Carbon dioxide nucleation as a novel cleaning method for ultrafiltration membranes

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ABSTRACT

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The use of low-pressure membranes, mainly ultrafiltration (UF), has emerged in the last decade and began to show acceptance as a novel pretreatment process for seawater reverse osmosis (SWRO) desalination. This is mainly due to the superior water quality provided by these membranes, in addition to reduction in chemicals consumption compared to conventional methods. However, membrane fouling remains the main drawback of this technology. Therefore, frequent cleaning of these membranes is required to maintain water flux and its quality. Usually, after a series of backwash using UF permeate chemical cleaning is required under some conditions to fully recover the operating flux. Frequent chemical cleaning will probably decrease the lifetime of the membrane, increase costs, and will have some effects on the environment. The new cleaning method proposed in this study consists of using a solution saturated with carbon dioxide (CO₂) to clean UF membranes. Under the drop in pressure, this solution will become in a supersaturated state and bubbles will start to nucleate on the surface of the membrane and its pores from this solution resulting in the removal of the fouling material deposited on the membrane. Different compositions of fouling solutions including the use of organic compounds such as sodium alginate and colloidal
silica with different concentrations were studied using synthetic seawater with different concentrations. This cleaning method was then compared to the backwash using Milli-Q water and showed an improved performance compared to it. An operational modification to this cleaning technique was then investigated which includes a series of sudden pressure drop during the backwash process. This enhanced technique showed an even better performance in cleaning the membrane, especially at severe fouling conditions. In most cases, the membrane permeability was fully recovered even at harsh conditions where conventional backwash failed to maintain a stable operation. Therefore, the new cleaning method might provide an efficient and environmentally friendly alternative cleaning technique to low-pressure membranes technology in the future.
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LIST OF ABBREVIATIONS

BW  backwash
BW(CO₂)  backwash using CO₂ saturated solution
BW(MQ)  backwash using Milli-Q (pure) water
CEB  chemical enhanced backwash
CIP  cleaning in place
CO₂  Carbon dioxide
DAF  dissolved air flotation
DMF  dual media filter
ED  electrodialysis
GC-TCD  Gas Chromatography - Thermal Conductivity Detector
GCC  Gulf Cooperation Council
HA  humic acid
LC-OCD  Liquid Chromatography - Organic Carbon Detection
MED  multi effect distillation
MENA  Middle East and North Africa
MF  microfiltration (membrane)
MQ  Milli-Q ultrapure water
MSF  multi-stage flash
MWCO  molecular weight cut off
NOM  natural organic matter
NTU  Nephelometric turbidity unit
pH  power of Hydrogen
psi  pounds per square inch
RO  reverse osmosis (membrane)
SA  sodium alginate
SD-BW(CO₂)  backwash using CO₂ saturated solution with sudden-drop technique
SDI  silt density index
SEM  scanning electron microscopy
SWRO  sea water reverse osmosis
TMP  transmembrane pressure
<table>
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<td>TOC</td>
<td>total organic carbon</td>
</tr>
<tr>
<td>TVC</td>
<td>thermal vapor compression</td>
</tr>
<tr>
<td>UF</td>
<td>ultrafiltration (membrane)</td>
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CHAPTER 1

INTRODUCTION

1.1 Background

Due to the lack of fresh water resources, desalination became a very essential practice for meeting the global demand of fresh water. Thus, it has been implemented in more than 150 countries including USA, China, Europe and Gulf Countries. The increase in the water demand caused by population growth and urbanization made the desalination market grow by more than 5% annually reaching a total capacity of more than 80 million m$^3$/day (IDA, 2015). The two main desalination technologies commonly practiced are thermal-based and membrane-based technologies.

Thermal-based desalination separates water from its impurities through evaporation and condensation. This type is still the dominating desalination technology in the Gulf Cooperation Council (GCC) countries due to several reasons, which include:

- The reliability and high production capacity of thermal based desalination technology.
- The availability of oil at low prices.
- The poor and unsuitable seawater quality for membrane-based technology which usually is described by 4H: High salinity, High temperature, High turbidity and High marine life (Fath, Sadik, & Mezher, 2013).
While it is more susceptible to feed impurity than thermal-based desalination, membrane-based technology, mainly reverse osmosis (RO), is generally more economical than the thermal technology (Ghaffour, Missimer, & Amy, 2013). For this reason, the capacity of membrane-based desalination plants has increased more rapidly than thermal-based plants during the last decade, including in the GCC countries (Figure 1.1) (IDA, 2015). However, the performance of the membrane technology (i.e. RO) is highly affected by the feed water quality. Therefore, extensive pretreatment is essential in order to optimize the process, enhance the plant’s performance, and reduce the cost of water production. A good example on the susceptibility of membrane processes to feed water quality is the severe bio-fouling in the seawater reverse osmosis (SWRO) plant at Al-Birk, in the southern region of the Red Sea coast of the Kingdom of Saudi Arabia (Hassan et al., 2002). Some of the problems that led to the shutdown of this plant include:

- Fast pressure drop (ΔP) build up across membrane that necessitates frequent membrane cleaning (intervals of 10 days or less).
- Decline in membrane flux.
- High conductivity readings in permeate.
- Clogging of media and micron cartridge filters.
Figure 1.1: Installed membrane and thermal capacity, 1980-2015 (cumulative) (IDA, 2015)

Even though many improvements have been achieved in pretreatment, which introduced different approaches in treating feed water to the required quality for RO membranes. The following general rule is still valid:

“The selection of a proper pretreatment technology is site-specific”

Therefore, one should consider the seawater intake condition before he or she prefers one pretreatment technology over another.

The current seawater reverse osmosis (SWRO) pretreatment technologies can be divided into two main categories; conventional and low-pressure membrane filtration technologies. Conventional pretreatment systems usually consist of coarse screens to filter the large objects from entering the plant, followed by granular filters (or dual media filters). These systems are commonly complemented with the addition of some chemicals to enhance the performance such as chlorine, acid, coagulants or flocculants (Voutchkov,
2008; Wolf, Siverns, & Monti, 2005), in addition to other chemicals for RO scaling control and protection, e.g. antiscalant and sodium metabisulfite. Conventional pretreatment systems usually provide a quality of water that is acceptable to RO membranes. However, in regions where the raw seawater fluctuates, the cost of pretreatment becomes higher due to the high chemical consumption needed to produce the required water quality for a safe RO operation (Prihasto, Liu, & Kim, 2009), and sometimes additional pretreatment steps are required to meet RO feed water quality standards (Missimer et al., 2013).

The low-pressure membrane filtrations are relatively new technologies and they are mainly two types; ultrafiltration (UF) and microfiltration (MF). These membranes provide a physical barrier, based on membrane pore size that will reject anything larger than these pores. The use of UF and MF membranes has emerged in the last decade and began to show acceptance in SWRO desalination plants, and it is expected to grow more rapidly as SWRO pretreatment in the next few years (Figure 1.2) (GWI, 2014). This is mainly due to the superior water quality these membranes usually provide, in addition to the lower chemicals consumption compared to conventional methods. Moreover, the better water quality provided by these membranes could lead to a higher operating flux and a longer life for the RO membranes, which could be a more economically viable option in the long run (Kim et al., 2009; Prihasto et al., 2009).
However, MF/UF membrane fouling remains the main drawback for its application. It is the accumulation of different substances on the surface of the membrane that causes the membrane to partially or fully block its pores. Some of the known types of fouling include particulate fouling, organic fouling, biofouling, or a combination of more than one type of fouling (Voutchkov, 2008). The rate of the foulants accumulating on the membrane’s surface depends on the feed water quality. Under harsh conditions, a rapid decrease in the permeate flux will occur (at constant feed pressure). Therefore, frequent cleaning of these membranes is required to maintain the required water flux and its quality. In current practice, usually a lot of chemicals are required to restore the membrane permeability after a series of backwash using UF permeate, which have several negative effects as described above. Finding better alternative cleaning techniques is essential to follow the rapid capacity increase and advancement in the UF membrane processes.
The proposed carbon dioxide (CO₂) nucleation cleaning technique is considered as a novel procedure that combines both hydraulic and chemical cleaning. It is based on the formation of CO₂ bubbles at the membrane surface or within its pores, which clean the membrane physically when they nucleate and move away from the membrane surface to the module vent, while also cleaning chemically through the reduction of the solution’s pH where it acts as a new acid-cleaning medium. Through an extensive literature search, only one paper was found which investigated this technique for an RO membrane system, where the spacer acted as the nucleation site (Ngene et al., 2010). The author of this paper found that the performance of this procedure was far better than air scouring and forward flushing.

1.2 Problem statement

Fouling of UF/MF membranes is the main drawback of the development of their application as SWRO pretreatment. Due to this problem, more frequent cleaning is required that if it is not done properly will lead to frequent, or longer, shutdowns and a decrease in the overall efficiency of the plant operation. The limitation of the current low-pressure membrane cleaning techniques that leads to high operational cost in addition to the effects using chemical cleaning agent on the surrounding environment necessitates the search for novel cleaning techniques. These novel techniques are expected to elongate the lifetime of the membranes, be friendly to the environment and be operated at lower operational cost.
1.3 Research hypothesis

This study is aimed at enhancing the operation of low-pressure hollow-fiber membranes by developing novel methods for cleaning the membranes. A novel cleaning technique is proposed in this study, which consist of backwashing the UF membranes using saturated CO$_2$ solution that nucleates bubbles through the membrane pores under the drop in pressure.

By using saturated CO$_2$ solution to clean the membranes as a backwash solution, bubbles will start nucleating within the pores of the membrane due to the drop in pressure since they are the most preferred sites for CO$_2$ bubbles nucleation. These bubbles are then expected to clean the membrane pores and its surface physically during their de-attachment from the membrane surface. Although the solution has a low pH value, it is not expected to have a major effect on the cleaning of most types of foulants used in this study.

1.4 Research Objectives

The main objective of this research is to control the fouling of low-pressure hollow-fiber membranes by using saturated CO$_2$ solution as an alternative novel method of cleaning. This technique has a potential to clean membranes more efficiently while providing more environmentally friendly operations. The main objective of this research can be divided into the following sub-objectives:

- Building a custom-made experimental setup to perform the testing on different UF/MF hollow-fiber membranes.
• Proof of concept: saturating a solution with CO$_2$ under different temperatures, pressures and salinities to analyze the nucleation of bubbles through the membrane pores.
• Using saturated CO$_2$ solution to clean the membrane.
• Studying the efficiency of using Milli-Q (MQ) water (ultrapure water).
• Studying the effect of sudden pressure drop during the backwash with saturated CO$_2$ solution on the nucleation and membrane cleaning.
• Evaluating the cleaning performance of saturated CO$_2$ solution for different compositions of fouling.

1.5 Thesis content

The research thesis consists of five chapters including this chapter and they are presented as follows.

Chapter 2: It presents a literature review on the state of the art of the current techniques used in controlling membrane fouling. It also discusses the need for developing alternative cleaning techniques that could minimize the use of chemical additives and enhance the pretreatment performance. The theory behind the use of the saturated CO$_2$ solution properties to clean the membranes is also presented in this chapter.

Chapter 3: the procedure and methodology used for the experimental investigation conducted in this research is presented in this chapter.
Chapter 4: the results and discussion of all experimental work conducted for this research project are presented in different sections and discussed in details.

Chapter 5: the research thesis concludes by giving a summary of the outcome of this research and gives some recommendations for further research work planned for the future.
1.6 References


CHAPTER 2

LITERATURE REVIEW

2.1 Summary

In this chapter, a comprehensive literature review of the thesis subject is presented. The first section describes the current water desalination technologies in use, its market growth and its importance in supplying fresh water to population in arid and semi-arid countries, focusing mainly on seawater reverse osmosis (SWRO) membrane desalination process and the need for an efficient pretreatment (conventional and low pressure membranes processes) for better and stable performance of the reverse osmosis (RO) desalination plants. The following section covers an overview of conventional RO pretreatment and ultrafiltration (UF) membranes used as an alternative pretreatment technology and discusses the different operational and fouling issues of UF membranes. Then, the current practical cleaning techniques of hollow fiber UF membranes typically used as pretreatment in RO systems are presented in the next section. Finally, the last section gives the basic principles of the novel carbon dioxide (CO₂) nucleation cleaning technique for UF membrane application, which is the main purpose of this study.

2.2 Water desalination

Water desalination technologies consist of removing all suspended solids, dissolved salts, organics and any other contaminants from feed water making
it safe for human consumption (or safe for its intended application). Many water-stressed countries, especially located in arid and semi-arid areas, are augmenting their water supply with desalinated water to meet the continuous increased water demand caused by growth triggered by industrial expansion, increased demand by population, agriculture, and tourism development. In some areas, including in the Kingdom of Saudi Arabia (KSA), desalination is no longer a marginal or supplemental water resource as very large cities and some countries rely fully (100%) on desalinated water for domestic and industrial supplies (Ghaffour, 2009).

Due to this huge lack of fresh water resources, desalination became a very essential practice for meeting the global demand of fresh water, not only in the Middle East and North Africa (MENA) region but it has been implemented in more than 150 countries including USA, China, and Europe, e.g. Spain, Cyprus and Malta.

The continuous increase in the water demand made the desalination market grow by more than 5% annually reaching, at present, a total capacity of more than 80 million m$^3$/day and it is expected to reach about 100 million m$^3$/d in the next few years (IDA, 2015). The two main desalination technologies commonly practiced are thermal-based (e.g. multi-stage flash (MSF), multi-effect distillation (MED), thermal vapor compression (TVC)) and membrane-based technologies (e.g., reverse osmosis (RO), electrodialysis (ED/ED Reversal which is mainly used for brackish water desalination)). While both of them are energy intensive, RO membrane technology is generally more economical than the thermal technology (Ghaffour et al., 2013). For this
reason, the capacity of membrane-based desalination plants has increased more rapidly than thermal-based plants during the last decade (see Figure 2.1). Of the global desalted water produced by the different technologies, 65% of the total capacity is produced by the RO membrane process, while 21% and 7% is produced by the thermal processes MSF and MED, respectively, and the remaining is produced by other technologies. The desalination source water is split with 59% from seawater and 22% from brackish water sources, and the remaining percentage from surface water and saline wastewater (Figure 2.2) (IDA, 2015).

Figure 2.1: Installed membrane and thermal capacity, 1980-2015 (cumulative) (IDA, 2015).
The increase of desalination capacity is caused primarily by increases in water demand as mentioned above but also by the tremendous reduction in water desalination cost as a result of significant technological developments that result in making desalinated water cost-competitive with other water sources (Reddy & Ghaffour, 2007).

SWRO process is dominating the current water desalination market although it requires a very extensive pretreatment to maintain a stable operation of the system, especially for challenging feed waters. Pros and cons of the different pretreatment technologies are presented in the next section.

2.3 Conventional and membrane pretreatment technologies for RO membrane desalination

Pretreatment is an essential part of the RO membrane desalination process. It consists of removing all potentially fouling compounds from the source water to ensure a stable and efficient operation of the desalinating membranes. Silt,
suspended solids and natural organic matter (NOM) that pass the pretreatment step to the desalinating RO membranes could cause a loss of production in these membranes, which is referred to as membrane fouling (Voutchkov, 2008). If these fouling compounds are accompanied with the existence of naturally occurring microorganisms, this could make it a perfect food source for these organisms and make them form a biofilm on the surface of the membrane. This is usually known as biofouling, and it usually causes a significant loss of membrane productivity over time. This loss of productivity will lead to increasing the energy to maintain the same level of production (increase of pressure drop through the membrane modules), and this might lead to a decreasing quality of the produced water as well. In addition, this would require more frequent cleaning and shutdown of the plant, and eventually reduce the lifetime of the membrane, and would ultimately cause a reduction in the overall efficiency of the plant. Therefore, pretreatment is an essential step in protecting the desalinating RO membranes and maintain its operation. Studies have shown that capital and operation costs for pretreatment systems could reach up to 50% of the total desalination plant cost (AlMashharawi, 2011).

Conventional pretreatment systems usually consist of coarse screens to filter the large objects from entering the plant, followed by granular filters (or dual media filters (DMF)). These systems are commonly complemented with the addition of some chemicals to enhance the performance (see Figure 2.4a), such as chlorine to control the biological growth, acid to control scaling, and coagulants or flocculants to enhance suspended solids removal (Voutchkov,
2008; Wolf et al., 2005). Other chemicals are also used in pretreatment, e.g. antiscalant to control RO membrane scaling and the addition of sodium metabisulfate to neutralize chlorine to protect the RO membranes from oxidation. Conventional pretreatment systems usually provide a quality of water that is acceptable to RO membranes. However, in regions where the raw seawater fluctuates, the cost of pretreatment becomes higher due to the high chemical consumption needed to produce the required water quality for a safe RO operation (Prihasto et al., 2009).

Low-pressure membrane filtration is relatively a new technology and consists mainly of two types: microfiltration (MF) and ultrafiltration (UF). These membranes provide a physical barrier, based on membrane pore size that will reject anything larger than these pores. The use of UF and MF membranes has emerged in the last decade and began to show acceptance in SWRO desalination plants, and it is expected to grow more rapidly as seawater reverse osmosis (SWRO) pretreatment in the next few years, as shown in Figure 2.3 (GWI, 2014). This is mainly due to the superior water quality these membranes usually provide, in addition to the lower chemicals consumption compared to conventional methods (Al-Mashharawi, Ghaffour, Al-Ghamdi, & Amy, 2013). Moreover, the better water quality provided by these membranes could lead to a higher operating flux and a longer life for the RO membranes, which could be a more economically viable option in the long term (Kim et al., 2009; Prihasto et al., 2009). Strainers of 80-100 microns are commonly used prior to UF membranes to remove large suspended solids (see Figure 2.4b). Low concentration (low dosing rates) coagulants are sometimes injected to
enhance the removal of small colloids or organics depending on the feed water quality though that some seawater desalination plants do not use any chemicals for the UF operation. Silt Density Index (SDI) which is commonly used in SWRO plants as an indicator to predict RO membrane fouling has always lower values for UF permeates than filtrate from conventional pretreatment (i.e. DMF) regardless of feed water quality (Rachman, Ghaffour, Wali, & Amy, 2013). In some cases where feed water quality is really challenging such as during red tide events, a combination of dissolved air flotation (DAF) enhanced by coagulation followed by UF membranes is used (Figure 2.4c).

Figure 2.3: The low-pressure membrane market 2005-2018: estimated new contracted permeate flow by year (GWI, 2014).
Table 2.1: Comparison of conventional and MF/UF pretreatment  
(Vedavyasan, 2007).

<table>
<thead>
<tr>
<th></th>
<th>Conventional pretreatment</th>
<th>MF/UF pretreatment</th>
<th>Benefits</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Capital costs</strong></td>
<td>Cost competitive with MF/UF.</td>
<td>Slightly higher than conventional pretreatment. Costs continue to decline as developments are made.</td>
<td>Capital costs of MF/UF could be 0–25% higher, whereas life cycle costs using either of the treatment schemes are comparable.</td>
</tr>
<tr>
<td><strong>Footprint</strong></td>
<td>Calls for larger footprint.</td>
<td>Significantly smaller footprint.</td>
<td>Foot print of MF/UF could be 30-50% of conventional filters.</td>
</tr>
<tr>
<td><strong>Energy requirements</strong></td>
<td>Less than MF/UF as it could be gravity flow.</td>
<td>Higher than conventional.</td>
<td>MF/UF requires pumping of water through the membranes. This can vary depending on the type of membrane and water quality.</td>
</tr>
<tr>
<td><strong>Chemical costs</strong></td>
<td>High due to coagulant and process chemicals needed for optimization.</td>
<td>Chemical use is low, dependent on raw water quality.</td>
<td>Less chemicals.</td>
</tr>
<tr>
<td><strong>RO capital cost</strong></td>
<td>Higher than MF/UF since RO operates at lower flux.</td>
<td>Higher flux is logically possible resulting in lower capital cost.</td>
<td>Due to lower SDI values, RO can be operated at 20% higher flux if feasible, reducing RO capital costs.</td>
</tr>
<tr>
<td><strong>RO operating costs</strong></td>
<td>Higher costs as fouling potential of RO feed water is high resulting in higher operating pressure. One experiences frequent cleaning of RO membranes.</td>
<td>Lower RO operating costs are expected due to less fouling potential and longer membrane lifetime.</td>
<td>The NDP (net driving pressure) is likely to be lower if the feed water is pretreated by MF/UF. Membrane cleaning frequency is reduced by 10–100%, reducing system downtime and prolonged element life.</td>
</tr>
</tbody>
</table>
2.3.1 Ultrafiltration (UF) membranes

UF membranes have typically pore sizes in the range of 5-20 nm, or molecular weight cut off (MWCO) in the range of 50-200 kDa. They are very effective in the removal of all particles larger than the pore size, such as colloids, suspended solids, bacteria, and dissolved organics with ferric salt addition. Turbidity and SDI values could be lowered 90% of the time to below 0.1 NTU and below 3, respectively (Voutchkov, 2008). However, it does not effectively remove organics and microorganisms that could potentially affect the operation of RO membranes (Figure 2.5).
2.3.2 Configurations of UF membranes

UF membranes are most commonly made in a hollow-fiber membrane configuration, however, it could also be offered in spiral wound configuration (flat sheet membranes), as shown in Figure 2.6.
Hollow-fiber membrane configuration provides several advantages over spiral-wound module, such as hydrodynamic efficiency, backwashability and integrity. Furthermore, feed water can flow in the lumen side of the fibers (in-out) or vice versa (out-in). The relatively high flux in UF membranes would likely result in a hydrodynamic inefficiency for spiral wound membranes. This is caused by the pressure drop in the sheets connected to the central collector. In addition, the multi-layers of a spiral wound membrane will make

Figure 2.6: Hollow-fiber UF membrane configuration (top). Dots on the outer surface represent the membrane pores, while the “id” represents the inner diameter of the fiber (Bahshwan, 2012). Spiral-wound membrane configuration (bottom) (AlMashharawi, 2011).
the backwash an issue due to a de-lamination possibility. Hollow-fiber membranes, on the other hand, provide higher integrity than spiral wounds, and defects in a hollow-fiber membrane could be repaired. Moreover, spiral-wound membranes are likely to get fouled by particulates and suspended solids near the feed spacer area if the feed quality is relatively bad. In this work, hollow fiber membranes (out-in configuration) have been used. Therefore, these types of membranes will be the focus in the subsequent chapters.

2.3.3 Modes of operation in UF membranes

UF membranes could be operated in a dead-end or cross-flow operation mode, as shown in Figure 2.7. In dead-end filtration mode, the water flows perpendicularly to the membrane surface and all feed water is going through the membrane. This will make the particles quickly accumulate on the membrane surface and clog the pores which will decrease the productivity, and hence, more frequent cleaning would be required, such as backwash cleaning technique. In cross-flow operation mode, the flow is parallel (tangential) to the surface of the membrane which will help in sweeping away the particles in the feed suspension and will allow the membrane to be operated for a longer time without backwash. However, operating in cross-flow mode requires more pressure to reach a productivity level similar to the dead-end mode, which makes the process energy intensive. This is the main reason for the wide application of dead-end mode in UF pretreatment in RO systems.
2.3.4 Materials of UF membranes

UF membranes are manufactured from different types of polymers that could offer a wide range of operational capabilities for the end-user. Most commonly, Polyethersulfone (PES), Polyvinylidene fluoride (PVDF), Polyacrylonitrile (PAN), Cellulose Acetate (CA), Polyethelene (PE) and Polypropylene (PP) are used.

2.4 Fouling of UF membranes

As it is the case for any membrane filtration process, UF membrane fouling remains the main drawback for its application (Al-Mashharawi et al., 2013). Fouling is the accumulation of different substances on the surface of the membrane that cause the membrane to internally, partially or fully block its pores leading to a reversible or irreversible fouling. Some of the known types...
of fouling include particulate fouling, organic fouling, biofouling, or a combination of more than one type of fouling (Voutchkov, 2008).

“It should be noted that natural organic matter (NOM), depending on its properties and origin, may also adhere to the surface of UF and MF membranes and cause significant productivity loss by plugging the membrane pores, adsorbing to the internal matrix of the membranes, and forming a cake of organic matter on the membrane surface.” (Voutchkov, 2008).

The rate of the foulants accumulating on the membrane surface depends on the feed water quality. Under harsh conditions, a rapid decrease in the permeate flux will occur (operation at constant feed pressure). Therefore, frequent cleaning of these membranes is required to maintain the required water flux and its quality. Current cleaning techniques include backwash mostly using chemicals to restore the membrane permeability. Finding better alternative cleaning techniques are essential to follow the rapid increase in capacity and advancements in the UF membrane processes.

2.5 Cleaning of UF hollow-fiber membranes

Cleaning of UF hollow-fiber membranes depend on several parameters and operational conditions, such as its configuration and feed water quality. Different cleaning methods are applied in practice, this include flushing, backwashing, air scouring or chemical cleaning. In order to ensure a sustainable operation and to minimize the operational cost, frequencies and intensities of these cleaning procedures are carefully selected and optimized.
The cleaning processes of UF hollow-fiber membranes are mainly two types; hydraulic cleaning and chemical cleaning.

2.5.1 Hydraulic cleaning

Hydraulic cleaning procedure depends on the type of filtration process used. For inside-out filtration process the hydraulic cleaning is usually conducted by a forward flushing to remove any loose foulants deposited on the membrane surface and then followed by a backwash with UF permeate where the flow is reversed (permeate to feed, in this case inside-out) to remove the particles and deposits that were resistant to forward flushing and to remove the foulants inside the membrane pores (Figure 2.8, bottom). In the outside-in type of filtration, the hydraulic cleaning is almost the same as inside-out filtration except that air scouring is sometimes used to enhance the hydraulic cleaning process (Figure 2.8, top). Air scouring is the flow of air bubbles around the hollow-fiber membranes. Its cleaning mechanism is achieved by causing the fibers to shake rapidly, and as a result, make the fouling layer get loose and then becomes easy to clean or to flush. Both shear forces and vibration are the main effective parts in this procedure (Cui & Taha, 2003; Guigui, Mougnot, & Cabassud, 2003; Ndinisa, Fane, Wiley, & Fletcher, 2006; Serra et al., 1999; Willems et al., 2009).

The hydraulic cleaning is usually repeated every 15-90 minutes for 20-60 seconds depending on the fouling rate and the type of the feed water. In many cases this process is efficient to some extent until the fouling becomes irreversible and the process becomes costlier to operate. In this case,
additional processes might be required, such as chemical cleaning, to recover the initial condition of the membrane.

Figure 2.8: MF/UF filtration and backwash flow regimes, (top) outside-in, (bottom) inside-out.
2.5.2 Chemical cleaning

The chemical cleaning procedure depends on the severity and irreversibility of the fouling on the membrane surface. If the fouling is not severe, then regular backwash procedure with the addition of some chemicals is applied which is referred to as Chemical-Enhanced Backwash (CEB). The addition of chemicals would enhance the removal of the fouling layer from the membrane surface and restore its flux (membrane regeneration). In extreme cases, this will require the membrane to be soaked in the cleaning solution for some time and is referred to as Cleaning in Place (CIP). Many chemicals can be used for cleaning the membranes depending on the fouling layer characteristics. For example, acids are used for cleaning inorganic substances, while organic substances are usually cleaned using a base. Chlorine and caustic soda are commonly used to clean the system. Finding a better cleaning method which is more efficient in terms of membrane permeability restoration, frequency of cleaning and its duration for each cycle as well as to be more environmentally friendly (no chemicals used) is essential for a more efficient and low-cost UF pretreatment systems. In this study, we propose the use of CO2 nucleation to clean the UF membranes.

2.6 CO2 nucleation

CO2 nucleation cleaning technique is considered as a new procedure that cleans through the nucleation of bubbles formed on the membrane surface. It is based on the formation of CO2 bubbles at the membrane surface or within its pores, which clean the membrane physically when they nucleate and move
away from the membrane surface to the module vent, while also might provide an additional cleaning chemically through the reduction of the solution’s pH to 4 where it acts as a weak acid-cleaning medium. Through an extensive literature search, only one paper was found which investigated this technique for an RO membrane system by applying a forward flashing using CO$_2$ solution in Milli-Q water, where the nucleation site occurred on membrane spacer channels aiming to remove biofilms fouling (Ngene et al., 2010). The authors of this paper found that the performance of this procedure was far better than air scouring, nitrogen sparging and forward flushing.

2.6.1 Solubility of CO$_2$ in water

CO$_2$ is considered as one of the most soluble gases in water, and this is mainly due to polarity. This means that under the same conditions of pressure, temperature, salinity and using the same volume of water, much more CO$_2$ gas is dissolved compared to other gases such as oxygen (O$_2$) or nitrogen (N$_2$). This is the main reason for selecting CO$_2$ rather than any other gas.

The solubility of gases is calculated using Henry’s law:

$$C = kP_{gas}$$  \hspace{1cm} \text{(Equation 2.1)}

where $C$ is the solubility of a gas at a fixed temperature in a particular solvent (in units of M or mL gas/L), $k$ is the Henry's law constant (often in units of M/atm) and $P_{gas}$ is the partial pressure of the gas (often in units of Atmosphere).
As shown in Figure 2.9, the solubility of CO$_2$ decreases with the increase of water temperature, especially at low temperatures where the CO$_2$ solubility decreases from 3.3 g gas/Kg water to 1.7 g gas/Kg water when water temperature increases from zero to 20 °C. At room temperature (25 °C) where our experiments have been conducted, the solubility of CO$_2$ is 1.5 g gas/Kg water.

![Figure 2.9: Solubility of CO$_2$ in water versus temperature.](image)

On the other hand, Tables 2.2-2.4 present the solubility of CO$_2$ in water, expressed as mole fraction of CO$_2$ in the liquid phase, for different partial pressures of CO$_2$ ranging from 5 kPa to one atmospheric pressure (101.325 kPa) and temperatures ranging from 0 to 100°C (Table 2.2), at various total
pressures ranging from 50 to 1,000 kPa and at various CO\textsubscript{2} partial pressures ranging from 50 to 500 kPa for temperatures ranging from zero to 160\degree C, Table 2.3 and Table 2.4, respectively. As shown in these Tables and Figure 2.10, the solubility of CO\textsubscript{2} increases with the increase of the partial and total pressures of CO\textsubscript{2} (Carroll, Slupsky, & Mather, 1991; Prini & Crovetto, 1989).

Table 2.2: Solubility of CO\textsubscript{2} in water for different partial pressures of CO\textsubscript{2} and temperatures. The estimated uncertainty is about 2\% (Carroll et al., 1991; Prini & Crovetto, 1989).

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<th>20</th>
<th>30</th>
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Table 2.3: Calculated solubility of CO\textsubscript{2} in water at various total pressures (Carroll et al., 1991; Prini & Crovetto, 1989).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Solubility of CO\textsubscript{2} in water at various total pressures (Solubility in mole fraction × 1000, pressure in kPa)</th>
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Table 2.4: Calculated solubilities for CO\textsubscript{2} in water at various CO\textsubscript{2} partial pressures (Carroll et al., 1991; Prini & Crovetto, 1989).

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<th>Temperature (°C)</th>
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Figure 2.10: Solubility of CO$_2$ in water for different pressures (1 to 30 atmospheres) and different temperatures.

Figure 2.11 shows the relation between CO$_2$ and pH. When CO$_2$ dissolves in water, it forms carbonic acid (H$_2$CO$_3$), as shown in the following reaction:

$$\text{CO}_2 \text{ (aq)} + \text{H}_2\text{O} \text{ (aq)} \rightleftharpoons \text{H}_2\text{CO}_3 \text{ (aq)}$$

Carbonic acid (weak acid) then dissociates into bicarbonate (HCO$_3^-$) and then to carbonate (CO$_3^{2-}$), as shown in the following reactions:

$$\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{O} + \text{H}^+ + \text{HCO}_3^-$$

$$\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{O} + \text{H}^+ + \text{CO}_3^{2-}$$

The reaction could be also represented as following:

$$\text{CO}_2 \text{ (aq)} + \text{H}_2\text{O} \text{ (aq)} \rightleftharpoons \text{H}_2\text{CO}_3 \text{ (aq)} \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$$
Each of these compounds will be dominant in a certain pH range, as it is shown in Figure 2.11. A water saturated with CO₂ is expected to have a pH value of 4.

![Figure 2.11: Fractional contribution of dissolved CO₂ versus pH (Zeebe, 2009).](image)

### 2.6.2 Nucleation theory

Nucleation of gas bubbles within a solution happens either when there is a high level of supersaturation of this solution, or if there are some gas cavities that usually exist within the walls of the container or within the solution bulk (Bauget & Lenormand, 2002; Jones, Evans, & Galvin, 1999). The latter is the most occurring case since it only needs low levels of supersaturation. This is
because the nucleation energy barrier for the gas cavities are much lower than in the classical case.

(Jones et al., 1999) described four different types of nucleation: Type I classical homogeneous nucleation, Type II classical heterogeneous nucleation, Type III pseudo-classical nucleation, and Type IV non-classical nucleation. At low levels of supersaturation, Type IV is the main type of nucleation occurring. This is due to the availability of pre-existing gas cavities within the container walls or in the solution that acts as nucleation sites since there is no energy barrier to overcome in this case.

The reason for choosing to dissolve CO$_2$ gas in the solution instead of any other gas is, besides being an easily available gas, it has a very high solubility in water compared to other gases. This will make it very beneficial during the degassing process where it will release more bubbles compared to other gases under the same conditions.

There are two types of CO$_2$ bubble formations: homogeneous nucleation and heterogeneous nucleation. The homogeneous nucleation is not expected to take place in the membrane cleaning process because it requires more than 100 atmospheres of pressure difference between the pressure inside the module and the dissolved gas pressure. Therefore, the main nucleation type will be heterogeneous where bubbles are formed within pre-existing gas pockets located at micro-cracks on the membrane surface, or what could be referred to as the pores within the membrane structure (see Figure 2.12) (Scardina & Edwards, 2000).
2.6.3 Techniques for enhancing nucleation

The rate of CO$_2$ bubbles nucleation is affected by several factors, which include:

1- Degree of super-saturation: the higher the degree of CO$_2$ super-saturation in a solution, the higher the driving force for bubble formation.

This degree of saturation can be controlled either by changing the solution’s pressure, temperature or its salt content. Increasing the pressure or reducing the temperature of CO$_2$ solution relative to the ambient conditions will increase the CO$_2$ saturation level and force more bubbles to dissolve in the solution (Figure 2.13). The increase in salt content to around seawater levels in the solution reduces the degree of CO$_2$ solubility, especially at higher temperature and lower pressure, by about 20%, as shown in Figure 2.13. The water activity will be more
saturated with more salt contents available in the same volume of water, and hence there will be less capacity for the CO₂ gas to dissolve in water. Therefore, water with less salinity is preferred to have higher saturation of CO₂.
Figure 2.13: Solubility of CO$_2$ under different temperatures, pressures and salinity values (calculated using the prediction models reported by (Duan, Sun, Zhu, & Chou, 2006)).
2- Nucleation surface properties: as mentioned previously, the presence of defects or roughness at the membrane surface aid the formation of gas pockets in these sites and become preferred nucleation sites for CO$_2$ bubbles. This means that the higher the number of these sites, which is expected to be very high in highly porous membranes, the higher the nucleation rate of CO$_2$ bubbles.

Further details on CO$_2$ nucleation at different operating conditions and its application in backwashing UF membranes as a novel cleaning technique will be discussed in the next chapters.
2.7 References


CHAPTER 3

MATERIALS AND METHODS

3.1 Summary

The first section of the materials and methods chapter describes the experimental set-up and materials used for the filtration and cleaning parts, and then more details on the different module designs used in this investigation are presented in the following section, followed by providing some details on the membranes used in the different experiments. The procedure for preparation of the saturated carbon dioxide (CO$_2$) solution and the different feeds used in this research as well as a description of water and membrane characterization and analysis using different analytical equipment and measurements are described in the following sections. Finally, the experimental procedure and matrix, including nucleation rate, transmembrane pressure recovery, determination of the cleaning frequency, flux comparison, and an improved method to enhance the cleaning performance, of all conducted experiments are given in the last section of this chapter.

3.2 Experimental set-up

A fully customized experimental unit comprising the filtration cell and cleaning components has been locally designed and built at KAUST’s workshop. A schematic diagram and picture of the unit are presented in Figure 3.1. This unit was made from materials, mainly SS316, Plexiglass and Polyvinyl
chloride (PVC), that are resistant to harsh conditions, e.g. high salinity and acids, due to the nature of feed and cleaning solutions used for testing. All sensors to measure flow-rate, pressure, temperature, and weight, were made of compatible materials and high accuracy (±0.25%, as given by the different manufacturers). All sensors have been calibrated and double-checked manually to confirm the accuracy of the measurements.

The setup is fully automated and controlled using Labview (a software from National Instruments Company). The software uses the feedback from the pressure and flow sensors to control the pump in order to operate at constant pressure or at constant flux, as desired, throughout the experiment. It also collects the data from all sensors, views the measurements and plots the experimental data on the monitor, and saves a copy of the data into a file for further analysis. Data collected include date, time, pressure, temperature and flux. The data are usually logged every 5 seconds to gather as much information as possible while maintaining a smooth and stable operation. The software is flexible to include any other data measurement and logging frequency as needed.
Figure 3.1: A schematic diagram of a software controlled experimental setup, and picture of the complete unit.
3.3 Module designs

Several new modules have been designed and built at KAUST workshop specifically for this study (Figure 3.2). After collection of feedback from a series of testing, better modules have been designed and manufactured at the same workshop. The selected module was made of Plexiglass where the transparent surface makes it easier to visually observe the accumulation of foulants during filtration, as well as observing the bubbles and detachment of the deposited foulants during the membrane cleaning operation. The module was specially designed with a unique fiber holder which held each fiber separately without being touched or compressed to other fibers (Figure 3.2). This makes it easier for observing the fibers from all directions and not having them affect each other during filtration, cleaning and bubbles observation.

Another upgraded setup containing a new module design enabling to avoid the deficiencies observed in the previous designs, such as the clarity of the surface, the simplicity and cost of replacing membrane fiber holders, and the ease of opening the module to replace or clean the membrane fibers has been used in all subsequent experiments (Figure 3.3). The new design is also smaller, lighter and looks much better. Moreover, it has the flexibility to run in both dead-end and cross-flow filtration modes using flow valves. The module has 20 cm length of fibers with a case diameter of 40 mm. Different number of membrane fibers could be installed in the module.
Figure 3.2: First generation of modules: top-left: empty fiber holder with the module shown in the background; top-right: fiber holder fixed in the module; and bottom: module holding fibers completely assembled and ready for testing.
Different commercially available microfiltration (MF) and ultrafiltration (UF) membranes fabricated with different materials, characteristics and configurations have been preliminary tested using different feed water quality (Al-Mashharawi et al., 2013; AlMashharawi, 2011; Bahshwan, 2012; Kalantan, 2013). The selected membrane that was used in this research was a UF hollow-fiber Polyvinylidene fluoride (PVDF) membrane type having a mean pore size of 0.03 μm operating in an outside-in operation mode. In all

3.4 Membranes

Figure 3.3: Improvement of the new module design generated from feedback from preliminary results. The right module was used for the experiments presented in the next chapters.
experiments, 5 membrane fibers with a length of 20 cm and a total surface area of 40.84 cm$^2$ were used. Figure 3.4 shows hollow fiber membranes assembled on different fiber holders.

![Figure 3.4: Hollow fiber PVDF membranes assembled on fiber holders.](image)

### 3.5 Preparation of the saturated CO$_2$ cleaning solution

A pressure vessel filled with de-ionized water connected to a CO$_2$ gas cylinder, and connecting this solution to the backwash side of the filtration module was added to the experimental setup to run the novel cleaning technique used in this study (Figure 3.5). This solution is prepared by firstly filling the pressure vessel with de-ionized water, then injecting CO$_2$ gas through gas diffusers in the solution while keeping the pressure vessel open.
to strip all other gases from the solution. After 10-15 minutes, the pressure vessel is closed and maintained under a specific pressure for a couple of days to ensure that the solution is fully saturated with CO\textsubscript{2}. The saturated CO\textsubscript{2} solution is then introduced into the membrane module as a backwash solution. The drop in pressure through the membrane will make the solution in a temporary supersaturated state. This will make the solution not in an equilibrium state and the gas will tend to escape until it reaches its equilibrium under the new pressure condition. This state of the solution, in addition to the pre-existing gas cavities (Bauget & Lenormand, 2002; Jones et al., 1999), will cause the solution to instantly release the CO\textsubscript{2} bubbles out of the solution. This rapid release of bubbles will help in detaching the foulants from the surface of the membrane and within its pores.

![Pressure vessel for CO\textsubscript{2} saturation](image)

Figure 3.5: Picture showing the pressure vessel used for CO\textsubscript{2} saturation in de-ionized water.
3.6 Feed solutions

The main fouling observed in low-pressure membranes in seawater reverse osmosis (SWRO) systems is due to organic fouling. Hence, this study focuses on the cleaning of the fouling caused by organic matter. Sodium alginate was used to represent the organic fouling in UF membranes, with the addition of colloidal silica in some experiments. These types of foulants are common model foulants widely used in the literature to represent organic and particulate fouling. Solutions with different concentrations of these compounds dissolved in Milli-Q (de-ionized) water were prepared and tested to ensure that an amount of 1-2 mg/L of total organic carbon is present in the solution to foul the membrane fibers in a reasonable time. Additionally, in order to test the efficiency of the proposed cleaning technique for other types of fouling which are typically found to severely foul the UF membranes in water treatment and desalination applications, colloidal silica have also been used in the feed solution. Ultra-high purity colloidal silica provided by Sigma-Aldrich with an average particle size of 23 nm, and Fuso Chemical Co. Ltd. (LUDOX® HS-40), with an average particle size of 113 nm, were used. Detailed characteristics of these colloids are presented in Figures 3.6-3.8 and Table 3.1. Characteristics (Figure 3.6 and Table 3.1) have been provided by the manufacturers and size distribution data (Figure 3.7 and Figure 3.8) have been performed in the laboratory using Malvern Zetasizer Nano ZS.

Several concentrations of sea salts were also added to the solutions to increase the ionic strength and to increase the fouling effect on the membranes, which mimics the actual marine salinity conditions. Several
research papers have shown that the use of divalent ions help attaching the fouling particles together and form a more difficult fouling condition (Costa, Depinho, & Elimelech, 2006; Katsoufidou et al., 2010).

Figure 3.6: Characteristics of the particle silica provided by Sigma-Aldrich.
Figure 3.7: Particle size distribution of SiO₂ purchased from Sigma-Aldrich, average particle size = 23 nm.

Table 3.1: Characteristics of the particle silica provided by Fuso Chemical Co. Ltd. (LUDOX® HS-40).

<table>
<thead>
<tr>
<th>TEST</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance (Color)</td>
<td>Colorless</td>
</tr>
<tr>
<td>Appearance (Form)</td>
<td>Viscous Liquid</td>
</tr>
<tr>
<td>Ludox HS-40</td>
<td>Confirmed</td>
</tr>
<tr>
<td>pH (@ 25 Deg C)</td>
<td>9.2 - 9.9</td>
</tr>
<tr>
<td>Specific Gravity (@ 60 Deg F)</td>
<td>1.292 - 1.312</td>
</tr>
<tr>
<td>Viscosity (@ 25 Deg C)</td>
<td>≤ 45.0 cps</td>
</tr>
<tr>
<td>Silica (% SiO₂)</td>
<td>39.0 - 41.0 %</td>
</tr>
<tr>
<td>Ratio (SiO₂:Na₂O)</td>
<td>89 - 101</td>
</tr>
<tr>
<td>Surface Area (m²/g)</td>
<td>198 - 258</td>
</tr>
<tr>
<td>Sulfate (as Na₂SO₄)</td>
<td>&lt; 0.080 %</td>
</tr>
<tr>
<td>Transmission</td>
<td>≥ 52.0 %</td>
</tr>
<tr>
<td>Registered Trademark</td>
<td>Confirmed</td>
</tr>
</tbody>
</table>

LUDOX is a registered trademark of W.R. Grace & Co.-Conn.
Figure 3.8: Particle size distribution of SiO₂ purchased from Fuso Chemical Co. Ltd., average particle size = 113 nm.

3.7 Characterization and analysis

Several water and membrane characterization methods were used to analyze the efficiency of the new cleaning technique. The feed and permeate waters were both characterized during each test. Typical analysis done on each sample includes the measurement of turbidity, pH, conductivity and total organic carbon (TOC) content. Turbidity was measured using Hach 2100Q Portable Turbidimeter, and pH was measured using CyberScan pH 6000, while conductivity was measured using OAKTON CON 510 Benchtop Meter, and TOC was measured using TOC-V CPH equipment from Shimadzu. However, in some cases, more analytical equipment was used to explore more details of the samples, such as Liquid Chromatography - Organic Carbon Detection (LC-OCD) to know more about the fractions of the organic matter. Some other measurements include the use of the Gas
Chromatography - Thermal Conductivity Detector (GC-TCD) to provide a qualitative analysis of CO\textsubscript{2} gas in the cleaning solution sample.

While mainly focusing on water analysis, a few more characterization techniques were used to analyze the effect of cleaning on the membrane surfaces, mainly using the Scanning Electron Microscopy (SEM) to take high-resolution images of the membrane surface before and after applying cleaning, and comparing it to clean membranes. This gives an indication on how efficient the cleaning is in removing all accumulating foulants from the surface of the membrane.

3.8 Experimental procedure

In order to investigate this innovative UF membrane cleaning technique, a series of experiments has been designed to measure some of the properties of this cleaning technique. These experiments are described in the following paragraphs.

3.8.1 Nucleation rate

The first parameter to check is to confirm the amount of CO\textsubscript{2} gas dissolved in water by visually observing the nucleation rate on the surface of the membrane. Higher amounts of dissolved gas are expected to show higher amounts of gas nucleated at the drop in pressure. This is tested at different pressure, temperature and salinity values of the CO\textsubscript{2} saturated water.

The experiments were conducted by diffusing CO\textsubscript{2} gas in water contained in a pressure vessel. The solution is then left under pressure for two days to make
sure that it reached saturation. Then the CO\textsubscript{2} saturated water is used to backwash the UF hollow-fiber membrane where the bubbles will start nucleating and showing on the surface of the membrane. These bubbles were visually observed, recorded and compared to all other conditions. Experiments are repeated for each condition of the tested parameters. Table 3.2 shows the experimental conditions of each test.

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Pressure (bar)</th>
<th>Temperature (\degree C)</th>
<th>Salinity (NaCl, g/l)</th>
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<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>20</td>
<td>0</td>
</tr>
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</tr>
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<td>10</td>
</tr>
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<td>9</td>
<td>1.0</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>10</td>
<td>1.0</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>11</td>
<td>2.0</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>12</td>
<td>2.0</td>
<td>20</td>
<td>50</td>
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<tr>
<td>13</td>
<td>2.0</td>
<td>20</td>
<td>100</td>
</tr>
</tbody>
</table>

3.8.2 TMP recovery

After selecting the best operating parameters for the cleaning solution, this solution was used to clean the UF hollow-fiber membrane after fouling it with sodium alginate (representing organic fouling). The experiments were conducted at constant flux of 73 L/h.m\textsuperscript{2}, and the increase in transmembrane pressure (TMP) was recorded. The recovery of TMP is measured after
cleaning with the CO$_2$ saturated solution and compared to cleaning with de-ionized water. Table 3.3 shows the experimental conditions of some tests.

<table>
<thead>
<tr>
<th>Number</th>
<th>Concentration of sodium alginate (mg/l)</th>
<th>pH</th>
<th>Sea salts (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
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</tr>
<tr>
<td>6</td>
<td>4</td>
<td>9</td>
<td>10</td>
</tr>
</tbody>
</table>

Preliminary results using 4 mg/L sodium alginate and 4 g/L of sea salts in feed water indicated that cleaning the membrane using Milli-Q water and UF permeate through backwash have similar performance, as shown in Figure 3.9. Therefore, in our subsequent experiments we used Milli-Q water to backwash the membranes, as we do not have sufficient UF permeate, especially when backwashing the membrane several times is required.
Figure 3.9: Flux decline with time of feed water containing 4 mg/L of sodium alginate and 4 g/L sea salts using two different backwash solutions (Milli-Q water and UF permeate), each cycle last for 30 minutes.

### 3.8.3 Cleaning frequency effect

Cleaning after each specific type of fouling could require longer cleaning times or more frequent cleaning cycles to recover the initial permeability of the membrane. This experiment is designed to compare the number of cleaning cycles required to recover the initial condition of the membrane by comparing the cleaning with CO2 nucleation to cleaning with Milli-Q water. 10 cycles of cleaning with Milli-Q water is compared to 1 cycle of cleaning with CO2 solution.
3.8.4 Flux comparison

The backwash solution composition affects the efficiency of the cleaning effect of the backwash. Using saturated CO$_2$ solution as the backwashing solution between cycles could enhance the efficiency of the operation. In this experiment, two different cleaning solutions were used as a backwash solution at different conditions of fouling. The UF hollow-fiber membrane was backwashed with Milli-Q water and compared to backwashing with CO$_2$ saturated solution.

3.8.5 Sudden-drop CO$_2$ backwash

In the previous sections of this chapter, we have introduced a new cleaning technique that utilizes the nucleation resulting from the use of saturated CO$_2$ solution to clean the UF membrane. This new technique showed better cleaning in all cases compared to cleaning with Milli-Q water. In this part, we have optimized the performance of the developed cleaning technique by modifying its procedure to achieve an even better cleaning performance for more severe membrane fouling cases, especially when dealing with challenging feed waters.

As it was discussed in the previous sections, the nucleation of bubbles occurs due to the high supersaturation level of the solution, or because of the occurrence of gas cavities that act as nucleation sites with very little energy barrier to overcome (Bauget & Lenormand, 2002; Jones et al., 1999). Also, it was discussed that the nucleation of bubbles is affected by the degree of supersaturation, and by the nucleation surface properties.
Experiments have shown that more bubbles are nucleated at higher depletion rates (Bauget & Lenormand, 2002). Figures 3.10-3.13 illustrate how the depletion rate could affect the number of bubbles nucleated. At instant pressure drop (one step depletion), all bubbles are formed instantly, and this is because the initial time corresponds to the maximum supersaturation level (Figure 3.10). When the depletion rate increases from 0.1 bar/day to 1 bar/day (faster reduction in pressure), and if the threshold of nucleation is reached, higher supersaturation level is reached for higher depletion rate (Figure 3.11 and Figure 3.12). The total number of activated bubbles is directly related to the supersaturation level, and hence, higher depletion rates will show a higher number of bubbles nucleated. Please note that after a time $t^*$, no more bubbles are produced (all sites have been activated). The number of bubbles formed for two depletion rates are shown in Figure 3.13. It is clear how the faster drop in pressure yields to a higher number of bubbles formed.

In the special case (sudden-drop of pressure), all bubbles are formed instantaneously (Bauget & Lenormand, 2002). This means that sudden-drop of pressure (1-step drop) would provide the (higher) maximum supersaturation level of the solution. Also, the cleaning is not effective anymore after time $t^*$. This is why we are introducing a modified cleaning procedure based on these principles to maximize the efficiency of the cleaning.
Figure 3.10: Simplified representation of the evolution of the number of bubbles and the liquid pressure vs. time during depletion by one step $\Delta P$ (Bauget & Lenormand, 2002).
Figure 3.11: Low depletion rate (0.1 bar/day): a) pressure as a function of time, and b) corresponding supersaturation as a function of time (Bauget & Lenormand, 2002).
Figure 3.12: High depletion rate (1 bar/day): a) pressure as a function of time, and b) corresponding supersaturation as a function of time (Bauget & Lenormand, 2002).
The principle of the sudden-drop backwash cleaning is shown in Figure 3.14. After the first sudden-drop in pressure, a few seconds are given to allow the bubbles to detach from the membrane surface and then another cycle of pressurizing and de-pressurizing is done. This is made intermittently for several cycles to achieve the maximum number of bubbles nucleated in the least amount of time.
The first experiment of this series represents a comparison of using backwash with Milli-Q (BW(MQ)) water against backwash using saturated CO$_2$ (BW(CO$_2$)), and also by using the advanced procedure of this novel cleaning method, namely the sudden-drop backwash technique using saturated CO$_2$ (SD-BW(CO$_2$)).

Several experiments have been conducted to test this new cleaning procedure. At first it was compared to using the original procedure of this novel cleaning as it was introduced in in the first part. After that, a few more experiments with more severe fouling condition were tested.

Figure 3.14: Principle of sudden-drop (intermittent) backwash using CO$_2$. 
3.9 References


CHAPTER 4

RESULTS AND DISCUSSION

4.1 Summary

The results and discussion chapter is divided into two main parts, namely:

i) proof of concept and experimental evaluation of carbon dioxide (CO₂) nucleation as a novel membrane cleaning method. In this technique, a saturated CO₂ solution prepared in a separate closed pressure vessel under specific conditions, which will be optimized in this investigation, such as pressure, temperature, salinity and pH, is used as a backwash solution (from permeate to feed side of the hollow fiber membranes) exactly in the same way as the current industrial practices where conventional backwash using UF permeate is widely applied. However, the objective of our work is not to replace the latter cleaning method only but we are expecting that the novel cleaning technique developed in this study will be proposed as an alternative solution for both the frequent conventional backwash using UF permeate and the periodic chemical cleaning required to restore the membranes after severe fouling.

ii) an advanced CO₂ backwash cleaning technique consisting of backwashing dissolved CO₂ intermittently, called ‘sudden-drop CO₂ backwash’. This is an improvement of the novel cleaning technique by applying an intermittent sudden drop in pressure to allow for more bubbles to be nucleated under the same time used for backwash.
4.2 Nucleation rate

As described in Section 2.6.1, different parameters affect the solubility of CO₂ in water, and hence will affect the efficiency of cleaning using this solution. Therefore, several experiments have been conducted by testing different operating parameters of the cleaning solution, mainly pressure, temperature and salinity.

Before testing the different parameters experimentally, the values of saturated CO₂ were calculated under these different conditions using the prediction models that were reported by (Duan et al., 2006), and an example is shown in Figure 2.13 (a, b and c) which is presented in Section 2.6.3. According to these calculations, it is clearly shown that the solubility of CO₂ increases with the increase in pressure. However, the solubility decreases with the increase in either temperature or salinity. These results are in line with reported data using different calculation methods (for different pressures and temperatures), as shown in Tables 2.2-2.4 and Figure 2.10 presented in Section 2.6.1 (Carroll et al., 1991; Prini & Crovetto, 1989).

These conditions were then experimentally compared to each other, and resulted in matching the trend shown in the previous calculations. Each tested condition was video recorded to make it more accurate in visual analysis. Snapshots of specific times (15s, 30s, 45s, and 60s) of these videos were captured to show the difference of each condition, as shown in Figure 4.1 and Figure 4.2. It is clear from these snapshots that more bubbles are present at higher pressures and lower salinity of the solution. The number of bubbles in each snapshot reflects the nucleation rate in each of the tested conditions,
and the higher rate of nucleation means that there is more CO$_2$ dissolved in the solution.

The optimum cleaning solution would be the solution that would produce more bubbles generated from nucleated CO$_2$ solution, leading to potentially more efficient cleaning of the membrane by lifting the foulants away from the membrane pores and its surface. From the previous results we conclude that the solution providing the best cleaning efficiency would be the one with higher pressure, lower temperature and with low or no salinity (see Section 2.6.3, Figure 2.13 (a, b and c).

Increasing the pressure from 1 bar to 2 bars exhibited higher bubbles at a shorter time. From Figure 4.1, we observe that a sufficient number of bubbles have been nucleated uniformly across the membrane fibers pores at 2 bars, while at 1 bar a longer backwashing time was required to reach a more uniform nucleation of CO$_2$ on the membrane surface. In addition, we observe that more bubbles are formed on the membrane fibers with backwashing time, especially at the first 30 seconds of the backwash and then a steady state is reached, suggesting that 30 seconds could be an optimum backwash time which is very attractive for practical applications. On the other hand, backwash time doesn’t seem to affect the cleaning efficiency for different salt concentrations except for very high concentration (100 g/L NaCl), as shown in Figure 4.2, which is typically above the range of ultrafiltration (UF) applications.
Figure 4.1: Screenshot after 15, 30, 45 seconds, and 1 minute of initiating the backwash using CO$_2$ saturated solution. (Top: 1 bar, Bottom: 2 bars; using room temperature and without salinity).
Figure 4.2: Screenshot after 30 seconds and 1 minute of initiating the backwash using CO₂ saturated solution. (Top left: 10 g/L NaCl, Top right: 50 g/L NaCl = 50 g/L NaCl, and Bottom: 100 g/L NaCl; using room temperature and pressure = 2 bars).
4.3 TMP recovery

Several tests have been conducted in a way similar to a chemical enhanced backwash (CEB) for a better comparison with the current practices of low pressure membrane cleaning methods, such as UF membrane pretreatment in seawater reverse osmosis (SWRO) systems. This will also help investigating the possibility of replacing the CEB with the new cleaning technique, i.e. using conventional backwash with water for a number of filtration cycles which is determined by the tolerated pressure drop and then apply CO$_2$ cleaning after a more severe fouling (when backwash with water cannot recover the transmembrane pressure increase or the membrane permeability between the cycles). By using it in this way rather than applying cleaning with CO$_2$ after each cycle means that less cleaning solution is required, and hence, reducing the cost of cleaning.

Figure 4.3 (a and b) show results of the experiments at constant flux of 73 L/h.m$^2$ with 6 cycles of filtration, each cycle lasts for 60 minutes followed by a 1 minute of backwash using MQ water, and then a backwash using CO$_2$ solution was applied. It is clearly shown that applying CO$_2$ cleaning significantly reduced the transmembrane pressure (TMP) for all experiments to almost the initial conditions of the tests (before fouling), including at very high sodium alginate concentrations (8 mg/L). We also observe that feed solutions with higher pH exhibited higher TMP but after backwash with CO$_2$ the TMP has stabilized for both cases (Figure 4.3).
Figure 4.3: TMP versus time using 4 mg/L sodium alginate at pH 6 and pH 9, respectively, running at constant flux of 73 L/h.m², followed by a backwash with Milli-Q water (after 6 cycles) followed by CO₂ backwash.
Figure 4.4: TMP versus time using 8 mg/L sodium alginate at pH 6 and pH 9, respectively, running at constant flux of 73 L/h.m², followed by a backwash with Milli-Q water (after 6 cycles) followed by CO₂ backwash.

The addition of sea salts (10 g/L for this case) to the 4 mg/L sodium alginate at the same pH values led to a higher TMP reaching 12 psi after the third cycle and it was hardly maintained at the same value using backwash with MilliQ water (it is widely reported that calcium enhances the fouling potential in presence of sodium alginate), however, as it is the case for sodium alginate only, the membrane permeability was recovered with one backwash using saturated CO₂ solution for both pH values, as shown in Figure 4.3 (a and b).
Figure 4.5: TMP versus time at different pH using Milli-Q water (after 6 cycles) followed by CO₂ backwash, 4 mg/L sodium alginate + 10 g/L sea salts, running at constant flux of 73 L/h.m².

Figure 4.6 shows the results of experiments at constant flux of 73 L/h.m² with 6 cycles of filtration, each cycle lasts for 60 minutes followed by a 1 minute backwash using Milli-Q water, and then a backwash using CO₂ solution for feed water containing 4 mg/L sodium alginate and 20 g/L sea salts. The experiment with backwash using Milli-Q water did not complete 60 minutes in the last few cycles because it reached the maximum TMP for the membrane (Figure 4.6). As shown in the figure, backwash with Milli-Q water was not able to recover the membrane from the severe fouling which is most probably irreversible fouling, however, backwash using CO₂ solution showed a very
stable operation from the first cycle. TMP remains very acceptable (for high feed concentration) between cycles suggesting that CO$_2$ bubbles have efficiently cleaned the membrane pores followed by sweeping away the deposit from the membrane surface, most probably due to the higher lift force created by the nucleation of CO$_2$, which was not observed for Milli-Q water. This result showing the high efficiency of CO$_2$ cleaning at higher salt concentration also suggests that the proposed cleaning method could be used for saline UF filtration application where typically UF permeate containing high concentration of salts is used for backwash. This also incorporates energy saving as well since the stable operation of the experiment using CO$_2$ backwash at a much lower TMP value compared to using Milli-Q water backwash is saving the energy used to pump the water through the membrane, typically with double flow rate value compared to feed flow rate during filtration. In addition, it will keep the plant operating with minimum shutdowns which are required to clean the membranes chemically in order to recover the membrane permeability after severe fouling.
Figure 4.6: A comparison between backwash using Milli-Q water and backwash using CO₂, for feed solution containing 4 mg/L of sodium alginate and 20 g/L of sea salts with pH adjusted at 8, running at constant flux of 73 L/h.m².

Figure 4.7 shows a possible mechanism of CO₂ bubbles nucleated through the membrane pores and scrubbing on its surface offering a lift force which is high enough to detach the foulants from the surface compared to the conventional backwash which is mostly based on flashing at relatively higher shear forces.

The reaction between carbon dioxide and water is an example of an equilibrium reaction (Equation 4.1). Aqueous CO₂ reacts with water forming carbonic acid, H₂CO₃ (aq). Carbonic acid may lose protons to form
bicarbonate, $\text{HCO}_3^-$, and carbonate, $\text{CO}_3^{2-}$. In this case the proton is liberated to the water and consequently decreasing the pH.

$$\text{CO}_2 (\text{g}) + \text{H}_2\text{O} (\text{l}) \leftrightarrow \text{H}_2\text{CO}_3 (\text{aq}) \quad \text{(Equation 4.1)}$$

Figure 4.7: Nucleated $\text{CO}_2$ bubbles through the membrane pores and on its surface during backwash.

$\text{CO}_2$ solution desorption in the pressure vessel versus time is presented in Figure 4.8. After the drop in pressure in the saturated $\text{CO}_2$ solution from 28 psi to 0 psi, the dissolved gas will start to nucleate and desorb from the solution. This process will continue until the solution reaches an equilibrium state. This process is expected to happen at the same rate as the sorption of $\text{CO}_2$ into water to form the $\text{CO}_2$ saturated solution. It is noted that the 50% of the equilibrium state is reached almost instantly (within a few seconds of the
drop in pressure). However, the rate decreases with time until equilibrium is reached after 54 hours (Figure 4.8).

![Figure 4.8: Release of pressure from 28 psi to 0 psi in a CO$_2$ saturated solution showing how long it takes to desorb the gas until equilibrium is reached.](image-url)

This solution (CO$_2$ saturated solution) was analyzed using Gas Chromatography - Thermal Conductivity Detector (GC-TCD). The results are presented in Figure 4.9. First, to set the reference, pure CO$_2$ gas was analyzed, as shown in Figure 4.9(a), then Milli-Q water was analyzed (Figure 4.9(b)). After that a solution with Milli-Q water with sparging CO$_2$ gas into it was analyzed (Figure 4.9(c)), and finally the CO$_2$ saturated solution from the pressure vessel was analyzed, as shown in Figure 4.9(d). It is clear that the
solution from the pressure vessel contains only water and CO₂, and it has a high concentration of CO₂. This qualitative analysis confirmed that the composition we are using in our novel cleaning technique is made of water and CO₂ only.
Figure 4.9: Gas Chromatography - Thermal Conductivity Detector (GC-TCD) results.
Figure 4.10 gathers the results of all tests under the studied operating parameters by showing the recovery of the initial TMP while cleaning with CO₂ solution compared to cleaning with Milli-Q water. It is very clear that cleaning with the CO₂ solution is more efficient in recovering the initial permeability of the membrane for all tested operating parameters. In most of the cases, CO₂ cleaning successfully recovered the initial permeability within 1 minute only of cleaning which is very helpful for its application in practice, especially when treating feeds with high fouling potential. Values above 100% might refer to a better cleaning that was achieved using this novel technique compared to conventional chemical cleaning (sodium hypochlorite was used in between experiments). In some cases, chemical cleaning did not fully recover the initial condition of the membrane, however, the range was within the accepted experimental error range (5%).

These results also show the possibility of using this novel cleaning technique as a replacement to chemical cleaning, as it could recover the initial permeability of the membrane in most of the cases studied.
Figure 4.10: TMP recovery of backwash using Milli-Q water versus backwash using saturated CO₂ solution for different feed concentrations (sodium alginate and sea salts), and different pH values (values above 100% remain within the experimental errors).

4.4 Cleaning frequency effect

Since one cycle of backwash was compared in the previous section between Milli-Q water and saturated CO₂ solution, more cycles of backwash were performed in a new set of experiments to see how many cycles of backwash could be able to recover the initial condition of the membrane.

Figure 4.11 and Figure 4.12 show the results of these experiments. 10 cycles of backwash using Milli-Q water were conducted for every tested fouling composition (see an example in Figure 4.11). Interestingly, in all the studied
experiments, the one cycle of backwash using saturated CO$_2$ solution recovered more than the combined 10 cycles of backwash using Milli-Q water, except for one case (4 mg/L sodium alginate and 10 g/L sea salts at pH 6) where one CO$_2$ cleaning cycle was not able to fully recover the membrane permeability, which might be due to a limitation of the performance under these operating conditions as it was also observed in similar case presented in Figure 4.10, but the flux recovery was higher than one cycle of a normal backwash using Milli-Q water (Figure 4.12). We can also observe that the repetitive backwash with Milli-Q water after the second cycle was not very helpful in recovering the membrane permeability, which again shows the possibility of using the novel cleaning technique (saturated CO$_2$ solution) to replace the CEB (in practice CEB is applied periodically to recover the membrane permeability when TMP becomes higher than the recommended value while applying the regular backwash using UF permeate).
Figure 4.11: TMP recovery of 10 cycles of backwash using Milli-Q water after 6 cycles of operation, running at constant flux of 73 L/h.m².
In order to test the efficiency of the proposed novel cleaning method for a more challenging situation, a set of experiments using feeds containing 4 mg/L sodium alginate, 50 mg/L of colloidal silica and 4 g/L of sea salts have been performed. As shown in Figure 4.13, TMP increases significantly throughout the filtration time, reaching 25 psi after 10 cycles. Backwashing the UF membrane fibers with Milli-Q water was not efficient starting from the second cycle. However, applying backwash with saturated CO$_2$ solution starting from the third cycle (backwash in the first 3 cycles using Milli-Q water) could recover the UF membrane fibers permeability, as shown in Figure 4.14. After the first CO$_2$ backwash (1 min duration), we observe a stabilization of TMP in the last cycles cleaned with 2 min CO$_2$ backwash, suggesting that the
applied first 1 min CO$_2$ backwash was very efficient in cleaning the severe membrane fouling observed in the first three cycles.

Figure 4.13: TMP increase versus time (backwash with Milli-Q water with 30 min cycles) for a solution containing 4 mg/L sodium alginate, 4 g/L sea salts, and 50 mg/L colloidal silica.
Figure 4.14: TMP increase versus time (backwash with Milli-Q water and saturated CO₂ solution after the third cycle with 15 min for each cycle) for a solution containing 4 mg/L sodium alginate, 4 g/L sea salts, and 50 mg/L colloidal silica.

A physical observation through 2 snapshots taken from a video before and after cleaning with saturated CO₂ solution, presented in Figure 4.15, shows clearly the detachment of foulants, mainly colloidal silica, from the membrane fibers. This detachment process has been observed for several minutes although the picture taken before the cleaning and the visual observation during the experiments do not really show a big amount of foulants deposited on the membrane surface. This is most probably because colloidal silica and other foulants might be transparent for eye observation when they are
deposited on the membrane surface or they have been continuously detached from the membrane pores and its surface as a result of CO$_2$ nucleation explaining the severe fouling observed in the first 3 cycles and the incapability of sweeping away these foulants hydraulically using backwash with Milli-Q water only, but also confirming our assumption of CO$_2$ nucleation occurring within the membrane structure (inside the membrane pores) and the efficiency of CO$_2$ solution in cleaning irreversible fouling.

Figure 4.15: Snapshot before and after cleaning with saturated CO$_2$ backwash for a feed solution containing 4 mg/L sodium alginate and 50 mg/L colloidal silica.
4.5 Flux comparison

In order to confirm our constant flux results, a set of experiments at constant pressure (5 psi) have been performed to investigate the efficiency of the cleaning methods. Figure 4.16 shows the experiments with 10 cycles of filtration, each cycle lasts for 30 minutes followed by 1 minute of backwash. During the first filtration cycles, backwash with Milli-Q water and CO₂ solution showed similar performance but starting from the third cycle backwash with Milli-Q water only was not sufficient to recover the membrane permeability. However, Backwash with saturated CO₂ solution maintained the initial flux until the last cycle suggesting again that this novel cleaning technique could be a promising method to replace the conventional CEB cleaning in UF membrane applications, such as surface water treatment or water desalination, even at high feed concentrations causing severe fouling.

By increasing the concentration of sea salts in the feed solution from 4 g/L to 20 g/L, the cleaning with saturated CO₂ solution showed the same trend, as shown in Figure 4.16. The decrease in the flux rate with CO₂ cleaning was showing even a more stable operation with a very slight decrease as compared to cleaning with Milli-Q water. However, by increasing sodium alginate concentration in the feed to 16 mg/L with 20 g/L sea salts, CO₂ cleaning could not recover the membrane permeability better than the conventional backwash using Milli-Q water although it looks like both methods reached a stable flux but it is much lower than that of the new membrane, as shown in Figure 4.17.
Figure 4.16: A comparison between backwash using Milli-Q water and backwash using CO$_2$ solution for a feed solution containing 4 mg/L sodium alginate and 20 g/L sea salts running at constant pressure of 5 psi.

The high sodium alginate concentration in the feed led most probably to a severe irreversible fouling with a significant flux decline observed mainly in the first half minute of operation, which represents typically standard fouling in UF and MF applications (Ghaffour, 2004), as shown in Figure 4.18. This result suggests that at such high organic concentration, a coagulation process might be required prior to UF filtration process (Tabatabai et al., 2014; Schurer et al., 2012; Li et al., 2016; Lee et al., 2000). In order to have a comparable results of our proposed cleaning method, all our UF experiments have been conducted without coagulation.
Figure 4.17: A comparison between backwash using Milli-Q water and backwash using CO₂ solution for a feed solution containing 16 mg/L sodium alginate and 20 g/L sea salts running at constant pressure of 5 psi.
Figure 4.18: A comparison between backwash using MQ water and backwash using CO₂ for a feed solution containing 16 mg/L of sodium alginate only running under constant pressure of 5 psi.

4.6 Water analysis

Feed and permeate water analysis of a few samples (selected randomly) collected from experiments done under different operating parameters and conditions, mainly turbidity, pH, conductivity, total organic carbon (TOC), zeta potential of particle sizes have been performed mainly to make sure that the UF filtration process didn’t show any anomalies. As shown in Figure 4.19 and Figure 4.20 as an example, turbidity of feed which was initially ranging from 0.7 to 1.98 NTU has come down to almost zero in the UF permeate in all cases regardless of the other operating parameters and conditions. On the
other hand, TOC removal was fluctuating from high rate (from 1.42 mg/L in feed to 1.26 mg/L in permeate) mainly at higher pH values to very low removal efficiency (from 2.84 mg/L in feed to 0.81 mg/L in permeate), which remains in the typical range of TOC removal in the UF process depending on the used feed water and membranes parameters and characteristics (Schurer et al., 2012; Li et al., 2016). Particles size results are also very reasonable except for tests done at high pH where we have experienced higher flux decline with time (Figure 4.21).
Figure 4.19: Turbidity analysis for some of the feed and permeate water samples
Figure 4.20: Total organic carbon (TOC) analysis for some of the feed and permeate water samples
In the first part of this chapter, we have introduced a new cleaning technique that utilizes the nucleation resulting from the use of saturated CO$_2$ solution to clean the UF membrane. This new technique showed better cleaning in all cases compared to cleaning with Milli-Q water. In this part, we optimize the performance of the developed cleaning technique by modifying its procedure to achieve even a better cleaning performance for more severe membrane fouling cases, especially when dealing with challenged feed waters.

As it was discussed in the first part, the nucleation of bubbles occurs due to the high supersaturation level of the solution, or because of the occurrence of...
gas cavities that act as nucleation sites with very little energy barrier to overcome. Also, it was discussed that the nucleation of bubbles is affected by the degree of supersaturation, and by the nucleation surface properties.

The higher the depletion rate, the higher the number of nucleated bubbles (see Figures 3.10-3.13). Please note that after a time $t^*$, no more bubbles are produced (all sites have been activated). In the special case (sudden-drop of pressure), all bubbles are formed instantaneously (Bauget & Lenormand, 2002). This means that a sudden-drop of pressure (1-step drop) would provide the (higher) maximum supersaturation level of the solution. Also, the cleaning is not effective anymore after time $t^*$. This is why we are introducing a modified cleaning procedure based on these principles to maximize the efficiency of the cleaning.

The first experiment of this series represents a comparison of using backwash with Milli-Q water against backwash using saturated CO$_2$ solution, and also by using the advanced procedure of this novel cleaning method, namely the sudden-drop backwash technique using saturated CO$_2$ solution.

It is clear from Figure 4.22 presenting experimental data of feed solution containing 4 mg/L of sodium alginate and 20 g/L of sea salts that the novel backwash cleaning method using saturated CO$_2$ solution is providing a significant advantage over backwash with Milli-Q water only as demonstrated in the first part of this Chapter. Moreover, the modified procedure, i.e. sudden-drop backwash using saturated CO$_2$ solution, proved even a better cleaning efficiency and recovery of the membrane permeability throughout the experiment. The membrane permeability in each cycle was always fully
recovered although we observe a slight increase of TMP throughout the cycles keeping in mind the harsh quality of the feed water used in these experiments.

![Figure 4.22](image_url)

Figure 4.22: A comparison of three types of backwash: using Milli-Q water, saturated CO₂ solution, and sudden-drop saturated CO₂ solution for feed solution containing 4 mg/L sodium alginate and 20 g/L sea salts with pH adjusted at 8, running at constant flux of 73 L/h.m².

It is worth mentioning here that although the difference in TMP levels between experiments with backwash using saturated CO₂ solution and the sudden-drop CO₂ backwash are not very significant, however, the behavior of the fouling accumulation is totally different. It clearly shows that the sudden-drop
CO₂ backwash technique is successfully recovering the initial condition of the membrane which means the membrane pores and its surface were efficiently cleaned, while the fouling is still accumulating on the normal backwash using saturated CO₂ solution but in a much slower rate than the conventional cleaning method. This different behavior in TMP rise which is shown as a different direction of the curvature on the graph will lead to a more significant difference that could be measured in terms of energy use.

Similarly, as discussed in the first part, the addition of colloidal silica (1 mg/L) to sodium alginate (4 mg/L) and sea salts (20 g/L) in feed water made the situation worst as cleaning with Milli-Q water was not able to recover the increase of TMP after the third cycle, after which TMP was stable at 17 psi even after backwash, as shown in Figure 4.23. However, even under these severe fouling conditions the TMP could be mostly recovered after each cycle of backwash using sudden-drop saturated CO₂ solution although TMP was significantly increased from 5 psi to 10 psi during each filtration cycle.
Figure 4.23: A comparison between backwash using Milli-Q water and backwash using saturated CO₂ solution for a feed solution containing 4 mg/L sodium alginate, 20 g/L sea salts and 1 mg/L colloidal silica with pH adjusted at 8, running at constant flux of 73 L/h.m².

An additional experiment was conducted to confirm this result by increasing the feed solution’s salinity. It is also clear from Figure 4.24 presenting experimental data of feed solution containing 4 mg/L of sodium alginate and 30 g/L of sea salts that the novel backwash cleaning method using saturated CO₂ solution is providing a significant advantage over using backwash with Milli-Q water only where the latter cleaning technique failed to recover the TMP increase which remained stable at a value of 11 psi. Again, we confirm here that high salinity in the feed significantly affects the membrane cleaning.
due most probably to the irreversible fouling which was enhanced by the presence of high concentration of salts, such as calcium, as it is widely reported in the literature. However, the sudden-drop saturated CO$_2$ advanced cleaning procedure provides a better alternative cleaning of UF membranes as it could reasonably recover the TMP increase throughout the experiment as it was the case in the first experiments, although it was difficult to fully recover the membrane permeability after a few cycles.

![Graph](image)

**Figure 4.24**: A comparison between backwash using Milli-Q water and backwash using saturated CO$_2$ solution for a feed solution containing 4 mg/L sodium alginate and 30 g/L of sea salts with pH adjusted at 8, running at constant flux of 73 L/h.m$^2$. 
4.8 References


CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, a novel cleaning technique for hollow-fiber ultrafiltration (UF) membranes using a saturated carbon dioxide (CO₂) solution was developed and tested. First, optimum conditions of the proposed cleaning solution were studied showing that this solution is dissolving more CO₂ gas at higher pressure. However, it dissolves less at higher temperature or salinity of the solution. The optimum conditions were then selected to dissolve the highest amount of gas possible so that more nucleation will occur at a drop in pressure during the cleaning process. Then, the solution was tested with different UF feeds containing different concentrations of sodium alginate with the addition of different concentrations of sea salts to study the effect of organic fouling under similar conditions to saline water environment. The results showed that in all cases, the backwash cleaning with saturated CO₂ solution showed a more significant cleaning performance compared to cleaning with the conventional backwash using Milli-Q water. Backwashing with saturated CO₂ recovered the initial condition (100%) of the membrane in most studied cases. It also showed that it could potentially be used as an alternative method for the conventional CEB chemical cleaning under these conditions, hence offering an efficient membrane cleaning without the use of chemicals. A couple of experiments were also conducted with the addition of
colloidal silica to mimic extreme conditions with severe membrane fouling conditions. In these experiments, backwashing with Milli-Q water was not able to maintain a stable operation or recover the membrane’s permeability, especially after a few cycles of filtration. However, when it was backwashed with saturated CO\(_2\) solution, most of the initial condition of the membrane was recovered throughout the whole experiment (6-10 cycles each). It was also observed that the addition of colloidal silica formed a whitish semi-transparent gel layer on the surface of the membrane, which was not cleaned with Milli-Q water. However, this layer was mostly completely removed during the first minute of cleaning with saturated CO\(_2\) solution.

A modification to this novel cleaning technique aiming to enhance its performance especially for severe fouling cases was then investigated. The addition of multiple sequences of sudden pressure drop was used as the modified cleaning technique. It was reported that all bubbles are initiated instantly if the pressure was dropped in one step (Bauget & Lenormand, 2002). So in this modified cleaning, the bubbles will nucleate multiple times during one backwash cycle. This gives it a better chance of cleaning under the same cleaning time. During these experiments with sudden pressure drop, it was observed that the backwash cleaning was even better than using saturated CO\(_2\) solution without the multiple sudden drop technique. It was also noticed that the cleaning with the sudden drop saturated CO\(_2\) solution showed a better performance of the following cycles of filtration (longer operation time). It was also found that this cleaning technique helps to clean not only the surface of the membrane but its pores due to repetitive nucleation
of CO₂ bubbles, which is helpful to recover the membrane from irreversible fouling. This different fouling accumulation in the consequent cycles also showed that a reduction in the energy requirement is achieved, and a longer operation before shutdown is expected (less cleaning frequency). All of these factors show the potential of this novel cleaning technique to replace the current chemical cleaning applied in practice and how potentially significant energy saving and more environmentally friendly process could be gained.

5.2 Recommendations for future work

With a good cleaning potential shown by using this novel cleaning technique, a few recommendations for future work are suggested. First, ways of speeding up the process of saturating the CO₂ solution is to be studied. A few recommendations of stirring the solution to speed up the saturation could be looked at. Also, initially cooling down the solution could provide a faster solubility of CO₂ in water since this process is faster during the first few minutes. Moreover, this study focused on cleaning the organic matter (in our case sodium alginate), with a few tests of adding colloidal silica. It is suggested that more types of fouling to be studied to see how effective this method is in cleaning multiple types of fouling. In addition to that, different types of membranes with different materials or pore sizes could show different behavior or cleaning efficiency. We also suggest to use a high speed camera as an advanced characterization tool to see the mechanism of the nucleation of CO₂ bubbles formation and growth on the membrane surface. Finally, although it is reported that air scouring or the use of other gas such as
nitrogen during cleaning doesn’t significantly help in improving the cleaning performance due to the formation of stagnant bubbles in the flow channel (Ngene et al., 2010), a comparison study using micro-bubbles could show the difference in the mechanism of cleaning by micro-bubbles flowing on the surface of hollow fiber membrane and CO$_2$ nucleation.
5.3 References
