and at the end of each CEB. From this modeling, it has been assessed that the best sustainable operating conditions are working at a backwash flux of 130 l/m^{2}h and doing a backwash every 120 min, a CEB every week and no CIP within three months. Using these conditions, the efficiency is increased from 88% to 96%, and the chemical concentration is minimized to 0.5 mg/l.

9.2.5 Chapter 5 – Backwash optimization III

This chapter uses both cleaning researches approaches done in previous chapters in order to give a unified view to both research and integrate them. Therefore, the backwash steps are simplified to the backwash top with air scour and the forward flush. These steps are demonstrated in Chapter 3 to be the ones that contribute the most to the fouling reduction during the backlash cleaning sequence. In addition, the number of backwashes done per day are reduced from a backwash every 30 min to a backwash every 90 minutes. This decrease is performed according to the results obtained from the assessment of each cleaning scenario done in Chapter 4. , where it is suggested the better approach in order to increase efficiency is to reduce the backwash cleaning frequency. Moreover, the backwash flux is decreased to 80 l/m^{2}h, a CEB of 350 mg/l is done every day and the operating flux is maintained at 70 l/m^{2}h. A new concept called total backwash time is introduced. This concept refers to the time per day dedicated in backwashing the fibers. As the new optimum identified reduces the number of steps and decreasing the number of backwash done per day, it exerts more stress to the membrane. Therefore, the step duration of the backwash top with air scour step is increased to 60 seconds and the forward flush is set to 30 s in order to helps sustaining the TMP within the two weeks validation period done. Finally, a model that predicts the TMP evolution over time is obtained. The model is proven to fit very well the experimental data obtained during the validation. Moreover, the equations obtained through this model are used to validate the new cleaning methodology. This is validated with a parallel ultrafiltration line running exactly the same conditions of a backwash every 90 minutes but doing all the five backwash cleaning steps with duration of 30 seconds. Analyzing the backwash efficiency, it is proven that the optimum conditions identified have the same backwash cleaning power as the reference conditions. Thanks to this research, the efficiency has been increased from 88% to 97%.

9.2.6 Chapter 6 – Backwash using brine

This chapter studies the effect of operating the ultrafiltration membrane doing a backwash that uses reverse osmosis concentrate. Reverse osmosis concentrate is also called brine and has a higher salinity value up to a 50% higher than feed seawater, as well as sodium metabislulfite ($Na_2S_2O_5$) and antiscalant. The benefit of using brine instead of filtrated water during membrane cleanings increases the efficiency of the process. This allows operating at 100% recovery since reverse osmosis concentrate is a waste that must be treated and no filtrated water is consumed. Long term evolution of three weeks of operation is gathered in order to make sure there is no precipitation of calcium carbonates or magnesium hydroxides that precipitate in the ultrafiltration membranes during the backwash cleanings which could clog the pores. This long term performance is assessed against a clone parallel line which uses filtrated water to backwash their fibers. Chemical enhanced backwashes are done with filtrated water to avoid scaling in the fibers due to a pH increase when adding sodium hypochlorite. In order to obtain the baseline, only the backwash frequency is set to 90 minutes while the five backwash steps are kept to 30 seconds. Operating flux is kept at 70 l/m²h and backwash flux to 80 l/m²h. A second validation period is done using brine during backwashes and the only two backwash steps identified as the most relevant in the previous chapters. These are the backwash top with air scour and the forward flush. The other line uses filtrated water during backwash and the five main backwash steps. This validation proves feasible to operate with these conditions. A new trigger based on only doing a CEB when it is needed is done. The value of one CEB every five days is chosen. This allowed saving chemicals and gaining some extra efficiency. This supposes an efficiency increase to 98% and a sodium hypochlorite chemical equivalent concentration saving from 0.28 mg/l to 0.06 mg/l. This represents filtrating 96 minutes extra per day and a reduction of 100% in the filtrated water used during backwashes. This allows a 7.1% savings in the ultrafiltration step and a 1.2% savings in the whole desalination process.

9.2.7 Chapter 7 – PVDF versus PES fibers

This chapter assesses the main operating differences between the two main commercially available ultrafiltration technologies. These are the outside-in flux configuration, represented by the PVDF membranes, and the inside-out flux configuration, represented by the PES membranes. The key benefit of outside-in flow technology is the possibility of using air scour during the backwash cleanings. Both technologies are operated through a side by side validation are rather challenging conditions for 55 days at the same average operating flux. These are a backwash frequency of 30 minutes and at two periods of a backwash flux of 80 l/m^{2}h and 160 l/m^{2}h although no strong correlation is found between backwash flux changes. Results show that both technologies deliver the same water quality in terms of turbidity and TOC rejection. However, PES membrane is shown to be more permeable for clean waters. Therefore at the beginning of the operation they show a higher permeability, but they lose their permeability faster than PVDF membranes. PVPF membranes shower initially worst permeability, but afterwards they lose permeability slower than PES membranes. Specifically, it is estimated that PES membranes need 2.5 more times CEBs than PVDF membranes to sustain the same operating flux. Thus, if no CEB is done to restore both membranes permeability to their initial conditions, PVDF membrane shows 55% higher permeability than PES membranes. Both fiber types are also analyzed in terms of cost competitiveness showing small differences. If the smaller active filtration area of PES modules is taken into consideration, savings up to 18% in the ultrafiltration pretreatment and up to 2% in the whole desalination plant can be achieved.

9.2.8 Chapter 8 – Reverse osmosis chlorination prevention

This chapter focuses on developing a chemical enhanced backwash which eliminates the risk of chlorinating reverse osmosis membranes due to the sodium hypochlorite (NaClO) used during these cleanings. Some improvements are developed in order to eliminate the chlorination risk. The first improvement refers to backwash top with NaClO dosing done during the CEB. If NaClO injection is not stopped some time before the backwash top finishes, chlorine might be drained through the booster pump causing it to reach reverse osmosis membranes and oxidizing them. The installation of injectors which prevents diffusion from chemical dosing pipe to the backwash pipe when there is no flow is also recommended. The second improvement deals with separating the backwash sequence done after the CEB. This backwash is done in order to flush the backwash line and thus remove all remaining NaClO. If the backwash done after the CEB is not completely independent than the conventional backwash done during normal operation, there is a reverse osmosis chlorination risk. This risk arises due to the fact that if the conventional backwash sequence is optimized, there is the possibility that there is not enough time to flush all the backwash line after a CEB. Therefore, the backwash done after each CEB must have an own independent backwash bottom step so that there is no chlorine accumulated at the bottom of the module, and a forward flush so all the module can be properly drained. These steps must have their independent time and flow set points. Moreover, the CEB is improved by adding a draining step before the CEB starts and after the soaking step. The first CEB enables a faster filling of the module with the targeted concentration, since the filling solution must not be dissolved in water. The second CEB enables a faster drainage of the module, thus removing very fast the pressure vessel chlorine content. Moreover, dead zones due to a bad design are identified. A residual and uncontrolled chlorination dosed by the water supply company to prevent biogrowth in the supply pipe is identified. To prevent occasionally reverse osmosis membrane chlorination, a low constant sodium metabisulfite ($Na_2S_2O_5$) addition is dosed to the reverse osmosis membranes. A logarithmic correlation between redox measurements and free chlorine concentration is found. This relationship tells that regardless of the chlorine concentration found, redox measurement will increase. Therefore online measurement of redox is only helpful qualitatively assessing chlorine detection, but it is not useful for quantitative analysis. These results are published under a confidentially agreement since they can eventually lead to an application patent to prevent chlorination combining novel plant and control design.

9.3 Final remarks

It is worth mentioning that most of the research done has been used to upgrade the current ultrafiltration plant design guidelines, which has enabled Dow to gain competitiveness when offering ultrafiltration technological solutions to its customers. Moreover, the pressurized ultrafiltration advance cleaning research findings are leveraged and implemented to the plant control systems of the different pilot plants and small industrial scale plants located in the Water Technology Application Development Global Center that Dow Water & Process Solutions has in Tarragona as well as the new Technological Development Center located in King Abdullah University of Science and Technology (KAUST) in the Kingdom of Saudi Arabia.

10. About the author

10.1 Biography

Guillem Gilabert Oriol was born in Tarragona on 18th May 1985. After completing his high school in Institut Martí i Franquès on 2003, he studied at the Universitat Rovira i Virgili (URV) in Tarragona, where he became a Chemical Engineer obtaining a Bachelor of Science (BSc) in 2008. During the third year of university, he was awarded in 2005 with a Sicue-Seneca scholarship to study in Universitat Autònoma de Barcelona (UAB). In 2007, he was awarded with an Erasmus Scholarship and he finalized his studies in the Technische Universität Berlin (TU Berlin) obtaining a Master of Science (MSc) in Chemical Engineering and Processes. In 2007, he was awarded with a scholarship to work in Evonik Industries (formerly known as Degussa) obtaining the highest academic degree for its work. In Berlin, he did his master thesis characterizing waste water foulants in membrane bioreactors (MBR) using sludge fractionation.

He started his PhD in Chemical Engineering in 2009 in Universitat Rovira i Virgili. He began researching Biomimetic Proton Exchange Membranes for Fuel Cells and Artificial Photosynthesis, receiving a scholarship from Fundación Mapfre. In 2010, he received a scholarship from Generalitat de Catalunya (FI). In 2010, he changed the topic of his PhD to research how to optimize the ultrafiltration cleaning process as a pretreatment for reverse osmosis in seawater desalination plants, and he stared working in Dow Water & Process Solutions in the Global Water Technology Development Center in Tarragona. Meanwhile, he worked also in the application development field for ultrafiltration and reverse osmosis as well as implementing the process control strategy of industrial plants running these technologies. He also learned to operate theses plants and worked managing various funding projects and coaching new students. In 2012, he obtained the Six Sigma Green Belt Project Leader certification. In Tuesday 5th March 2013 he will defend this PhD.

10.2 Grants

- Generalitat de Catalunya (FI) scholarship to do the PhD, 2010–2011
- Fundación Mapfre scholarship to do the PhD, 2009–2010

10.3 Conferences

- Co-author in Saudi Water & Power Forum (SWPF) 2012, Jeddah, Saudi Arabia, 3rd – 5th December 2012. N. Moosa, V. Garcia Molina, G. Gilabert Oriol, M. Bahshwan, Optimisation of Ultrafiltration Operational Strategy for the Red Sea in the Kingdom of Saudi Arabia.
- Euromembranes 2012 (EMS), London, England, 23rd – 27th September 2012.
- Presentation in European Desalination Conference (EDS) 2012, Barcelona, Spain, 23rd – 26th April 2012. G. Gilabert Oriol, N. Moosa, R. Garcia-Valls, M. Busch, V. Garcia-Molina, Optimizing seawater operating protocols for pressurized ultrafiltration based on advanced cleaning research.
- Presentation in 12th Network Young Membrains (NYM) 2010, Lappeenranta, Finland, 7th – 9th June 2010. G. Gilabert Oriol, M. Giamberini, R. Garcia-Valls, Proton exchange membranes based on biomimetic ion channels for the artificial photosynthesis.

10.4 Stages

- PhD stage in Institut Européen des Membranes, Montpellier, France, 2010

10.5 Courses

- Six Sigma Green Belt Project Leader, The Dow Chemical Company, September 2012
- Summer school on microtechnology and solids handling, Universitat Rovira i Virgili, Tarragona, Spain, 2010

10.6 Published articles

- V. Garcia-Molina, G. Gilabert Oriol, J. Suárez Martín, Ultrafiltration Advanced Cleaning Research and Modeling applied to Seawater, Water Conditioning and Purification, 54 (2012) 24-29.
- G. Gilabert Oriol, N. Moosa, R. Garcia-Valls, M. Busch, V. Garcia-Molina, Optimizing seawater operating protocols for pressurized ultrafiltration based on advanced cleaning research, Desalination and Water Treatment, 51 (2013) 384-396.
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10.8 Published confidential articles

- G. Gilabert Oriol, V. Garcia-Molina, M. Busch, Pressurized Ultrafiltration competitive benchmarking between PVDF outside-in technology and PES inside-out filtration mode, Dow CRI Report (2012).
- G. Gilabert Oriol, V. Garcia-Molina, M. Busch, F. Gutierrez, M. Cornejo, J. Dewisme, P. Carmona, N. Carpi, Reverse osmosis chlorination risk and prevention approaches in integrated systems (ultrafiltration & reverse osmosis), Dow CRI Report (2012).
- G. Gilabert Oriol, N. Moosa, M. Busch, V. Garcia-Molina, Optimizing seawater operating protocols for pressurized Ultrafiltration based on advanced cleaning research, Dow CRI Report (2012).
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- M. Bahshwan, N. Moosa, V. Garcia Molina, G. Gilabert Oriol, The design of a two-train ultrafiltration seawater reverse osmosis (UF-SWRO) pilot plant for development of UF-SWRO technology in the Red Sea and Arabian Gulf region, Dow CRI Report (2012).
- M. Bahshwan, Mohanad, N. Moosa V. Garcia Molina, G. Gilabert Oriol, T. Waly, Advanced Cleaning Research in a UF-SWRO System Using Red Sea Water, Dow CRI Report (2012).
- V. García Molina, G. Gilabert Oriol, P. Welle, J. Dewisme, DOW™ ULTRAFILTRATION performance optimization in the MFT SW UF+RO installation. DIPS vs DOTS evaluation and key operation learnings, Dow CRI Report (2012).
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10.9 Submitted confidential articles

- G. Gilabert Oriol, M. Hassan, J. Dewisme, V. Garcia-Molina, M. Busch, Backwashing using reverse osmosis brine in seawater desalination and it potential cost savings, Dow CRI Report.
- G. Gilabert Oriol, M. Hassan, J. Dewisme, M. Busch, V. Garcia Molina, High efficiency operation of pressurized ultrafiltration based on seawater advanced cleaning research, Dow CRI Report.
- V. Garcia-Molina, G. Gilabert Oriol, J. Suárez Martín, Ultrafiltration Advanced Cleaning Research and Modeling applied to Seawater, Dow CRI Report.
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- N. Moosa, V. Garcia-Molina, G. Gilabert Oriol, M. Bahshwan, Optimisation of Ultrafiltration Operational Strategy for the Red Sea in the Kingdom of Saudi Arabia.

Back cover

This thesis gives an overview on how to improve efficiency of the ultrafiltration filtration process in seawater desalination. This is achieved by optimizing different cleaning processes such as the backwash and the chemical enhanced backwash. Key success factors rely on reducing the number of backwash steps, improving the backwash frequency, using reverse osmosis brine for backwashing and reducing the chemical consumption. A new methodology to analyze these cleanings cycles is proposed through modeling the process. Different fibers types are also analyzed according to its permeability and its fouling tolerance. A methodology to prevent reverse osmosis chlorination from upstream chemical enhanced backwash cleaning is presented. All the findings are validated through real plant operating data. The proposed improvements increase the process efficiency to 98% and lead to a 7% cost reduction in the ultrafiltration process.