Assessing feasibility of reverse osmosis treatment of anaerobic membrane bioreactor industrial permeate, focusing on fouling characteristics

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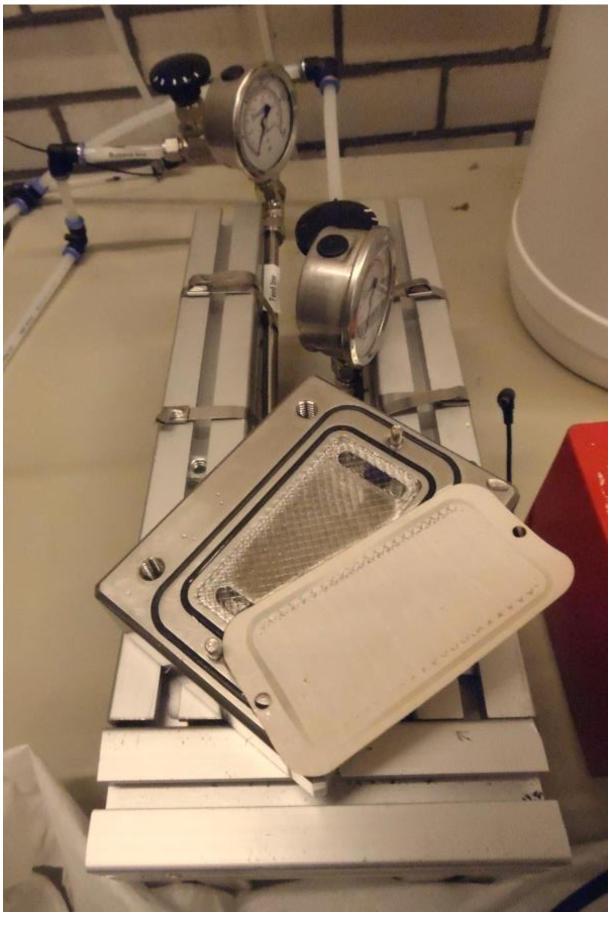

Assessing feasibility of reverse osmosis treatment of anaerobic membrane bioreactor industrial permeate, focusing on fouling characteristics

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Abstract

According to United Nations, 700 million people around the world suffer water scarcity, value that will probably double over the next ten years. Now a days, wastewater reclamation is a viable water source for irrigation, industrial purposes and even drinking water is increasing. Furthermore, anaerobic treatment has proven to be an efficient treatment compare to aerobic ones, due to reduction of up to 90% of sludge production and footprint, production of energy (as methane gas) and high applicable organic loading rates. Anaerobic Membrane Bioreactors (AnMBR) are particularly useful when treating particulate high organic load wastewater, as dairy industry one. When treating dairy industry wastewater, if AnMBR is coupled with a second step of anaerobic Reverse Osmosis (RO), high quality effluent is achieved, with almost none restriction regarding its reuse in agricultural irrigation.

AnMBR dairy industry permeate has a silt density index around 3, which implies that it is suitable to use as RO feed without provoking extreme fouling and scaling of the membrane. Moreover, this research is focus on the differences of keeping the AnMBR permeate anaerobic as RO fed, compare to aerating it. This latter brings as a consequence, 10 times higher amounts of particle formation than the anaerobic one, but with similar particle size distribution. Main salts that precipitate are calcium carbonate and calcium phosphate.

Setting, starting up and running a laboratory scale anaerobic Reverse Osmosis system coupled with batch scale AnMBR has its difficulties and challenges. System is allow to run up to a pressure of 23 bars, but no stable conditions regarding pressure or recovery are achieve. Maximum recovery is 4.2 % per meter of membrane, and high removal efficiencies are achieved in the process. However, bacteria present in AnMBR permeate and RO permeate may compromise its reuse. Values of 25 and 2 millions of active cells are found in RO concentrate (AnMBR permeate) and permeate respectively. Permeate characteristics allows its reuse with almost none restriction for irrigation, and also, for industrial processes such as cooling and boiling towers, cleaning, etc., where no direct contact with dairy industry products is expected. In order to achieve better recoveries and removal efficiencies, and less constrains in streams reuse, especial considerations regarding sterilization and disinfection must be carried out.

Acknowledgements

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Abbreviations

AnMBR	Anaerobic membrane bioreactor
AS	Activated Sludge
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
CSTR	Continuous flow stirred-tank reactor
DINAGUA	National Directorate of Water
DINAMA	National Directorate of Environment
DNA	Deoxyribonucleic Acid
EGSB	Expanded sludge bed
EPS	Extracellular Polymeric Substances
FAO	Food and agriculture organization of the United Nations
FCM	Flow Cytometric
FOG	Fat, Oils and grease
HRT	Hydraulic retention time
LPRO	Low pressure reverse osmosis
MBR	Membrane bioreactor
MF	Microfiltration
MFI	Modify Fouling Index
MLSS	Mixed liquid suspended solids
MVOTMA	Ministry of Housing, Land Planning and Environment
OLR	Organic Loading Rate
OSE	Sanitary Works of the State
PI	Propidium iodide
PVDF	Polyvinylidene fluoride
RNA	Ribonucleic Acid
RO	Reverse Osmosis
SBR	Sulphate reducing bacteria
SDI	Silt density Index
SRT	Solid retention time
SS	Suspended Solids

TDS	Total dissolved solids
TKN	Total Kjeldahl nitrogen
TMP	Transmembrane pressure
TSS	Total suspended solids
UASB	Up flow anaerobic sludge blanket
UEI-IM	Industrial Effluent Unit
UF	Ultrafiltration
UNIT	Uruguayan Institute of Technical Standards
VFA	Volatile fatty acids
VSS	Volatile suspended solids
WHO	World Health Organisation
WWTP	Wastewater Treatment Plant

CHAPTER 1

Introduction

1.1. Background

Anaerobic digestion dates from over 100 years ago, but most advances in this technology were conducted since 1970s, mainly due to the energy crisis (Van Lier, et al., 2001). When high rate reactors were developed, such us Up Flow Anaerobic Sludge Blanket (UASB) in the 1970s, it was recognised to be an effective alternative in comparison to aerobic treatment, mainly to treat industrial wastewater. Some of the core advantages on anaerobic wastewater treatment are (Henze, 2008): high treatment efficiencies, reduction of up to 90% of sludge production and footprint, production of energy (as methane gas) and high applicable organic loading rates.

Nowadays, broader applications of anaerobic wastewater treatment technologies are being carried out, and one of the most recent developments in this subject is the anaerobic membrane bioreactor (AnMBR). This technology can ensure the decoupling of sludge and hydraulic retention time, holding all biomass in the reactor and allowing degradation of even slow-degradable compounds (Dereli, et al., 2012).

Reverse osmosis technology (RO) is widely use in drinking water treatment, especially when desalination of brackish or seawater is needed. However, several countries are using RO as a post treatment of conventional wastewater treatment, for wastewater reclamation. One of the main drivers to use this technology is due to water scarcity, which may lead to an increase in water cost, compromise economic development and social crisis. When couple with AnMBR, RO has proven to be a technology well suited for treating domestic wastewater, allowing nutrient recovery and a high quality effluent (Grundestam and Hellström, 2007).

Finally, Uruguay situation regarding industrial wastewater treatment is quite diverse. Several pollution problems in Río Santa Lucía basin have arisen due to improper wastewater discharge, where dairy industries are in the top 3 of most pollutant ones, regarding organic load and nutrient (phosphorus and nitrogen) discharge (JET / DINAMA, 2010). High organic loads and nutrient concentration (primarily nitrogen and phosphorus) are the central complications in the basin, causing a significate danger to the main source of drinking water in the country. AnMBR coupled with RO systems seems to be an adequate technology for cases such as the ones of dairy industries, because a high quality effluent can be reached (low organic loads and nutrient concentration), and additionally, besides that treated wastewater can be reused for industrial purposes, there might be a possibility to recover nutrients from RO concentrate.

1.2. Problem statement

According to United Nations, 700 million people around the world suffer water scarcity, value that will probably double over the next ten years (Www.un.org, 2016). Reuse water policies will be key to prevent water crisis from getting worse, even in countries with no water limitations. Industrial water use represents around 20% of the total water consumption (Caridad Canales, et al., 2012), and reuse of treated wastewater may lead to reduce water consumption by millions of cubic meters per year. Furthermore, according to Fritzmann, et al. (2007), as water resources are used, agriculture, industry and public water users compete for them, leading to higher water prices, restrained economic development and social issues in water stress countries.

On the other hand, world estimated demand for fertilizer in 2018 will overcome the supply possibilities in several areas (FAO, 2015), causing massive impacts in agriculture and worldwide economy. Whilst the annual growth rate of nitrogen and phosphate will be around 1.4% and 2.2%, this values will reach 3.3 and 3.6% respectively for Latin America and Caribbean, contributing to 7% and around 15% of the World nitrogen and phosphate consumption (FAO, 2015). Moreover, in Latin America, fertilizer balance (supply/demand) indicates that even now, the region depends on nitrogen and phosphate imports, situation that will be worst by 2018, with a demand of nitrogen above 3,200 and almost 3,000 thousands of tons per year of phosphate, over the possible supply (FAO, 2015). Nutrients situation across the World is not only important due to its imminent scarcity, but also because wastewater discharge with high nutrient concentration into water bodies causes pollution.

In Latin America, Uruguay situation regarding pollution from excess of nutrients and organic loads in Río Santa Lucía basin is critic. Aguas Corrientes, the main drinking water treatment plant of the country, which provides fresh water to around half of Uruguay inhabitants (Ose.com.uy, 2015), use Santa Lucía Rivers as water source. Industries that discharge their wastewater into this river, agriculture and livestock are the principal pollution causes. There is an increasing need to upgrade wastewater treatment plants in the area, to improve water quality of the river, prevent further problems and, promote water reuse.

Among the most pollutant commercial enterprises in Río Santa Lucía Basin, dairy industries are in top 3 (JET / DINAMA, 2010). Dairy industry wastewater can be categorize as strong and particulate, with high organic load, suspended solids content, fats, oils and grease (Demirel, et al., 2005). Currently, high strength wastewater is mostly treated by anaerobic high rate systems and conventional wastewater processes (like Activated Sludge among others). Soluble high rate wastewater is well treated by several high rate anaerobic reactors, such as up flow anaerobic sludge blanket (UASB) and expanded sludge bed (EGSB) reactors (Liao, et al., 2006). However, wastewater with high particulate matter and high strength is hard to treat by this technology, mainly because of: slow growing biomass is not retained enough time to actually degrade all compounds, large HRT is needed for sufficient hydrolysis (Liao, et al., 2006), and finally, this type of wastewater may hamper the development of granular sludge formation and stability (Visvanathan and Abeynayaka, 2012).

Bearing in mind the provision of the preceding paragraphs, anaerobic membrane bioreactors couple with reverse osmosis systems, seems a capable technology to apply in this cases with particulate and high organic load, not only due to its high quality effluent and water reuse possibilities, but also because of the nutrient recovery potential. Reverse osmosis membranes (RO) is an effective technology to remove dissolved matter, pathogens (up to a certain extent), and nutrients, allowing wastewater reuse. When previously couple with anaerobic membrane bioreactors (AnMBRs), which allow complete retention of biomass, with a small footprint and methane production (energy recovery), RO treatment seems like a promising technology, where permeate flux (after passing through the RO) may be reclaim for industrial purposes and the concentrated flux as fertilizer. This latter may be the case when treating some industrial wastewater, with a high content of nutrients (such as nitrogen and phosphorus).

Lack of information about the characteristics of permeate of AnMBR, and treatment system of AnMBR plus RO for handling industrial wastewater, implies a challenge and gap in knowledge regarding possible and feasible applications of this technology. Assessing the possibility of coupling both system when treating dairy industry wastewater, analyse permeate and concentrate flows for reuse and nutrient recovery, may have an important impact on industrial water demand, and a better understanding in the main constrains and benefits of these technology.

CHAPTER 2

General and specific objectives

The aim of this research is to assess the feasibility and analyse the performance of an RO system, fed with permeate from an AnMBR system treating dairy wastewater. To carry out the above, a laboratory scale RO reactor will be installed and operated at Biothane-Veolia in Delft. The general research question is: *Can the permeate of an AnMBR be feasibly treated by an anaerobic reverse osmosis system for water reuse and nutrient recovery?*

The four specific objectives of the current research are as follows:

- to identify RO fouling potential fed with permeate from an AnMBR treating dairy wastewater (keeping the permeate at anaerobic conditions);
- to link the AnMBR permeate characteristics to the RO operability and efficiency;
- to assess the RO performance in terms of pollutants rejection (removal efficiencies);
- to characterize the permeate and concentrate flows of the RO systems, considering the reuse of these streams in an industrial context.

The specific objectives presented above are directly linked to the specific questions as follows:

- Which are the particulate size distribution, ions content (Cl^-, NO_3^-, Ca_2^+, K^+, Mg_2^+ among others), TSS/VSS ratio, conductivity, Langelier Saturation Index (LSI), Sild Density Index (SDI), and Modified Fouling Index (MFI) of the RO feed?
- Does the oxygen concentration influence fouling potential of the RO membrane?
- What are the operational conditions such as RO membrane flux, permeability, recovery, and rejection established during the assessment of the RO membrane?
- Which is the impact of pressure on the RO system performance? Considering the feed flow characteristics, which is the feed pressure range at which the RO system adequately perform?
- Which are the concentrations of organic matter, nutrients, pathogens, and solids on the RO permeate? What are the removal efficiencies on these compounds?

- Which are the concentrations of organic matter, nutrients, pathogens, and solids on the RO concentrate?
- Is it possible to reuse the concentrate of the RO system? For what purpose?

CHAPTER 3

Literature review

In this section, the current state of relevant literature is summarized.

3.1. Industrial water consumption and wastewater treatment: worldwide situation

As stablished in the Sustainable Development Goals (Sustainabledevelopment.un.org, 2016) *Sanitation involves the adequate management and disposal of different types of wastes with a view to minimizing harmful effects to human health and the environment*. Within this wide definition, having an adequate industrial effluent treatment plays a key role in pollution prevention and development of sustainable cities.

Water use in industries is around 20% of the whole word consumption of freshwater and continuous increase over the years (Caridad Canales, et al., 2012). These values goes up to 90% in some European countries (Europa.eu, 2016), which lead to greater volumes of wastewater produced. According to data collected by the statistical office of the European Union (Eurostat), industrial wastewater produced in 17 European countries reached up to around 14.000 millions of cubic meters per year, and the range of wastewater treated previous it is discharge into different water bodies varies from 8% (Croatia) to 60% (Czech Republic) (Europa.eu, 2016).

Since the 20th century, several wastewater treatment technologies have arisen throughout the years. These new developments were strongly influenced by what happened at time, like increase in organics loads (because of rapid growth of cities), necessity of smaller footprints, eutrophication of surface water due to an increase of nutrients in water bodies, and energy crisis. Furthermore, water scarcity issues lead to water reuse policies and new advance treatments, which are not only restricted to water shortage regions (Henze, 2008).

3.1.1. Uruguay industries and wastewater treatment

In 2014, around 14% of the Gross Domestic Product (GDP) of Uruguay was due to industrial activity, where manufacturing of food products, drinks and tobacco represent 50% of it. According to data from 2013, industries embodied 4% of the total consumption of surface water of the country, and 18% of ground water (MVOTMA-DINAMA, 2014). Water consumption for industrial purposes is about 390 million of cubic meters per year, and total effluent discharge into different water bodies around 67 million of cubic meter per year (MVOTMA-DINAGUA, 2016). Monitoring and controlling that discharges of industrial wastewater treatment plants (WWTP) are done according the require standards is responsibility of the National Directorate of Environment (DINAMA) all over the country but in the capital city, Montevideo, where the Industrial Effluent Unit (UEI-IM) is the accountable entity. Data collected is divided and evaluated regarding the main hydrographic basins: Laguna Merín, Atlantic Ocean (Océano Atlántico), Río Santa Lucía, Río de la Plata, Río Negro, and Río Uruguay, as shown in Figure 3-1.

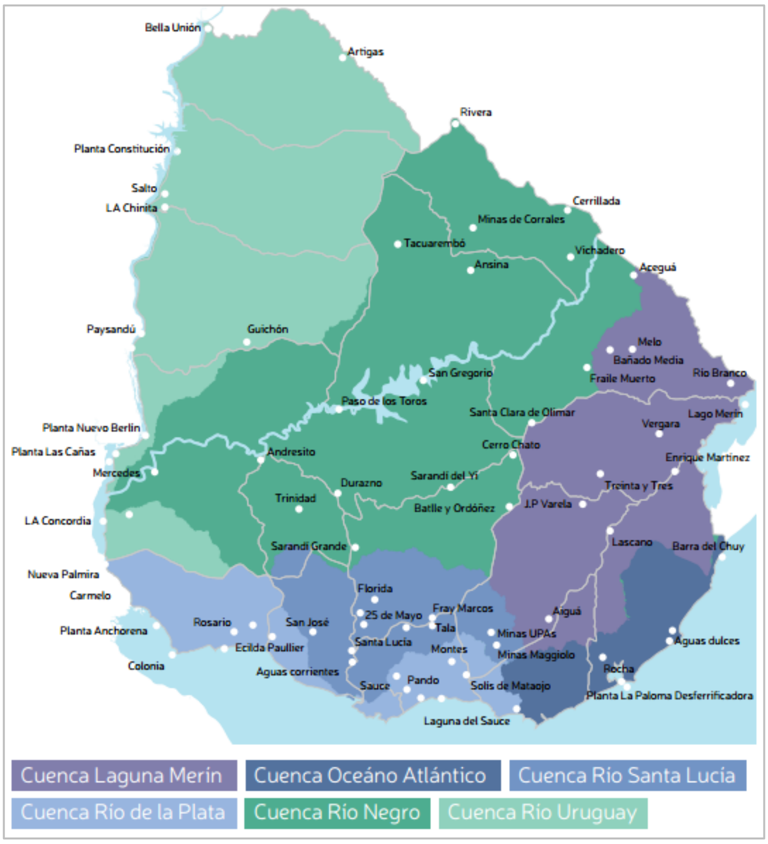


Figure 3-1: Uruguay most important hydrographic basins. Source: MVOTMA-DINAGUA (2016)

Of the 550 registered industries located all over the country, 80 are situated in the capital (Montevideo), and discharge around 7.1 million of cubic meters per year of effluents into different water bodies (IM-UEI, 2015). Decree 253/79 (Uruguay Government, 1979) stablishes that all industries generating wastewater in the production process must have an effluent treatment plant approved by the National Environment Directorate, and the treated effluent must cope with the require standards according to its final disposal (water bodies, sewer system, etc.). Allocation and amount of industrial and domestic wastewater treatment plants in the whole country are shown in Figure 3-2.

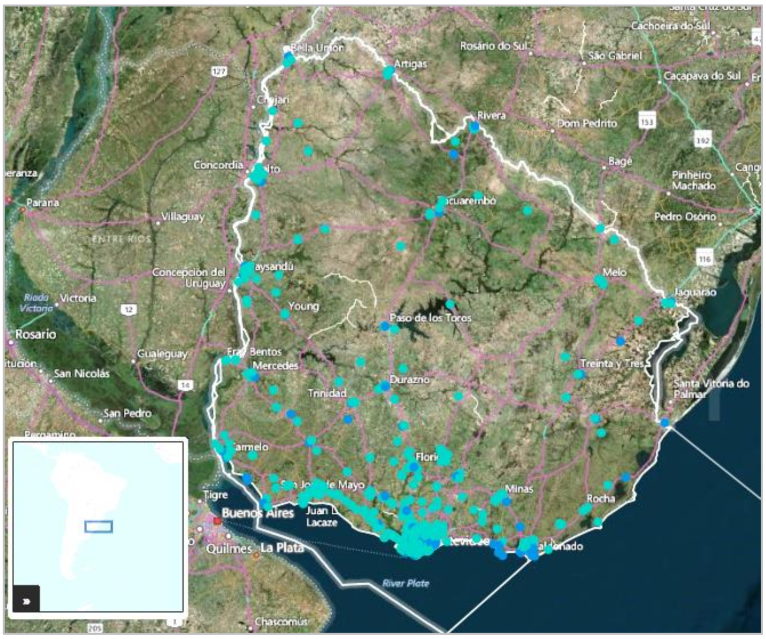


Figure 3-2: Allocation of wastewater treatment plants in Uruguay. The sky blue dots represent the industrial WWTP while the blue dots corresponds to the domestic ones. Source: Dinama.gub.uy (2016)

Even though several industries count with WWTP's, these do not adequately treat the effluent (according to the needed standards), and are responsible of discharging grater amount of organic loads and nutrients into water bodies, seriously polluting and compromising water quality. Pollution in Río Santa Lucía basin is one of the main concerns of the Uruguayan government and population, due to the fact that Santa Lucía River is one of the most important sources of drinking water and where the main drinking water treatment plant is located. As an example of problems arise, total phosphorus concentration in Río Santa Lucía basin has increased during the years, with values up 30 times higher than the required standards. Concentration of this nutrient in two main reservoirs in Río Santa Lucía basin is shown in Figure 3-3. In this particular subject, Uruguayan government has shown great concern and developed in 2013, an Action Plan to protect water of Río Santa Lucía basin (MVOTMA, 2013), which embrace a more exigent control in industrial discharge of total nitrogen and phosphorus.

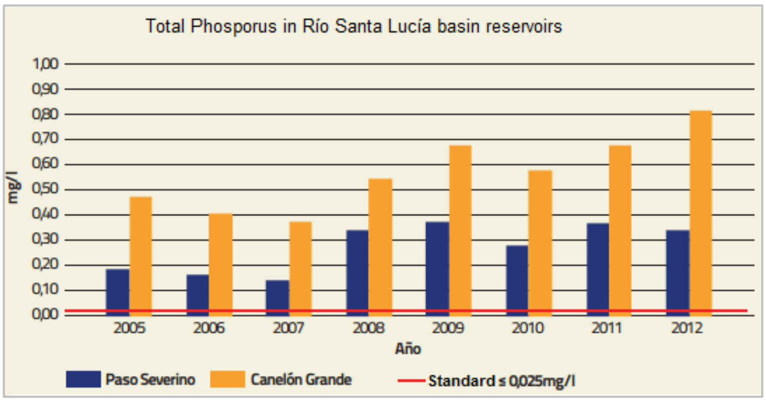


Figure 3-3: Total phosphorus in Río Santa Lucía basin reservoirs throughout the years. Source: MVOTMA-DINAMA (2014)

Besides the problem of excess amount of nutrients in water bodies, most of industries are located in the south region of Uruguay, which is the densest one. Lack of space to build or upgrade WWTP in Montevideo city is a key matter. The capital city has around 1.5 million of inhabitants, and 80 industries registered in DINAMA, of which several but not all are located in the peri-urban area (Figure 3-2). Coexistence between population and industries is delicate, and presses the latter into embracing smaller footprints for their WWTP, deal with noxious odours to prevent unrest in neighbouring, etc.

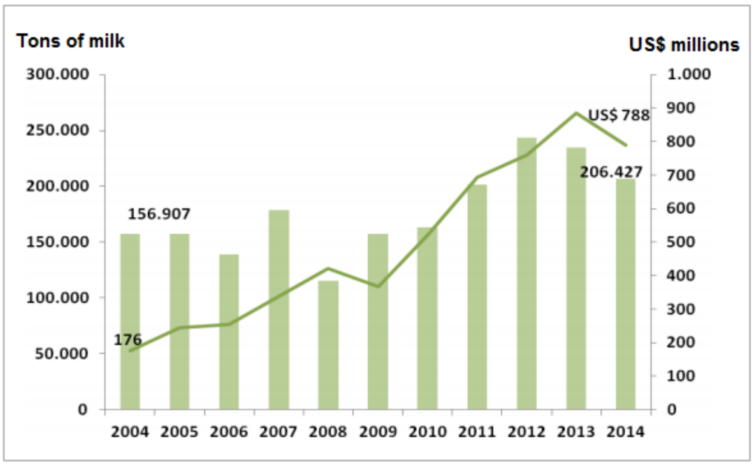
3.1.2. Worldwide dairy industry situation and in Uruguay: need to improve wastewater treatment plants

According to IDF (2014), milk consumption has increase worldwide over the years, reaching in 2014 around 110 kg per capita per year (including fresh milk and dairy products, butter, cheese, milk powder, skim milk powder and others). Furthermore, this value rise up to 165 and 270 kg per person per year in South America and Europe respectively.

The top three industries regarding 2012 sales are located in Europe, two in France (Danone and Lactalis) which sum up represent around 32 billion euros in sale, and one in Switzerland (Nestlé) with sales that reach up 23 billion euros per year (Rabobank.com, 2016). Additionally, as stated by PMMI (2013), dairy market is part of the fastest market growing sector, and forecasts made for 2020 consider worldwide milk production of 827 million tons (compare to 692 million tons in 2013).

Dairy sector plays a key role in Uruguayan economy and it is one of the industrial sectors that generates more added value. Furthermore, in 2014 dairy exports represented around 8% of the total goods sales in Uruguay (Uruguay XXI, 2015). Overall, since 2012 milk productivity index has increase around 12%, value that reach to 60% when compare to 2007 data (Uruguay XXI, 2015). In 2014, milk production in Uruguay was above 2,300 million litters, where the principal cause of production increase is due to an improvement of production per animal and surface area (DIEA, 2016). The growing milk production goes hand in hand with the increase in the price aid to the producer, which was USD 0.46 per litter of milk.

High per capita consumption of milk in Uruguay was not enough for the offer to overcome the domestic market supply, what forced industries to expand exports, given the comparative advantages of the country (contrasting to some other Latin America countries) (Uruguay XXI, 2015). Even though dairy exportations slightly decrease in 2014, it represented almost 800 million dollars and above 200,000 tons of milk (Figure 3-4), data revealing the importance of this market in Uruguay. Most exports can be divided between 5 main dairy companies, where CONAPROLE stands out with 64% of the total exports (Uruguay XXI, 2015).



Destination	Thous. US$	Tons	US$/Tons
Venezuela	148.727	35.860	4.147
Brasil	84.037	21.692	3.874
China	50.685	20.253	2.503
Argelia	45.043	9.169	4.913
Cuba	25.757	5.700	4.519
Chile	13.828	3.025	4.571
Federación Rusa	8.816	2.150	4.100
Colombia	8.503	1.881	4.521
Vietnam	5.789	2.058	2.812
Sudáfrica	5.141	7.288	705
Total general	408.545	118.934	3.435

Figure 3-4: On the left, Tons of milk exported in Uruguay from 2004 to 2014, and its corresponding economic gain. On the right, milk exportations from Uruguay. Source: Uruguay XXI (2015).

One of the main concerns regarding dairy industry in Uruguay is about its (treated) wastewater discharge. As shown in Figure 3-5, in Río Santa Lucía Basin is where the highest percentage of milk production in dairy farms, which is of main concern of Uruguayan government. Therefore, this industries are especially pressure by the government and population, to upgrade their wastewater treatment plants, minimizing discharges into water bodies.

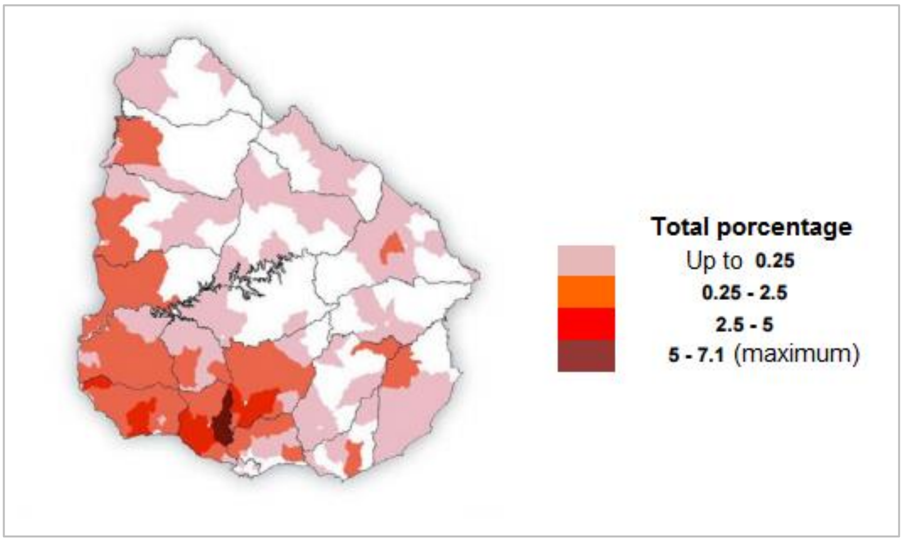


Figure 3-5: Percentage of milk production in dairy farms per police department, for the period 2010/2011. Source: (Uruguay XXI, 2015)

According to Vourch, et al. (2007), dairy industry is among one of the most pollutants (considering volume) of food industries, producing between 0.2 to 1 L of wastewater per litter of treated milk. Furthermore, studies conducted in 11 dairy plants in France, show a water consumption between 800 to 3,400 m^3/day, corresponding to 1.2 to 3.4 L of water consumed per litter of processed milk.

3.2. Technology selection: anaerobic wastewater treatment

Anaerobic wastewater treatment was developed more than 100 years ago, and studied worldwide mainly due to the energy crisis in the 1970s (Henze, 2008). Anaerobic digestion is a process where microorganism break down material (digestion) in the absence of O_2. Considering its process, digestion can be divided into four phases (Van Lier, et al., 2008):

- Hydrolysis: enzymes convert undissolved matter into dissolved and less complex one, which can then pass through cell membranes. This process may be the slowest and bottleneck of all anaerobic digestion phases.
- Acidogenesis: this is the fermentation step, where the small and dissolved matter from hydrolysis is taken by fermentative microorganisms and converted into volatile fatty acids (VFA), alcohols, lactic acid, CO_2, among others.
- Acetogenesis: step where digestion products are transformed into acetate, hydrogen (H_2) and CO_2.
- Methanogens: methanogenic bacteria convert the latter compounds from acetogenesis into methane (CH_4), CO_2, and new cell material.

Whilst anaerobic wastewater processes started to be important due to the energy crisis, they also have outstanding advantages over aerobic treatment technologies, such as (Van Lier, et al., 2008):

- around 90% less of sludge is produced,
- up to 90% of smaller footprint needed,
- high applicable organic loading rates (in comparison with aerobic processes),
- production of methane (that can be transformed into energy) and reduction on overall energy consumption,
- and none or very little use of chemicals.

These pluses are counterbalance by the slow growth rates of some organisms (specially the methanogenic ones), and system complexity (Liao, et al., 2006). Morover, providing a long enough solids retention time (SRT) is key to the development of organisms and, organics effluent concentration achieved by anaerobic treatment is lower than the one achieved by aerobic ones. Additionally, anaerobic processes have two core limiting steps: hydrolysis and methanogensis. The first one is the limiting step for wastewater with high particulate content, and both strongly depend on temperature, pH, hydrolyzing concentration, toxicity, amount of nutrients and particulate organic type (Visvanathan and Abeynayaka, 2012). Last constrain conisder is that, overall, anaerobic treatments have a minimum nutrient removal, needing further treatment in case of water reuse (Visvanathan and Abeynayaka, 2012).

According to Van Lier, et al. (2008) a big share of agroindutrials wastewater is treated by anaerobic reactor systems in the Netherlands. In 2008, the total amount of registered scale installations of anaerobic high rate reactors reach to 2,226, almost twice the amount of installations ten years before. High rate anaerobic systems are those in which hydraulic retention time (HRT) and sludge retention time (SRT) are uncoupled, allowing higher organic loading rates with smaller footprints (due to high biomass concentration and retention). Anaerobic granular sludge is one of the main pros for this type of reactor (Visvanathan and Abeynayaka, 2012). However, various industrial wasewaters characteristics, like high amount of suspended solids, high oil, fat and grease content, salinity, toxicity, flow variations, etc., may affect negatively the granular sludge formation and stability, worsen the performace of the anaerobic reactor (Visvanathan and Abeynayaka, 2012). Furthermore, according to Dereli, et al. (2012), changes in organic loading rates (OLR), high amount of fats, oil and grase (FOG), high temperature and amount of suspended solids (SS) are key drivers that hamper granular sludge development.

3.2.1. Anaerobic membrane bioreactor

Anaerobic Membrane Bioreactors (AnMBRs) were developed first in the late 1980s and are an excellent solution to alleviate the main disadvantages related with conventional high rate anaerobic treatment. AnMBR is biological treatment with membrane separation by microfiltration or ultrafiltration (MF or UF respectively) without oxygen (Henze, 2008, Liao, et al., 2006). Membranes are permselective materials, which implies that while wastewater (or any other flow) is passing through it, several compounds (physical, chemical and biological) are reteined by it, according to the pore size of the material. The flow that passes through the membrane is called the permeate, while the one rejected is the retentate (or concentrate).

Wastewater can be categorized based on two features, concentration of consituents (e.g. wastewater with high concentration of organics is known as ‘strong’), and their particulate nature (solubable or particulate) (Liao, et al., 2006, Visvanathan and Abeynayaka, 2012). According to this, wastewater can be clasified into 4 categories, as shown in Figure 3-6.

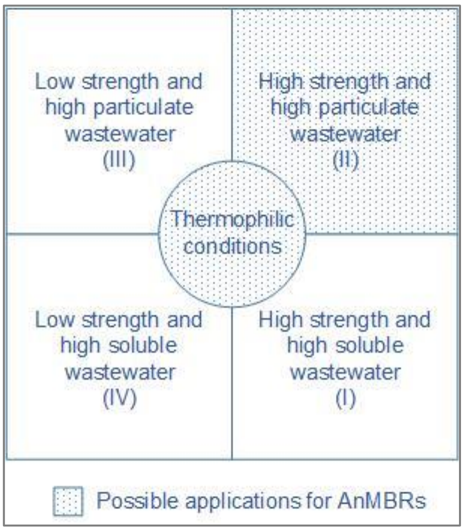


Figure 3-6: Applications of AnMBRs to different types of wastewater modified from Liao, et al. (2006).

Nowadays, the high strength soluble wastewater is well treated by high rate anaerobic reactors, especially UASB (Visvanathan and Abeynayaka, 2012). Hence, AnMBR application in this type of effluent is striking mainly in case water is reuse after treated. Additionally, AnMBRs used for low strengh effluents (quadrants III and IV of Figure 3-6) would also be necessary only when wastewater reclamation is inteended. However, this technology provides a suitable option for high strength flows, especially particulate ones, like dairy industry wastewater. This is due the fact that membrane allows the complete retention of partiulates and hence, a total degradation of slowly degraded compounds (Liao, et al., 2006). Several industries have an effluent corresponding with the characteristics of quadrant II, which makes them suitable for AnMBR treatment. From 2008 to 2009, the amount of articles on AnMBRs research for application in industries trebled, from 10 to 30 journal publications (Visvanathan and Abeynayaka, 2012), many of them, outstanding the posibilities and constrains of the technology.

According to Liao (Liao, et al., 2006), one of the strongest point of AnMBRs is that they are able to completely retein biomass, which leads to smaller footprints and decouple the hydraulic and sludge retention time of the process. Other advantajes of this process are:

- high quality treated effluent (permeate), clarified and lagerly free of pathogens,
- operation at high values of MLSS (mixed liquid suspended solids), compare to processes like Activated Sludge (AS),
- allowance to operate with high SRT, promoting an enhance treatment due to the growth of slow growing bacteria,
- and reduction of sludge produced.

Although AnMBR present several benefits, it also has two main drawbacks: larger process complexity, and higher capital equipment and operating costs (Henze, 2008). Additionally, membrane fouling represents one of the core tailbacks (Dereli, et al., 2012), reducing the flux due to setting of solid material onto the membrane surface and within its structure (Henze, 2008). Membrane fouling depends on several variables, like influent characteristics, biomass propoerties, and reactor features and operation. According to several authors cited by Dereli (Dereli, et al., 2012), *cake layer formation was identified as the most important fouling process for AnMBR.* Furthermore, when AnMBR are used for treating industrial wastewater, membrane fouling do to inorganic compounds (like calcuim and phosphorus) tend to increase compare to the performance of MBRs.

3.2.2. Reverse Osmosis for wastewater treatment

Reverse Osmosis (RO) is a pressure driven process, based on the rejection of dissolved and particulate compounds in the feed water by a semi-permeable membrane (Malaeb and Ayoub, 2011). It is able to remove smaller particles than ultra, nano or microfiltration, dissolved organic compounds, free atoms and small organic monomers, are shown in Figure 3-7.

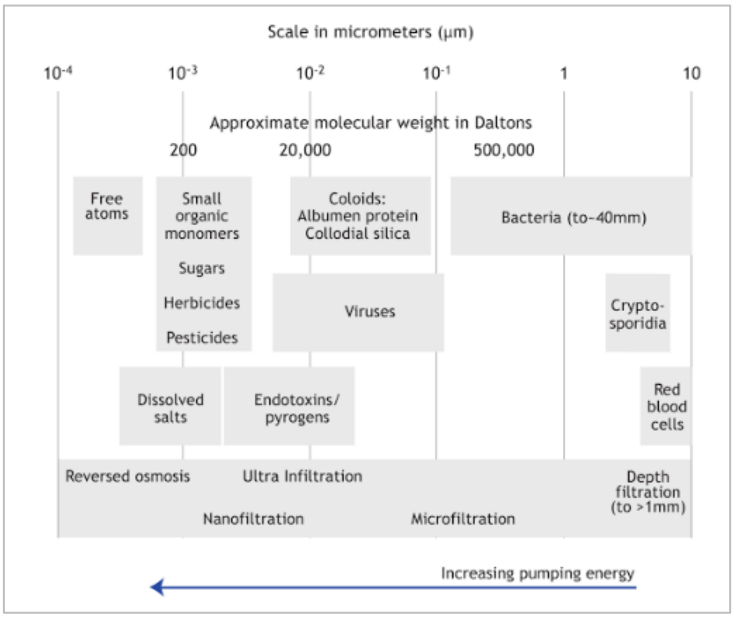


Figure 3-7: Membrane separation processes. Source: Henze (2008)

RO technology is widely use to obtain drinkable water from brackish and seawater (desalination), and for tertiary treatment of wastewater, due to the possibilities of reuse the treated effluent. Furthermore, according to Tanuwidjaja (2002), RO technology will be broadly used in industrial wastewater treatment to take over large conventional wastewater treatment systems.

RO membranes are very permeable to water, but they are capable to retain dissolved substances and particulate compounds. By applying pressure, water that is in the feed flow passes through the membrane, and end up having less concentration of different composites. To overcome the feed side osmotic pressure, which will naturally lead into water flowing from the less concentrated solution into the more concentrated one, high feed pressure is needed, as shown in Figure 3-8. External pressure applied in RO is very diverse, and can vary from 15 bar (brackish water desalination) to 200 bar (landfill leachate treatment).

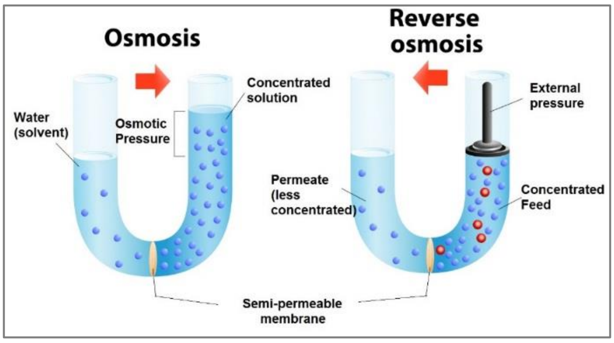


Figure 3-8: Reverse osmosis. Source: modified from kandrwaterservice.com (2016).

Water that passes through the RO membrane is called permeate, and the one that does not is the concentrate. The relation between this two flows is entitled recovery, and it affects the passage and product flow. Additionally, as water permeates through the membrane and different compounds are rejected, the retained solutes gather on the membrane surface, gradually increasing their concentration. This phenomenon is called Concentration of Polarization and have numerous negative impacts on the RO performance (Fritzmann, et al., 2007), of which the main ones are:

- salt and other compounds rejection decrease, leading to higher concentrations in the permeate (although this may not be a problem when the feed flow of the RO is pre-treated by AnMBR),
- precipitation of divalent ions on the membrane,
- reduction of water flux as a result of higher osmotic pressure,
- cake formation in the membrane surface due to particles accumulation.

RO (and all membranes) have two main hydrodynamic conditions: membrane flux and transmembrane pressure. The first one is considered as the key parameter to assess RO performance (Liao, et al., 2006). Moreover, membrane fouling capacity (and foulants removal) have a direct relation with flux and a range for optimal and sustainable process conditions can be define. Furthermore, according to Lin, et al. (2013), flux across the membrane is one of the limiting factors for full scale application. On the other hand, transmembrane pressure (TMP) refers to the pressure differential through the membrane cell to obtain a certain flux. RO can be operated at constant TMP, where the flux is variable, or a constant flux variating the TMP.

RO processes have some limitations that can be diminished when coupling this systems with membrane bioreactors. This drawbacks are not only regarding the increase of the osmotic pressure attributable to the effect of concentration of polarisation, but also by membrane deterioration and blocking (Fritzmann, et al., 2007). The former may well occur due to the use of some chemicals that harm the active layer, like oxidants or cleaning chemicals. Moreover, membrane surface type can be critical when evaluating their susceptibility to pH variation (like the polymeric ones, which are affected by high or low pH).

Membrane fouling can be categorized into reversible and irreversible one, based on the cleaning practice. Furthermore, reversible fouling can be divided into two subcategories: removable or irremovable (Lin, et al., 2013). The latter corresponds with the fouling that has to be remove by adding chemicals, while the removable one only requires physical means (like backwash). The irreversible fouling is a permanent one, which cannot be eradicated by any means without damaging the membrane. Whilst these membrane fouling classification is widely approve, there is other way to classify the fouling types, included in a broader category called blocking.

Membrane blocking is one of the primary limitations of RO (Bartels, et al., 2005), and can be divided into two main mechanism: fouling or scaling, shown in Figure 3-9. The former one is caused by supersaturation of inorganic compounds, which are concentrated on the feed side of the membrane. Furthermore, the downstream part of the RO in a cross flow type is the most prone to scaling, due to the increase of different compounds that cannot pass through the membrane (Fritzmann, et al., 2007). The most often scaling substances when treating wastewater are calcium carbonate, silica and calcium phosphate (Bartels, et al., 2005). To alleviate this problem, the use of antiscalants and pH adjustments are common activities performed.

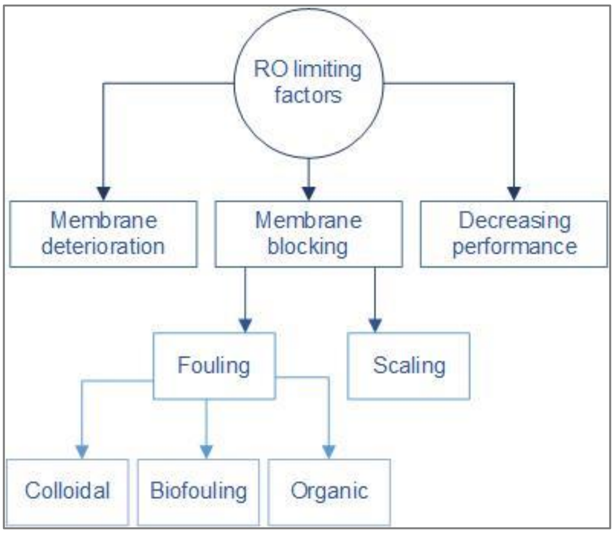


Figure 3-9: RO membrane limiting factor mechanisms. Source: modified from Bartels, et al. (2005).

Membrane fouling can also be categorize into three main kinds: colloidal fouling, organic fouling and biofouling (Bartels, et al., 2005). The former type is one of the most frequent RO fouling when treating wastewater, but can be controlled by an adequate pretreatment, especially with ultrafiltration (UF) or microfiltration (MF) (Bartels, et al., 2005, Malaeb and Ayoub, 2011). Particulate and colloidal matter may form a layer on top of the membrane and decrease significantly the RO performance. These process is known as cake formation.

Biofouling is caused by microbial growth sticking in the feed side of the RO membrane, producing a layer that seems like a gel (Fritzmann, et al., 2007). This type of fouling causes lower permeability and higher pressure drops in RO membrane channels. As in colloidal fouling, having a pretreatment that reduce the amount of bacteria and microorganism is key to prevent and diminish biofouling of the RO membrane.

Last but not least, organic fouling is mainly due to high concentrations of dissolved organic material present in wastewater. Beside a decrease in flux, adhesion of organic matter to the membrane enhance microbial growth due to the amount of nutrients present in the system, and therefore enlarge biofouling. While there are some measures that can be carried out to prevent and minimize all types of fouling, it can never be fully avoided. Hence, periodical cleaning of the membrane must be performed. According to Fritzmann (Fritzmann, et al., 2007), cleaning must be done when either the flow decrease by 10%, rejection increase 10% from the initial conditions in the first 48 hours of operation, or when pressure losses reach up to 15% in the feed channels.

3.3. System configuration

Dairy industry wastewater is a strong high particulate wastewater, characterized by its high organic matter and FOG concentration, adequate to be treated by AnMBR. Taking into account that this type of industry consume a great amount of water (mainly for cleaning processes), reuse of treated wastewater for industrial purposes seems a solid option to pursue. Wastewater treatment with RO system allows to reuse the permeate flow for several purposes. Moreover, according with numerous authors (Bartels, et al., 2005, Fritzmann, et al., 2007, Grundestam and Hellström, 2007, Xu, et al., 2010) when RO is couple with a previous step of ultrafiltration (UF) or microfiltration (MF), optimal process conditions can be achieve: minimal membrane fouling and best effluent quality.

RO systems were mostly developed for desalination purposes. High conductivity of sea water leaded to apply high transmembrane pressure in order to be able to increase as much as possible the permeate flow, while having high salt rejection. However, when RO is used to treat wastewater, especially after a membrane pretreatment (AnMBR in this particular case), conductivity of the feed flow (permeate of AnMBR) is not as high as the one of seawater. Therefore, low pressure reverse osmosis systems (LPRO) are possible to apply, drastically reducing the energy consumption.

3.3.1. Wastewater characterization

Among different industrial effluents possibilities to analyse the efficiency of an AnMBR couple with RO system, dairy industry wastewater seems to be a perfect option. High rate anaerobic reactors (like UASB) have several difficulties when dealing with this effluent, mainly due to effluent fluctuation, high lipid content and high amount of suspended solids. Dairy industries produce a huge variety of products, and each one had and effluent with different characterization. Also, such properties are likely to vary from industry to industry. Furthermore, one of the main characteristics of dairy industries is flow variation, mainly due to seasonal, diurnal and hourly fluctuations. Several papers present considerable variations of this industrial wastewater (Andrade, 2011, Demirel, et al., 2005, Janczukowicz, et al., 2008, Multilateral Investment Guarantee Agency, 1996). Nevertheless, similar characteristics and proportions amongst parameters can be detected, enabling the definition of a reasonable wastewater constitution.

According to Andrade (Andrade, 2011), the main constituents of the dairy industry effluent are: proteins, carbohydrates, lactose, fats, suspended solids, nitrogen, phosphorus and inorganic pollutants. Besides such parameters the following might also be present in this wastewater: detergents, disinfectants and some compounds used in cleaning, oil and lubricants from machinery and domestic sanitary sewage. Between all parameters mentioned, the ones that define the reactor characteristics and efficiency (main ones) are: biological and chemical oxygen demand (BOD and COD respectively), total suspended solids (TSS), volatile suspended solids (VSS), pH, fats, oils and grease (FOG), alkalinity, total phosphorus, and total Kjeldahl nitrogen (TKN). Values of this parameters are shown in Table 3-1 and 3-2.

Table 3-1: Dairy industry wastewater characterization. Source: Janczukowicz, W et al (2008)

The sewage origin	BOD_5 (mg l^{-1})	COD (mg l^{-1})	BOD_5/COD (mg l^{-1})	Total suspended solid (mg l^{-1})	Fats (mg l^{-1})	Reaction (pH)
Apparatus room	3470.0	14639.5	0.27	3821.2	3105.2	10.37
Butter section	2423.3	8925.9	0.27	5066.5	2882.4	12.08
Milk reception point	797.6	2542.9	0.31	653.6	1056.8	7.18
Cheese section	3456.7	11753.0	0.29	939.5	330.5	7.90
Cottage cheese section	2599.0	17645.4	0.15	3375.3	950.3	7.83
Hard cheese whey	29480.0	73445.0	0.4	7152.2	994.4	5.80
Cottage cheese whey	26766.0	58549.6	0.46	8314.0	491.5	5.35
Pumping station	1748.0	4441.5	0.39	1071.8	573	8.35

Table 3-2: Dairy industry wastewater characterization. Source: Demirel, B, et al (2005)

Effluent type	COD (mg/l)	BOD_5 (mg/l)	pH (units)	Alkalinity (mg $CaCO_3$/l)	Suspended solids (mg/l)	Volatile suspended solids (mg/l)	Total solids (mg/l)	TKN (mg/l)	Total phosphorus (mg/l)
Creamery	2000–6000	1200–4000	8–11	150–300	350–1000	330–940		50–60	
Not given	980–7500	680–4500			300				
Mixed dairy processing	1150–9200		6–11	320–970	340–1730	255–830	2705–3715	14–272	8–68
Cheese whey	68814[a]							1462[a]	379[a]
Cheese	1000–7500	588–5000	5.5–9.5		500–2500				
Fresh milk	4656[a]		6.92[a]						
Cheese	5340[a]		5.22[a]						
Milk powder/ butter	1908[a]		5.80[a]						
Mixed dairy processing	63100[a]		3.35[a]		12500[a]	12100[a]	53000[a]		
Cheese whey	61000[a]				1780[a]	1560[a]		980[a]	510[a]
Cheese			4.7[a]		2500[a]			830[a]	280[a]
Not given			4.4–9.4		90–450				
Fluid milk	950–2400	500–1300	5.0–9.5		90–450				

[a] Mean concentrations are reported.

In what denotes to pathogens, not mentioned in previous references, dairy effluent may contain organisms prevenient from production process (Multilateral Investment Guarantee Agency, 1996), even though no information regarding possible pathogens concentration in dairy industry effluent was found. Since permeate from the RO is likely going to be reuse for industrial processes, pathogen analysis in the treated effluent is key parameter to consider.

3.3.2. Legislation of treated wastewater reuse

Several drivers can be found for treated wastewater reuse, like increasing water prices, water scarcity, and strict environmental regulations for wastewater discharge among others. Wastewater reuse for agricultural purposes is worldwide studied and a variety of standards, guidelines and recommendations can be found for this purpose. According to Kramer and Post (NY), three central criteria should be analyse when reusing treated wastewater for irrigation: salt concentration, heavy metals and dangerous organic compounds, and health safety. Furthermore, World Health Organisation (WHO) developed in 2006 wastewater reuse in agriculture guidelines entitled: “Guideline for the safe use of wastewater, excreta and greywater” (World Health Organization, 2006).

Even though vast standards and recommendations can be found for wastewater reuse in agricultural, limited information is available for industrial purposes reuse. Industrial processes are very diverse and water may be use differently, like cleaning and cooling (among others). Hence, treating wastewater for industrial reuse purpose requires to be tailored according the particular applications (Hoinkis, et al., 2012).

World Health Organization (2006) and FAO (Ayers and Westcot, 1985) developed guidelines for wastewater reclamation in agricultural purposes, restricting wastewater reuse according to the crop type, in none, moderate and severe restrictions in wastewater reuse. Figures 3-10 and 3-11, shows a summary of some restrictions for wastewater reuse in agriculture by WHO and FAO.

Category	Reuse conditions	Exposed Group	Intestinal nematodes [b] (arithmetic mean no. of eggs per liter) [c]	Fecal coliforms (geometric mean no. per 100 ml) [c]	Wastewater treatment expected to achieve the required microbiological guideline
A	Irrigation of crops likely to be eaten uncooked, sports fields, public parks [d]	Workers, consumers, public	≤ 1	≤ 1000	A series of stabilization ponds designed to achieve the microbiological quality indicated, or equivalent treatment
B	Irrigation of cereal crops, industrial crops, fodder crops, pasture and trees [e]	Workers	≤ 1	No standard recommended	Retention in stabilization ponds for 8–10 days or equivalent helminthes and fecal coliform removal
C	Localized irrigation of crops in category B if exposure to workers and the public does not occur	None	Not applicable	Not applicable	Pretreatment as required by irrigation technology but not less than primary sedimentation

a In specific cases, local epidemiological, socio-cultural and environmental factors should be taken into account and the guidelines modified accordingly.
b Ascaris and Trichuris species and hookworms.
c During the irrigation period.
d A more stringent guideline limit (□ 200 fecal coliforms/100 ml) is appropriate for public lawns, such as hotel lawns, with which the public may come into direct contact.
e In the case of fruit trees, irrigation should cease two weeks before fruit is picked, and no fruit should be picked off the ground. Sprinkler irrigation should not be used.

Figure 3-10: WHO guidelines for using wastewater in agriculture[a]. Source: (Kramer and Post, NY).

Potential Irrigation Problem				Units	Degree of Restriction on Use		
					None	Slight to Moderate	Sever-e
Salinity *(affects crop water availability)*[2]							
	EC_w			dS/m	< 0.7	0.7 – 3.0	> 3.0
	(or)						
	TDS			mg/l	< 450	450 – 2000	> 2000
Infiltration *(affects infiltration rate of water into the soil. Evaluate using EC_w and SAR together)*[3]							
SAR	= 0 – 3	**and EC_w**	=		> 0.7	0.7 – 0.2	< 0.2
	= 3 – 6		=		> 1.2	1.2 – 0.3	< 0.3
	= 6 – 12		=		> 1.9	1.9 – 0.5	< 0.5
	= 12 – 20		=		> 2.9	2.9 – 1.3	< 1.3
	= 20 – 40		=		> 5.0	5.0 – 2.9	< 2.9
Specific Ion Toxicity *(affects sensitive crops)*							
	Sodium (Na)[4]						
	surface irrigation			SAR	< 3	3 – 9	> 9
	sprinkler irrigation			me/l	< 3	> 3	
	Chloride (Cl)[4]						
	surface irrigation			me/l	< 4	4 – 10	> 10
	sprinkler irrigation			me/l	< 3	> 3	
	Boron (B)			mg/l	< 0.7	0.7 – 3.0	> 3.0
	Trace Elements (see Table 21)						
Miscellaneous Effects *(affects susceptible crops)*							
	Nitrogen (NO_3 - N)[5]			mg/l	< 5	5 – 30	> 30
	Bicarbonate (HCO_3)						
	(overhead sprinkling only)			me/l	< 1.5	1.5 – 8.5	> 8.5
	pH				**Normal Range 6.5 – 8.4**		

Figure 3-11: Guidelines for interpretation of water quality for irrigation. SAR corresponds to Sodium adsorption ratio and ECw electrical conductivity. Source: (Kramer and Post, NY).

Particularly in Uruguay, treated wastewater for industrial purposes must cope with the drinking standards. Sanitary Works of the State public company (OSE), is the state agency responsible for supplying drinking water and sanitation to all the country (but Montevideo department), and is also in charge of stablishing the require standards for drinking water. Applied standards undertaken by OSE are regarding what it is stablished by Uruguayan Institute of Technical Standards (UNIT) (2010), which is based on WHO recommendations. Most important parameters and allowable values are presented in Table 3-3. Therefore, permeate parameters of the RO system must be compare to the values given by UNIT 833:2008.

Table 3-3: Uruguay most important parameters for drinking water with their corresponding maximum allowable values. Source: UNIT 833:2008.

Parameter	**Standards**	**Units**
Total Coliforms	Absence in 100 ml	c.f.u/100ml
Faecal Coliforms	Absence in 100 ml	c.f.u/100ml
Pseudomonas aeruginosas	Absence in 100 ml	c.f.u/100ml
Heterotrophic	500	c.f.u/ml
Enterococci	Absence in 100 ml	c.f.u/100ml
Clostridios sulphate reducers	Absence in 100 ml	c.f.u/100ml
Colour	15	Esc.Pt-Co
Conductivity (at 25°C)	2000	µS/cm
Odour	Absence	-
Taste	Absence	-
pH	6.5-8.5	uPH
Turbidity	1	NTU
Ammonia	1.5	$mgNH_4/L$
Arsenic	0.02	mgAs/L
Chlorides	250	mgCl/L
Hardness	500	$mgCaCO_3/L$
Fluoride	1.5	mgF/L
Iron	0.3	mgFe/L
Manganese	0.1	mgMn/L
Mercury	0.001	mgHg/L
Nitrate (NO_3^{-})	50	$mgNO_3/L$
Nitrite (NO_2^{-})	0.2	$mgNO_2/L$
Lead	0.03	mgPb/L
Sodium	200	mgNa/L
Total dissolved solids	1000	mg/L
Sulphate	400	$mgSO_4/L$
Zinc	4	mgZn/L
Cyanide	0.07	mgCN/L
Sulphide	0.05	mgS/L
Total Chromium	0.05	mgCr/L

CHAPTER 4

Materials and methods

4.1. RO setup

4.1.1. Pretreatment step: AnMBR

A bench-scale AnMBR is coupled to an RO flow cell at the laboratories of Biothane, located in Delft, Netherlands. AnMBR systems are marketed by Biothane, under the trade name Memthane® (www.Veoliawatertechnologies.com). The bench scale AnMBR system consists of an anaerobic continuously stirred tank reactor (CSTR), with a volume of 10L and mechanical mixers. The CSTR is connected to a tubular inside out ultrafiltration (UF) membrane of 3 meters, operated under cross-flow mode. The UF membrane consists of polyvinylidene fluoride (PVDF).

The AnMBR-RO system is evaluated using synthetic dairy industry wastewater as feed flow. Permeate from the AnMBR is drawn from the membrane column by a pump, allowing (and controlling) a certain flux through the membrane. Sludge retention time and cross flux of the AnMBR are 20 days and around 10 Litters per hour and square meter of membrane (lmh) respectively.

To the date, two bench-scale Memthane® reactors are set-up in Biothane’s laboratory, and operating with synthetic dairy industry wastewater (diluted milk and macro nutrients). These systems, are operated by PhD student Alejandra Szabo, for achieving stabilised conditions prior to coupling to the LPRO system, using AnMBR permeate as the feed of the latter. AnMBR setup is shown in Figure 4-1.

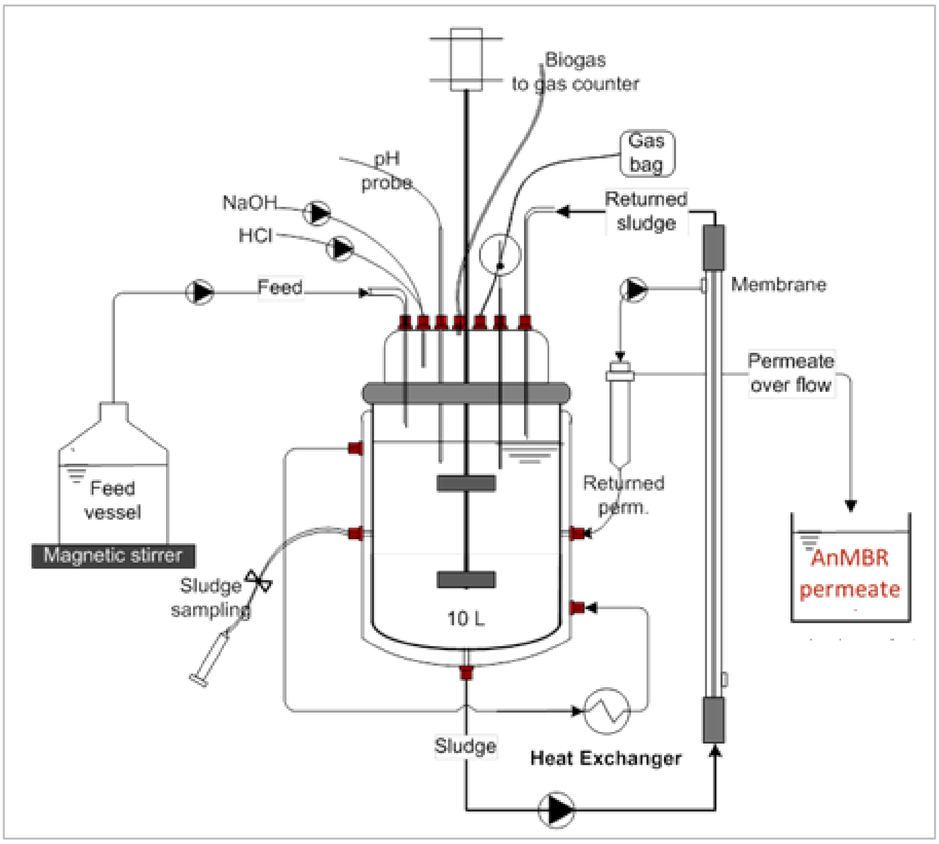


Figure 4-1: AnMBR laboratory scale setup. Source: Biothane.

4.1.2. Experimental set up

RO system is a cross flow membrane flow cell, developed by STERLITECH. The cell is designed to evaluate RO membranes and simulates the flow dynamics of larger, commercially available membrane elements, such as spiral wound membrane elements. The material is stainless steel, and it is able to handle a maximum pressure of 69 bar (1,000 psi) and 88°C. Figure 4-2 shows the RO parts and different components.

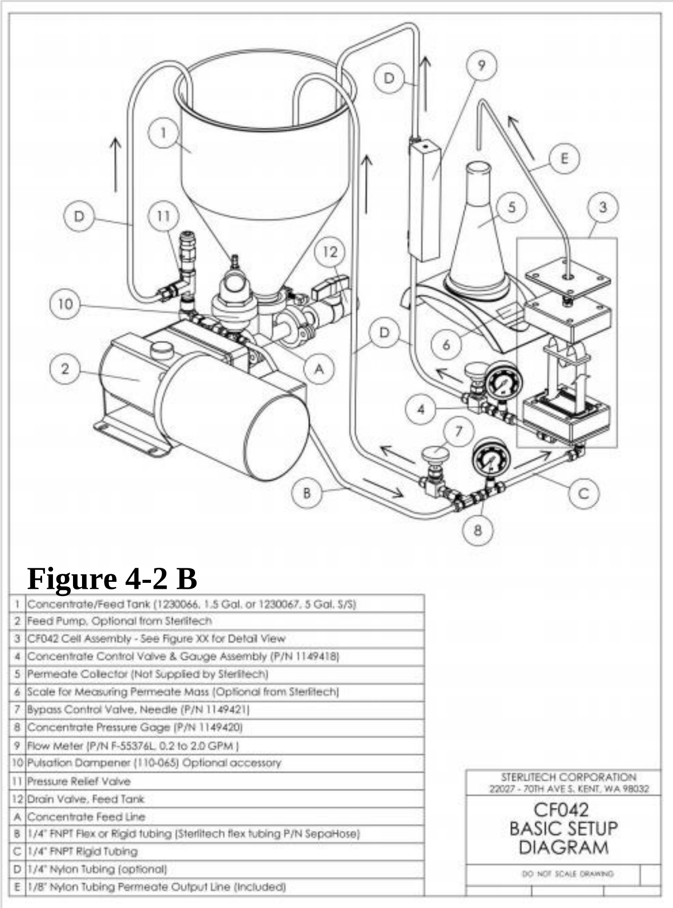


Figure 4-2: Figure A, system parts to be assemble. Figure B, suggested set up according to manufacturer.

Features and technical specifications of the RO cell are presented in Table 4-1. Apart from the membrane constituents, other components need to be installed. The main ones are: feed pump and tank, filtration membrane pack, conductivity meter, and permeate retention tanks. Due to the fact that there is few literature about AnMBR and RO coupling for industrial wastewater treatment, there is no information regarding optimal flux or applicable Net Driving Pressure (NDP). While these parameters are key for the membrane performance, they must be identify regarding the type of membrane that will be used.

Table 4-1: CF042SS RO membrane specific characteristics. Source: modified from STERLITECH Corporation (NY) and Sterlitech.com (2016)

Parameter	Description
Membrane Active Area	42 cm² (6.5-inch²)
Maximum Pressure	69 bar (1000 psig)
Maximum Temperature	80 °C (190 °F)
O-rings:	Viton (Other materials available)
pH Range:	Membrane Dependent
Cross Flow Velocity	0.1 - 0.5 m/s
CF042SS	Stainless Steel
Dimensions	
Slot depth	2.28 mm (0.09 inches)
Slot width	39 mm (1.54 inches)
Active Membrane Area	42 cm^2
O-Ring	Buna-N or Viton
Outer Dimensions	12.7 x 10 x 8.3 cm
Active Area Dimensions	9.207 x 4.572 cm
Membrane Support	20 µm Sintered Stainless Steel
Hold-Up Volume	17 mL

Laboratory scale AnMBR (Memthane®) is coupled with a LPRO, and the experimental setup and lab scale set up are shown in Figure 4-3 and Figure 4-4 respectively.

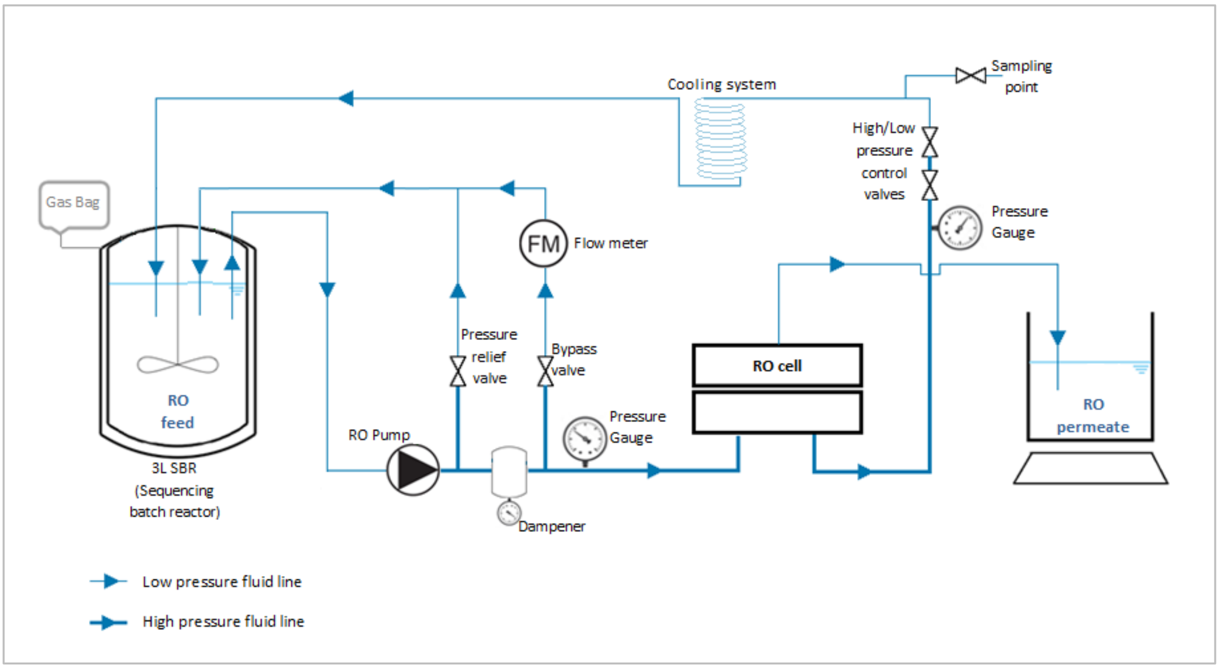


Figure 4-3: Experimental setup.

Figure 4-4: Experimental laboratory scale setup in Biothane.

Considering the system set-up, the LPRO should run at constant feed flow and Net Driving Pressure (NDP), variable cross flow velocity, normalized flux and recovery. These are key parameters to identify fouling potential of treating AnMBR permeate with RO systems.

4.1.3. Membrane and spacers chose

A vast variety of membranes can be chosen, considering the type of water to be treated and desire rejection (removal efficiency). Among the most known brands, Dow Filmtec™ is widely used. For this particular research, three different types of membranes were bought, but only one used. Membrane characteristics and rejections, according the type of feed wastewater are presented in Table 4-2. Two Dow Filmtec™ membrane are bought: one for sea water and one for brackish water, with similar operational conditions but maximum allow pressure of 83 for the first one and 41 for the second one. Additionally, a Toray™ membrane for brackish water is also bought. This have similar characteristics than the Dow Filmtec™ for brackish water.

Table 4-2: Membrane specifications and operating conditions. Sources: (DOW-FILMTEC, 2017), (Toray.com, 2017), (Sterlitech.com, 2017)

Series	**Dow Filmtec™ Flat sheet membrane SW30XLE**	**Dow Filmtec™ Flat sheet membrane BW30XFR**	**Toray™ Flat sheet membrane 73AC**
Feed	Seawater	Brackish water	Brackish water
Type	Extra Low energy	Fouling resistant, extra low energy	High rejection, low energy, Cl resistant
pH range (25°C)	2 - 11	2 - 12	2 - 11
Cleaning pH range	1 - 13	1 - 13	1 - 13
Maximum feed temperature	45 °C	45 °C	45 °C
Design flux range , maximum flux (lmh)	13-20 (24)	13-20 (24)	-
NaCl rejection (%)	99.5	99.7	99.8
Maximum Feed Silt Density Index	SDI <5	SDI <5	SDI <5
Maximum operating pressure (bar)	83	41	41
Polymer	Polyamide	Polyamide	Polyamide

Dow Filmtec™ BW30XFR is the membrane used for the research trials, due to the fouling resistance, low energy, literature available and worldwide use.

Besides membrane type, spacers are used in flat sheet membranes to simulate spiral wound RO. According to Bucs, et al. (2014), spacers have a crucial role in spiral wound RO systems, keeping membranes away from each other and enhancing fluid mixing. Feed spacers may be classify according to: space between spacer filaments, angle of the filaments, flow angle, and the spacer thickness (Li, et al., 2002). Geometry corresponding to five commercially available spacers were bought by Biothane, but only one was used for this research. Four different spacers thickness are contemplated: 17, 31, 47 and 61 mil (1 mil = 25.4 µm), and two different filaments angles: diamond and parallel (Figure 4-5).

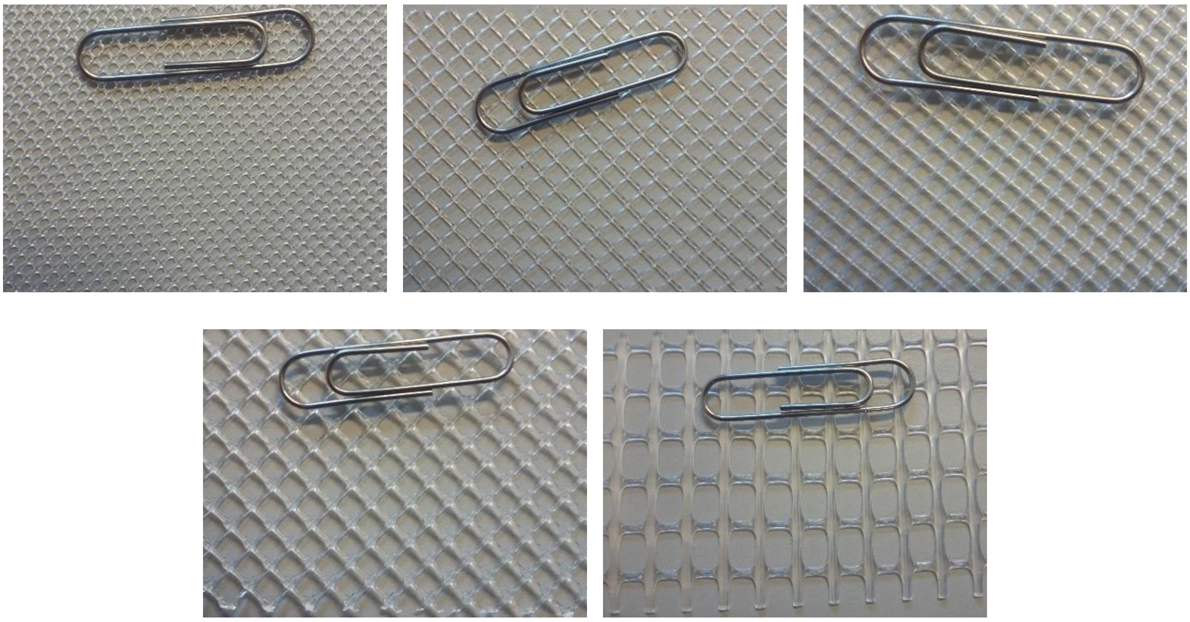


Figure 4-5: Spacers type available for the research. From left to right and top to bottom: 17 mil diamond, 31 mil diamond, 47 mil diamond, 65 mil diamond, and 47 mil parallel.

The chosen feed spacer is the one of 31 mil and diamond shape. This spacer is considered low foulant, and used in several researches (Bucs, et al., 2014, Farhat, et al., 2016, Li, et al., 2002, Vrouwenvelder, et al., 2009a, Vrouwenvelder, et al., 2009b).

4.1.4. Pumped feed flow

Feed is pumped into the RO by a Hydra-Cell positive displacement pump (Appendix A) with performance characteristics according to what is shown on Figure 4-6. The system can work at a frequency range from 2 to 20 Hz (corresponding to speeds from 100 to 1750 rpm respectively), and for pressures between 6.9 to 69 bar. Considering the overall pump workable frequencies, the desire applied frequency will be between 10 to 15 Hz (600 - 900 rpm), to keep settings around the middle of the working pump rate. In this conditions, the feed flow should be between 2.5 and 3.5 L/m. If smaller cross flows are needed compare to the ones achieved at 10 Hz, due to membrane resistance, then a bypass needle valve is used, and a share of the flow is recirculated to the feed vessel.

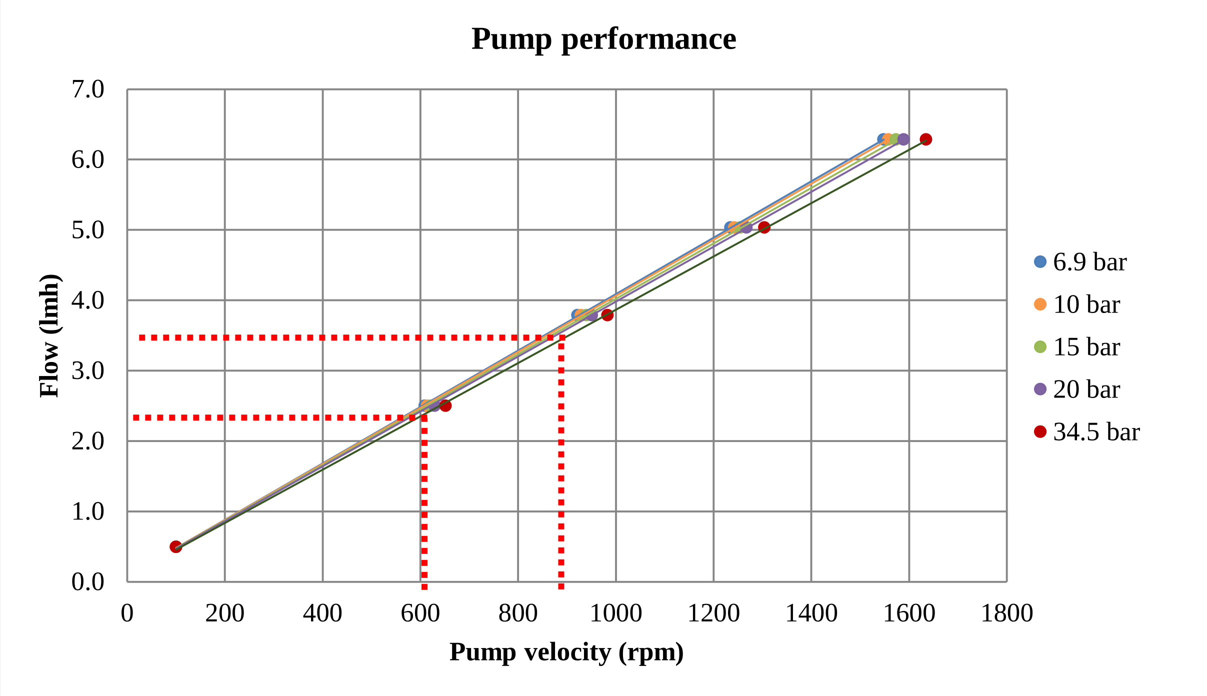


Figure 4-6: Pump performance for different given pressures. In between the red dots lines is the desire working frequency of the laboratory scale reactor.

As said by the pump manufacturer, suction line should be one size larger than the pump inlet (12.7 mm), and inlet velocity should not exceed 0.9 m/sec, in order to avoid cavitation and undesired head losses. Considering the inlet tube diameter (12 mm), then frequencies equal and below 10 Hz ensure an inlet pump velocity below 0.9 m/sec.

4.1.5. Cross flow velocity

According to the manufacturer, cross flow velocities should be between 0.1 to 0.5 m/s, but on average, systems are design to operate al velocities between 0.1 to 0.2 m/s (Vrouwenvelder, et al., 2011). Bearing this in mind and the flows given by the pump between 10 and 15 Hz, calculations were conducted to find out if there is the need to bypass a share of the feed flow in order to ensure cross flow velocity range. The calculations for the velocities are based on findings of Vrouwenvelder, et al. (2009a) and shown in the equation below , where *Q* is the feed flow at the membrane module, *h* is the flow channel height, *w* its width and ε the feed spacer porosity, established as 0.85 (Vrouwenvelder, et al., 2009b).

$$v = \frac{Q}{hw\epsilon} \quad (1)$$

Considering a cross flow velocity between 0.1 and 0.5 m/s, feed and bypass flows per pump frequency were calculated.

4.1.6. Safety considerations

Even though the system is operated as a batch process, during working hours (maximum 8 hours per day) to minimize possible pressure problems, there are several issues that may arise. The pump can run at pressures between 6.9 to 69 bars, but it is operated at pressures below 30 bar (435 psi). Therefore, a pressure relief valve is installed in the pump, allowing a maximum pressure of 24.3 bar. However, pressure is not the only critical share from the whole system regarding safety concerns, and problems related to leakages or high pressure must be considered to avoid further complications and risky procedures. Two PVC plates located around the pump and the RO cell, protects the user in case of any inconvenient. Furthermore, the pump is placed on top of rubber to prevent its movement.

Frequency may vary from 2 to 29 Hz (100 to 1750 rpm) and the desire one is below 15 Hz. To do this, a frequency meter is installed. The device is located near the pump but the furthest away from liquids, to prevent any electrical cut off. Additionally, an acrylic plate is installed around the RO cell (as shown in Figure 4-7). This helps to prevent liquid leakages outside a secure area, where the system runs at high pressure. Acrylic (Plexiglas) is used as a lid due to its characteristics: transparency, lightweight, high impact resistance, good chemical resistance, among others.

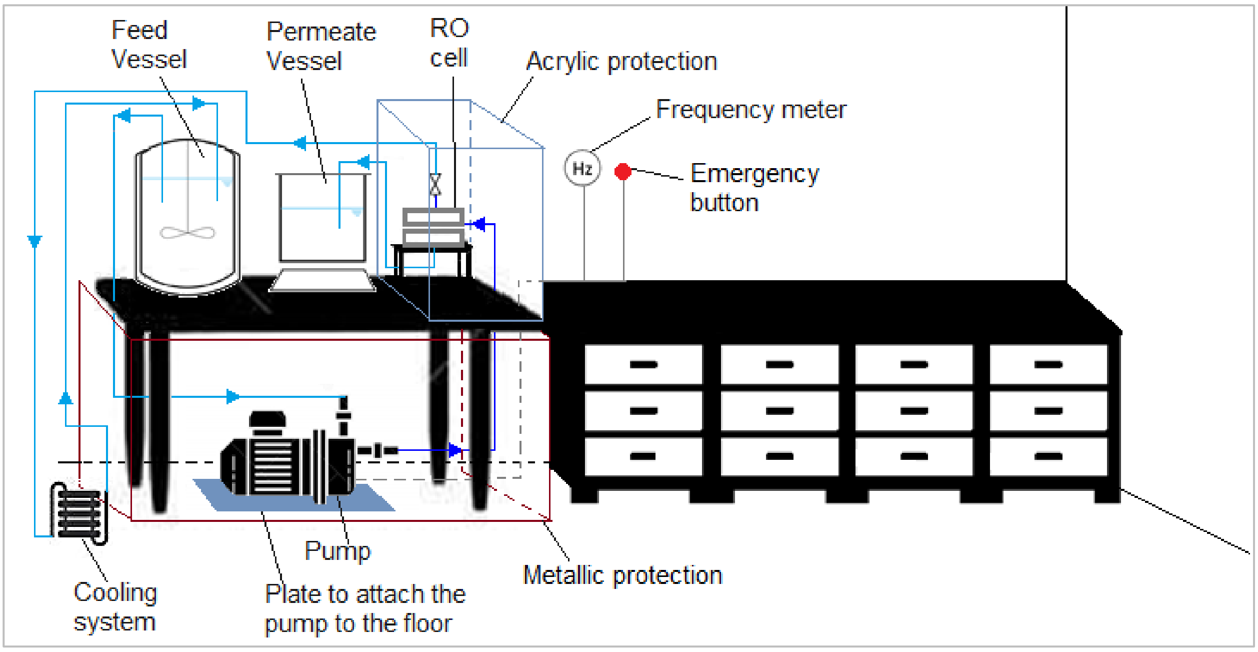


Figure 4-7: System configuration location sketch.

According to pump manufacturer, the feed vessel should be able to cope with twice the flow at which the pump is working. Considering the pump performance, the feed flows is below 4 L/min, leading to a feed vessel that needs to be able to handle 8 L/min. This recommendation is to avoid pump cavitation. Hence, an air tight feed vessel of 20 L is considered for running the experiments Taking into account a working frequency between 10 and 15 Hz, then the inlet velocity will be around 0.8 m/sec regardless the system pressure.
Besides working pressure, one of the main concerns regarding the system is the heating of the feed line due to the pump. To prevent it, a coil cooling system is mounted in the concentrate line (as shown in Figures 4-3 and 4-7). Calculations of the stainless steel coil have been conducted considering worst case scenarios, which led to have 30 m length of cooling pipe.
Finally, and emergency button is located near the frequency meter. This will allow the user to cut off all energy to the system, avoiding further complications in case something goes wrong.

It is important to highlight that the emergency bottom is located close enough to the system and easy to reach, to minimize possible negative outcomes.

4.2. Experimental analysis

4.2.1. Sampling points

Three main sampling points are defined and located in the feed, permeate and concentrate flows of the RO. Taking into account that the main driver of applying RO systems to AnMBR permeate is to reuse the treated effluent for industrial purposes, identify the membrane fouling potential, and the concentrate reuse possibilities, different parameters and sampling frequency will be measure in each flow.

To begin with, AnMBR permeate (initial RO feed) must be analysed in detail to assess the possibility of using it as a RO feed, bearing in mind the fouling capacity of the system. Hence, several parameters must be measured, where the most critical ones are the Silt Density Index (which should be below to 5 in order to be able to use RO systems according to Fritzmann, et al. (2007)), bacteria count, ion composition (to assess scaling potential), total dissolve solids (and conductivity), and total solids (TS). Measurements performed on the RO feed (AnMBR permeate) are done only once, due to the system setup characteristics, where concentrate stream is recirculated into the feed vessel, as described in previous section (Figure 4-3).

Furthermore, based on parameters measured by Fritzmann, et al. (2007), master thesis of Azadeh Rahimpour (2015) and María Cecilia Ceiter Techera (2016) (who evaluated an AnMBR for the treatment of pot ale and MBR for a brewery factory, respectively), key parameters to be measured in the concentrate and permeate flows of the system were defined, and shown on Table 4-3.

Table 4-3: Suggested analysis parameters and sampling frequency per batch test.

Parameter	Sampling frequency per stream			Analysis Location
	Feed	Permeate	Concentrate	
pH	Once	Once per day	Hourly	Biothane
Temperature	Once	Once per day	Hourly	Biothane
COD	Once	Three times per week	Daily	Biothane
TSS/VSS	Once	--	--	UNESCO-IHE
TS/VS	Once	Three times per week	Daily	Biothane
VFA	Once	Three times per week	Daily	Biothane
TKN	Once	Three times per week	Daily	Biothane
NH_4^+ -N	Once	Three times per week	Daily	Biothane
TP	Once	Three times per week	Daily	Biothane
PO_4-P	Once	Three times per week	Daily	Biothane
Alkalinity	Once	Three times per week	Daily	Biothane
TDS*	Once	Once per day	Hourly	Biothane
Conductivity*	Once	Once per day	Hourly	Biothane
E Coli	Once	Once	Once	UNESCO-IHE
Anions (Cl^-, NO_3^-, SO_4^-, HCO_3^-)	Once	Twice per week	Twice per week	External Laboratory
Cations (Ca^{2+}, K^+, Mg^{2+}, Ba^{2+}, Na^+)	Once	Twice per week	Twice per week	External Laboratory
PSD	Once	--	--	TU Delft
Particle count	Once	--	--	UNESCO-IHE
Silt density Index (SDI)	Once	--	--	UNESCO-IHE
Modify Fouling Index (MFI)	Once	--	--	UNESCO-IHE
Bacteria count	Once	Once	Once a month	UNESCO-IHE
CaCO3 Langelier Saturation Index (LSI)	Once	--	--	UNESCO-IHE

*TDS and Conductivity are measured together.

** This parameters are outsourced to an external lab.

Moreover, four more parameters will be measured to identify membrane performance, fouling potential, and assess the applicability of this particular system configuration. These parameters will be used to calculate flux and normalized flux, net driving pressure (NDP), recovery and permeability, key aspects to understand fouling potential. A list of the main analysis required to evaluate the RO fouling prospective are shown in Table 4-4.

Table 4-4: Suggested parameters and sampling frequency to evaluate RO performance

Parameter	**Frequency**
Bypass flow	Every 5 minutes
Feed Pressure	Every 5 minutes
Concentrate pressure	Every 5 minutes
Volume of permeate produced	Every 5 minutes

Based on these parameters, equations for flux, normalized flux, NDP, recovery and permeability are shown below (Water Environment Federation, 2006).

$$J = \frac{Q_{permeate}}{A_{membrane}} \quad (2)$$

$$J_{20} = J \times e^{[-0.032 \times (Temp-20)]} \quad (3)$$

$$NDP = P_{feed-} \frac{P_{feed} - P_{concentrate}}{2} - P_{permeate} - \Delta\pi \quad (4)$$

$$R = \frac{Q_{permeate}}{Q_{feed}} \times 100 \quad (5)$$

$$K = \frac{J}{NDP} \quad (6)$$

Where *J is the flux*, $Q_{permeate}$ is the permeate flow, $A_{membrane}$ *is the total area of the* system, J_{20} is Normalized Flux at 20°C, *P* indicates pressure (feed, concentrate or permeate), $\Delta\pi$ represents the change in osmotic pressure, *R* is the recovery and *K* the permeability.

4.2.2. Analysis

<u>*Wastewater characterization*</u>

Table 4-5 presents the analysis for wastewater characterization carried out, the standard measuring method and range if applicable. In several cases, Standard methods for the examination of water and wastewater were used (APHA, et al., 2005).

Table 4-5: Standard measuring method by parameter.

Parameter	**Standard measuring method**	**Test ID and range**
pH	HACH pH meter	
Temperature	HACH temperature meter	0 - 60°C
COD	HACH Lange	914, 5-60 mgO_2/L 514, 100-2000 mgO_2/L 014, 1000-10000 mgO_2/L
TSS/VSS	Standard methodology by gravimetric analysis	
TS/VS	Standard methodology by gravimetric analysis	
VFA	Quantitative determination by gas chromatography	
TKN	Quantitative determination by chemical decomposition, distillation and titration	
NH_4^+ -N	Quantitative analysis by distillation and titration	
TP	HACH Lange	350, 2-20 mg PO_4-P/L
PO_4-P	HACH Lange	350, 2-20 mg PO_4-P/L
Alkalinity	Standard methodology by centrifuge and titration	
Conductivity*	HACH Conductivity meter	0.01 µS/cm-200mS/cm
E Coli	Standard methodology by plate count	
Anions (Cl^-, NO_3^-, SO_4^-, HCO_3^-)	External Lab (IC and ICP)	
Cations (Ca^{2+}, K^+, Mg^{2+}, Ba^{2+}, Na^+)	External Lab (IC and ICP)	

Particle Size distribution and Particle count

Particle Size distribution is measured in TU Delft using a Blue Laser Diffraction Particle Size Analyser (BLUEWAVE), with a measuring range between 0.01 to 2800 µm. This technology use three different types of lasers (one red and two blue) in order to recognize particles below 1 µm. When measuring AnMBR permeate (RO feed), approximately 200 mL of sample is needed in order to perform the analysis. Furthermore, particles are considered as absorbent or transparent, and with irregular shape, and flow is set up in 30%. Additionally, Bluewave performs three runs with the same sample, and gives results of particle size distribution of each, and an average one conducted based on the three distributions found before.

Particle count is measured in UNESCO-IHE Laboratory using Crystalline Particle Viewer (PV), which combines temperature and turbidity measurements with real time particle imaging (Crystallizationsystems.com, 2017). Crystalline PV counts particles from 2 to 200 µm passing through a define window in 5 seconds, and gives the total particle count per size (from 2 to 200 µm). For this particular case, samples were stirred and measure for 20 minutes.

Bacteria count

Bacteria is quantify using flow cytometry, discriminating between the total and the intact cell share by staining the sample and then analysing it using BD Accuri™ C6 software. In flow cytometry, particles and suspended cells pass through a pulsed beam of laser light, and two lasers, two scatter detectors, and four fluorescence collect the signal and digitalize them for computational analysis (Gatza, et al., 2013). Furthermore, by adding to the sample two different kinds of dyes: SYBR® Green I and Propidium iodide (PI), total bacteria count of damage and intact cells can be differentiate from the intact one. The first dye stains double–stranded DNA, and when excited by a certain electromagnetic wavelength emits red and green light, enable the count of total amount of bacteria. PI fixes to DNA and RNA in cells that lost membrane integrity (damage cells). Hence, when a damage cell is stained with PI, no light is emitted.
Since the device was design to work in a range of 10^2 to 10^7 cell/mL, concentrate and feed samples were diluted 200 times, and permeate was measured with no dilution needed (500µL).

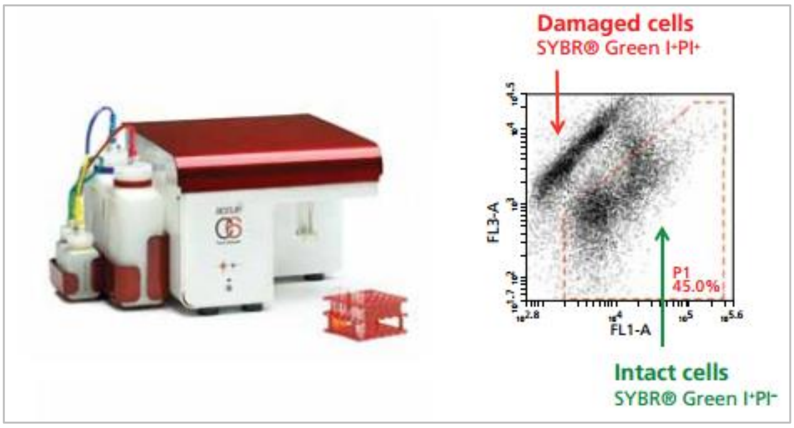


Figure 4-8: On the left, BD Accuri™ C6; on the right, and example of visualization of bacteria count. Source: Gatza, et al. (2013)

SDI and MFI

Silt density index and modify fouling index are measured in UNESCO-IHE laboratory. They are performed to characterize fouling potential of feed water, were desire SDI values are generally below 3. AnMBR permeate is passed through a membrane of 0.45 μm pore size and at a pressure of 210 kPa (2.1 bar). Weight of volume of feed passing through the membrane is recalled over time in order to calculate the parameters, where the decay in filtration rate (SDI) is stated as a percentage per minute, according to the equation below, where Δt are the time needed to collect the first and second fixed volume ΔV, *T=T* is the time when the second volume is starting to be collected, an *T=0* the start of collection of the first volume.

$$SDI = \frac{\frac{\Delta V}{\Delta t}_{T=0} - \frac{\Delta V}{\Delta t}_{T=T}}{\frac{\Delta V}{\Delta t}_{T=0}} \times \frac{100}{T} \quad (7)$$

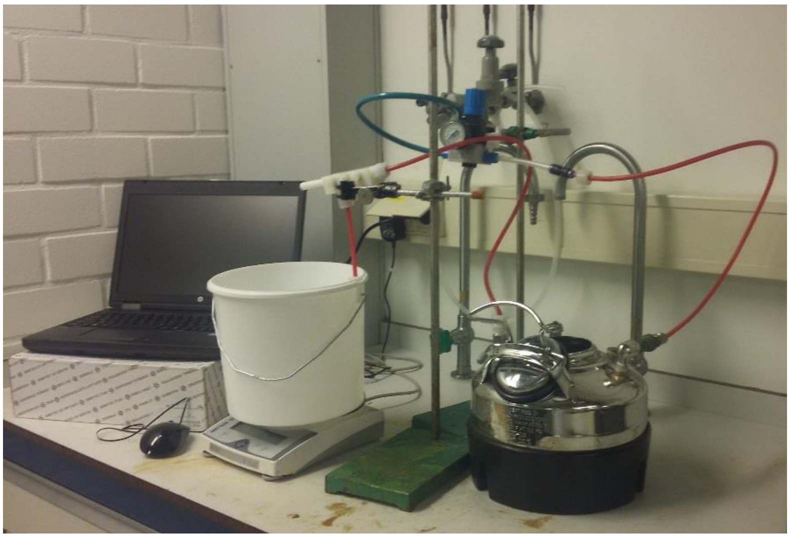


Figure 4-9: SDI and MFI

Since one of the main issues when measuring SDI in effluents of MF and UF (like the AnMBR permeate), is that values are relatively high, MFI was developed. It is define as the minimum value of the slope in the graph *t/V* versus *V*, during cake filtration.

$$MFI = \frac{\eta \times I}{2 \times P \times A^2} \quad (8)$$

η refers to viscosity at 20°C, *I* is the fouling index, *P* is pressure set as 200 kPa and *A* is area of $13.8 \times 10^{-4} m^2$.

4.3. Experimental methods

Three main phases are defined: the start up, with no membrane and demineralized water, Phase 1 with membrane and demi-water keeping aerobic conditions, and finally, the trials with AnMBR permeate as feed. In the first one, the main objective is to evaluate system safety and pump characteristics. The second one is performed to assess the system when working with demi-water an aerobic conditions. Finally, phase 2 is the core of the research, and permeate and concentrate characteristics apart from the operational conditions of the system are studied.

4.3.1. Phase 0: Start up with demineralized water and no membrane.

- Pump is started at a Frequency of 2 Hz (minimum frequency). System leakages and pressure build up are assess, while feed flow is being measured. This procedure is repeated for 5, 7, 10, 15 and 20 Hz.
- Real values of feed flow given by the pump are analysed and compare to the ones given by pump manufacturer.

4.3.2. Phase 1: Trials with demineralized water and membrane, keeping aerobic conditions

- The system is tested for 5 and 10 Hz, considering that the maximum cross flow velocity should be below 0.2 m/s.
- Real feed flows with membrane are calculated and compare to values obtained in Phase 0.
- Pressure build up, recovery, temperature and valve configuration are evaluated.

4.3.3. Phase 2: Trials with AnMBR permeate as feed and membrane, keeping anaerobic conditions

- Considering the feed values obtained from Phase 1, the system is ran at 10 Hz, and with assume constant feed flow.
- Volume of permeate, pressure in feed and concentrate lines, bypass flow and temperature are recorded every 5 minutes.
- Temperature, pH and conductivity of concentrate is measured every hour, and once a day in permeate produced.

CHAPTER 5

Results and discussion

This chapter comprehends a detailed description of outcomes obtained, evaluation and discussion of them. They are presented considering the specific objectives, and an assessment is conducted keeping in mind research questions.

Results include RO feed and its complete characterization, focusing on the differences in particle count and size distribution when the feed is kept anaerobic versus aerobic conditions. Furthermore, AnMBR permeate is evaluated as RO feed, and operational conditions when performing trials are detailed.

Finally, concentrate and permeate concentrations from RO system, ions, pH, etc., are presented and assess for reuse possibilities.

5.1. RO feed characterization

RO system is utilized as a second step of synthetic dairy industry wastewater treatment. Whilst this latter has a wide variation regarding the products made (milk, cheese, etc.), for this particular research, diluted milk plus macro nutrients (Ca, Mg and K) and Vithane® (micro nutrients) are used as feed of an AnMBR (Appendix B: Vithane characteristics). Hence, permeate of AnMBR treating synthetic dairy wastewater is used as RO feed. AnMBR chose works at mesophilic conditions (around 36 °C), 20 days SRT, flux around 10 lmh, volumetric load rate of 5 gCOD/Lday, and permeate production of approximately 4 L per day. The system is started at mid-November and Figure 5-1 shows the AnMBR system in Biothane.

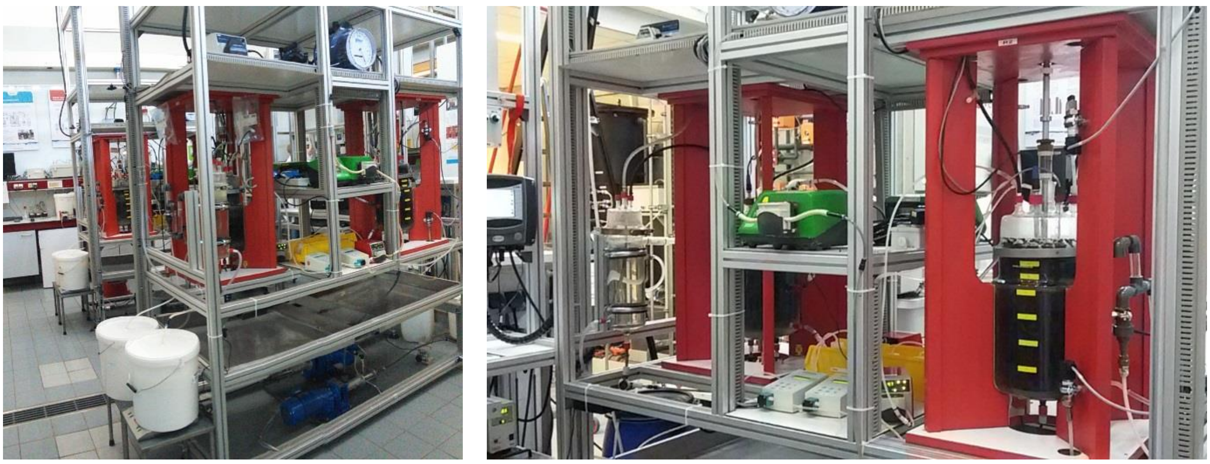


Figure 5-1: AnMBR set-up in Biothane.

Due to system characteristics, approximately 3 SRT are needed to ensure stable conditions (Dagnew, et al., 2011). Therefore, RO feed characteristics are assess from 1st of January on, even though, RO batch tests with AnMBR permeate are started on the 15th of February, after accumulating permeate for 3 days (14.77 L). Permeate storage is changed from aerobic to anaerobic, and measurements were done bearing in mind that they should be as anaerobic as possible.

Figure 5-2: On the left, the new anaerobic accumulation vessel; on the right, the previous accumulation and feed buckets of AnMBR.

Hence, Tables 5-1 and 5-2 show RO feed characteristics of the volume accumulated in the anaerobic vessel between the 13th and 15th of January. With values of parameter found and average values of AnMBR feed, removal efficiencies are calculated. Furthermore, even though feed characteristics for RO system are analysed ones due to the fact that all trails are going to be conducted with the same initial feed that will get concentrated, AnMBR permeate is analysed several times, and standard deviation is calculated from data of 1st of January on.

Table 5-1: RO feed wastewater characteristics and AnMBR removal efficiencies.

Parameter	Unit	Value	Standard Deviation	AnMBR removal efficiencies
pH	-	7.3	-	-
Conductivity	mS/cm	3.48	-	-
TCOD	mg/L	58.7	35	99%
TS	mg/L	2073	121	66%
VS	mg/L	740	100	86%
TSS	mg/L	30	0	99%
VSS	mg/L	0	0	100%
VFA	meq/L	0	0	100%
TP	mg/L	30.4	2	-
PO4-P	mg/L	30.2	2	0%
TKN	mg/L	216	21	21%
NH4-N	mg/L	191	30	-
Alkalinity	meq/L	31.5	7	Build up
MFI	s/L^2	210	-	-
SDI	-	3	-	-
CaCO3 Langelier Saturation Index (LSI)	-	0.86	-	-
Intact Bacteria count	Events/mL	26,000,000	-	-

Table 5-2: RO feed anions and cations

Cations	mg/L	Anions	mg/L
NH_4^+	179	Cl^-	220.0
Al^{3+}	0.0098	SO_4^-	12.9
Na^+	400	HCO_3^-	2196
K^+	106	NO_3^-	<6
Ca^{2+}	92.2	PO_4^-	31
Mg^{2+}	31.6		
Ba^{2+}	0.0208		
Mn^{2+}	0.012		
Fe^{2+}	0.055		
Sr^{2+}	0.17		

In light of AnMBR removal efficiencies obtained, RO feed characteristics are according to what is expected (Demirel, et al., 2005). Since the system is kept anaerobic, no nitrification or biological phosphorus removal is expected, due to the fact that the system is not only not design for phosphorus and nitrogen removal, but also because this processes are aerobic ones. Thus, nutrients removal efficiency is extremely low for this kind of systems, and in this particular case, it corresponds to 0 and 21 percent for orthophosphate and Total Kjeldahl Nitrogen respectively. Moreover, total solids removal is quite low (66%), while the one for suspended solids reaches almost 100%. When analysing conductivity and TS values of AnMBR permeate, it can be concluded that almost all solids are presented as dissolved ones, since a conductivity of 3.52 mS/cm corresponds to a total dissolved solids (TDS) of around 2,000 mg/L. Conductivity and TDS are comparable in diluted samples, with a comparison factor between 0.5 to 0.7 (Walton, 1989). Some dissolved solids are able to pass through ultrafiltration membrane, and are found in AnMBR permeate.

AnMBR pH is controlled and in a range around 7.1. Furthermore, its permeate pH is 7.3, which leads to assume that all alkalinity is presented mostly as bicarbonate, as shown in Figure 5-3.

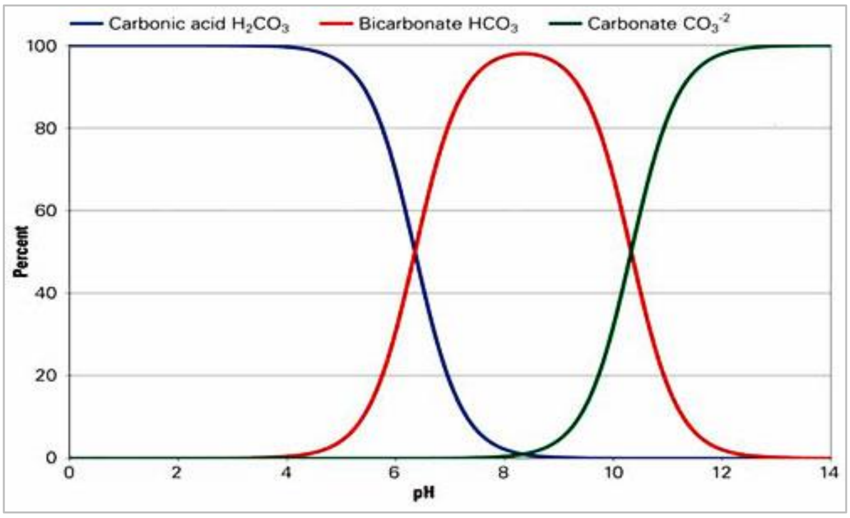


Figure 5-3: Alkalinity and pH diagram. Source: Chardonlabs.com (2016)

Feed alkalinity of AnMBR is zero, but anaerobic processes build up alkalinity, due to anaerobic digestion. McCarty developed a stoichiometric equation for the overall conversion of organic matter to methane, cited by Pavlostathis and Giraldo-Gomez (1991) and shown below:

$$C_nH_aO_bN_c + \left(2n + c - b - \frac{9sd}{20} - \frac{ed}{4}\right) H_2O \rightarrow \frac{de}{8} CH_4 + \left(n + c - \frac{sd}{5} - \frac{de}{8}\right) CO_2 + \frac{sd}{20} C_5H_7O_2N + \left(c - \frac{sd}{20}\right) NH_4{}^{+} + (c - \frac{sd}{20}) HCO_3{}^{-} \quad (9)$$

Where $d = 4n + a - 2b - 3c$; s = fraction of waste converted to cells; e = fraction of waste converted to methane gas for energy $(s + e = 1)$, $C_nH_aO_bN_c$ is an empirical formula of waste being digested, and $C_5H_7O_2N$ is the empirical formula for bacteria dry mass.

High values of ammonium, sodium, potassium, calcium, magnesium and chloride are typical from dairy industry wastewater, as shown in Table 5-3. Moreover, calcium, magnesium and potassium are added as macronutrients to AnMBR feed (24, 29 and 47 mg of Ca, Mg and K respectively per litter of feed).

Table 5-3: Concentration of selected ions in dairy industry wastewater. Source: Demirel, et al. (2005)

Effluent type	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Fe (mg/l)	Co (mg/l)	Ni (mg/l)	Mn (mg/l)
Creamery	170–200	35–40	35–40	5–8	2–5	0.05–0.15	0.5–1.0	0.02–0.10
Cheese/whey	735[a]	42.8[a]	47.7[a]	11.4[a]				
Cheese/alcohol	423[a]	41.2[a]	54.3[a]	8.3[a]				
Cheese/beverages	453[a]	8.6[a]	33.6[a]	16.9[a]				
Cheese/whey	419[a]	35.8[a]	52.3[a]	11.0[a]				
Mixed dairy	123–2324	8–160	12–120	2–97	0.5–6.7	0	0–0.13	0.03–0.43
Cheese	720–980		530–950					

[a] Mean concentrations are reported.

According to RO membrane manufacturer, feed of this type of system should have a SDI below 5 in order to be able to obtain permeate without overstressing the membrane, and pH between 2 and 11. MFI values between 180 and 225 s/L^2 corresponds to SDI values below 3, which is coherent with what is stablished before. When SDI and MFI are conducted, dilution of permeate sample are needed to do, in order for permeate to pass through the 0.45 µm filter. Then, in 10 times dilution, MFI values obtained is multiply by 10 to find the real value, and SDI serves as an indicative value. AnMBR permeate has then, an MFI value of 210 s/L^2 and SDI approximately 3.

Thus, after assessing RO feed characteristics, it can be conclude that AnMBR permeate of synthetic dairy industry wastewater meet the necessary characteristics that allows its use as RO feed (in the given conditions).

5.1.1. Modelling feed characteristics

Based on feed characterization, Genesys membrane master 3vc software is used to predict membrane scaling and prevent severe membrane damage. Calculations are conducted considering an estimated recovery of 8%, design pressure of 15 bar, feed flow of 350 mL/m (corresponding to a cross flow velocity of 0.2 m/s), and temperature of 18 °C. RO feed ions compositions is loaded into the software and considering the operational parameters mentioned above, software is ran. Genesys gives results regarding feed scaling and fouling potential, ion composition of concentrate, and the possibility to calculate final recovery is a real scale with several trains system is installed. Fouling and scaling potential of RO feed (AnMBR permeate) are shown in Figure 5-4. Feed water chart showed in figure, contains the usual solutes that precipitate considering brackish water in the abscissa (given by Genesys software), and saturation index on the ordinate.

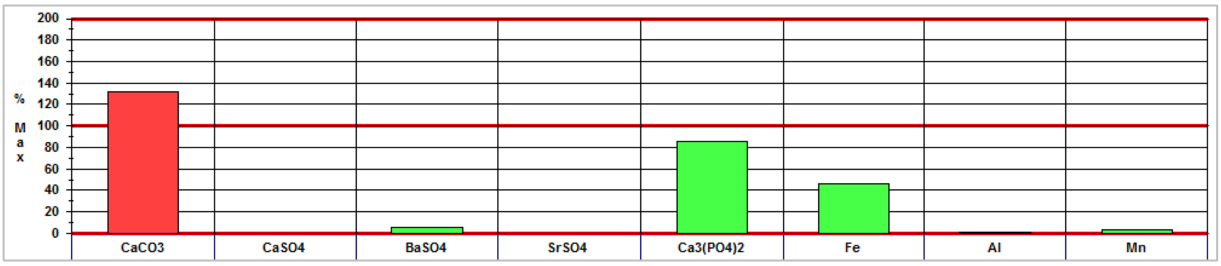


Figure 5-4: Fouling and scaling potential in Ro feed water.

As can be seen in Figure 5-4, calcium carbonate exceeds the saturation limit (100%) and it is oversaturated, which means is going to precipitate promoting membrane fouling. Apart from calcium carbonate, calcium phosphate and iron are also prone to precipitate, but in smaller quantities. The rest of the possible compounds to precipitate have saturation levels below 10%. However, pH variations have a significant impact on saturation and precipitation of different compounds, and as an example, calcium carbonate may not precipitate if pH decrease enough.

Calcium carbonate is a salt formed from a weak acid (carbonic acid), according the equation shown below:

$$CaCO_3 + H_2O \leftrightarrow Ca^{2+} + HCO_3{}^{-} + OH^{-} \quad (10)$$

If pH increase, then we will have a lower concentration of H^+ and a higher one of OH^-, shifting the reaction the left, and producing more $CaCO_3$. Thus, calcium carbonate ion product (define as the product of Ca^+ and CO_3^- actual concentration) increase, and when higher than the solubility product (K_{sp} is $2.8x10^{-9}$), precipitation occurs. Therefore, to avoid $CaCO_3$ precipitation, RO feed pH should decrease to obtain better results regarding scaling and fouling potential.

Calcium phosphate is also formed from a weak acid (phosphoric acid), and a pH decrease will also produce a decrease in its saturation and precipitation possibilities. Furthermore, calcium phosphate is more prone to precipitate than struvite, because smaller concentrations are needed in order to have a super saturated solution. Experimental values of struvite solubility constant varies from $3.89x10^{-10}$ to $4.37x10^{-14}$ Rahaman, et al. (2006), while this value for calcium phosphate is $2.07x10^{-33}$. K_{sp} equations for calcium phosphate and struvite are shown below:

$$Ksp_{Ca_3(PO_4)_2} = [Ca^{2+}]^3 \times \left[PO_4{}^{3-}\right]^2 = [3s]^3 \times [2s]^2 = 108s^5 \quad (11)$$

$$Ksp_{MgNH_4PO_4} = [Mg^{2+}] \times [NH_4{}^{+}] \times \left[PO_4{}^{3-}\right] = [s] \times [s] \times [s] = s^3 \quad (12)$$

Where *s* represents the mols of each compound. When the concentration of actual solutes exceed the solubility product, then ions will precipitate as salts. For calcium phosphate, the limiting concentration *s* is $1.13x10^{-7}$ mol/L, while for struvite is between $4.9x10^{-6}$ to $5.06x10^{-5}$ mol/L. Thus, considering Mg^{2+}, Ca^{2+}, PO_4^{3-} and NH_4^- concentration in AnMBR permeate, calcium phosphate formation is more possible than struvite.

As a result from Genesys membrane master 3vc model, antiscalant to prevent scaling and obtain higher recoveries is recommended. Considering feed characteristics, a broad spectrum antiscalants is recommended: Genesys WB (Appendix C). A similar antiscalant is bought, but from Veolia brand: HYDREX 4103. However, it arrived after all test are concluded.

5.1.2. Bacteria in RO feed

Bacteria count value is high considering an ultrafiltration membrane, were pore size is 0.03 µm, and in theory, no bacteria should pass through the membrane. However, AnMBR permeate is reach in nutrients, and therefore, a medium prone to bacteria proliferation. Additionally, permeate is store for three days in the vessel, so enhanced growth conditions may be achieved. To evaluate this latter hypothesis, samples from different locations are taken: in the accumulation tank and before it, as shown in Figure 5-5.

Figure 5-5: Measurements of bacteria count. On the left, the accumulation tank, on the right the

Total and intact (alive) cells are calculated in duplicates, and values are shown in Table 5-4.

Table 5-4: Total and Intact cell count in two sampling points.

Location	**Accumulation vessel**	**Before Vessel**
Total count (Events/mL)	31,500,000	14,500,000
Intact count (Events/mL)	26,000,000	10,250,000

Either for total or intact count, values from the accumulated vessel are more than twice the ones found before it. Nevertheless, taking into consideration that both orders are the same (10^7), there is no significant difference between samples. This leads to conclude that the accumulation vessel is not the only system component where bacteria are prone to grow. Furthermore, it can be concluded that lines and accumulation tank are contaminated and not properly sterilize, which entails into higher RO fouling potential.

Bacteria count is performed by FCM and BD Accuri™ software is used to analysed data obtained. This latter is able to count all intact cells, which correspond to bacteria and viruses. This latter size is between 0.01 to 0.1 µm, while bacteria varies from 0.1 µm up to 40 mm. AnMBR pore size is 0.03 µm, hence, small viruses may pass through the membrane and can be found in permeate. Furthermore, membrane pore size is an average, but bigger pores are present in it, which means that larger particles (bacteria and viruses) than 0.03 µm can be found in permeate

5.1.3. Particle count and size distribution in RO feed

Particle size distribution on AnMBR permeate is measured in TU Delft four different days: January 18th, February 1st, 3rd, and 14th. Average particle size distribution found from 3 runs per sample are shown in Figure 5-6.

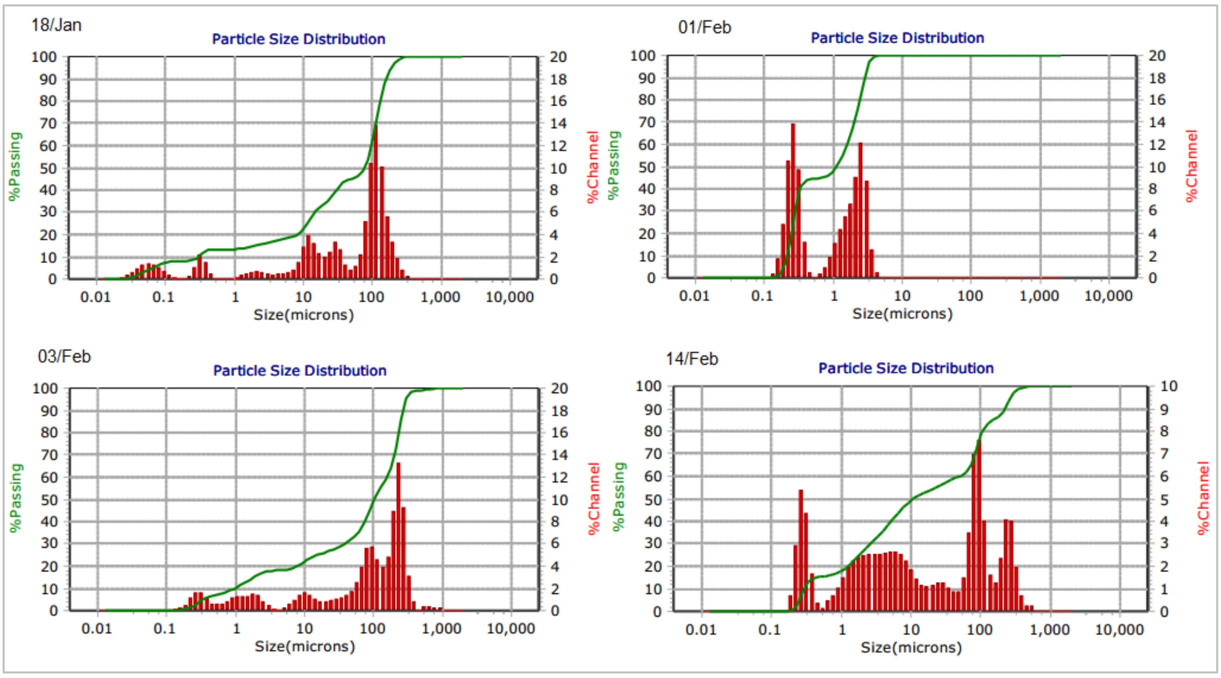


Figure 5-6: AnMBR permeate average particle size distribution, from different dates.

Results show a great variation between samples, even though they were measure under the same conditions. Differences between the 1st and 3rd of February are especially important, considering that samples were taken from the anaerobic accumulation vessel, which stored AnMBR permeate from 23rd January until 27th January, and was kept at temperatures around 8°C, hence, they are the same sample. Table 5-5 presents d_{10}, d_{50}, and d_{90} values for all measurements.

Table 5-5: Diameters at which 10, 50 and 90% of sample's mass is comprised of smaller particles, in different sampling days.

Sample	d_{10} (µm)	d_{50} (µm)	d_{90} (µm)
18/01/2017 Average	0.3	79	155
01/02/2017 Average	0.2	1	3
03/02/2017 Average	1	103	266
14/02/2017 Average	0.3	11	221

Moreover, considerable deviation among particle size distribution happens not only for different samples, but also for different runs of the same sample, as shown in Figure 5-7.

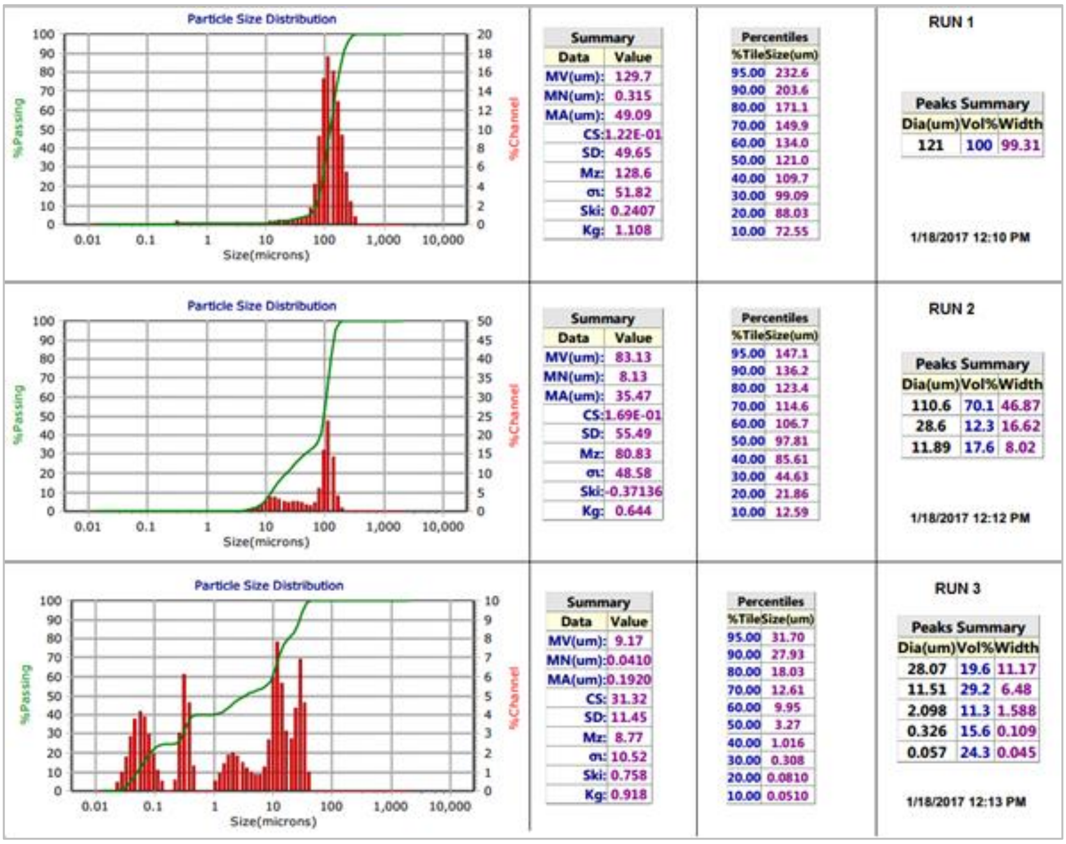


Figure 5-7: Deviation between 3 runs of the same sample taken the 18th of January, on particle size distribution.

In order to further study and understand the different results of PSD, analysis are also performed in UNESCO-IHE with Crystalline Particle Viewer (PV), which counts particles from 2 to 200 µm. Same sampling points used for bacteria count, are also used to measure particle count and particle distribution (accumulation vessel and before it). Moreover, the sample took in the feed vessel was divided into two, and one was saturated with air, while the rest of the samples are taken under anaerobic conditions. In the aerated sample, pH increase from 7.0 to 8.2, and more particles were visually detected (Figure 5-8).

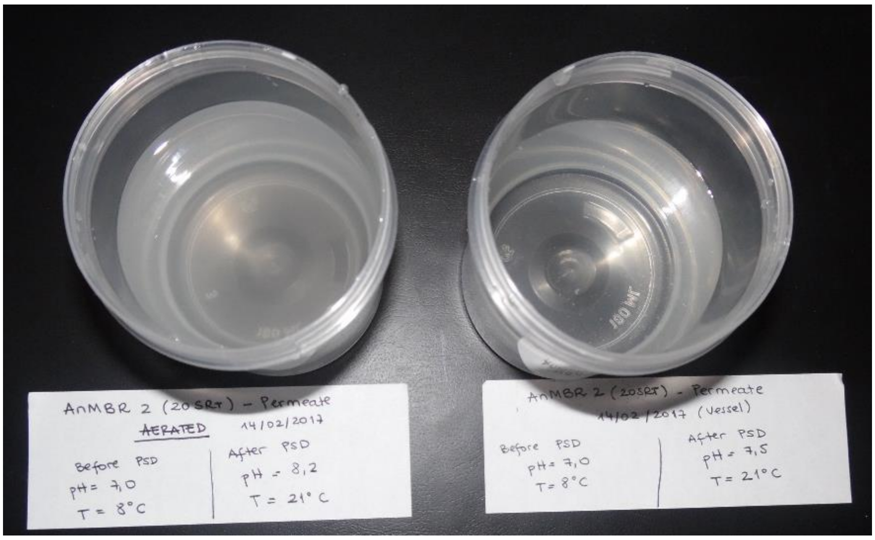


Figure 5-8: On the left, aerated sample, and on the right the anaerobic one after performing all the measurements. Both samples were taken from the accumulation vessel.

Increase in pH when aerating the sample is due to CO_2 exchange with the atmosphere. Aqueous CO_2 reacts with water forming carbonic acid (H_2CO_3). If pH is between 7 and 10, carbonic acid is mainly dissociated into HCO_3^- and H^+ (as shown in Figure 5-3, Section 5.1). Then, CO_2 equation follows:

$$CO_2 + H_2O \leftrightarrow HCO_3{}^- + H^+ \tag{13}$$

When CO_2 is released, the equilibrium shifts to the left, and as a consequence, the system has lower concentrations of HCO_3^- and H^+. Thus, pH increase.

Samples were stirred and measure for 20 minutes, where data is collected every 5 seconds. Relative particle size distribution and its standard deviation are shown in Figure 5-9.

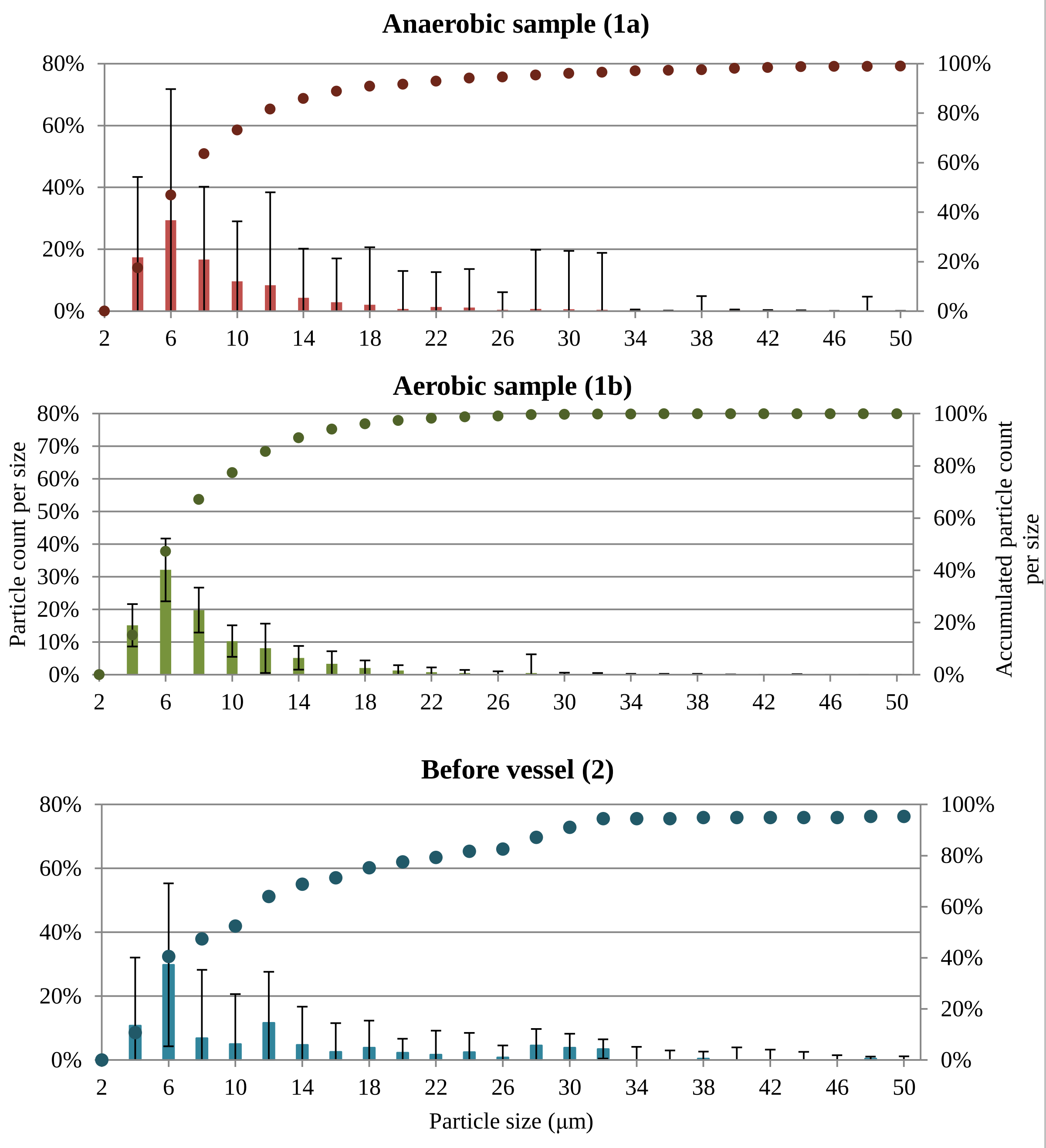


Figure 5-9: Relative particle size distribution. The dots represent the accumulated while relative count per particle size (diameter size) is expressed in bars with their standard deviation.

When analysing relative particle size distribution with Crystalline PV, all samples have a similar distribution, where around 30% of the total count represent particles of 6 µm size, and d_{50} is 6 µm. The distributions have a considerably different standard deviation per particle size, and the content of particles higher than 20 µm is slightly higher in the sample taken before the accumulation vessel. If instead of analysing PSD in the 20 minutes ran, it is done every 30 seconds (as the Bluewave particle size distribution), PSD has a considerable deviation, as shown in Figure 5-10. However, d_{50} values are below 10 µm.

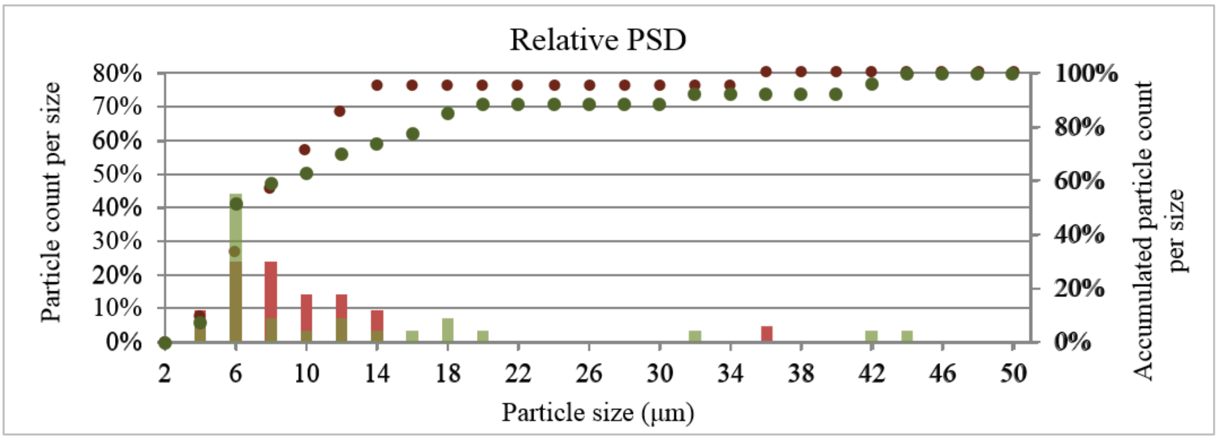


Figure 5-10: On red, PSD of a sample measure for 30 seconds at initial time 1 minute, and on green, measurements for 30 seconds at initial time 10 minutes.

According to Lousada-Ferreira, et al. (2016), permeate analysed in 450 MBR present with a pore size of 0.04 µm, particles in the range from 2-100 µm were counted. This corresponds to the values found (when Crystalline PV is used), in all samples of the research, where d_{50} (6 µm approximately) is around 100 time higher than the membrane pore size (0.03 µm). Furthermore, AnMBR integrity is studied considering data of anaerobic sample from accumulation vessel. Graphical representation followed indications given by (APHA, et al., 2005): normalization of data by dividing particle count in a given size range by the size interval, and presenting particle size in logarithmic scale. Hence, PSD is presented as a power-law function as shown below:

$$logN(d_p) = A \times log(d_p) + logB \tag{12}$$

Where $N(d_p)$ is the derivate of particle diameter (d_p), and A and *logB* are power-law coefficients. Figure 5-11 shows the graphical results obtained for the above considerations.

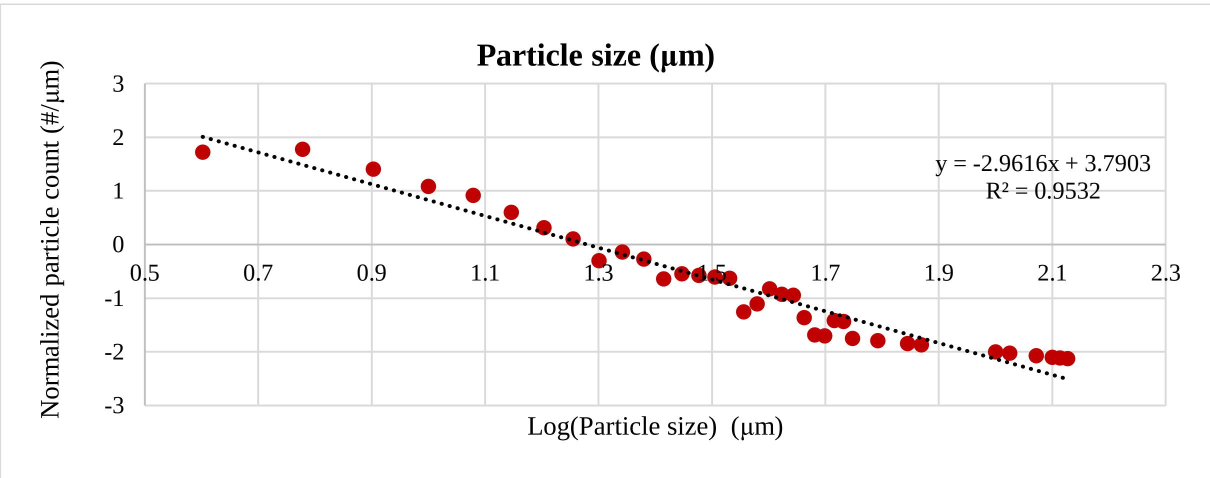


Figure 5-11: Normalized particle count, from anaerobic sample taken in the accumulation vessel.

PSD permeate sample has a R^2 power-law above 0.95, which according to Lousada-Ferreira, et al. (2016), means that AnMBR membrane does not present integrity failure. Additionally, VSS values are zero, and if membrane integrity is compromise, then several suspended solids are able to pass through it and TSS and VSS values should be above zero, which is not the case in this research.

Aside from studying PSD, total particle count is asses in the 3 samples: anaerobic and aerobic from the accumulation vessel, and before the accumulation tank. Total particle count in 20 minutes is shown in Figure 5-12.

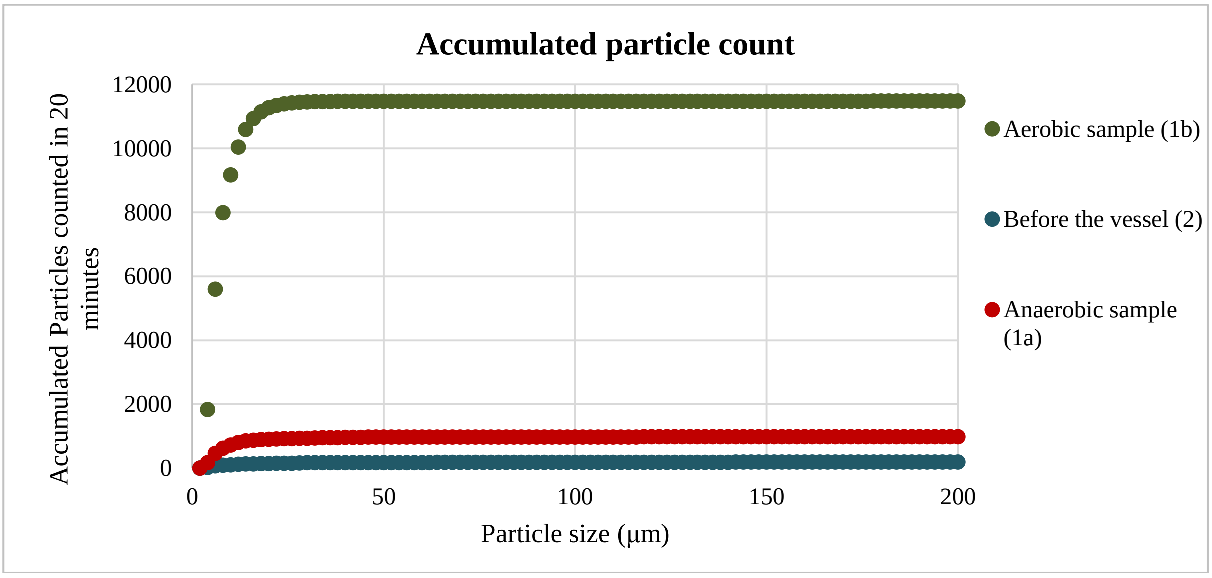


Figure 5-12: Total particle count in 20 minutes of measurements.

Total particle count have massive differences in the three samples. In the aerated sample, values reach up to almost 11,500 while in the anaerobic one is almost 1,000, and in the one before the vessel it is almost 200. Hence, when aerating AnMBR permeate (RO feed), more particles are developed than if it is kept anaerobic. Particles can be formed due to precipitation and crystallization of certain compounds, like calcium carbonate and calcium phosphate, among others, which precipitate when samples are aerated due to higher pH. As a conclusion for this experiment, aerating feed of RO that can be kept anaerobic, without controlling pH, leads to have around 10 times more particles than if we keep it anaerobic, but with a similar distribution.

5.2. System operability

5.2.1. Set-up and start-up of the system

RO set up is build up in the work space of Biothane laboratory, in view of safety considerations mainly regarding the pump. Experimental set up design is shown in Figure 5-13.

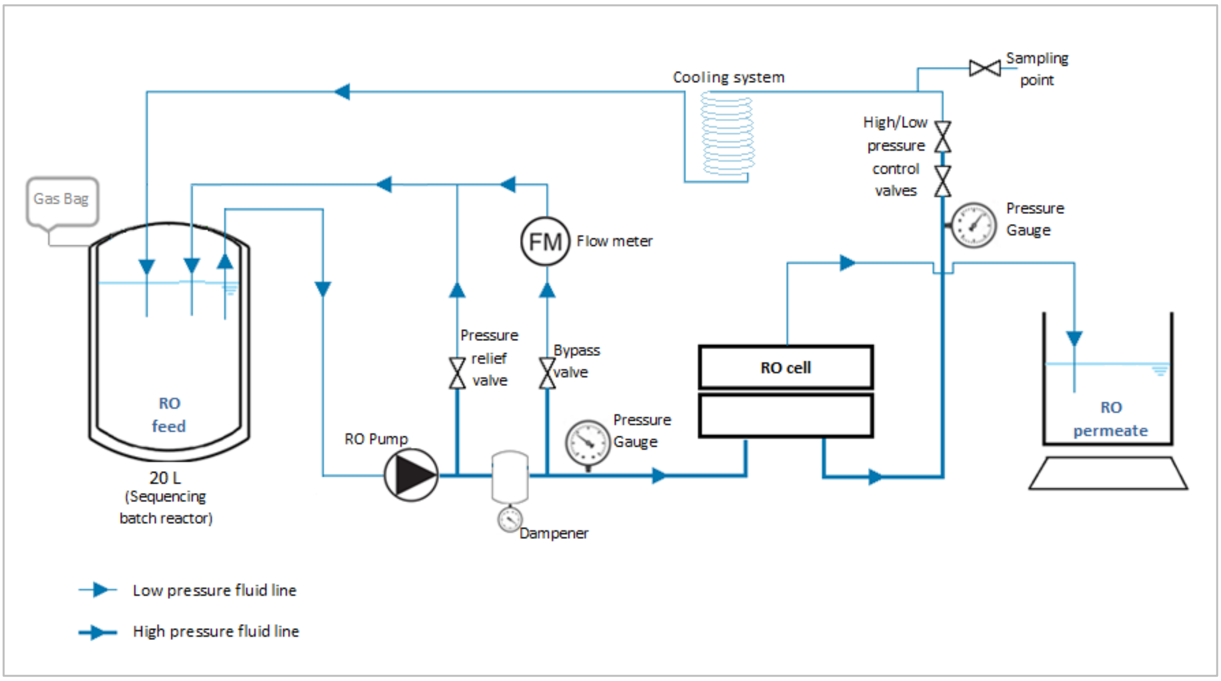


Figure 5-13: RO experimental setup.

Feed vessel is connected to the pump which increments line pressure, measurable with a pressure gauge located in the RO feed line. The gauge is able to measure a difference of 2 bars, and a range from 0 to 100 bars, as shown in Figure 5-14.

Figure 5-14: Pressure gauges.

Permeate of RO is accumulated in a glass tank, located on top of a weight scale. Concentrate (or brine) line is also connected to a pressure gauge and high/low pressure valves, to decrease pressure to atmospheric one and recirculate concentrate into the feed vessel. Before arriving to the vessel, concentrate passes through a coil cooling system which decrease the line temperature. Since all concentrate is recirculated into the feed vessel, after a certain amount of time, wastewater characteristics of the feed vessel are almost the same as the one in the concentrate (depending on RO rejection, recovery and feed flow). Therefore, only two sample points are needed: one in the permeate line, and another in the concentrate line. This latter will provide information regarding the feed characteristics to RO membrane.

RO cell is a solid prism of around $15x10^{-4}$ m^3 (10cm x 10cm x 15cm) that weights around 6 kg. Permeate line is in the top of the cell, while concentrate and feed ones are located in the bottom, as shown in Figure 5-15.

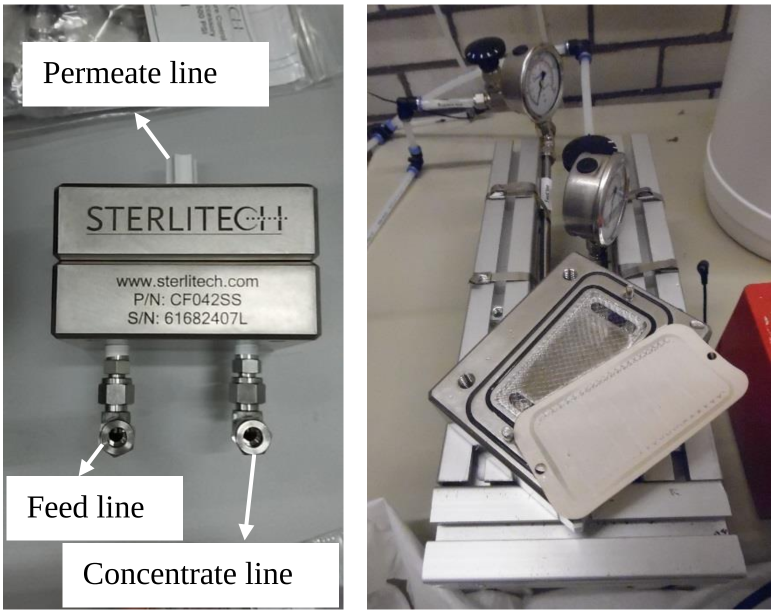


Figure 5-15: RO cell system. On the left, the whole RO cell, with permeate, feed and concentrate lines. On the right, the cell opened, where feed spacers and membrane can be seen.

A frequency meter is installed to control the pump given frequency and assure a constant feed flow from the pump. However, when the system is being set up, the original frequency meter is burned out due to an electrical connection error. Therefore, a new system with the same frequency range is bought and installed (Figure 5-16).

Figure 5-16: On the left, the original frequency meter that was burned out. On the right, the installed frequency meter.

Flow meter is installed in the bypass line, but can be also connected in the concentrate line. Since cross flow velocities should be between 0.1 to 0.5 m/s, feed flow to RO membrane should be between 200 and 1000 mL/m (0.05 to 0.26 gpm). Nevertheless, the flow meter is able to measure flows from 750 to 7500 mL/m (0.2 to 2.0 gpm) as shown in Figure 5-17, and possible concentrate flows (which are below 100 mL/m) may be outside the meter range.

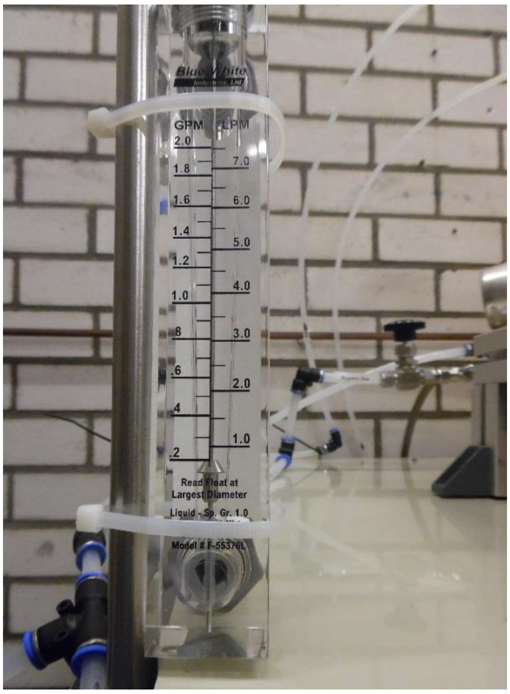


Figure 5-17: Installed flow meter.

Additionally, since RO membrane has 10 cm length, small flow changes have a significant effect in recovery percentage, but flow meter is able to measure 0.1 gpm differences (350 mL/min). Hence, the installed device is not appropriate for the system conditions. It is connected to the concentrate or bypass line, considering which is the largest flow and therefore, measurable.

Stainless steel coil cooling system of 15 m is mounted in the concentrate line and connected to a cooling device. The coil is firstly immerse into a 20 L bucket filled with tap water, and connected through two lines to the cooling device. However, when the system is installed, it is found that the cooling device has a pump to push water from it to the bucket, but it works in close systems (like water jackets), were water entering the system is the same as the one leaving it. Since the bucket is not a close system, water started overflow. Therefore, another coil is used to cool down the system. The final setup has two stainless steel coils submerge in a 40 L bucket. One is used to cool down the concentrate coming from the RO membrane, and the other, cools down the water were both coils are submerged, which consequently chills the concentrate line. Initial cooling system and final one are shown in Figure 5-18.

Figure 5-18: On the left, the cooling system; on the right, the installed one.

Once the cooling structure is installed, the system is ready to run. A trial with demineralized water and no membrane is conducted to assess leakages. Several tubes are changed, due to the fact that connections between tubes were done considering European metric system (cm), while some setup pieces are bought in USA. Therefore, differences of 0.5 mm are found in tubes diameters and several connections leak when the system is started. Figure 5-19 show the final system setup.

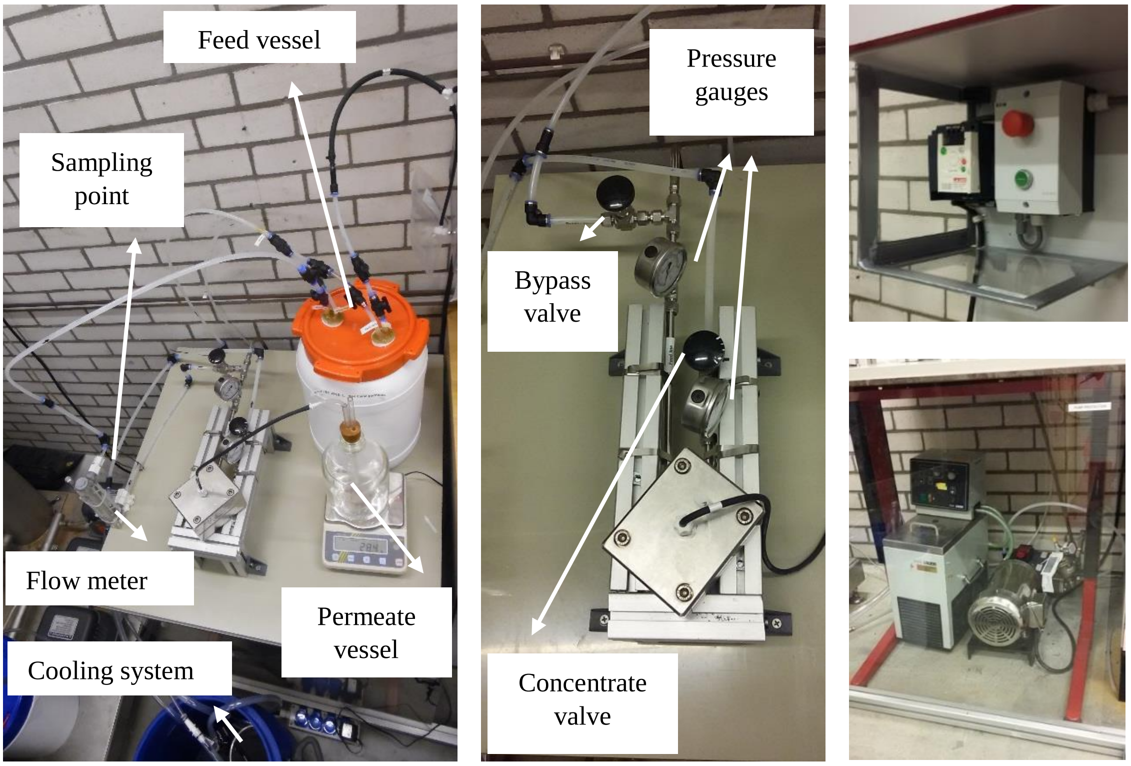


Figure 5-19: RO system setup. On the left and centre, RO cell, feed and permeate vessels; on the right, in the upper picture is the frequency meter and emergency button, while at the bottom are the pump and cooling system.

5.2.2. Trials with demineralized water

Once leakages are fixed, the system is ran with demi-water and no membrane, to assess feed flows and compare them to the ones given by the pump manufacturer. Flows are found for 2, 5, 7, 10, 12, 15 and 20 Hz and results are shown in Table 5-6 and Figure 5-20.

Table 5-6: Average flow and standard deviations for different pump frequencies, with no membrane and demineralized water.

Parameter	**Unit**	**Frequency (Hz)**						
		2	5	7	10	12	15	20
Average Flow	mL/m	74.3	365.5	511.0	675.8	900.8	1124.0	1520.0
Standard deviation	mL/m	1.0	1.9	2.7	10.8	11.3	7.8	10.0

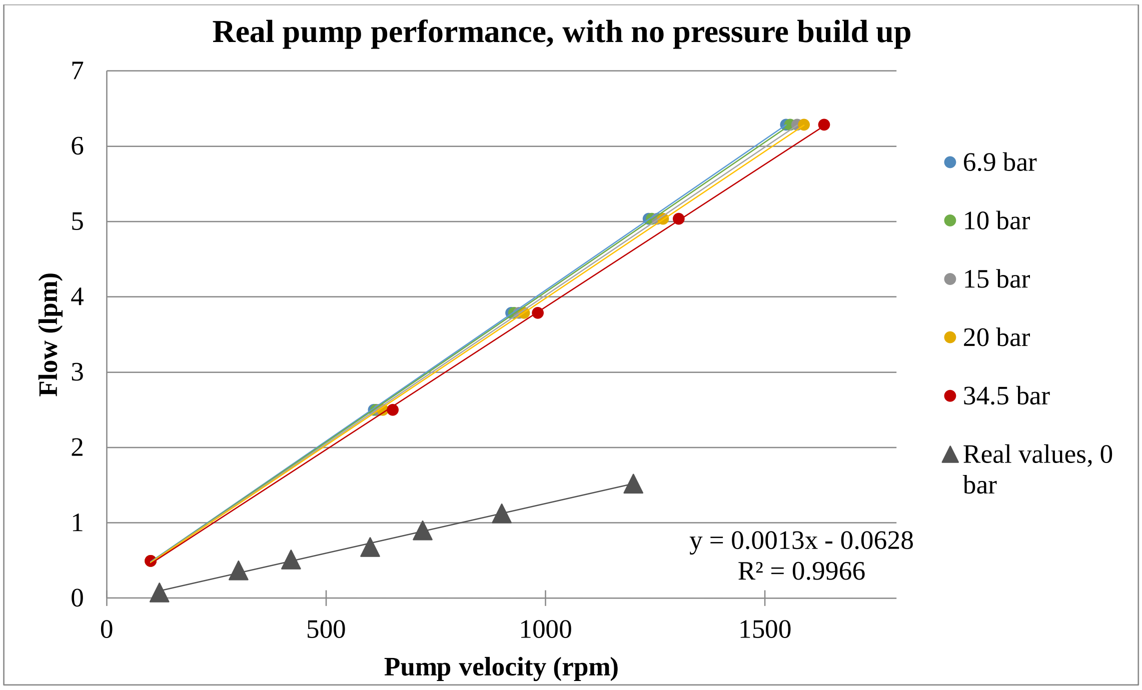


Figure 5-20: Comparison of flows obtained when the RO system is started out.

Flows are measured as the volume of concentrate plus permeate obtained per minute (no bypass flow is admitted), and trials were conducted for around 10 minutes. Time limitation is because laboratory weight scale used support a maximum of 15 kg. Graphical results shown in Figure 5-20 corresponds to average values obtained per frequency. Moreover, standard deviation is calculated in each case, and values are always below a 2% difference from average flows. Real flows are considerable lower than the ones given by the pump manufacturer. This can occur because pump performance is assess from pressures in the range of 6.9 to 69 bars. However, while this trial is carried out, no pressure is detected by the pressure gauges, and no permeate is obtained (recovery zero).

As a second step, the system is evaluated using demineralized water, spacer (31 mil and diamond shape) and selected RO membrane: DOW-FILMTEC BW30XFR, keeping aerobic conditions. Since membrane crossflow velocities should be below 0.5 m/s, and usually, between 0.1 and 0.2 m/s, pump frequencies are kept below 10 Hz. Hence, trails, with 5 and 10 Hz are conducted. The main objectives of this step is to measure pumped flows, pressure build up, maximum recoveries achieved and changes in temperature.

To begin with, pump frequency is established at 5Hz. During 25 minutes, volume of concentrate and permeate produced over time are weight every 2 minutes, and feed and concentrate pressures are measured. Permeate flow is asses, and results are shown in Figure 5-21.

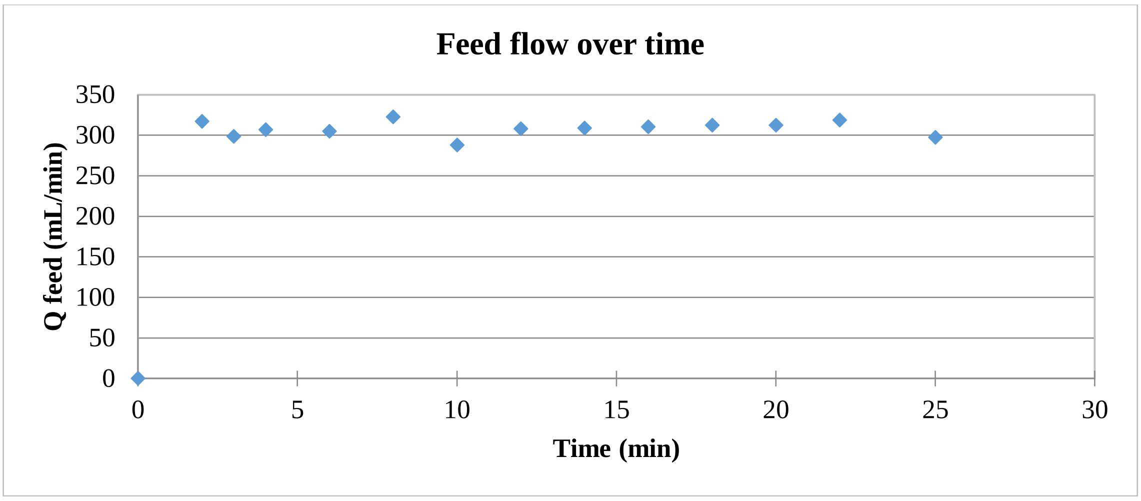


Figure 5-21: Feed flow over time when using demi-water in aerobic conditions, for a pump frequency of 5 Hz.

Average feed flow found is 308 mL/m, with a standard deviation of 9 mL/min (less than 3%). Therefore, it can be assume that at the given conditions, feed flow is constant. This value will be further assume for larger trials, due to weight scale limitations in the laboratory (maximum of 15 kg). Although a constant flow is achieved, system pressure increased as shown in Figure 5-22.

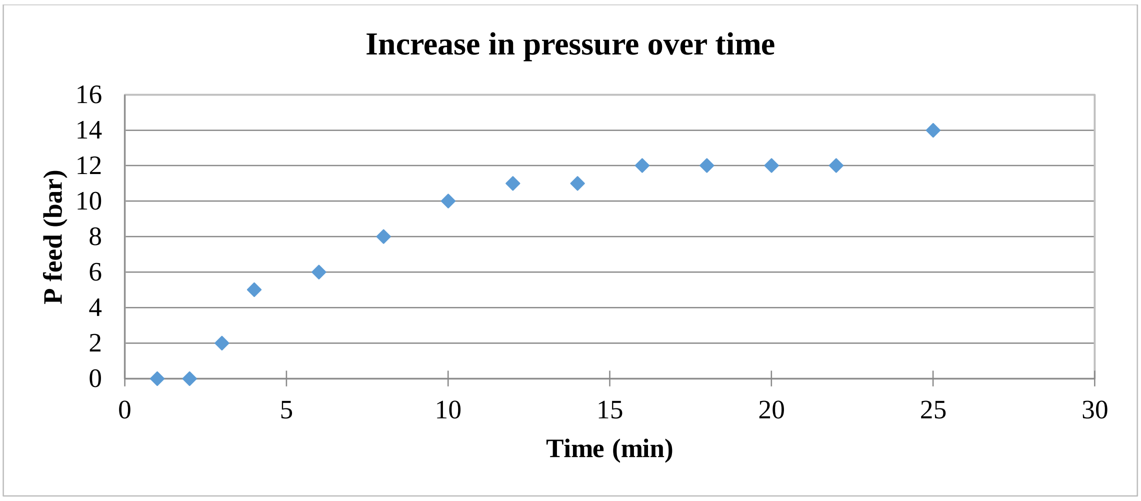


Figure 5-22: Feed pressure increase over time when using demi-water in aerobic conditions, for a pump frequency of 5 Hz.

RO system is design to work at constant feed pressure when feed characteristics remain constant. Hence, more trials are conducted assuming the found feed flow, in order to achieve constant pressure by changing the concentrate valve opening. It is important to highlight that during trials with demi-water and pump frequency of 5 Hz, no bypass flow is needed because cross flow velocity is 0.15 m/s. While performing trials with 5 Hz, concentrate valve open position affects pressure build up and recovery achieved. When concentrate valve is opened approximately 45° from the closed position, a constant feed pressure of 13 bar is achieved during 40 minutes (in an hour duration trial), with a maximum recovery per meter of membrane near 9%. Furthermore, cooling system is not turned on during trial, and total increase of temperature in 60 minutes is 1.4°C. Figure 5-23 shows feed pressure, recovery per meter of membrane and temperature variation over time, through the whole trial.

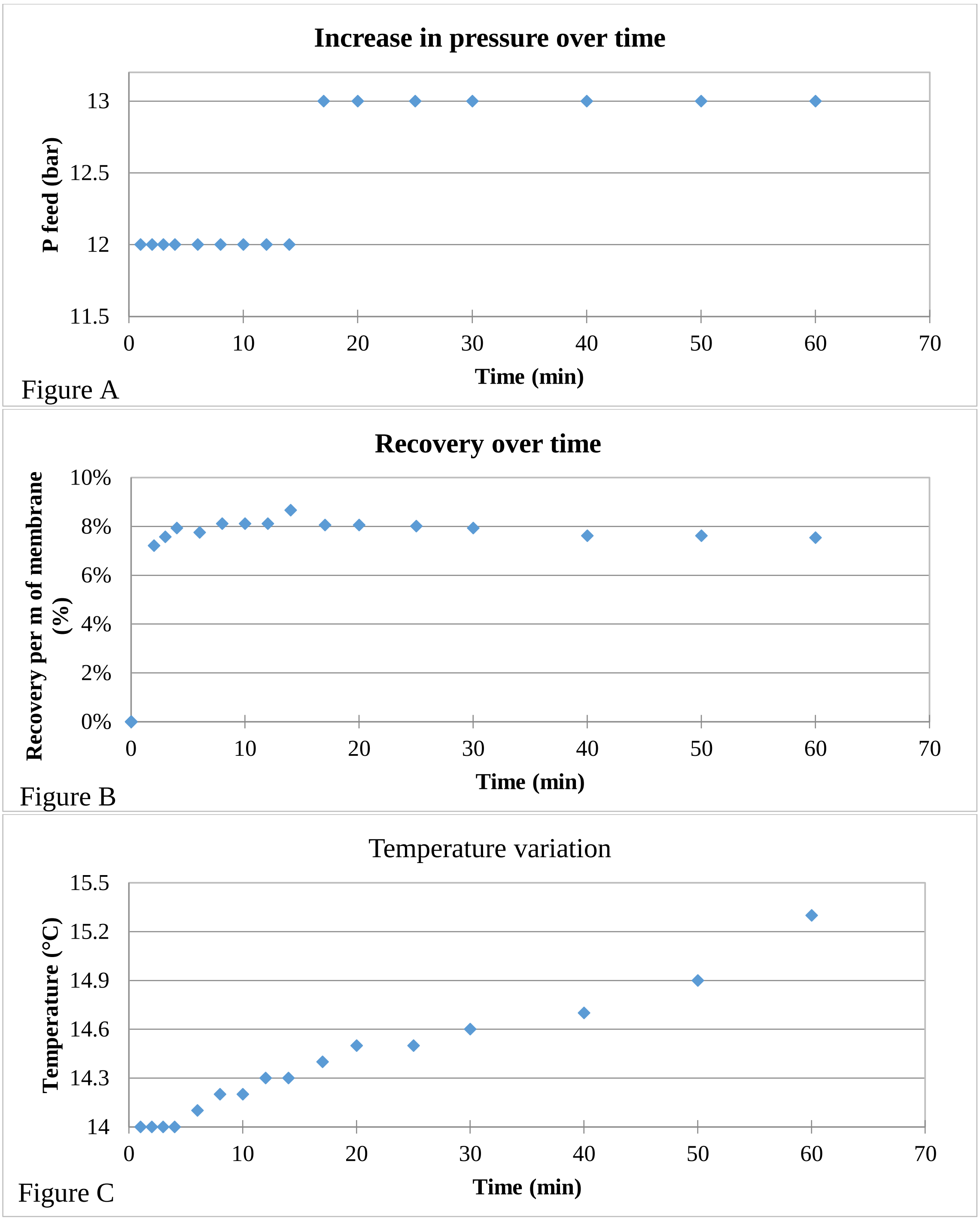


Figure 5-23: Increase in pressure over time (Figure A), recovery per meter of membrane over time (Figure B), and temperature variation over time (Figure C), of RO system ran with demi-water, pump frequency of 5 Hz, constant feed flow of 308 mL/min, concentrate valve opened 45°, and Dow-Filmtec BX30XFR membrane.

Similar procedure as the one conducted for 5 Hz is done for 10 Hz. Two trails with RO membrane, of 12 minutes each where bypass valve is closed are conducted in order to find pump feed flow at 10 Hz (concentrate vale is opened). Average feed flow found is 1060 mL/m, with a standard deviation of almost 100 mL/m (around 9%). This value is used as pumped feed flow for the rest trials performed (with demi-water and AnMBR). Additionally, in demi-water trials where no bypass is allowed, concentrate flux is measured by a flowmeter.

A 75 minutes trial with demi-water, pump frequency at 10 Hz, no bypass flow, and a concentrate valve angle of around 65° is conducted. Concentrate valve angle is stablished in 65° from closed position in order to start the system with a feed pressure below 10 bars and be able to observe pressure build up but giving the system enough margin. If concentrate valve is kept at 45 °, initial system pressure is around 15 bar, and in less than 30 minutes increase to 22 bars, which is the maximum allowed pressure. A maximum recovery of 2.2% per meter of membrane is obtained and feed pressure is stabilized at 12 bar after 45 minutes ran. Figure 5-24 shows evolution of recovery and pressure over time.

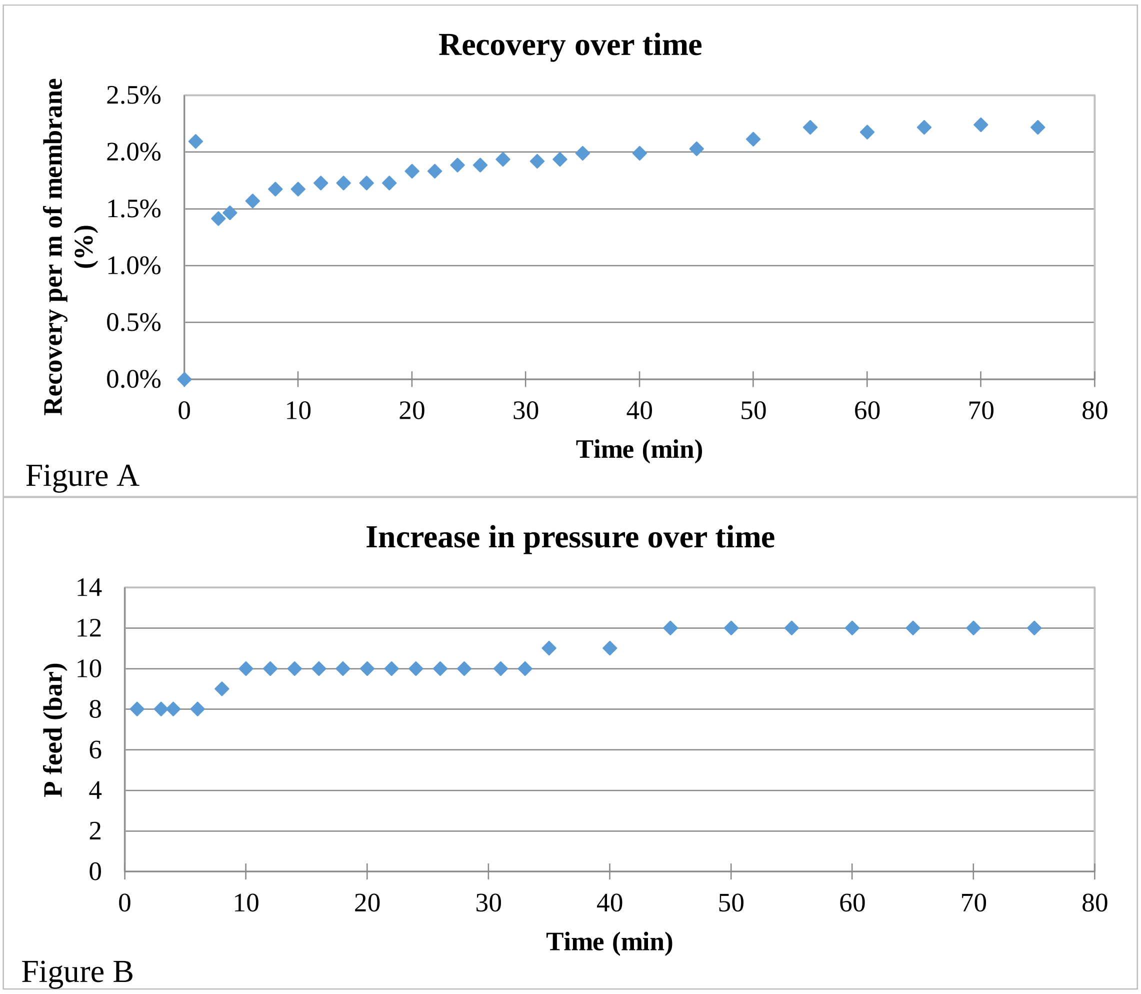


Figure 5-24: Recovery per meter of membrane over time (Figure B) and increase in pressure over time (Figure A), of RO system ran with demi-water, pump frequency of 10 Hz, constant feed flow of 1060 mL/min and Dow-Filmtec BX30XFR membrane.

5.2.3. Trials with AnMBR permeate

AnMBR permeate collected anaerobically between 13th and 15th of January is used as RO feed. The system is ran in batch, at 10 Hz and for a total of 21 hours 45 minutes, where the membrane is cleaned twice. Due to working hours in Biothane laboratory, the system cannot be ran for more than 4 hours continuously. Laboratory is opened from 8:30 until 16:30, a lunch break is compulsory and no one is allow to stay in the laboratory during that period.

Most pilots and real scale RO systems run at constant recovery and variable pressure, where feed pump frequency is increased when recovery decrease outside a certain range. This leads into an increase of feed pressure, and as consequence, an increase in permeate flow and recovery. Therefore, first five trials, with a total duration of 9 hours, are conducted in order to try to achieve certain operational conditions which allow the system to be ran at constant pressure or constant recovery, and a bypass flow between 350 to 750 mL/min. Moreover, bypass and concentrate valves are tested for different opening angles, to assess their effect on the system. Since concentrate and bypass flows are recirculated into the feed vessel, pumped feed flow for 10 Hz is assumed as 1060 mL/m, considering results found in trials with demi-water and membrane performed before (section 5.2.2).

In the first trail, valves positions and effect are analysed. Once the system is started, pressure of feed and concentrate lines build up. When bypass valve is closed, smaller bypass flows are achieved and as consequence, higher flows through the membrane. Thus, feed and concentrate pressures increase, and higher permeate flows can be achieved. On the other hand, if concentrate valve is closed while the rest of the system is kept unchanged, higher pressures in concentrate and permeate lines are achieved, but also bypass flow increase due to feed pressure. Subtle changes in bypass flow have a significant effect on permeate flow and recovery. Furthermore, small permeate flow variations have a massive impact on recovery values, because these are calculated based on a meter length membrane, while the one used for this research has 9 cm of length.

In the second trial, a constant bypass flow of 0.16 gpm (605 mL/m), which corresponds to a constant feed flow through the membrane of around 450 mL/min, is established and maintained during the whole trial. Net driving pressure increase from 8 to 13 bar, which corresponds to an increase of feed pressure from 11 to 16 bar. Differences between feed and concentrate pressure is never greater than 2 bars, as shown in Figure 5-25.

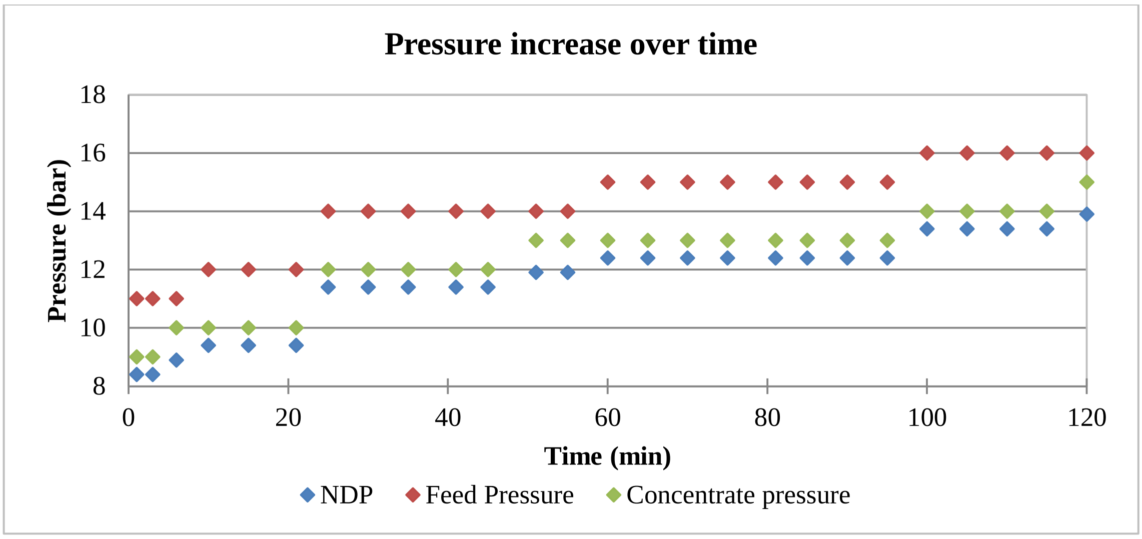


Figure 5-25: Increase in net driving pressure, permeate and concentrate pressure over time, when ran with AnMBR permeate as RO feed, at constant feed flow of 450 mL/min, pump frequency of 10 Hz.

Recovery increase during the first hour, up to a value of 4.2 % per meter of membrane, and then started to decrease until 3.9 % after 2 hours ran. The same happens to flux over membrane, which reach a maximum value of 24.3 lmh after one hour ran, as shown in Figure 5-26.

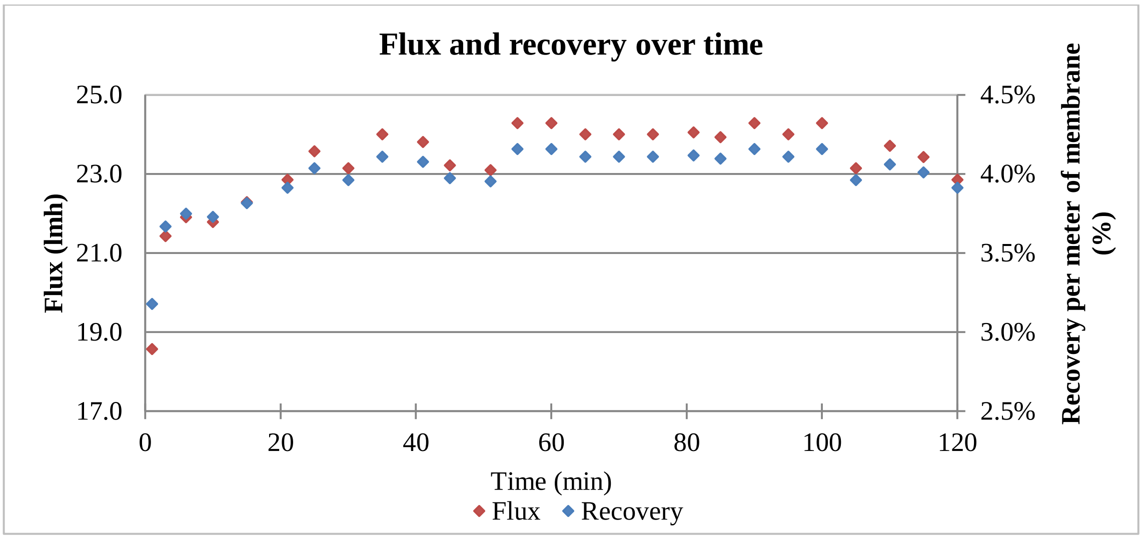


Figure 5-26: Flux and recovery over time, when ran with AnMBR permeate as RO feed, at constant feed flow of 450 mL/min, pump frequency of 10 Hz.

Fifth trial, performed on 22nd of January is entitled to obtain constant recovery. Thus, a peristaltic pump is connected to the permeate line. Pump frequency is established to achieve a recovery of 8%, when feed flow through membrane is 685 mL/m (bypass flow of 0.10 gpm). Figure 5-27 shows new system setup.

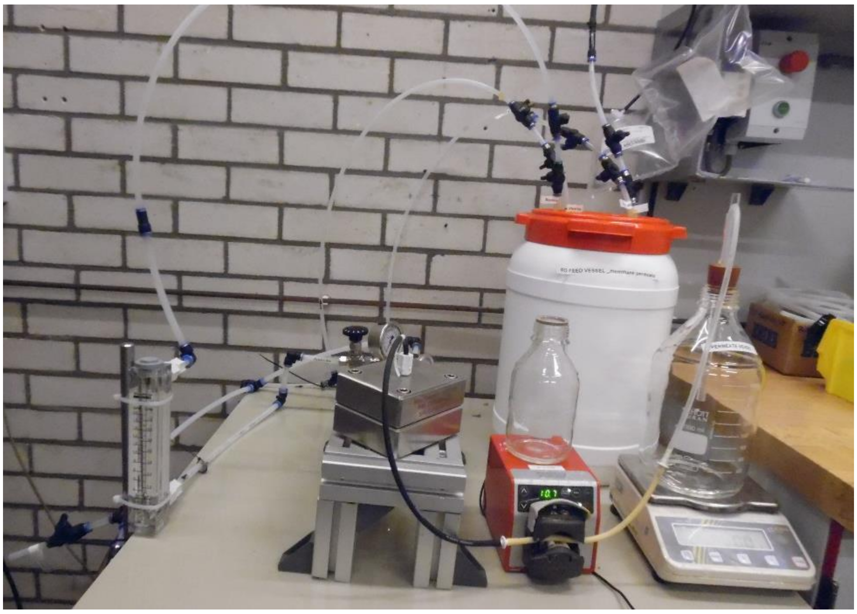


Figure 5-27: RO setup with a peristaltic pump in permeate line to achieve constant recovery.

During 30 minutes, permeate flow is pumped at constant frequency, but no stable recovery is achieved. Permeate flow vary from 1.3 to 2.4 mL/m, while feed pressure increased from 6 to 18 bar. After 30 minutes, pump is disconnected and the system is allowed to run unchanged, while parameters mentioned above are further evaluated. After pump is disconnected, permeate volume reduced for one minute, associated to a negative pressure build up in the line. Set recovery of 8% is never achieved, and once the system is let to run without permeate pump, recovery values fluctuate from 2.0 to 1.5 %. Peak recovery of 2.0 % is achieved after 115 minutes ran, and corresponds to a permeate flow of 2.0 mL/m, as shown in Figure 5-28. After system is ran for 90 minutes, feed pressure reached 22 bars and reactor is stopped.

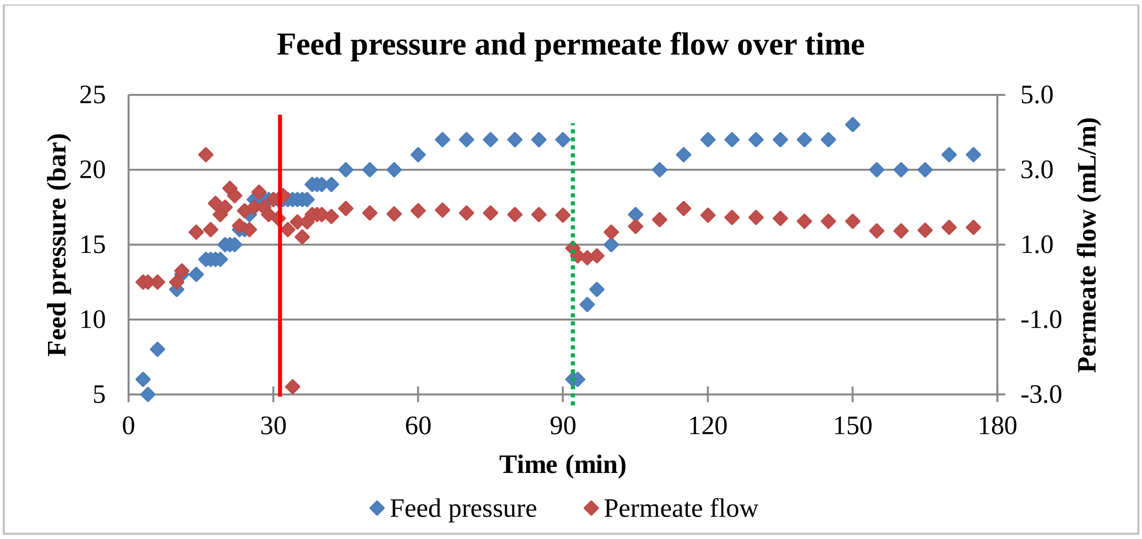


Figure 5-28: Feed pressure and permeate flow over time. With a red line is represented the time until permeate pump is connected to the system (30 minutes). Additionally, dotted green line indicates when system was stopped at 90 minutes, and started again after concentrate and bypass valves were opened around 50°.

Recovery values in this trial are below the desire one. Thus, after 3 hours the system is stopped and membrane is cleaned. Cleaning procedure and characteristics are explained ahead in this section. Final trial is started after membrane cleaning, and it last for 12 hours 15 minutes (4 days).

When last trial is being started (6th trial), system conditions are kept the same as before, where bypass flow is sat at 0.10 gpm (375mL/min) and kept constant. Pressure, bypass flow, volume of permeate produced and temperature measurements are taken every 5 minutes and further analyse.

While net driving pressure increase from 10 to 21 bars over 12 hours (feed pressure from 12 to 23 bar), recovery decrease from 2.9% to 1.5% (Figure 5-29). Maximum recoveries are achieved minutes after the system is turned on, and corresponds to 2.3%, 2.6%, 2.5%, 2.9%, 2.1% and 2.3% at 4, 190, 305, 376, 545, and 621 minutes ran (respectively). It is important to highlight that system is stopped due to lunch hours (where no one is allow to be in the laboratory) and laboratory schedule, but not because system issues.

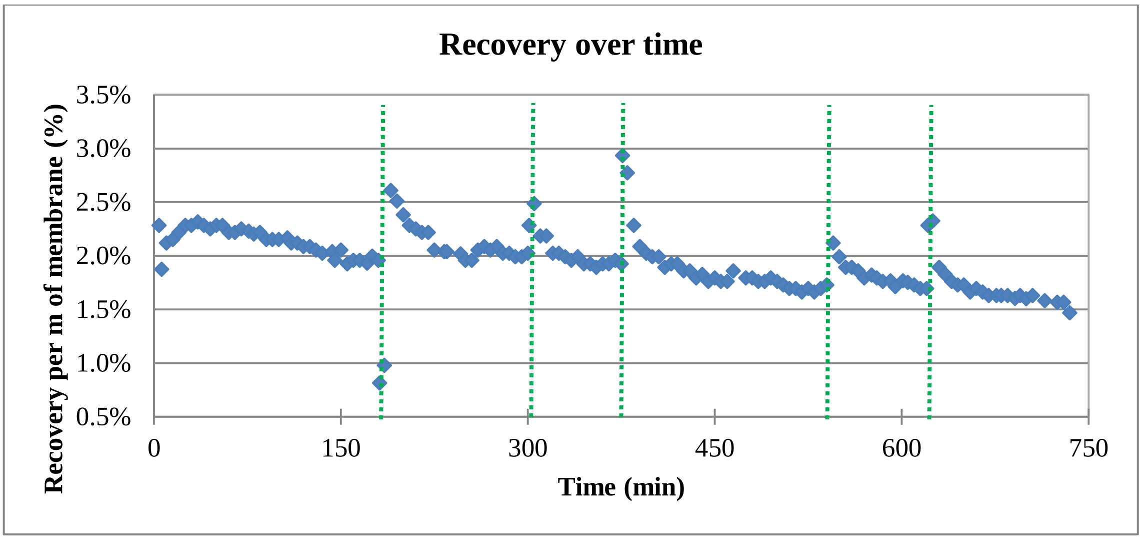


Figure 5-29: Recovery over time, when ran at constant feed flow of 685 mL/min and pump frequency of 10 Hz. Additionally, dotted green line indicates when system is stopped (180, 300, 375, 545 and 620 minutes).

During the 12 hours and 15 minutes trial, system is stopped 5 times. Once the system is started up again, around 30 minutes needs to pass in order to achieve previous values of pressure and permeate flow. During this time, pressure increase rapidly in the first 5 minutes, but permeate flow needs around 30 minutes to reach to previous conditions, as shown in Figure 5-30. Therefore, in the minutes after the system is restarted, permeability increase mainly due to the fact that pressure is building up faster than the decrease in permeate flow. The apparently increase in this latter is reflected in recovery rise between 0.2 to 1.6% from values before shut down (right when the system is started), followed by an exponential decrease in the next 30 minutes. Furthermore, variations of 0.05 mL/m in permeate flow corresponds to differences of 0.1 % in recovery, thus, recovery values are extremely sensitive to permeate volumes obtained over time and membrane feed flow (assume as a constant value of 685 mL/m).

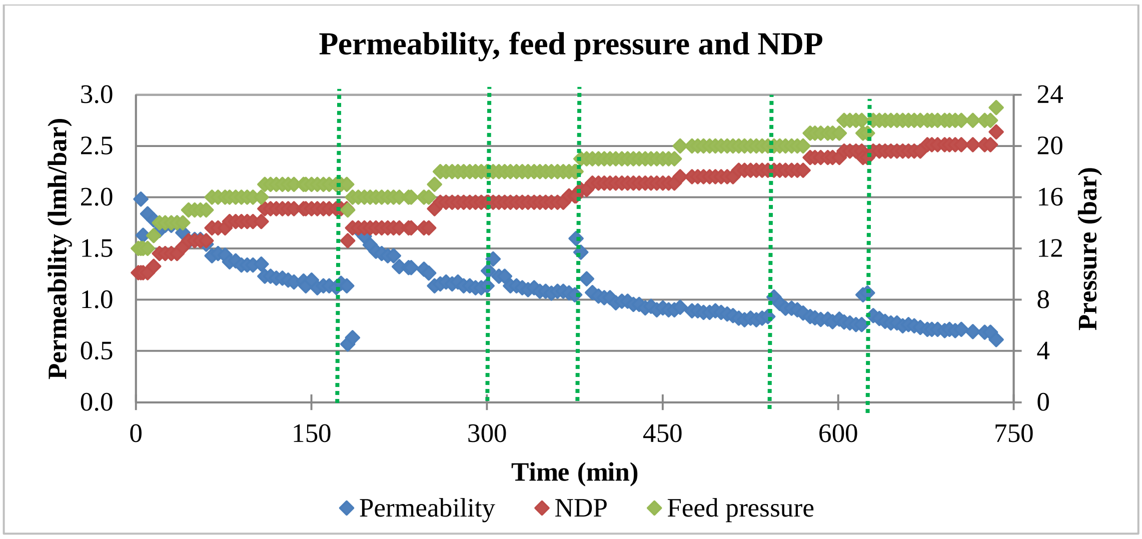


Figure 5-30: Increase in feed pressure and net driving pressure while membrane permeability decrease, when ran at constant feed flow of 685 mL/min and pump frequency of 10 Hz. Additionally, dotted green line indicates when system is stopped.

Hence, maximum recovery achieved is 2.9 %, value below the one obtained in the second trial (4.2%). Furthermore, while NDP increase, membrane permeability decrease from 2 to around 0.5 lmh/bar, as shown in Figure 5-30. Additionally, permeate and concentrate lines pressure differ always less than 2 bars, and osmotic pressure (calculated based on anions and cations) is around 1.5 bar, thus, NDP is about 2 bars below feed pressure values.

Flux also decrease over time, from 20 to 15 lmh. If this value is normalized considering temperature, which increase over time, as shown in Figure 5-32, then normalized flux decrease from 23.5 to 14.5 lmh (Figure 5-31).

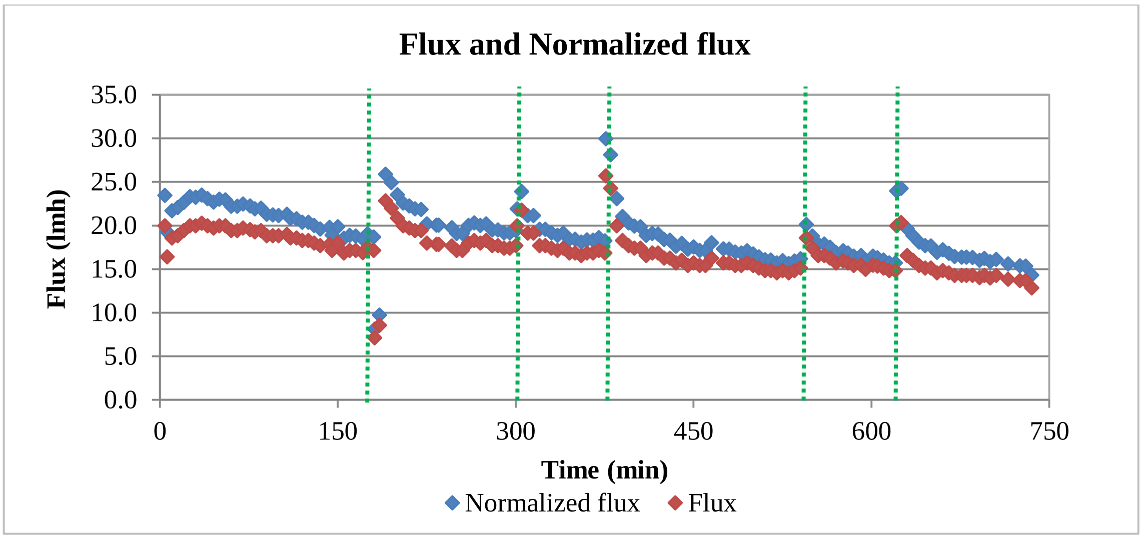


Figure 5-31: Differences between flux and normalized flux considering temperature, when ran at constant feed flow of 685 mL/min and pump frequency of 10 Hz. Dotted green line indicates when system is stopped.

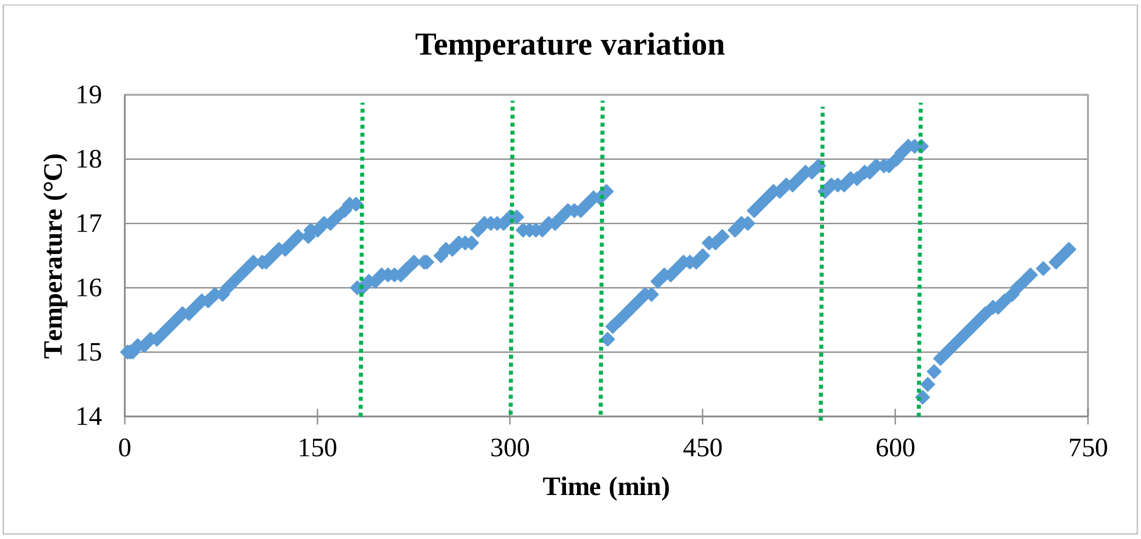


Figure 5-32: Temperature variation over time when ran at constant feed flow of 685 mL/min and pump frequency of 10 Hz. Dotted green line indicates when system is stopped.

Temperature variation follows a direct relation with minutes ran, with R^2 power law for each ran (6 in total) above 0.95. The lowest the starting temperature, the fastest temperature increase.

Membrane fouling and cleaning

Cleaning of membrane is conducted twice: before the last trials is started and after it is finish (when reaching a feed pressure of 23 bars). Cleaning procedure is similar to the cleaning in place (CIP) carried out for MBR. In this case, RO membrane is cleaned ex-situ, by submerging it in base and then in acid solutions.

According to membrane manufacturer, Dow-Filmtec BW30XFR membranes work at pH range from 2-11, but for short term cleaning (around 30 minutes), pH range may vary from 1 to 13 (DOW FILMTEC BW30XFR Product data sheet in Appendix D). Therefore, as a cleaning procedure, membrane is submerged for 15 minutes in a solution of citric acid (1 g of monohydrate citric acid per 100 mL solution) with a pH of 2, rinse with demineralized water for 5 minutes, and then submerged for 15 minutes in a sodium hypochlorite solution (1 mL of sodium hypochlorite per 100 mL solution) with a pH of 10.

When membrane is cleaned for the first time, no visual fouling is found in spacers, but membrane has a greyish and blackish colour, as shown in Figure 5-33.

Figure 5-33: Membrane fouling before the star- up of the sixth and last trial with AnMBR permeate.

Additionally, once the cleaning procedure started, membrane is visually cleaned after being submerged for 10 minutes in citric acid. Acid cleaning is associated with removal of inorganic compounds which precipitate (Wang, et al., 2014), and due to the colour found, it can be Manganese or Magnesium. In order to assess this latter, concentration of this compounds is measured in concentrate line (results are shown in section 5.3). Furthermore, even though the system is kept anaerobic, trials with demineralized water are conducted under aerobic conditions. Thus, demi-water can cause stainless steel corrosion and loose its demineralized characteristics. Therefore, greyish and blackish colour can be also due to Zinc and Chromium deposition. While demi-water is needed to perform some trials with RO membrane without enhancing fouling, it can be corrosive to the cell system used, and therefore, have a negative impact on the system operational conditions.

A second membrane cleaning is conducted after the last trial, when pressure reached 23 bars. However, membrane fouling is considerable different from the first one, as can be seen in Figure 5-34.

Figure 5-34: Membrane fouling after the last trial is performed.

In this case, biofouling in feed spacers can be visually identify, while in the RO membrane it can be perceived deposition of an oily layer. Figure 5-35 shows in detailed the biofouling in the feed spacers.

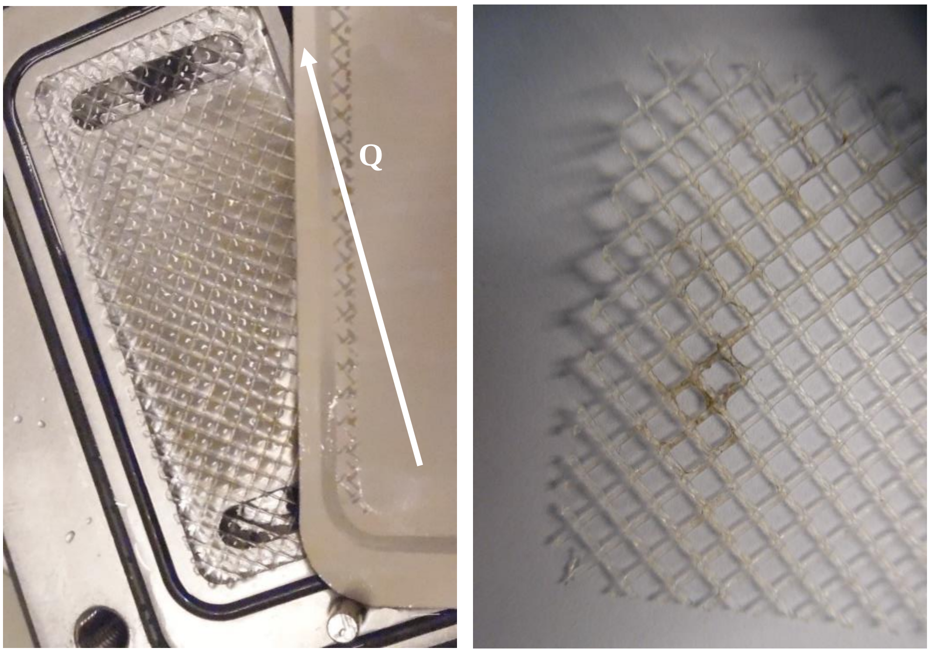


Figure 5-35: Visual spacer biofouling. The white arrow is used to indicate flow direction.

Moreover, few changes in membrane are observed after being cleaned with citric acid, but it visually looked clean after using sodium hypochlorite, which is linked with organic fouling (Wang, et al., 2014). Total cleaning lasted for 40 minutes, 15 minutes soaked in citric acid, 15 minutes in sodium hypochlorite and around 10 minutes rising the membrane with demi-water.

Since both membrane fouling are completely different, another trial is to be carried out. However, when assembling the RO cell, two screws are badly introduce, producing thread galling, and tests are stopped. When removing the screws, one gets locked in the cell, as shown in Figure 5-36, and it has to be sent to an external repair.

Figure 5-36: Thread galling and broke screws in the RO cell.

Due to the screws issue, no more runs are conducted, even though further analysis must be conducted in order to assess system fouling and operational conditions. Total recovery achieved during last trial considering feed and permeate volume is 8%, corresponding to an entire permeate volume of 876 mL. Since system is not operated at constant feed pressure or constant recovery, it is hard to compare operation conditions to literature review. One of the main reasons why constant pressure is not achieved is because feed characteristics change over time. Thus, recirculating concentrate into feed vessel causes an increase in pollutants concentration, which needs higher pressures to pass through RO membrane. Pilot and real scale systems have several trains (steps), and high recoveries values of around 75% can be achieved (Vrouwenvelder, et al., 2011). Furthermore, Biothane has a pilot scale RO plant located in South Africa, fed by AnMBR permeate which is treating dairy industry wastewater. This plant operates at variable pressure and average constant recovery of 8%.

Maximum recovery achieved when using AnMBR permeate as feed is 4.3% when system ran 3 hours and a half. This values is not achieved even after membrane cleaning, where the maximum recovery is 2.9%. In any case, maximum recovery is below the one obtained for demineralized water. Antiscalants can be used for decreasing fouling and scaling potentials, and thus, increase recovery. Even though an antiscalants (HYDREX 4103) is ordered, it did not arrive on time when trials are conducted.

5.3. Concentrate and permeate characteristics: reuse possibilities

RO permeate and concentrate are evaluated based on measurements done from the 17th until 24th of February, with AnMBR permeate as feed. As a key aspect, since concentrate is recirculated to the feed vessel, feed characteristics change overtime. Furthermore, RO membrane is design to achieve a constant rejection of pollutants. Thus, while concentrations are increasing over time in feed line, permeate characteristics will also be worst over time. Initial feed volume is or around 13 L, pump feed flow is 1062 mL/min, with bypass flow of 375 mL/min. Therefore, it is needed less than 20 minutes for the whole feed to pass through the membrane, and after that time has passed, characteristics of the feed are almost the same as the ones from the concentrate.

All samples are taken at the end of the day. TCOD, TS, VS, VFA, TKN, NH_4-N, Total P, PO_4 and alkalinity of concentrate are measure daily, while permeate once every other day. Results are shown in Tables 5-7 and 5-8 (between the 17th and 20th of February is weekend, and Biothane is closed).

Table 5-7: Concentrate parameters measured in Biothane laboratory.

Parameter	Unit	Concentrate					
		17-Feb	20-Feb	21-Feb	22-Feb	23-Feb	24-Feb
TCOD	mg/L	53	57	59	67	91	86
TS	mg/L	1650	1760	1710	1770	1790	1810
VS	mg/L	180	290	330	170	270	190
VFA	mg/L	0	0	0	-	-	-
TKN	mg/L	188	190	193	196	201	203
NH_4-N	mg/L	186	189	186	191	196	199
Total-P	mg/L	29	29	30	31	30	29
Ortho-P	mg/L	30	29	30	30	30	29
Alkalinity	meq/L	32.8	32.3	34.0	34.0	34.4	32.9

A total of 1305 minutes (around 22 hours) ran, conforming 6 different trials with AnMBR permeate as RO feed conducted, and total permeate produced is approximately 1,720 mL (corresponding to a total recovery of 13%). Concentrate samples taken the 17th, 22th, 21st, 22nd, 23rd, and 24th of February correspond to 390, 565, 750, 945, 1190 and 1305 minutes ran respectively, and 535, 843, 1078, 1324, 1600 and 1720 mL of permeate produced respectively. Overall, TCOD, TS, TKN and NH_4-N values in concentrate are more concentrated over time. This is align with what is expected for the RO system. While values of NH_4-N and TCOD from the 21st and 24th respectively are slightly smaller than the ones from the previous day, this can be due to errors when measuring samples. On the other hand, neither alkalinity, total phosphorus nor orthophosphate concentrations have a representative variation over time. Moreover, all phosphorus presented on concentrate is orthophosphate, since measurements of this latter are the same as TP. Finally, volatile solids vary from 170 to 330 mg/, but it is not related with TS variation. VS values increase until the 21st, and then vary 100 mg/L in a day.

Even though this is a considerable difference, total amount of VS is still very low, bearing in mind the AnMBR VS feed concentration (around 5,400 mg/L).

Table 5-8: Permeate parameters measured in Biothane laboratory.

Parameter	Unit	Permeate			
		17-Feb	**20-Feb**	**22-Feb**	**24-Feb**
TCOD	mg/L	3	1	7	9
TS	mg/L	60	70	70	80
VS	mg/L	40	40	50	60
VFA	mg/L	0	0	-	-
TKN	mg/L	9	7	8	12
NH4-N	mg/L	9	6	7	12
Total-P	mg/L	<2	<2	<2	<2
Ortho-P	mg/L	<2	<2	<2	<2
Alkalinity	meq/L	3.1	0.6	0.4	0.0

Between permeate samples taken the 17^{th} and 20^{th}, RO membrane is cleaned on the 20^{th} morning. Thus, permeate parameters may differ from one another, like COD values. However, a trend of higher concentrations of pollutants over time can be observed from the 20^{th} of February on. VFA is measured only at the beginning to check because there is no VFA in concentrate (feed) samples and therefore, it should not be in the permeate either. Total and orthophosphate values are below the minimum detectable by the kit available in Biothane. Moreover, TS increase from 60 to 80 mg/L, and VS from 40 to 60. Finally, removal efficiencies comparing concentrate and permeate from the same day are found and shown in Table 5-9.

Table 5-9: RO removal efficiencies.

Parameter	Removal efficiencies			
	17-Feb	**20-Feb**	**22-Feb**	**24-Feb**
TCOD	94%	99%	90%	89%
TS	96%	96%	96%	96%
VS	78%	88%	71%	68%
VFA	-	-	-	-
TKN	95%	96%	96%	94%
NH4-N	95%	97%	96%	94%
Total-P	>93%	>93%	>94%	>93%
Ortho-P	>93%	>93%	>93%	>93%
Alkalinity	91%	98%	99%	100%

High removal efficiencies are achieve with RO, especially regarding nutrients (nitrogen and phosphorus). All parameters but VS has a removal efficiency variation of less than 10 %, and are above 89%. VS removal is between 68 and 88%, mainly due to concentrations in concentrate stream, and is the one with highest variation. Furthermore, anions and cations from permeate and concentrate are analysed twice, and rejection factors (removal efficiencies) are shown in Table 5-10.

Table 5-10: Ion composition of permeate and concentrate, and removal efficiencies achieved with RO.

Parameter	Unit	Concentrate		Permeate		Rejection rate	
		21-Feb	24-Feb	21-Feb	24-Feb	21-Feb	24-Feb
NH_4^+	mg/L	186	196	6	7	97%	96%
Na^+	mg/L	398	439	11.5	46	97%	90%
K^+	mg/L	97.8	137	27.4	50.8	72%	63%
Ca^{2+}	mg/L	96.2	104	4	60.1	96%	42%
Mg^{2+}	mg/L	36.5	41.3	2.5	41.3	93%	0%
Cl^-	mg/L	213	209	3.5	3.5	98%	98%
SO_4^-	mg/L	67.2	57.6	86.5	183	build up	
NO_3^-	mg/L	43.4	0	6.2	18.6	86%	-

As shown in Table 5-10, higher ions removal efficiencies are obtained from samples of the 21st of February. Rejection rates of ammonium and chloride are the uppermost among the ones measured, with values above 97%. On the other hand, potassium removal vary from 63 to 72%, and is the lowest rejection achieved. Magnesium removal is once 93% and in the other sample 0%. While Magnesium is one of the ions with the smallest relative radii from the ions measured (Figure 5-37), it is not possible that RO membrane does not retain Mg^+. Furthermore, since concentrations of this parameter are the same on concentrate and permeate for samples of the 24th of February, it is possible that a typing error occur, and concentration found in concentrate line is written for both permeate and concentrate lines.

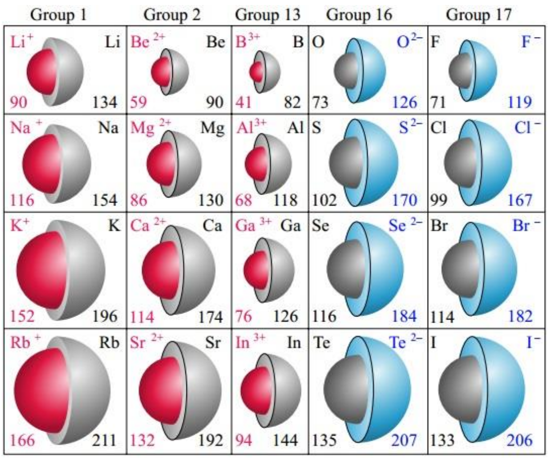


Figure 5-37: Relative radii of some ions in picometers (100pm=1Å). Source: Shannon (1976)

Moreover, sulphate values in concentrate line are particularly peculiar, because the system is kept anaerobic. When asked about the measurement of this parameter to the external laboratory, it is found that actually the quantity is not of sulphates but of total sulphur in the sample. Furthermore, nitrate is not presented in RO original feed, but it reaches a value of 43 mg/L in concentrate. Nitrate may be formed from ammonium by nitrification, which is an aerobic process, and if this is the case, it means that oxygen may be entering the RO system. Besides this possible explanation (even though nitrifying bacteria should grow in order to be able to reduce ammonium into nitrate), an error measuring nitrate concentration on the 21st of February may also have occur. Nevertheless, values of this parameter are zero in the next sample. System is not changed during the whole process, and therefore, same conditions are kept. All inconsistencies in anions concentrations measures make the data found not reliable. Hence, a sample of concentrate and permeate from 24th is send to UNESCO-IHE to analyse anions, in order to compare data obtained. Results are show in Table 5-11.

Table 5-11: Anions measured in UNESCO-IHE for permeate and concentrate samples taken the 24th of February.

Parameter	**Unit**	**Concentrate 24-Feb**	**Permeate 24-Feb**	**Rejection rate**
Cl^-	mg/L	238	7.8	97%
SO_4^-	mg/L	41.4	<4	>90%
NO_3^-	mg/L	<6	<0.6	-
PO_4^-	mg/L	31.2	<0.6	>98%

From data obtained at UNESCO-IHE, it can be concluded that actual orthophosphate removal is higher than 98%. Furthermore, there is minimal or none presence of nitrate, which means that no nitrification is carried out. Chloride concentrations in concentrate and permeate are similar to the ones measured by the other laboratory, but sulphate ones are considerably different. Permeate sample has less than 4 mg/L of sulphate, and concentrate has a bit more than 40 mg/L. Sulphate is an alternative electron acceptor, and in anaerobic processes, sulphate reducing bacteria (SBR) competes with methanogenic bacteria and consumes COD, but if this is the case, lower quantities of COD will be removed (Henze, 2008). However, SBR should grow in order to consume sulphate, and therefore, lower concentrations of sulphate can still be present on AnMBR permeate. In RO system, sulphate rejection higher than 90%.

Bearing in mind membrane fouling, magnesium, manganese, and chromium concentrations in concentrate line are also analysed. The first one is slightly concentrated than in the initial feed. On the other hand, Manganese concentration is reduce into half, from 12 to 6 µg/L. Decrease in Mn concentration can be linked with RO scaling, mentioned in section 5.2.3. During the first clean of the membrane, deposition of a blackish particles are found, and this may correspond to Manganese and Chromium found in the concentrate.

Chromium concentration is measured for the first time, and its value is of 7 mg/L. This latter is extremely high considering that is from treated synthetic dairy industry, where Chromium should not be present. Thus, high values of Chromium may indicate that when ran with demi-water, corrosion of the stainless steel system occurred. Even though after demi-water trials system was cleaned with tap water (and no membrane), pressure build up when performing trials with membrane may release certain compounds that were stacked in tubes before.

Apart from concentrate and permeate parameters measured and mentioned above, pH and conductivity of concentrate is measured hourly, and twice per day in permeate line. Results obtained for Trial 6 (last trial performed), are shown in Figures 5-38.

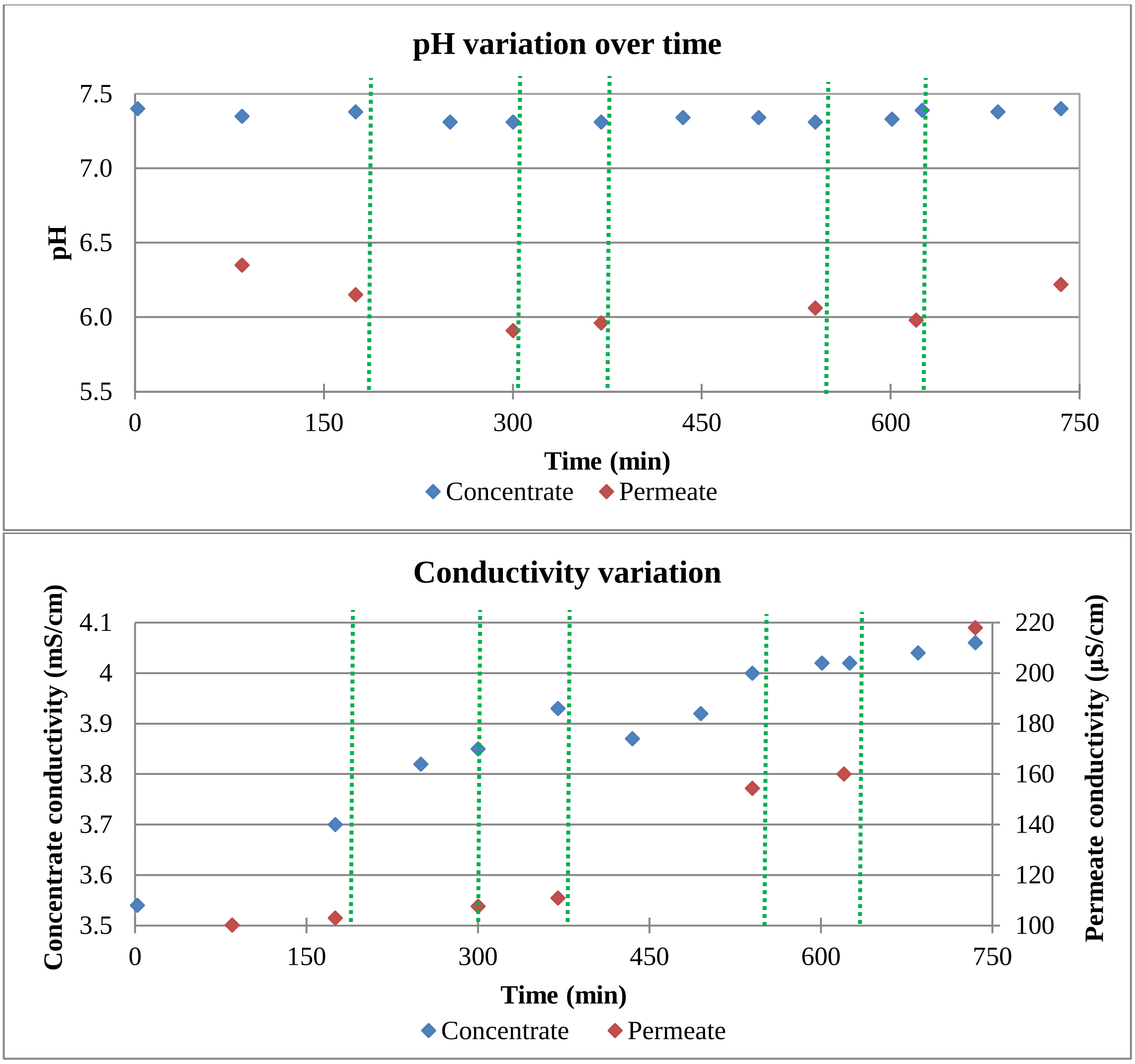


Figure 5-38: pH and conductivity variation over time, for the last trial conducted with AnMBR permeate as feed, pump frequency of 10 Hz, and feed flow of 685 mL/m. Dotted green line indicates when system is stopped.

Concentrate pH is expected to increase over time, due to the effect of increasing concentrations. However, this is not the case for the 6th trial, where little fluctuates of pH are observed. This can be due to the fact that actually only 8% of permeate is recover, causing a minimum impact on pH. Moreover, there is almost no variation in pH before and after the set-up is turned off and started again. On the other hand, permeate pH vary more than the concentrate one, from 5.9 to 6.4.

In both, permeate and concentrate, conductivity values increase over time, as shown in Figure 5-38. This is due the fact that total solids concentration increase over time in concentrate line (and therefore, total dissolved solids also), leading to an increase of this parameter in permeate stream (RO rejection coefficients should remain approximately the same). Furthermore, concentrate conductivity rejection rate varies from 95 to 97% as shown in Table 5-12. Moreover, conductivity is related with TDS, with a comparison factor between 0.5 to 0.7 (Walton, 1989). Table 5-12 shows TDS values considering a 0.5 factor, thus, a conductivity of 1 mS/cm corresponds to a TDS of 500 mg/L.

Table 5-12: Conductivity variation over time in permeate and concentrate lines of RO system.

Date	**Time**	**Concentrate**		**Permeate**		**Rejection rate**
		Cond	**TDS**	**Cond**	**TDS**	
	min	**mS/cm**	**mg/L**	**µS/cm**	**mg/L**	
21-Feb	2	3.54	1770			
21-Feb	85			100.2		
21-Feb	175	3.70	1850	103.0	52	97%
22-Feb	250	3.82	1910			
22-Feb	300	3.85	1925	107.6	54	97%
22-Feb	370	3.93	1965	110.9	55	97%
23-Feb	435	3.87	1935			
23-Feb	495	3.92	1960			
23-Feb	540	4.00	2000	154.4	77	96%
23-Feb	601	4.02	2010			
23-Feb	620			160.0	80	
24-Feb	625	4.02	2010			
24-Feb	685	4.04	2020			
24-Feb	735	4.06	2030	218.0	109	95%

Calculated TDS values are close to TS ones. Therefore, as concluded before, most of solids in concentrate and permeate are dissolved ones, while suspended solids are almost negligible. In concentrate sample taken on the 24^{th}, some particles are visually observed, and there is a clear difference between permeate and concentrate turbidity, as shown in Figure 5-39.

Figure 5-39: Concentrate and permeate samples from RO system taken on the 24th of February.

Huang, et al. (2015) conducted a research in assessing methods for reverse osmosis membrane integrity. Among several studies, TDS after RO system for wastewater reclamation is evaluated, and results are around 5 mg/L, value 10 times higher than the ones obtained in this research. Furthermore, Huang also counted bacteria and virus in RO feed and permeate samples using FCM and BD Accuri™. Feed samples are microfiltration MBR permeate, with total virus count around 6.2×10^6 VLP/mL (VLP corresponds to virus like particles). RO permeate samples has values below the detectable limit of 10^4 and 10^2 counts per mL, for bacteria and viruses respectively. For this research, two more analysis are conducted in permeate and concentrate lines: bacteria count and faecal coliforms. Total and intact cell count are measured from samples of the 21st of February, while coliforms are analysed from samples taken the 24th. Cell count results are shown in Table 5-13.

Table 5-13: Total and intact bacteria count measured on permeate and concentrate of RO system, the 21st of February.

Parameter	Unit	Concentrate	Permeate
Total cell count	Events/mL	29,068,667	3,486,000
Intact cell count	Events/mL	25,068,667	2,906,333

Despite the fact that one log removal is obtained with RO system, bacteria and viruses should not be present in permeate line due to its size in comparison with RO pores. Values in concentrate are according to what is found in original dairy industry AnMBR permeate (section 5.1.3). RO permeates samples are taken and stored in the fridge at 6°C, and measurements of cell count are conducted on the 3rd of March. Permeate accumulation vessel and sample bottles are not sterile ones, and it may occur contamination during storage. Furthermore, Van Nevel, et al. (2017) found a difference higher than 300,000 cell/mL counted by flow cytometry and heterotrophic plate count (HPC), where the latter has a peak of around 2,000 c.f.u/mL (compare to 350,000 total cell/mL by FCM) in a spring sample, and correlation between HPC and FCM (flow cytometric) is particularly weak ($R^2 < 0.1$).

Faecal and E.Coli are measured the 3rd of March, with samples taken the 24th and stored in the fridge. A volume of 1mL of permeate and concentrate are added to chromocult agar plate, and colony formed units are counted. Since bacteria count is high, 10 times dilutions are also measured. Results obtained after 24 hours growth at 37°C are shown in Figures 5-40 and 5-41.

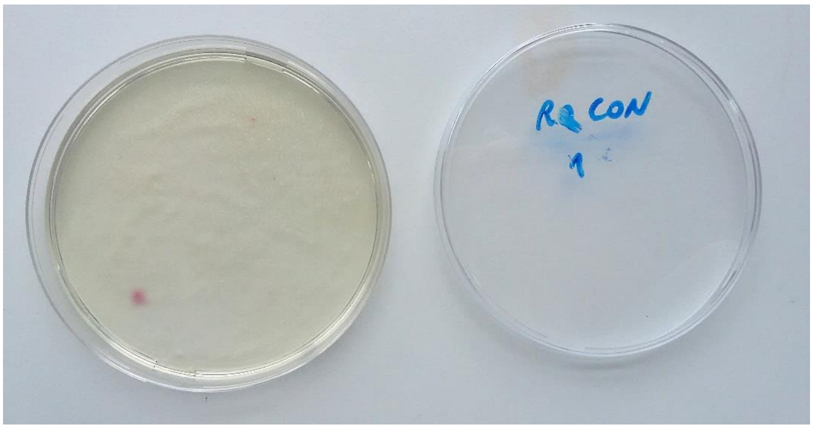


Figure 5-40: Concentrate measurement of Coliforms. Pink dots corresponds to Faecal Coliforms and white dots to other Enterobacter. No E. Coli are found in the samples.

Faecal coliform colonies counted vary from one to three per mL of concentrate sample. No E.Coli is found in either samples, but Enterobacter abound. Furthermore, in samples 10 times diluted, only the latter can be seen.

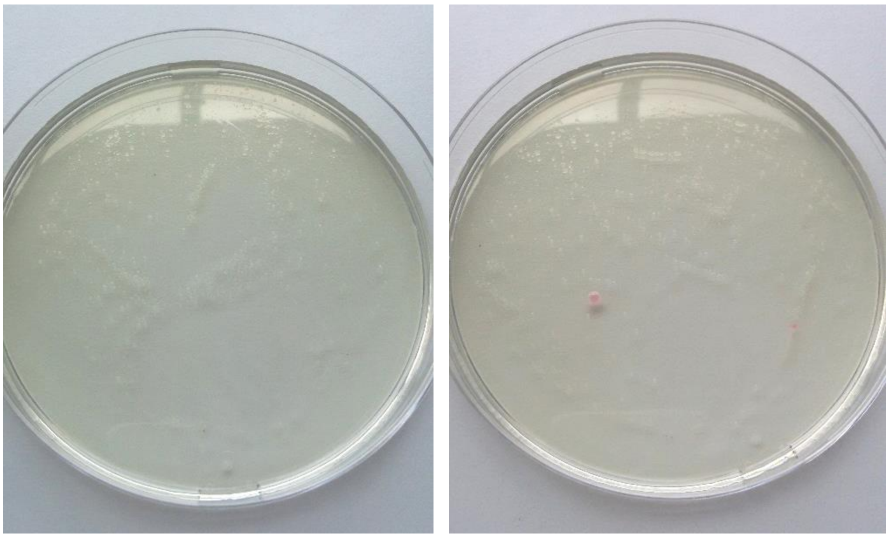


Figure 5-41: Permeate measurements of Coliforms. Duplicates of the same sample are down and shown in this figure. Pink dots corresponds to Faecal Coliforms and white dots to other Enterobacter. No E. Coli are found in the samples.

Presence of one colony of Faecal coliform per mL of sample is counted in one permeate sample, while in the other one only Enterobacter can be seen. Furthermore, there is no E. Coli in any sample. In samples 10 times diluted, only Enterobacter can be seen. Bacteria presence is align with the results of bacteria count measurements performed on permeate sample. However, considering that feed of AnMBR is synthetic dairy industry wastewater, no presence of Coliforms should be found in samples. Moreover, it is recommended that samples are analysed right away after being taken, because presence of F. Coliforms in concentrate and permeate does not directly imply that this streams are contaminated, due to the fact that contamination could occur while samples are being stored.

Considering all data analysed from permeate and concentrate, average values and standard deviation are calculated when corresponds. Results are shown in Table 5-14. Moreover, this values will be further scrutinise when considering reuse possibilities of the streams. Regarding ions measurements of concentrate and permeate, data given by UNESCO-IHE is accepted as reliable. Finally, both stream pollutant concentration increase over time. Thus, characteristics will worsen and considering the average between all measurements conducted is not the safest assumption. However, permeate is accumulated on the same vessel, and therefore, mixed.

Table 5-14: Average concentrate and permeate of RO system parameters.

Parameter	**Unit**	**Concentrate**		**Permeate**		**Removal efficiency**
		Value	**Standard deviation**	**Value**	**Standard deviation**	
pH	-	7.4	0.0	6.1	0.2	
Conductivity	mS/cm	3.9	0.16	0.14	0.04	96%
TCOD	mg/L	62.1	15.6	4.9	4.2	92%
TS	mg/L	1,750	60	70	10	96%
VS	mg/L	240	70	40	30	83%
VFA	meq/L	0	0	0	0	-
TP	mg/L	29.7	0.7	<2	-	<93%
PO_4-P	mg/L	29.7	0.5	<2	-	<93%
TKN	mg/L	195	6	9	2	95%
NH_4-N	mg/L	191	5	8	3	96%
Alkalinity	meq/L	33.4	0.8	1.0	1.4	97%
E. Coli	CFU/mL	0	-	0	-	-
F. Coliforms	CFU/mL	2	-	1	-	-
Intact Bacteria count	Events/mL	25,068,667	-	2,906,333	-	-
Na^+	mg/L	419	29	29	24	93%
K^+	mg/L	117	28	39	17	67%
Ca^{2+}	mg/L	100	5	32	40	68%
Mg^{2+}	mg/L	39	3	2.5	0	94%
Cr^+	mg/L	7	-	ND	ND	-
Mn^{2+}	µg/L	9	3	ND	ND	-
Cl^-	mg/L	211	2.8	3.5	0	98%
NO_3^-	mg/L	<6	-	<6	-	-

Given the RO permeate parameters mentioned above, then AnMBR coupled with RO system for dairy industry wastewater treatment achieve high removal efficiencies, as shown in Table 5-15.

Table 5-15: Coupling of AnMBR and RO system for treating dairy industry wastewater removal efficiencies.

Parameter	**Unit**	**AnMBR + RO removal efficiencies**
TCOD	mg/L	99.95%
TS	mg/L	98.84%
VS	mg/L	99.25%
TSS	mg/L	100.00%
VSS	mg/L	100.00%
VFA	meq/L	100.00%
PO4-P	mg/L	>93%
TKN	mg/L	96.70%

Big differences between nutrient and solids concentrations, between AnMBR and RO permeate, lead to considered RO permeate for industrial reuse apart than irrigation. Thus, considering that plenty of water is being used by dairy industries, recirculating RO permeate may have a significant effect on water consumption and water costs.

5.3.1. Reuse possibilities

According to Uruguayan standards, wastewater for reuse purposes have to comply with drinking water standards. Thus, both permeate and concentrate are assess according to the same standards stablished by Uruguayan Institute of Technical Standards (UNIT) (2010). Neither treated wastewater streams have reuse possibilities when being compare to Uruguayan standards, and Table 5-16 shows parameters in both streams that do not cope with the needed regulation.

Table 5-16: Concentrate and Permeate parameters that do not comply with standards given by Uruguayan Institute of Technical Standards (UNIT) (2010)

Parameter	Unit	UNIT Standards	Concentrate		Permeate	
			Value	Compliance with standards	Value	Compliance with standards
pH	-	6.5-8.5	7.4	Yes	6.1	No
Conductivity	mS/cm	2	3.9	No	0.14	Yes
NH_4-N	mg/L	1.5	191	No	8	No
Na^+	mg/L	200	419	No	29	Yes
Cr^+	mg/L	0.05	7	No	ND	-
F. Coliforms	CFU/mL	Absence in 100 mL	2	No	1	No

Permeate stream limitations for drinking water are regarding pH, ammonium and pathogens. This latter can be avoid by adding a disinfection step, like UV or chloride. However, addition of chloride will further decrease pH, which must increase to a minimum of 6.5 to be considered as neutral. Maximum allowed ammonium in drinkable water is 1.5 mg/L. Thus, permeate did never cope with this standard. To nitrify ammonium a biological process must happen, with growth of ammonia oxidizing bacteria (AOB) and nitrate oxidizing bacteria (NOB). Moreover, since there is almost none alkalinity in permeate and pH is below 6.5, nitrification processes are not likely to happen even if the sample is aerated. Additionally, COD content in permeate is not enough to nitrify ammonium up to the standard limits of 1.5 mg/L. According to the stoichiometry conversion of ammonium into nitrate, 4 g of COD (as oxygen) are required to convert 1 g of ammonium into nitrate (or 4.57 g of O_2 are needed to convert 1 g of NH_4^--N into NO_3^-—N, as shown in the equations below:

$$NH_4{}^+ + \frac{3}{2}O_2 \rightarrow NO_2{}^- + H_2O + 2H^+ \quad (14)$$

$$NO_2{}^- + \frac{1}{2}O_2 \rightarrow NO_3{}^- \quad (15)$$

Furthermore, pre-aeration for ammonium removal before RO treatment is not recommended, since as found in section 5.1.3, aeration produce crystallization of several compounds incrementing the total amount of particles. Other possibilities for decreasing ammonium concentrations are adding alkalinity (which will also increase pH) in order to be able to nitrify ammonium, ammonia stripping (where pH must be increase up to values around 10), or dilution.

Chromium content in concentrate line can be avoid by performing prolonged wash of the RO system with tap water, after demi-water trials. Besides, as few demineralized water trials as possible should be carried out, in order to prevent stainless steel corrosion.

Considering the Guidelines and Standards for Wastewater Reuse , complied by Kramer and Post (NY), and the Guideline for the safe use of wastewater, excreta and greywater developed by World Health Organization (2006) concentrate and permeate have reuse possibilities for irrigation, but depending on the type of crop or final use, which means that case to case assessment must be conducted.

To begin with, WHO guidelines for using treated wastewater in agriculture recommends less than a 1,000 F. Coliforms per 100 mL for irrigation of crops likely to be consumed raw. Thus, both permeate and concentrate streams are in the limits. Pathogens may be an issue and disinfection is recommended in any case.

Secondly, WHO gives recommendations on concentrations range base on the degree of restriction in use (none, moderate and severe), for conductivity, sodium, chloride, bicarbonate and manganese. Table 5-17 shows restriction levels according to WHO for the above mentioned parameters, where it can be observed that concentrate have mostly severe restrictions for irrigation purposes, but permeate has no limitations. Furthermore, maximum recommended concentration of Chromium is 0.10 mg/L, value assume due to lack of knowledge in its level of toxicity in plants. Hence, concentrate is not suitable for irrigation purposes. However, if chromium concentration is taken care off, by reducing trails with demineralized water and properly flushing the RO system, then it is possible to reuse it under severe restrictions. This restrictions allows it use only for localized irrigation of cereal crops, industrial crops, fodder crops, pasture and trees (no fruit trees), where there is no exposure to workers or any type of public (World Health Organization, 2006). Furthermore, nitrogen concentration in concentrate stream must be considered, since excessive amounts of it while irrigating, may lead into groundwater contamination.

Table 5-17: Restriction levels for reuse in irrigation of several compounds, according to World Health Organization (2006)

Parameter	Unit	Concentrate		Permeate	
		Value	Restriction level	Value	Restriction level
Conductivity	mS/cm	3.9	Severe	0.14	None
Na^+	mg/L	419	Severe	29	None
Cl^-	mg/L	211	Moderate	3.5	None
HCO_3^-	meq/L	33.4	Severe	1.0	None
Mn^{2+}	µg/L	9	None	ND	None

Finally, FAO developed guidelines for evaluating suitability of water for irrigation purposes (Ayers and Westcot, 1985), where several compounds concentrations range are presented. Among others, nitrate concentrations between 5 to 30 mg/L have a moderate restriction. Thus concentrate and permeate may have a moderate or none restriction regarding this value.

Bearing in mind WHO and FAO guidelines for irrigation reuse, permeate has almost none limitations or reuse. However, pH should be in the range of 6.5 to 8, and therefore, it is recommended to increase it. Furthermore, disinfection of both streams is endorsed to reuse treated wastewater for irrigation. Permeate can be directly use for irrigation of crops likely to be eaten uncooked, sports fields and public parks. Additionally, low solids concentration in permeate made this stream reusable for industrial purposes. One of the main drawbacks of RO concentrate is the high amount of calcium in the stream, which may lead (as discuss in section 5.1.3) into calcium phosphate precipitation. Therefore, concentrate is not recommended for industrial reuse since it is prone to bloke pipes. On the other hand, permeate low concentrations of calcium, orthophosphate, and other ions make this stream suitable to recycling it into industrial processes, such as cooling and boiling towers, cleaning purposes, bathrooms, firefighting, etc., where no expected contact with dairy products may occur.

Finally, according to Vourch, et al. (2007), who researched about dairy industry water consumption and wastewater production in 11 French companies who consume between 800 to 3,400 m^3 of water per day, boiler make up water consumption may vary from 30 to 275 m^3/day, cooling water from 70 to 370 m^3/d, and cleaning and outside washing between 40 to 950 m^3/day. Therefore, replace a share of water used for the previous processes mentioned have a significant impact on dairy industry water consumption.

CHAPTER 6

Recommendations

Assessing RO system to treat AnMBR permeate from dairy industry wastewater is a broad subject, difficult to be fully analyse in the short time of this research. Furthermore, setup and start-up of the system took around 3 months and a half, leading to a short time of trials. Biothane is planning to continue operating the system when fed with different types of industrial wastewater. Thus, some recommendations for the further studies are mentioned below.

Sterilize permeate line of AnMBR system to prevent bacteria growth. Considering the membrane pore size and the bacteria one, this latter should not pass through the membrane. However, since AnMBR systems in Biothane work with a full scale length membrane, permeate produced is recirculated into the CSTR vessel and passed through the membrane several times. This and mesophilic working temperature around 36°C enhance bacteria formation. Furthermore, accumulation vessel that will be used as a feed for RO system should be located as close as the exit of membrane permeate. In this way, contamination is minimize as much as possible. Moreover, all accumulation vessel in RO systems should also be sterilize, and if bacteria count and coliforms measurements are going to be carried out, it is recommended to have sterile bottles to accumulate samples.

Regarding dairy industry AnMBR permeate characteristics, use of antiscalants is highly recommended for further treatment with RO. This will reduce fouling and scaling potential and therefore, higher recoveries will be achieved. In case other type of permeate is used as RO feed, analysis of antiscalants needed is suggested.

Laboratory scale RO system is useful to assess permeate and concentrate characteristics, but is hard to compare operational conditions to real scale plants. Several upgrades of the system should be carried out in order to minimize errors and work with reliable data. To begin with, given the membrane area and length (42 cm^2 and 9 cm respectively) and cross flow velocity admissible range (0.1 to 0.5 m/s), RO feed flow should be between 410 and 1,030 mL/min. Therefore pump and flowmeter are oversized. Pump bought is able to give flows up to 6,500 mL/min, corresponding to 6 times higher than the maximum admissible one for the membrane, and if no bypass flow is desire, the pump needs to work a low frequencies which decrease its efficiency. Flowmeter measures flows between 0.2 and 2.0 gpm (760 to 7,600 mL/m), with mark measurements every 0.1 gpm (375 mL/min). If concentrate is measured using the actual flowmeter, representative variations which have a significant effect on recovery, are not perceptible in the flowmeter. Hence, a more sensitive flowmeter is recommended.

Secondly, pressure gauges are also oversized and no less than a difference of one bar can be measure. Maximum setup pressure is 69 bars, and bought membrane do not withstand pressures above 45 bar. Digital pressure gauges are recommended for the RO system, since this are able to measure small variations.

Thirdly, it is recommended to continuously measure conductivity, pH and temperature on the feed vessel of RO system. During trials, samples of around 70 mL are taken to perform the above measurements. However, considering that permeate flow achieved were around 2 mL/min, volume extraction is significant compare to permeate production. Furthermore, while volume of permeate produced is measure every 5 minutes on a weight scale, important changes can be performed if the weight scale is connected to computer and data is automatically recorded. As shown in the research, when the system is turned off and started again, it needs around 30 minutes to get to previous conditions. However, if system is connected to PLC and data is recorded, it can run continuously for around 8 hours per day, which will help in assess better its fouling and biofouling potential.

Considerable deviation in anions and cations concentration make results less reliable. Therefore, it is recommended to change the laboratory where ions samples are being analysed, or contact them in order to perform more trustworthy measurements. When working with anaerobic systems, it is important that samples and measurements are performed under anaerobic conditions, or introducing the less amount of air as possible.

Finally, it is recommended to minimize as much as possible trials with demineralized water, since this is corrosive for stainless steel material. Once demi-water has been used, flush the system several times with tap water and no membrane, to avoid undesired pollutants in trials with AnMBR permeate.

CHAPTER 7

Conclusions

Setting, starting up and running a laboratory scale anaerobic Reverse Osmosis system coupled with batch scale AnMBR has its difficulties and challenges. A feasibility assessment of using anaerobic RO system as a second step in treatment of synthetic dairy industry wastewater, where the first stage is AnMBR treatment, is carried out. Feed, concentrate and permeate conditions are studied, focusing on fouling characteristics, and operational conditions of the laboratory scale RO are assess. The following conclusions, can be drawn from results and discussions of this research:

- Permeate of ultrafiltration AnMBR treating synthetic dairy industry wastewater, has SDI around 3 and therefore, can be used as RO feed.
- Accumulation vessel of AnMBR permeate for RO feed should be avoided, since it is an environment rich in nutrients and prone for bacteria growth. Furthermore, permeate flow from AnMBR should be directly conducted to RO system to minimize bacteria growth.
- AnMBR permeate has less particles when kept anaerobic than if it is aerobic, even though particles have the same size distribution. When AnMBR is aerated, pH increase and particles counted are around 10 time higher than in anaerobic conditions. Furthermore, average particle diameter is 6 μm, which is 100 times bigger than the AnMBR pore size (0.03 μm). Even though particles in permeate are bigger than the membrane pore size, integrity of the AnMBR is ensure.
- AnMBR permeate is kept under anaerobic conditions, but when samples are being analysed it is impossible to ensure anaerobic conditions, even when special considerations are taken. Thus, results may deviate from reality.
- RO laboratory scale ran with Dow Filmtec™ BW30XFR membrane has a maximum achievable recovery of 9% per meter of membrane when ran with demineralized water. This value is achieved when system is ran at 5 Hz, no bypass and a feed flow of around 300 mL/min.
- Maximum recovery of 4.2% is achieved, when RO lab scale system is ran with AnMBR permeate as feed.
- When RO system is turned off and started up again, it needs approximately 30 minutes to reach the same operational conditions (regarding pressure and recovery) as before it is turned off.
- Given the RO setup, it is not possible to achieve stable feed pressure or recovery. Thus, operational conditions are not comparable with full scale RO plants, which operate generally at constant recovery and variable feed pressure, but also in some minor cases the other way around.

- Pollutants concentrations in RO permeate stream increase over time due to the fact that RO feed concentrations are also increasing (RO brine is recirculated to the feed vessel).
- High removal efficiencies are achieve with RO: 96% of Nitrogen (as ammonium), more than 93% of Phosphorus, 92% of TCOD, and 96% of conductivity is removed (same removal efficiency as total solids). Moreover, almost all solids found in AnMBR permeate and RO permeate are dissolved ones. Finally, coupled system of AnMBR and RO achieved extremely high removal efficiencies when treating dairy industry wastewater: TCOD of 99.95%, TS of 98.84%, VFA of 100%, Phosphorus removal (as orthophosphate) is higher than 93%, and Nitrogen (as TKN) 96.70%. Ammonium in RO effluent is around 8 mg/L and orthophosphate is below 2 mg/L.
- According to Uruguayan legislation, neither concentrate nor permeate streams have reuse possibilities due to the fact that they do not comply with drinkable water standards. Furthermore, values of NH_4 found in RO permeate are more than 5 times higher than require standard (8 versus 1.5 mg/L). However, when this streams are evaluated bearing in mind WHO and FAO recommendations, then permeate flow has almost none restriction in reuse for irrigation purpose, but pH should be in the range from 6.5 to 8. On the other hand, concentrate stream has severe irrigation restrictions, mainly due to conductivity, concentration of sodium and bicarbonate. Furthermore, due to low concentration in permeate stream, especially low concentration of solids, calcium and orthophosphate, permeate may be used for industrial purposes, such as cooling and boiling towers, cleaning and washing, among others, where no contact with dairy industry products is expected.

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Appendices

Appendix A **Pump data sheet**

Hydra-Cell®

Seal-less Pumps

Versatile, Reliable Pumps for a Wide Range of Applications

M03 Series

- Pumps the full spectrum of low-to-high viscosity fluids.
- Features a seal-less design and horizontal disk check valves that enable the pump to handle abrasives and particulates that might damage or destroy other types of pumps.
- Simple, compact design reduces initial investment and lowers maintenance costs.
- Operational efficiencies reduce energy costs.
- Able to run dry without damage (or additional maintenance) to the pump in case of accident or operator error.
- Tolerates non-ideal operating conditions.
- Minimizes maintenance and downtime because there are no seals, packing or cups to leak or replace.

Wanner Engineering, Inc.

M03 Series

Maximum Flow Rate: 3.1 gpm (11.7 l/min)

Maximum Pressure: 1200 psi (83 bar) for Metallic Pump Heads

350 psi (24 bar) for Non-metallic Pump Heads

M03 Close-coupled with Brass pump head

M03 Close-coupled with Polypropylene pump head

D03 Shaft-driven with Stainless Steel pump head

M03 Series Performance

Capacities

Flow

Model	Max. Input rpm	Max. Flow @ 1000 psi (69 bar) gpm	l/min
M03-X	1750	3.1	11.7
M03-E	1750	2.2	8.3
M03-S	1750	1.7	6.4
M03-B	1750	1.0	3.6
M03-G	1750	0.6	2.3
		@ 1200 psi (83 bar)	
M03-E	1750	2.1	8.1
M03-S	1750	1.6	6.3
M03-B	1750	0.9	3.5
M03-G	1750	0.6	2.2

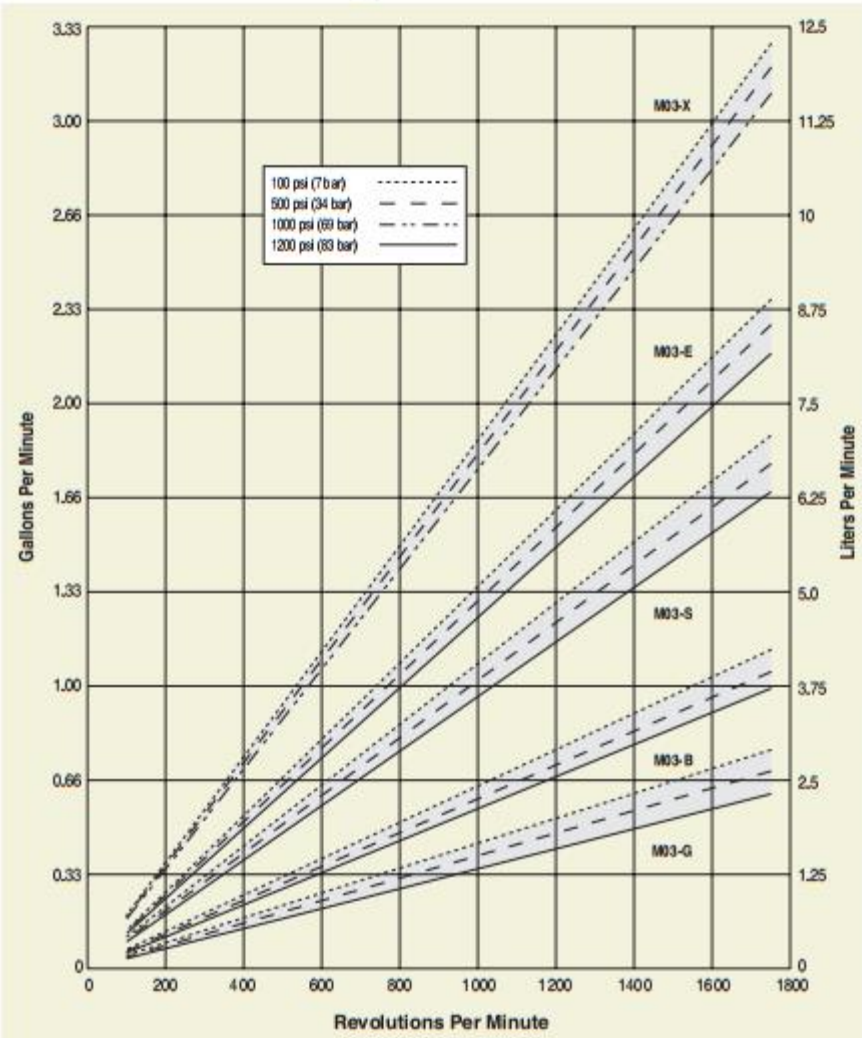
Pressure

Maximum Inlet Pressure
250 psi (17 bar)

Maximum Discharge Pressure
Metallic Pump Heads:
M03-X to 1000 psi (69 bar)
M03-S, E, B, G to 1200 psi (83 bar)
Non-metallic Pump Heads:
250 psi (17 bar) Polypropylene
350 psi (24 bar) PVDF

Performance and specification ratings apply to M03 Kel-Cell and D03 Shaft-driven configurations unless specifically noted otherwise.

Maximum Flow at Designated Pressure



M03 Series Specifications

Flow Capacities @1000 psi (69 bar)			
Model	**rpm**	**gpm**	**l/min**
M03-X	1750	3.10	11.73
M03-E	1750	2.18	8.25
M03-S	1750	1.69	6.40
M03-B	1750	0.96	3.63
M03-G	1750	0.62	2.35

Delivery @1200 psi (83 bar)		
Model	**gal/rev**	**liters/rev**
M03-E	0.0012	0.0046
M03-S	0.0009	0.0036
M03-B	0.0005	0.0020
M03-G	0.0003	0.0013

Delivery @1000 psi (69 bar)		
Model	**gal/rev**	**liters/rev**
M03-X	0.0018	0.0067
M03-E	0.0013	0.0047
M03-S	0.0010	0.0037
M03-B	0.0005	0.0021
M03-G	0.0004	0.0013

Maximum Discharge Pressure	
Metallic Heads:	M03-X to 1000 psi (69 bar) M03-S, E, B to 1200 psi (83 bar)
Non-metallic Heads:	250 psi (17 bar) Polypropylene 350 psi (24 bar) PVDF
Maximum Inlet Pressure	250 psi (17 bar)
Maximum Operating Temperature	
Metallic Heads:	250°F (121°C) - Consult factory for correct component selection for temperatures from 160°F (71°C) to 250°F (121°C).
Non-metallic Heads:	140°F (60°C)
Maximum Solids Size	200 microns
Inlet Port	
Primary:	1/2 inch NPT
Secondary:	3/8 inch NPT (plugged from factory)
Discharge Port	3/8 inch NPT
Shaft Diameter	M03: 5/8 inch (15.9 mm) hollow shaft D03: 7/8 inch (22.2 mm)
Shaft Rotation	Reverse (bi-directional)
Bearings	Precision ball bearings
Oil Capacity	1.0 US quart (0.95 liters)
Weight	
Metallic Heads:	28 lbs. (12.7 kg)
Non-metallic Heads:	19 lbs. (8.6 kg)

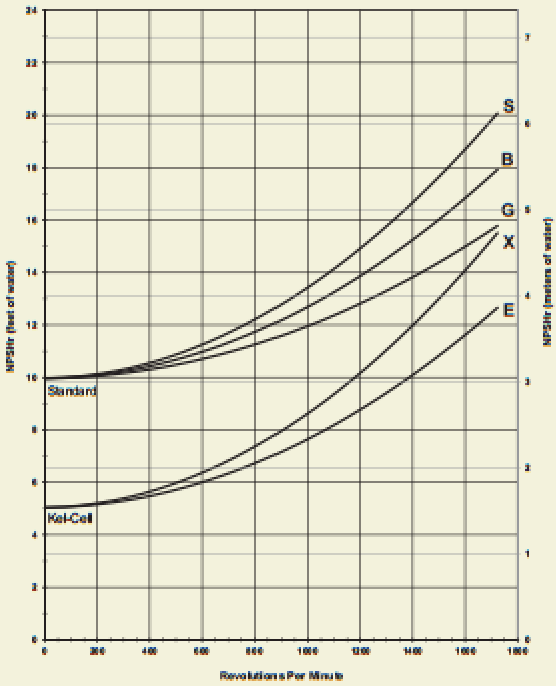
Calculating Required Power

$$\frac{6 \times rpm}{63{,}000} + \frac{gpm \times psi}{1{,}460} = \text{electric motor hp}$$

$$\frac{6 \times rpm}{84{,}428} + \frac{l/min \times bar}{511} = \text{electric motor kW}$$

When using a variable frequency controller (VFD) calculate the hp or kW at minimum and maximum pump speed to ensure the correct hp or kW motor is selected. Note that motor manufacturers typically de-rate the service factor to 1.0 when operating with a VFD.

Net Positive Suction Head (NPSHr)



Note: Positive inlet pressure required with PTFE diaphragms.

Self-priming:

Each Hydra-Cell pump has different lift capability depending on model size, cam angle, speed, and fluid characteristics. To ensure that your specific lift characteristics are met, refer to the inlet calculations regarding friction, and acceleration head losses in your Hydra-Cell Installation & Service Manual. Compare those calculations to the NPSHr curves above.

M03 Series How to Order

Ordering Information

1	2	3	4	5	6	7	8	9	10	11	12

A complete M03 Series Model Number contains 12 digits including 9 customer-specified design and materials options, for example: M03XKSTHFECA.

Digit	Order Code	Description
1-3		**Pump Configuration**
	D03	Shaft-driven (NPT Ports)*
	M03	Close-coupled to NEMA 56C footed motor (NPT Ports)
		*Pump/motor adapters ordered separately. See previous page.
4		**Hydraulic End Cam**
	X	Max 3.1 gpm (11.7 l/min) @ 1750 rpm
	E	Max 2.2 gpm (8.3 l/min) @ 1750 rpm
	S	Max 1.7 gpm (6.4 l/min) @ 1750 rpm
	B	Max 1.0 gpm (3.6 l/min) @ 1750 rpm
	G	Max 0.6 gpm (2.3 l/min) @ 1750 rpm
5		**Pump Head Version**
	A	Standard NPT Ports (S, B & G cams)
	K	Kel-Cell NPT Ports (X & E cams)
6		**Pump Head Material**
	B	Brass
	M	PVDF
	P	Polypropylene
	S	316L Stainless Steel
	T	Hastelloy CW12MW
7		**Diaphragm & O-ring Material**
	E	EPDM (requires EPDM-compatible oil - Digit 12 oil code J)
	G	FKM
	J	PTFE (available with X and E cams and standard A version only; cannot be used with Kel-Cell pumps)
	P	Neoprene
	T	Buna-N
8		**Valve Seat Material**
	C	Ceramic
	D	Tungsten Carbide
	H	17-4 Stainless Steel
	S	316L Stainless Steel
	T	Hastelloy C

Digit	Order Code	Description
9		**Valve Material**
	C	Ceramic
	D	Tungsten Carbide
	F	17-4 Stainless Steel
	N	Nitronic 50
	T	Hastelloy C
10		**Valve Springs**
	E	Elgiloy
	S	316L Stainless Steel
	T	Hastelloy C
11		**Valve Spring Retainers**
	C	Celcon
	H	17-7 Stainless Steel
	M	PVDF
	P	Polypropylene
	T	Hastelloy C
	Y	Nylon
12		**Hydra-Oil**
	A	10W30 standard-duty oil
	G	5W30 cold-temp severe-duty synthetic oil
	J	EPDM-compatible oil
	K	Food-contact oil

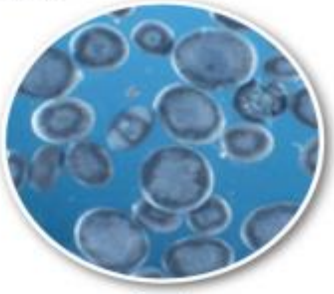
Consult the Hydra-Cell Master Catalog for:

- Motors, bases, couplings and other pump accessories
- Hydra-Oil selection and specification information
- Design considerations, installation guidelines, and other technical assistance in pump selection

Appendix B **Vithane**

Vithane™

A nutrient can be defined as any element that is utilized by microorganisms for energy generation and cellular growth. The exact mixture of nutrients required for optimal growth varies between species of microorganism. Of course some elements (macronutrients) such as carbon, oxygen, nitrogen, hydrogen, phosphorus and sulphur are essential to all organisms and are usually present in abundance in most wastewaters. However there is often a shortage of other minerals and trace elements (micronutrients).



Granules

- Many metals are involved in important enzymatic activities and play an important role in the removal efficiency of the biomass. These metals are required in very small quantities but they are crucial for proper methanogenic activity. Not all wastewaters contain sufficient amounts of these specific metals and therefore trace element addition is common for industrial anaerobic treatment systems. Typical industries that require trace element addition are chemical and paper.
- Biothane provides a nutrient solution containing all necessary micronutrients which is called Vithane. This micronutrient solution is often mixed together with Iron, which is an essential nutrient for anaerobic bacteria. For this reason Biothane can also offer pre-mixed nutrient solutions of $FeCl_3$ and Vithane.
- Wastewaters produced by the chemical industry typically do not contain any micronutrients and also lack some macronutrients. Therefore Biothane has developed a special mixture (Vithane Complete) for the chemical industry. Vithane Complete contains all the necessary nutrients to promote granular formation and to achieve optimal performance. A key advantage of Vithane Complete is that all micronutrients are provided in a single solution, which reduces the handling requirement. Vithane Complete is discharged directly to a storage tank thereby eliminating any potential hazardous situations.

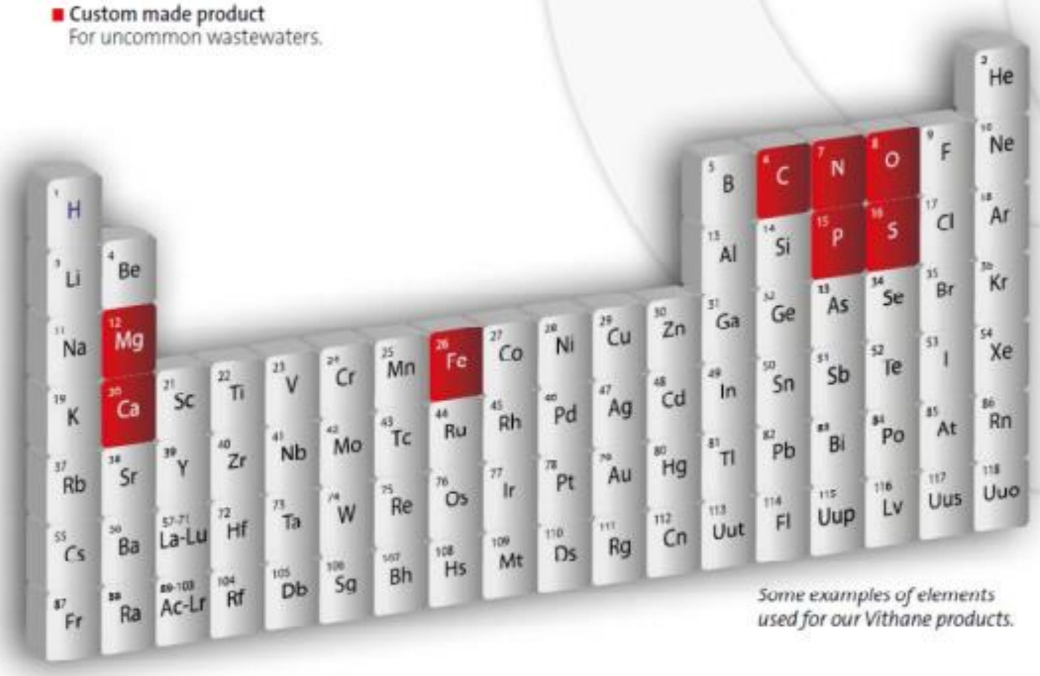
VEOLIA WATER
Solutions & Technologies

We can offer the following products:

- **Vithane – Basic**
  The standard Biothane trace element solution. The main precursor for our other mixtures.
- **Vithane – $FeCl_3$ mixture**
  Iron Chloride pre-mixed with Vithane.
- **Vithane Complete**
  A complex mixture with among others, Vithane, $FeCl_3$, $MgSO_4$, etc. Developed for wastewaters with very low concentrations of nutrients (e.g. Chemical).
- **S-Vithane**
  Vithane developed for Sulfothane application.
- **Custom made product**
  For uncommon wastewaters.

References

Industry	Country
Chemical	Poland
Starch	France
Dairy	The Netherlands
Chemical	Portugal
Paper	Poland
Food - Candy	Switzerland
Beer	Czech Republic
Paper	Norway



Some examples of elements used for our Vithane products.

VEOLIA WATER
Solutions & Technologies

BIOTHANE SYSTEMS INTERNATIONAL
Veolia Water Solutions & Technologies
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2623 EW Delft, The Netherlands
Tel +31 (0)15 2700111
www.biothane.com

Appendix C **Genesys WB Antiscalant**

Genesys WB
Broad Spectrum Antiscalant

G E N E S Y S
I N T E R N A T I O N A L

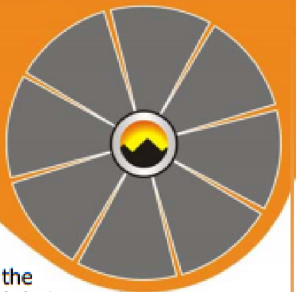
www.genesysro.com

The Complete Solution

Inhibits Scale formation

Prevents Iron Fouling

- ✓ Suitable for Reverse Osmosis (RO) and Nano-Filtration (NF) membranes
- ✓ Compatible with all types of polyamide membrane
- ✓ Allows high recovery rates
- ✓ Replaces acid addition
- ✓ Simple test method
- ✓ Metabisulphite removes chlorine from feed water
- ✓ Inhibits common scalants
  - Calcium carbonate/sulphate
  - Barium/Strontium sulphate
  - Calcium phosphate
  - Iron/Manganese



Description

Genesys WB has been developed as a broad spectrum antiscalant for use in very small Reverse Osmosis and Nano-Filtration systems using less than 30 M^3/day feed water. Genesys WB contains sodium bisulphite which removes residual chlorine from mains fed feed waters, thus protecting the membranes from oxidation without additional dosing equipment.

It is particularly effective in preventing calcium carbonate formation and all commonly found scaling species. It's effectiveness at a single dose rate means that a detailed water analysis is not necessary.

Genesys WB will continue to give maximum protection even when water analyses and operating conditions change.

Application

Genesys WB should be dosed continuously to the feed water upstream of the cartridge filter and should be diluted with good quality water.
The standard feed water dose rate is 50 mg/L.

Health and Safety

Genesys WB is an aqueous solution of phosphonic acid. It is compatible with carbon steel and all commonly used materials of construction. A material safety data sheet is available on request.

Classification

CHIP: Not Classified | UN: Non Hazardous

Typical properties

Appearance:	pale colourless liquid
pH as supplied:	6.0 – 6.5
Specific gravity:	1.09 – 1.13
Freezing point:	<-2ºC

Packaging

Available in 25 kg kegs and 200 kg drums.
Shelf life 12 months under normal storage conditions.

THE QUEEN'S AWARDS FOR ENTERPRISE 2005

For more information contact:
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Middlewich, Cheshire, CW10 0HS, UK
E-mail: info@genesysro.com
www.genesysro.com

Release 12/07/2010

Genesys Latin America - Chile
Genesys North America - USA
Genesys Membrane Products - Spain

Appendix D **DOW FILMTEC™ BW30XFR Data sheet**

Product Data Sheet

DOW FILMTEC™ BW30XFR-400/34i Element

Description

Ideal for: reverse osmosis plant managers and operators dealing with challenging waters and wastewaters and seeking consistent high performance, long element life, increased productivity and higher water quality coupled with outstanding fouling resistance.

With proven performance, DOW FILMTEC™ BW30XFR-400/34i:

- Delivers high quality permeate water while minimizing CAPEX and OPEX
- Offers the most effective cleaning performance, robustness and durability due to its widest cleaning pH range (1 – 13) and chemical tolerance, and the support of Dow representatives
- Includes iLEC™ interlocking end caps, reducing system operating costs and the risk of o-ring leaks that can cause poor water quality

Product Type

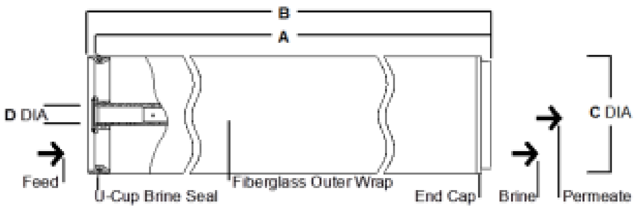
Spiral-wound element with polyamide thin-film composite membrane

Product Specifications

DOW FILMTEC™ Element	Active Area (ft²)	Active Area (m²)	Feed Spacer Thickness (mil)	Permeate Flow Rate (GPD)	Permeate Flow Rate (m³/d)	Typical Stabilized Salt Rejection (%)	Minimum Salt Rejection (%)
BW30XFR-400/34i	400	37	34-LDP	11,500	43	99.65	99.4

1. Permeate flow and salt (NaCl) rejection based on the following standard test conditions: 2,000 ppm NaCl, 225 psi (15.5 bar), 77°F (25°C), pH 8, 15% recovery.
2. Flow rates for individual elements may vary but will be no more than ± 15%.
3. Stabilized salt rejection is generally achieved within 24-48 hours of continuous use; depending upon feedwater characteristics and operating conditions.
4. Sales specifications may vary as design revisions take place.
5. Active area guaranteed ± 3%. Active area as stated by Dow Water & Process Solutions is not comparable to nominal membrane area often stated by some manufacturers. Measurement method described in Form No. 609-00434.

Element Dimensions



DOW FILMTEC™ Element	A (in.)	A (mm)	B (in.)	B (mm)	C (in.)	C (mm)	D (in.)	D (mm)
BW30XFR-400/34i	40.0	1,016	40.5	1,029	7.9	201	1.125 ID	29 ID

1. Refer to Dow Water & Process Solutions Design Guidelines for multiple-element applications. 1 inch = 25.4 mm
2. Element to fit nominal 8-inch (203-mm) I.D. pressure vessel.
3. Individual elements with *iLEC* endcaps measure 40.5 inches (1,029 mm) in length (B). The net length (A) of the elements when connected is 40.0 inches (1,016 mm).

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August 2015

Operating and Cleaning Limits

Maximum Operating Temperature [a]	113°F (45°C)
Maximum Operating Pressure	600 psig (41 bar)
Maximum Element Pressure Drop	15 psig (1.0 bar)
pH Range, Continuous Operation [a]	2 – 11
pH Range, Short-Term Cleaning (30 min.) [b]	1 – 13
Maximum Feed Silt Density Index (SDI)	SDI 5
Free Chlorine Tolerance [c]	< 0.1 ppm

[a] Maximum temperature for continuous operation above pH 10 is 95°F (35°C).
[b] Refer to Cleaning Guidelines in specification sheet 609-23010.
[c] Under certain conditions, the presence of free chlorine and other oxidizing agents will cause premature membrane failure. Since oxidation damage is not covered under warranty, Dow Water & Process Solutions recommends removing residual free chlorine by pretreatment prior to membrane exposure. Please refer to technical bulletin "Dechlorinating Feedwater" for more information.

Additional Important Information

Before use or storage, review these additional resources for important information:

- Usage Guidelines for DOW FILMTEC™ 8" Elements
- System Operation: Initial Start-Up

Regulatory Note

These membranes may be subject to drinking water application restrictions in some countries; please check the application status before use and sale.

Product Stewardship

Dow has a fundamental concern for all who make, distribute, and use its products, and for the environment in which we live. This concern is the basis for our product stewardship philosophy by which we assess the safety, health, and environmental information on our products and then take appropriate steps to protect employee and public health and our environment. The success of our product stewardship program rests with each and every individual involved with Dow products—from the initial concept and research, to manufacture, use, sale, disposal, and recycle of each product.

Customer Notice

Dow strongly encourages its customers to review both their manufacturing processes and their applications of Dow products from the standpoint of human health and environmental quality to ensure that Dow products are not used in ways for which they are not intended or tested. Dow personnel are available to answer your questions and to provide reasonable technical support.

DOW FILMTEC™ Membranes
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