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# Technical and environmental feasibility of membrane technologies in water treatment:

## NF in drinking water process and MBR for wastewater reuse

PhD Thesis

Gemma Ribera Simon

# UNIVERSITAT POLITÈCNICA DE CATALUNYA

## Doctorat en Recursos Naturals i Medi ambient

# Technical and environmental viability of membrane technologies in water treatment

## NF in drinking water process and MBR for wastewater reuse

**PhD Thesis**

**Gemma Ribera Simon**

**March 2013**

**Supervised by:**

**Xavier Martínez Lladó**
**Frederic Clarens Blanco**
**Miquel Rovira Boixaderas**

**MIQUEL ROVIRA BOIXADERAS**, director de l'Àrea de Tecnologia Ambiental de la Fundació CTM Centre Tecnològic, **XAVIER MARTÍNEZ LLADÓ i FREDERIC CLARENS BLANCO**, investigadors i responsables de les línees de tecnologia de l'aigua i d'ecologia industrial de la mateixa àrea, respectivament, juntament amb el **XAVIER GAMISANS NOGUERA** professor i investigador al Departament d'Enginyeria Minera i Recursos Naturals de la Universitat Politècnica de Catalunya (UPC) a Manresa (EPSEM)

CERTIFIQUEM,

Que el present treball, titulat "**Technical and environmental viability of membrane technologies in water treatment: NF in drinking water process and MBR for wastewater reuse**", que presenta **GEMMA RIBERA SIMON** per a l'obtenció del Grau de Doctor per la Universitat Politècnica de Catalunya, ha estat realitzat sota la nostra direcció i tutoria.

I per què així consti, signem el present document,

Dr. Miquel Rovira Boixaderas

Dr. Xavier Martínez Lladó

Dr. Frederic Clarens Blanco

Dr. Xavier Gamisans Noguera

Manresa, Febrer 2013

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## ACRONYMS AND SYMBOLS

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BDCM ($BrCl_2CH$): bromodichloromethane, bromodichloroform
BOD: biological organic demand
CAS: conventional activated sludge
ChC.: chemical cleaning
COD: chemical oxygen demand
CP: concentration polarization
DBCM ($Br_2ClCH$): dibromochloromethane, dibromochloroform
DBP: disinfection by-products
DWTP: drinking water treatment plant
EC: European Community
EEA: European Environmental Agency
EPS: extracellular polymeric substances
$EPS_c$: extracellular polymeric substances with relative content of carbohydrates
$EPS_p$: extracellular polymeric substances with relative content of proteins
ESNA: energy saving nanofiltration
FAO: Food and Agriculture Organization
FTIR: Fourier transformation infrared radiation
GAC: granular activated carbon
HA: humic acid
HHR: human health risk
HRT: Hydraulic retention time
IC: inorganic carbon
iMBR: immersed membrane bioreactor
IRIS: integrated risk information system
IS: ionic strength
ISO: International Standardization Organization
IWMI: Institute Water Management Institute
KWR: Water Research Institute in Netherlands
LAS: linear alkyl sulphonate
LCA: life cycle assessment
LMH (lmh): liters/square meter/hour
MBR: membrane bioreactor
MF: microfiltration
MLSS: mixed liquor solids in suspension

NF: nanofiltration
NOM: natural organic matter
NPOC: non-purgable organic carbon
PAC: powdered activated carbon
RAIS: risk assessment information system
RD: Royal Decret
RO: reverse osmosis
sMBR: sidestream membrane bioreactor
SMP: soluble microbial products
SMP$_c$: soluble microbial products with relative content of carbohydrates
SMP$_p$: soluble microbial products with relative content of proteins
SRT: sludge retention time
SUVA: specific ultraviolet light absorbance ($L \cdot \mu g^{-1} \cdot cm^{-1}$)
TBM: tribromomethane, bromoform
TCM: trichloromethane, chloroform
TFC: thin-film composite
TFC-SR: thin-film composite selective rejection
THM: trihalomethanes
THMFP: trihalomethane formation potential
TMP: transmembrane pressure
TMF: transmembrane flux (lmh or LMH)
TSS: total suspended solids
UF: ultrafiltration
UFC: unit formation counts
UNDESA: United Nations Department of Economic and Social Affairs
UNEP: United Nations Environmental Program
UNESCO: United Nations Educational, Scientific and Cultural Organization
USEPA: United States Environmental Protection Agency
UV: ultraviolet light
UVA: ultraviolet light absorption
VSS: volatile solids in suspension
WHO: World Health Organization
WWTP: wastewater treatment plant

## RESUM

La present tesi doctoral tracta de l'estudi de la tecnologia de membranes des d'un punt de vista aplicat: com és el cas de la nanofiltració (NF) pel tractament d'aigua potable i de l'ús d'un bioreactor de membranes (MBR) per la depuració d'aigües residuals.

La primera part ha estudiat la capacitat de la NF per reduir el contingut de precursors de subproductes de desinfecció presents en l'aigua potable, especialment dels trihalometans (THM). En canvi, la segona part ha avaluat la capacitat de la tecnologia MBR per tractar els efluents de la indústria vinícola i dotar a l'aigua residual de la qualitat necessària per a la seva reutilització.

Les membranes de NF s'han estudiat des d'escala laboratori, en configuració de mòdul pla, fins a planta pilot utilitzant 18 mòduls en espiral. Els estudis previs a nivell de laboratori han permès comparar 10 membranes comercials de NF en funció de la seva permeabilitat i capacitat de reducció del potencial de formació de trihalometans (PFTHM). La majoria d'elles permeten reduir el PFTHM en més del 95%, tot i que presenten rebutjos variables respecte les sals inorgàniques, fet que afecta la permeabilitat i consum energètic del sistema. En aquest estudi també es va tenir en compte com afecta la variabilitat estacional i el punt de captació sobre la qualitat de l'aigua d'entrada a les membranes.

Es van seleccionar dues membranes per a l'estudi en paral·lel en la planta pilot obtenint un bon rendiment en ambdós casos sota condicions d'operació òptimes. Amb l'objectiu final d'optimitzar el procés de tractament, es van avaluar diferents aspectes: capacitat de separació de diferents components inorgànics i orgànics, requeriments de pressió d'entrada per treballar a igual recuperació per a un mateix cabal d'entrada, pretractament, reducció del flux inicial de permeat i efectivitat de les neteges químiques. Els resultats obtinguts a ambdues escales es van comparar per poder validar la predicció des del nivell de laboratori, juntament amb els programes de disseny dels proveïdors.

Finalment, en aquest treball també es va avaluar l'impacte ambiental d'aquesta tecnologia mitjançant l'anàlisi de cicle de vida (ACV) utilitzant les dades obtingudes de la planta pilot i aproximacions per a una possible instal·lació a escala real de la NF. Els resultats d'aquest estudi indiquen un increment de l'impacte ambiental, respecte el procés actual, degut principalment al major consum energètic durant l'operació de les

membranes. Combinant l'estudi d'ACV amb l'anàlisi de risc per a la salut humana en funció de la qualitat de l'aigua obtinguda s'ha desenvolupat una eina que ajuda al disseny del escalat de la planta real. De fet, en l'estudi s'observa que es pot arribar a obtenir una reducció del 75% del risc associat a la presencia de THM a l'aigua potable.

D'altra banda, per avaluar la tecnologia MBR es va instal·lar una planta pilot a la depuradora d'una empresa vinícola. Durant els mesos d'operació es va comparar la qualitat dels efluents del sistema convencional i del MBR. Demostrant que el MBR presenta una qualitat final molt superior que en permet la seva reutilització en diferents aplicacions. També es va demostrar com la tecnologia MBR es capaç d'absorbir les variacions de càrrega i cabal que presenten els efluents d'aquesta indústria, fet que demostra la seva aplicabilitat en aquest sector.

Les dades obtingudes d'aquesta planta pilot també es van utilitzar per avaluar l'impacte ambiental derivat de la implementació a escala real de la tecnologia MBR. Els resultats obtinguts es van comparar amb el procés existent, basat en la digestió aeròbica de fangs activats, on s'observa un trasllat de l'impacte entre vectors ambientals, degut a que la millora de la qualitat de l'aigua i per tant reducció en categories d'impacte ambiental com la eutrofització implica l'augment del consum energètic i per tant un augment de l'impacte en categories com el canvi climàtic o la formació de partícules o del *smog* fotoquímic.

## ABSTRACT:

The present thesis is about membrane technology implementation for two cases of water processes: nanofiltration (NF) to produce drinking water and membrane bioreactor (MBR) to treat wastewater effluent.

The first part has evaluated NF capacity to reduce contents of disinfection by-products precursors, especially for trihalomethanes (THM). On the other hand, the second part is focused to evaluate MBR capacity to treat winery industry effluents giving the required quality for wastewater reclamation and reuse.

NF membranes have been studied in laboratory set-up (flat-sheet module) and in pilot plant (18 spiral-wound elements). Initially, laboratory results allowed to select two of the ten membranes tested at this scale, in function of the permeability and the reduction of trihalomethane formation potential (THMFP). Most of the membranes rejected THMFP at levels of 95%, however the separation capacities in front of inorganic salts were highly variable, which may have important consequences in permeability and energy demands for a full-scale system. This study also considered factors influencing feed water quality for the NF membranes, such as seasonal variations and different catchments of raw water.

Two NF membranes were selected in order to be compared simultaneously in a pilot plant. Under optimum conditions, good performances were obtained for both membranes. With the final aim to optimize treatment process, several aspects were evaluated simultaneously for each membrane: separation capacities for different inorganic and organic components, feed pressure requirements to operate with the same recovery for the same feed flow, pretreatment, initial flux decline and chemical cleaning efficiencies. Results obtained from both scales were compared to validate prediction for solutes rejection in a real plant from laboratory experiments, together with the calculations using suppliers' design software.

Finally, in this work environmental impact for this technology was also evaluated by means of life cycle assessment (LCA), using pilot plant data and approximations for the NF implementation in a full-scale drinking water treatment plant (DWTP). Results indicated how increase the environmental impacts using NF in front of the current treatment, mainly as a result of higher energy demands during membrane process.

These results have been correlated with results calculated by means of human health risk (HHR) assessment, developing a multicriteria tool in order to design a full-scale DWTP. Is important to note that carcinogenic risk index can be lowered near to 75%, associated to the reduction of THM precursor material (THMFP), if NF plant produces 100% of the final drinking water.

On the other side, a MBR pilot plant was installed in the wastewater treatment plant (WWTP) to treat effluents of winery industry. Quality of effluents from the current conventional activated sludge (CAS) plant and from the MBR pilot plant was compared during the experimental campaign, demonstrating that MBR effluent presented a higher quality that accomplished with legislated requirements for some reuse applications. In addition, MBR technology was able to maintain permeability although organic loads fluctuations in winery industry take place, what demonstrated its applicability in this sector.

Data obtained from MBR pilot plant were also employed to evaluate environmental impact associated to full-scale implementation of MBR technology, together with those obtained for the actual CAS system. Among other environmental impact categories, observed impacts related to wastewater emissions into water bodies (freshwater eutrophication) were diminished while impacts on climate change and particulate material (or photochemical compounds) formation were increased as a result of energy consumption.

# PREFACE

In the last century, global water situation has suffered important changes and nowadays the implementation of new technologies plays an important role to improve drinking water quality or to provide water reuse options. Drivers and actions in both cases pretend to give a sustainable framework to manage water situation, implying different measures because between other aspects, water is unequally distributed worldwide.

Considering drinking water treatments, it has been demonstrated the low effectiveness of conventional processes to remove undesirable substances, for example synthetic organic compounds (pharmaceuticals, pesticides), natural hormones, microorganisms, and inorganic trace elements (arsenic and other heavy metals from both natural and anthropogenic origin). A wide range of undesired substances have been studied and toxicological studies elucidate their potential to endanger human health, some of them have been classified as endocrine disrupting compounds (EDC), affecting hormonal systems in human and animal life, while others have carcinogenic effects, such as disinfection by-products (DBP).

In case of water reclamation and water reuse it is important to firstly consider the reuse application to define quality parameters. In this way, legislation in several parts of the world has been developed taking into account the minimization of potential risks for human health in the final fate of reclaimed water. Aquifer recharge, agricultural and landscape irrigation are typical water reuse applications and quality requirements are variable between them.

In the introduction part (Chapter 1) the aforementioned issues related to water aspects are described in more detail in order to give a water context evolution from the point of view of technologies implementation. Alternative technologies lately employed in water treatment to upgrade its quality are based on pressure driven membrane filtration, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Following this order, water suffers higher resistance to pass through the membrane, hence pressure and energy required to produce water permeate increase. On the other hand, membranes present fouling tendencies which decrease productivity and requires tools to prevent its formation; as suitable pretreatments, or corrective measures; as chemical cleaning and it last extent membrane replacement.

However, some benefits regarding the quality of the membrane permeate have been elucidate in many applications, for example the improvement in drinking water or the change for water reclamation and reuse. Technical and other aspects with regards membrane technologies are described in the introduction of this thesis, indicating some real cases of NF and membrane bioreactor (MBR) applications.

Advantages and drawbacks of membrane technologies in front of other technical options can be evaluated using tools such as life cycle (LCA) and human health risk (HHR) assessment in order to study environmental impacts and benefits in public health.

Once described the main technical aspects in the introduction, next chapters are related to check the reliability for two membrane cases: NF improving drinking water quality and membrane bioreactor (MBR) treating wastewater for reuse proposals. Laboratory and pilot plant results for NF are detailed from Chapter 4 to Chapter 7, to finally evaluate its environmental impact (LCA) in a case study where a virtual full-scale plant would treat 43% of final drinking water (Chapter 8). Additionally, in this chapter HHR benefits have been determined taking into account the trihalomethanes (THM), with potential carcinogenic effects when drinking water is consumed. THM concentrations were experimentally estimated as trihalomethanes formation potential (THMFP). Results from HHR and from LCA have been related in function of NF production capacity as a tool to choose the most suitable dimensions for a NF plant scale-up considering both criteria (drinking water quality and environmental impact).

The performance of a MBR using MF membranes in a pilot plant located in a winery industry was evaluated in Chapter 9 in order to validate this process and the treated effluent quality for some reuse applications. In this case, a LCA study has been carried out in Chapter 10 to evaluate the differences in environmental impacts of a MBR system in front of the conventional (CAS) treatment process, currently operating in the WWTP without reuse options.

# Chapter 1: Introduction

## 1.1. GLOBAL WATER SITUATION

Every habitant of the current world population requires clean and safe access to drinking water, in addition to the water required to grow and prepare food, industrial processes and cleaning or sanitation services. In this sense, the use of water implies abstraction and suitable treatment of this natural resource with the associated environmental impacts, such as the discharges into water bodies altering physicochemical properties that could endanger its future availability and quality.

Water occupies 72% of the Earth surface, although 97% of this water is contained in the seas and oceans as salt water, and only 3% is considered freshwater. Additionally, the 70% of this low percentage is in form of glaciers on the poles, being groundwater of difficult access the most part of the remaining freshwater. As summary, the amount of liquid water theoretically available to satisfy all humanity's needs is approximately 0.5% of total water in our planet (Figure 1.1).

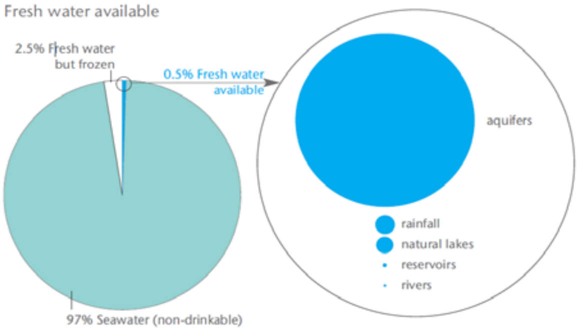


Figure 1.1: Water availability in Earth planet from a report of World Business Council for Sustainable Development (WBCSD, 2005)

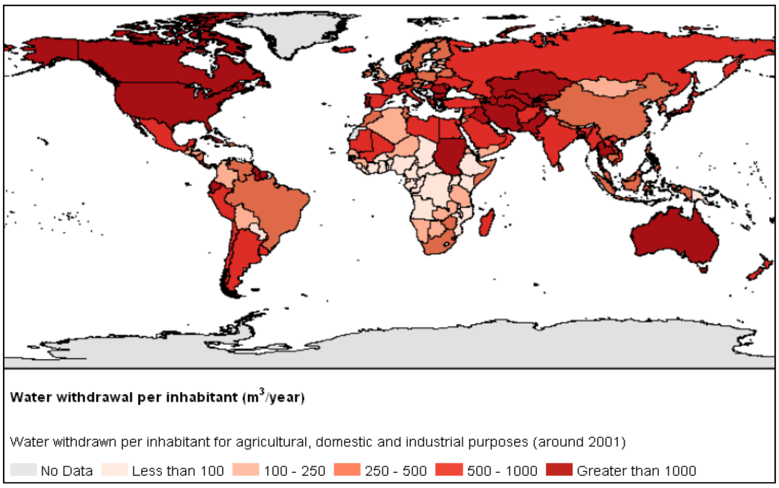
Global water situation has suffered important changes in the last century because, while population has tripled, water consumption has multiplied by six as a result of a great number of services and activities demanding water. To make things worse, different geographical distributions make some regions deficient in this natural and essential resource.

Despite the provision of water services cannot cope with the actual rate of growing demand, the international community reaffirmed the commitments proposed in the Millenium Summit in New York (September 2000) about reducing 50% the proportion of people without sustainable access to safe water between now and 2015 (FAO, 2003).

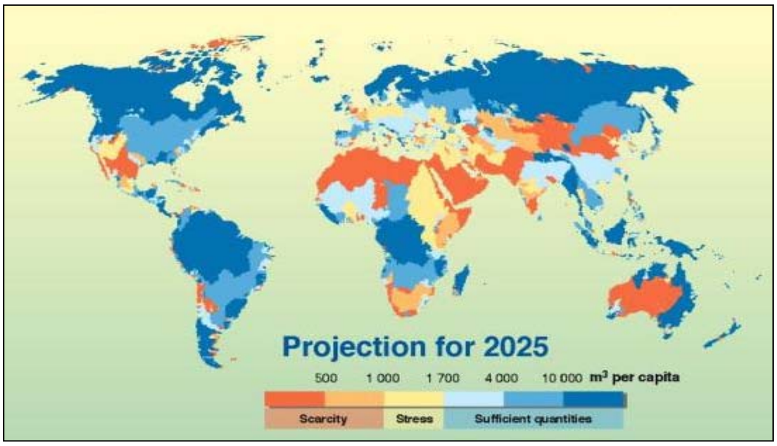
Meanwhile water from rivers, lakes and sea has been increasingly polluted around the world as a result of agricultural, industrial and urban activities. Technological solutions must be developed in order to increase water availability and quality, minimizing the risks for the human health and the environmental impact derived from its treatment and consumption.

### 1.1.2. Water demands

Actual water demand per habitant usually takes into account all sectors involved in human life, but quantities largely vary around the world: from less than 5 L·capita$^{-1}$·day$^{-1}$ (in very poor rural areas) to more than 2500 L·capita$^{-1}$·day$^{-1}$ (in developed countries). A map with annual water demand per capita around the world is shown in Figure 1.2a, in comparison to the projection of renewable water supply per capita for 2025 presented in Figure 1.2b.



a) Water demands per capita in 2001 (FAO-AQUASTAT, 2008)



b) Renewable freshwater supply per capita expected for 2025 (UNEP/GRI-Arendal, 2005)

Figure 1.2: Differences in water demand and future renewable freshwater supplies worldwide

A simplified definition of renewable freshwater supply would be the upper limit to the amount of water consumption that could occur in a region on a sustained basis (Asano et al., 2007; IWMI, 2000). A country is considered water-scarce when its annual supply of renewable freshwater is less than 1,000 m$^3$ per capita.

Places with water scarcity are often associated to regional water conflicts, limited economic development, food shortages, and environmental degradation. Nevertheless, the balance between water demand and availability has reached a critical level in many areas of Europe and Mediterranean zone, as a consequence of over-abstraction and periods of low rainfall or drought.

In general, for each region, water demands are classified into agriculture, industry and municipal sectors and the respective withdrawals are limited by the requirements to maintain minimum flows in streams leaving the region for navigation, hydropower, fish and other instream uses. Figure 1.3 shows the percentages for the major water demanding sectors in different parts of the world.

Water use in agriculture sector, which has increased 1.8 times in the last 40 years, requires approximately 70% of all water withdrawal, although in least developed countries this sector can reach 90% of total water withdrawal (IWMI, 2007; UNESCO, 2012).

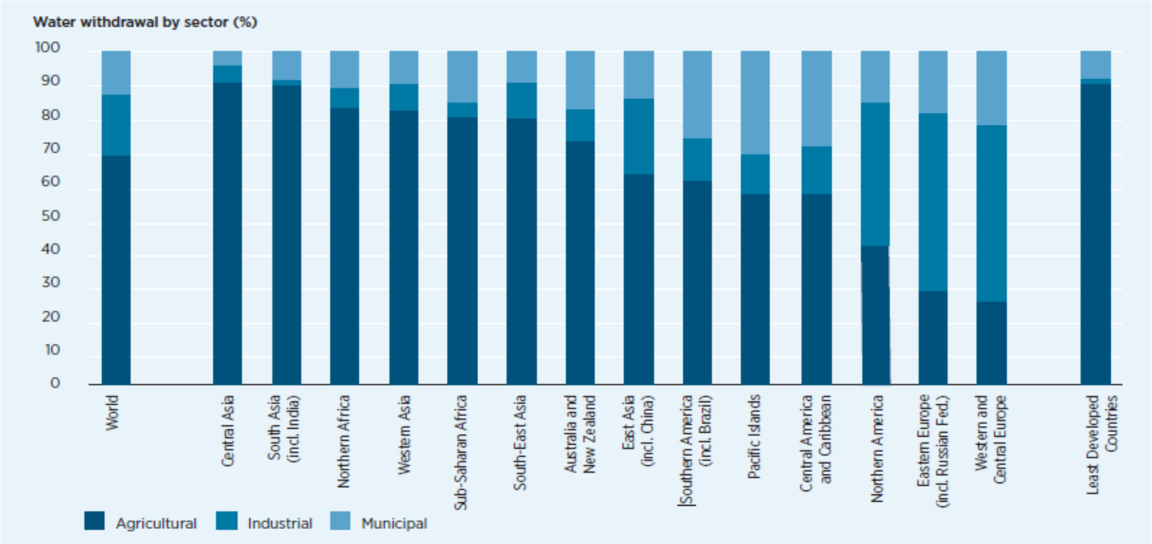


Figure 1.3: Water withdrawal by sector by region (2005) (UNESCO, 2012)

Industrial regions, such as North America and most part of Europe, can have higher water consumption in industry than in agriculture, approximately between 40-55%. Industry contains a wide variety of sub-sectors with very different water consumptions and water quality requirements (UNESCO, 2012). For example, water abstracted for energy production accounts for about 44 % of the total freshwater abstracted across Europe, although no direct consumption is done for this industrial sector, water is discharged to a receiving water body at a higher temperature also having undesirable effects on the environment.

By the contrary, in manufacturing industries, water is consumed in a number of different ways: for cleaning, heating and cooling, to generate steam, to transport dissolved substances or particulates, as a raw material, as a solvent and as a constituent part of the product itself (e.g. in the beverage industry). In this way, food industry plays an important role in global water balance, also including the part required from agriculture. Figure 1.4 shows the annual water requirements per capita in function of the food consumption patterns in 2003 for each region.

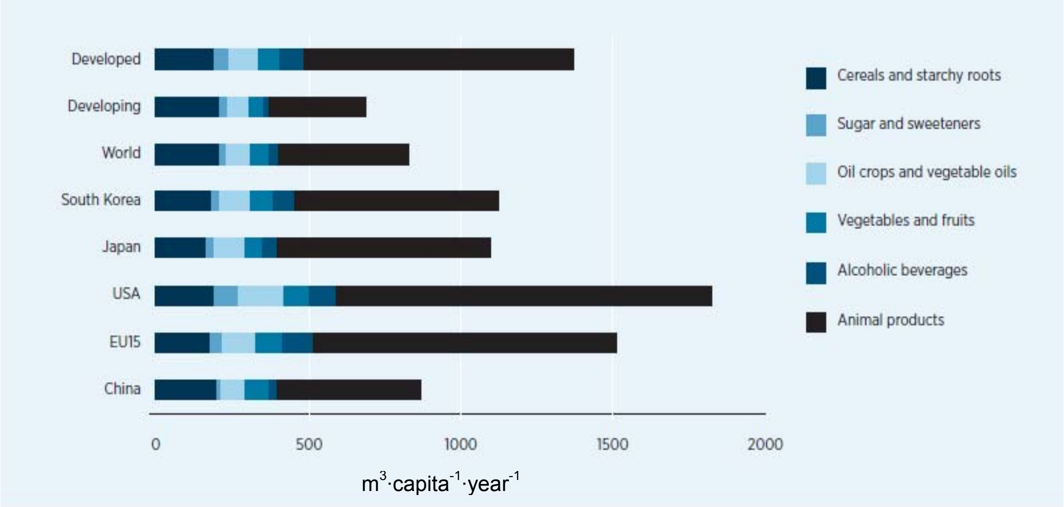


Figure 1.4: Annual water requirement for food production per capita in function of the country (2003) (UNESCO, 2012)

From the graphic above can be observed how developed countries have higher meat consumption in the diet habits of their inhabitants, implying higher water requirement per capita. Changing food-consumption patterns can be the main cause of worsening water scarcity, for example in China (Liu et al., 2008). However, in the current world, food is exported or imported being necessary to take into account the dependency on water resources elsewhere, not only from an environmental point of view, but also to assess national food security (Mekonnen and Hoekstra, 2011).

The last water demanding sector is related to municipal use of water, which presents differences around the world from 5% to 20% of total water abstraction depending on the region (Figure 1.2). Household duties such as cooking, bathing or drinking uses of water, requires previous raw water treatment to improve drinking water quality to guarantee the safety in its consumption, and consequently reduce the possible risk in human health. World health organization guidelines (WHO, 2004) give safe drinking water standards by terms of biological, chemical and physical parameters but still one billion of people do not have access to safe drinking water (UN-Habitat, 2003).

### 1.1.3. Water resources

The two principal water resources are groundwater and surface water, both having different qualities and requiring different treatments to reach potable water standards. Traditionally, water resources encompass the freshwaters of the world into the hydrological cycle, which include precipitation falling as rain or snow, infiltrating into soils and groundwater aquifers, running off into stream networks, evaporating from lakes and reservoirs, transpiring from vegetation, or flowing back into the deltas and estuaries along the continental margins. Figure 1.5 shows a scheme of the global hydrological cycle where the annual water fluxes is estimated around $10^3$ $km^3$/year.

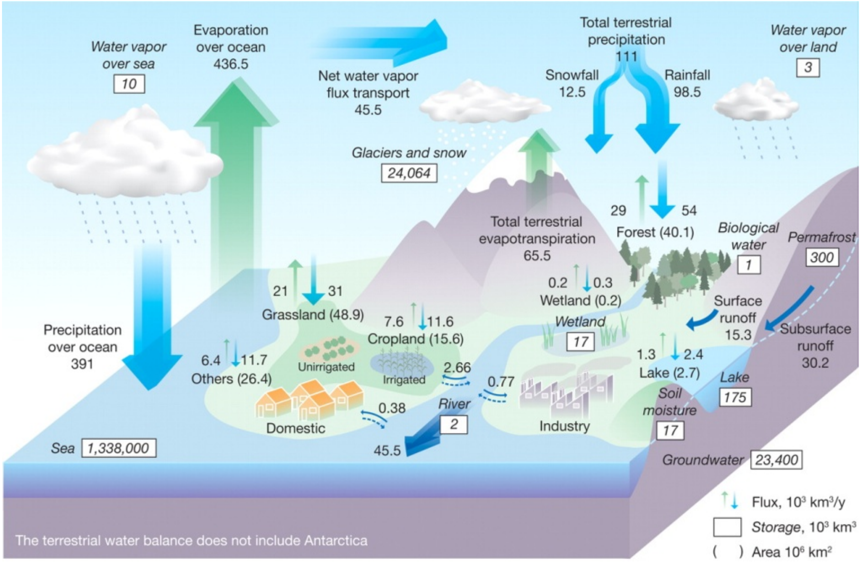


Figure 1.5: Global hydrological fluxes and storages with natural and anthropogenic cycles (Oki and Kanae, 2006)

The geographic distribution and flow of freshwaters is not homogeneously distributed all over the globe. The uneven distribution affects supplies available for human use, and lead to associated problems such as scarcity and pollution. From this point of view, non-conventional or alternative water sources, such as seawater desalination, rainwater harvesting or reclaimed wastewater, have become the main alternatives to solve some water demands in the current frame of water scarcity.

Today, some countries depend on desalination of seawater or brackish water to meet their freshwater requirements (i.e. Arabia Saudi, Kuwait, Florida), estimating that over 75 million people worldwide obtain freshwater from this alternative source. By the end of 2008, the total installed capacity of desalination plants worldwide was 42 million $m^3$·day and installation of desalination plants is expected to double between 2005 and 2015, with a major increase expected for membrane technology (Crittenden et al., 2012).

Another solution to water scarcity is the application of water regeneration and reuse strategies, such as irrigation of some crops or landscapes, aquifer recharge or specific industrial cleaning. In addition, the collection and storage of rainwater can supplement existing water supplies, alleviating some problems related to droughts and floods (Lye, 2009).

In the continuum of the global water cycle, an interesting debate emerges regarding alternative water sources and their uses, while desalination is widely accepted, reclaimed water reuse and rainwater harvesting have lower acceptance. However, improvements in technologies, control procedures and legislation can lead to establish these non conventional water resources as safe water supplies for human health.

### 1.1.4. Water quality

While the natural quality of water depends primarily on the geology and soil of the catchment for the different water demands, other factors such as land use and disposal of pollutants are of huge importance. Human use of water degrades its quality as a result of returning it into environment with different physicochemical characteristics to the initially found in water bodies. Additionally, water scarcity leads to reduce the dilution effect of wastewater discharges, hence increasing pollutants concentrations. All these events accentuate the depletion of the environmental flows in natural water systems and the decrease in healthy levels in drinking water reservoirs, including groundwater systems.

Agricultural practices can also cause water pollution, such as promoting water eutrophication (exceeding levels of nitrogen and phosphorous nutrients) and releasing of chemical products applied over the crops, such as pesticides, or veterinary medication in case of farms (Crittenden et al., 2012). High levels of mineral salts in water bodies and even soil mineralization have also been detected as negative agricultural practices (UNESCO, 2012).

On the other side, urban wastewaters can content industrial effluents in addition to domestic ones. Developed countries, such as Europe, regulate urban effluents before its discharge into water natural systems (91/271/EEC). In the best case, industrial effluents with high or toxic pollutant loads have to be treated previously to its discharge in the sewage system in order to maintain efficiency in urban wastewater treatment plants (WWTP).

Technical solutions to reduce different types of pollution can be adopted in the origin of the pollutant source or in the point before final use. Generally, the first option is applied in cases of synthetic organic compounds (SCO) and heavy metals , as a consequence of their toxic effects (carcinogenic effects, organ damaging) or persistence in the environment. The second option considers the water quality for final water application and the risk associated to it, being the case of pathogens removal in drinking water to reduce the incidence of epidemic waterborne diseases (i.e. dysentery, cholera or diarrhea).

In last years many attention have been dedicated to emergent contaminants, which can come from different origins. In case of endocrine disrupting compounds (EDC), pharmaceuticals and personal care products (PCP), conventional sewage treatments are not enough to remove them from water. This lack of effective wastewater treatment makes more probable to find undesired compounds in water resources downstream. In this context, advanced technologies have been applied to improve drinking water quality and to face up more restrictive legislations.

### 1.1.5. Future water situation

Future water situation will be aggrieved because worldwide population is expected to reach 9 bilions to 2050 (UNDESA, 2009). Water demands will depend not only on the increasing amount of food, energy, industrial activity, and rural and urban water-related services, but also on how efficiently we can use limited supplies in meeting these needs.

Additionally, over the next 20-50 years climate change is expected to be noticeable in temperatures, precipitation and sea levels, becoming another threat to water quantity and quality. Decrease in water availability and increase in drought periods will affect mainly mid-latitudes and semi-arid low latitudes, instead of higher water availability in moist tropic and high latitudes (IPCC, 2007). In case of lakes and reservoirs, warmer temperatures make undesirable species to dominate, as in case of some algae species which release algae toxins deteriorating water quality. As a result of sea level rise, floods and changes in flow regimes can occur having important consequences in this kind of ecosystems, such as salt intrusion in coastal aquifers.

Considering the region of Europe, some changes are expected to happen regarding water availability and abstraction for 2030, most of them due to climate change but also as a result of current groundwater over-abstraction in some regions (i.e. Belgium, Finland, Cyprus). For European continent, only one third or less of water supplies come from surface waters, which a tenth part for this is contained in Danube, Rhine and Loire rivers. Figure 1.6 shows regional variations from present and future of water availability in Europe.

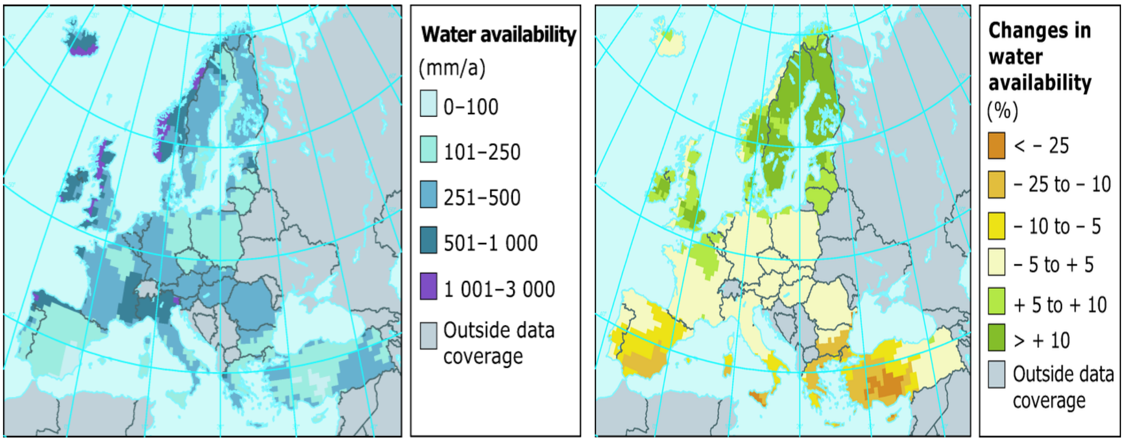


Figure 1.6: Present and future water availability in Europe (EEA, 2009a)

Observing the Figure 1.6, variations between -5 and 5% are projected in most part of Europe, except in cases such as United Kingdom, Norway, Sweden or Finland where water availability increase. In other parts, mainly located in the Mediterranean region, a reduction of water availability is expected, for example in Spain, Portugal, south of Italy and Turkey (EEA, 2009b).

In this framework, technological advances will have to play an important role to solve problems in water availability and quality, for example in drinking water supplies or to implement non conventional water sources, such as wastewater reclamation and reuse for agriculture, industry and urban sectors. Better integrated water management should lead to evaluate advantages and limitations for new water treatments from an economic, social and environmental point of view.

## 1.2. DRINKING WATER PROCESSES

Potable water must be free from pathogens and must present very low concentrations of chemical substances that could endanger life, whilst being clear and maintaining agreeable taste and smell. The availability of safe drinking water has been the main factor for human health development.

Historically, the developments in drinking water supply have been related to the reduction of some diseases, such as typhus or dysentery. The environmental protection agency of United States (USEPA) has been recollecting information about outbreaks and water contamination since 1971 with the intention to discover the biological or chemical origin of some diseases related to water uses (Borchardt and Walton, 1971; Craun G.F., 2002). Current legislation all over the world elucidates the concept of potable water giving the quality standards for the most important physical, chemical, microbiological, aesthetical properties and radiological parameters (98/83/EC; USEPA, 2001 ; WHO, 2004).

The selection of treatment and the design for a drinking water process not only depends on the required final quality, but also on the raw water composition. A first classification for water resources is considering total dissolved salts (TDS): freshwater (< 1000 $mg \cdot L^{-1}$ TDS), brackish water (between 1000 and 10000 $mg \cdot L^{-1}$) and seawater (approximately 35000 $mg \cdot L^{-1}$ TDS). Brackish and seawater can be used as drinking water under specific circumstances with adequate treatment, such as desalination.

Considering freshwater for drinking proposals, European Water Framework Directive, (WFD) classifies these resources in three categories ($A_1$, $A_2$ or $A_3$) considering the quality in the point of water abstraction with the degree of necessary treatment to obtain the desired final quality (2000/60/EC):

- Type $A_1$: simple physical treatment and disinfection (e.g. rapid filtration and chlorination);
- Type $A_2$: normal physical treatment, chemical treatment and disinfection (e.g. pre-chlorination, coagulation, flocculation, decantation, filtration and final chlorination);
- Type $A_3$: intensive physical and chemical treatment, extended treatment and disinfection (e.g. chlorination to break point, coagulation, flocculation, decantation, filtration, adsorption (activated carbon) and disinfection (ozone or final chlorination)).

Surface water that falls outside the mandatory limits for $A_3$ waters is normally excluded for drinking purposes, although it can be blended with better quality water prior to treatment. Each of the predominant types of water sources, including natural or man-made lakes and rivers, requires a different management strategy. For this reason, general procedure in the selection and implementation of water treatment plants involve several disciplines (engineering, microbiology, chemistry, geology, architecture and economics) and the main following steps:

- Characterization of the source water quality and definition of the treated water quality goals or standards
- Predesign studies, including pilot plant testing, process selection an development of design criteria
- Detailed design of the selected alternative
- Construction
- Operation and maintenance of the completed facility

According to the first point, for the implementation of new technology in a conventional water treatment plant, accomplishing with legislations is the first step to protect public safety but complementary tools, such as the assessment of human health risk or the evaluation of environmental impacts for a process, can be useful to establish new goals for future legislations or to establish criteria for technical options selection.

### 1.2.1. Conventional drinking water treatments

Initially, drinking water processes implied physicochemical processes to eliminate colour and particles in suspension. Alumina addition, for example, was employed since Egyptian. At the end of S.XIX the bacteriologist Robert Koch demonstrated that hypochlorite can destroy microorganisms, discovering its potential to avoid waterborne diseases (Crittenden et al., 2012). Since then, a disinfection step, using in most cases chlorine and its derivates, have been included in drinking water treatment to produce biological safe water.

The selection of water resources for supply purposes simultaneously depends on factors such as the nature of the raw water, the ability of the resource to meet consumer demand throughout the year, and the cost of treating the water. Conventional water sources are usually called freshwater sources, characterised for the low salt content and lately for their small volume occupying the planet. Considering inland water bodies, the basic classification consists in surface and groundwater, including a wide range of water sources (rivers, springs, lakes, streams, shallow lakes, aquifers). Groundwater is generally less contaminated than surface water in terms of organic content, requiring less steps or unit processes to clean the raw water in order to produce safe drinking water. However, local or punctual pollution in groundwater may require more complex process, for example to treat arsenic, nitrates or pesticides contents (Duran and Dunkelberger, 1995; Gorenflo et al., 2003; Karim, 2000; Kosutic et al., 2005; Van der Bruggen and Vandecasteele, 2003).

A generic scheme for conventional drinking water treatment plant (DWTP) can be seen in Figure 1.7.

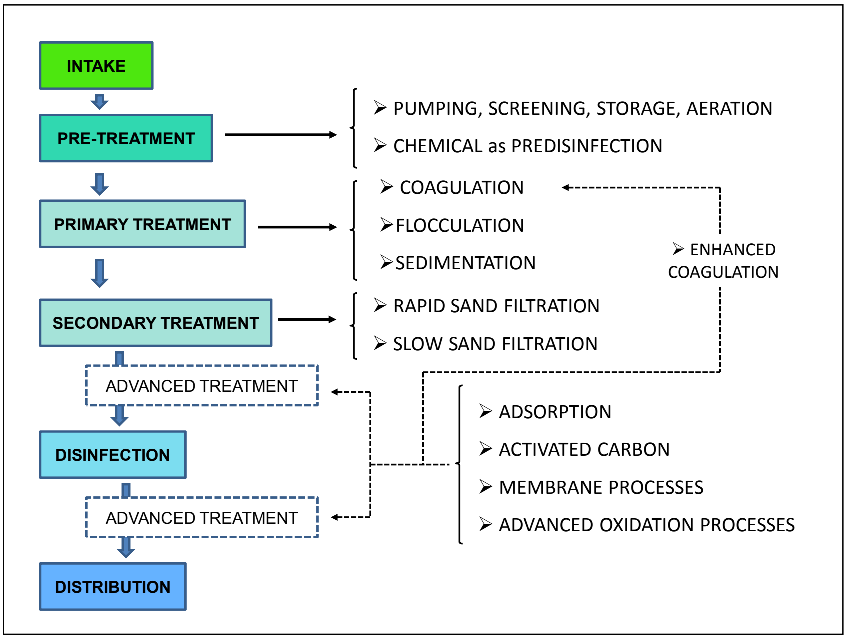


Figure 1.7: Basic scheme for drinking water treatment from raw water to final potable water

After pumping raw water, some aeration step can be required in cases of groundwater or very low oxygenated water (from the bottom of stratified reservoirs or eutrophic polluted rivers). Usually, chemical pre-treatment such as pre-disinfection is employed to prevent biological growth and maintain correct conditions for the installations and next operations. Prechlorination is a typical practice in this point when high counts of microorganisms can exist in raw water.

The step that allows reducing turbidity and colour in drinking water usually implies a coagulation-flocculation-sedimentation process and it is usually called primary treatment. Reduction of particulate and suspended matter take place with the aid of chemical products, aluminium or ferric chlorides, hydroxides, or sulphates ($AlSO_4$, $AlCl_xOH_y$, $FeCl_3$, $FeSO_4$). In some cases, uncharged and negative charged organic polymers (polyacrilamides, polyethylenes) are used as flocculants with the intention to form stronger floc than in single coagulation. Activated silica is an important inorganic flocculant and it can be effectively used with alum in cold water (Crittenden et al., 2012). Finally, suspended solids present in raw waters or those formed during coagulation are eliminated from water by sedimentation or clarification, implying a residue which will usually requires further treatment (sewage discharge or sludge thickener).

Filtration is the most typical separation technique in water treatments and takes part as a secondary treatment. A wide range of filters depending on the size of their pores and particles can be applied taking into account the size of particle to remove. Carbon and sand beds are employed in different modes of filtration; these modes can be slow or rapid, by gravity or under pressure. Rapid filtration usually involve chemical and physical adsorption (no biodegradation), requiring some backwashings during the day. In contrast, phenomena occurring in slow filtration, where smaller grains of sand are used (between 0.15 and 0.3 mm in diameter), additionally implies biofilm formation to degrade organics compounds (Gray, 2010b).

A final disinfection step is required because predisinfection treatment is not enough to assure biological and bacteriological stability until final point of drinking water consumption. Traditionally, chlorine and its derivates have been employed worldwide as the major disinfection agent, but their high oxidation potential leads to the formation of undesirable disinfection by products (DBP), specially chlorinated ones. In the last two decades, disinfection in drinking water has been widely studied and improved to avoid or reduce the formation of toxic DBP, such as trihalomethanes (THM), haloketones or chloroamines (Bougeard et al., 2010; Goslan et al., 2009; Singer, 1999).

Depending on the country and their concerns in drinking water treatment, the evolution in disinfection step has followed different ways. For example, Central Europe (Amsterdam, Berlin, Zurich, Viena) paid attention to reach biological stability of water and current efforts are in this direction, with minimum or no addition of chlorinated based disinfectant agents. Other European countries and United States employed alternative disinfectants such as chloroamines, chlorine dioxide, ozone, ultraviolet radiation (Karanfil, 2008). Generally, alternative disinfectants formed lower levels of halogenated DBP than chlorine, although less is known about these DBP. For this reason, in the last decade many investigation works in this sector are dedicated in new DBP (Hebert et al., 2010; Pressman, 2010; Richardson et al., 2012).

### 1.2.2. Improvement of drinking water quality

Excellent drinking water can be obtained from a high pure raw water intake or with an extensive treatment process with the intention to face up new challenges for suppliers and stakeholders implied in this sector. That means constant revisions taking into account scientific and technological developments into a concrete political and economical framework, which ultimately also takes into account the environmental perspective in terms of new technologies applied in water treatments (Vince et al., 2008).

New technologies are able to provide the desirable final drinking water quality from more deteriorated raw water qualities, in some cases related to water scarcity concerns. However its implementation generally increases capital and operational costs. In case of pollution of water bodies for drinking proposals, another option would be its preservation taking into account preventive measures in the origin of the pollution focus (Smit, 1998), which could reduce the need of treatment in DWTP.

In last years more attention has been paid in drinking water regarding the following main groups as a result of their intrinsic toxicity: DBP and organic, inorganic and trace elements pollution.

#### 1.2.2.1. Disinfection by-Products (DBP)

The nonselective oxidation power of disinfectant agents promotes the formation of disinfection by-products (DBP). Mainly, it consists in the reaction of disinfectant with natural organic matter (NOM) and other water components, such as bromide, ammonium species or iodide (Von Gunten, 2003). The great interest of DBP levels in potable water is consequence of their toxicology for human being (USEPA, 2001).

The typical use of chlorine or hypochlorous acid can form trihalomethanes (THM) and haloacetics acids (HAA) when NOM is present in water. These are the most representative groups for halogenated DBP, and consequently the most extensively studied regarding its reactivity and toxicity in drinking water (Chang et al., 2006; Chowdhury et al., 2009).

Although waterborne diseases have decreased dramatically during the 20th century as a result of disinfection of drinking water, DBP usually have intrinsic toxicity, such as carcinogenic effects in case of THM group: chloroform, bromodichloromethane, dibromochloromethane and bromoform (USEPA, 2009a; b; 2012). Haloacetic acids, on the other side, are the second predominant group of DBP and include bromoacetic acid, dibromoacetic acid, chloroacetic acid, dichloroacetic acid and trichloroacetic acid. Toxicity of HAA is also associated with some cancer, such as bladder or colon cancers (Hebert et al., 2010; Richardson et al., 2007).

Alternative disinfectants (ozone, chlorine dioxide, chloroamines) may also interact with dissolved organic matter to produce its own characteristic set of chemical DBP in final water

(Richardson et al., 2000; Singer, 1999; Swietlik and Sikorska, 2004; Yang et al., 2007). Although the use of an alternative disinfectant or a combination of them can minimise the formation of THM, HAA and total organic halogen (TOX), other dangerous DBP may be formed (Dotson et al., 2010; Liu et al., 2006). Table 1.1 indicates the formation for some emerging DBP in function of the disinfectant employed (Hebert et al., 2010).

Table 1.1: Emergent DBP formation qualitatively related with the disinfectant agents employed

| **Disinfectant agent** | | **Chlorine (gas)/ Hypochlorous acid** | **Chlorine dioxide** | **Chloroamines** | **Ozone** |
|---|---|---|---|---|---|
| **Halogenated Organics** | MX and Halofuranones | ++ | + | + | |
| | HEX and TEX | | | | |
| | Iodo THMs | + | | + | |
| | Iodoacids | | | + | |
| | Haloketones | | | + | |
| | Haloacetonitriles | + | + | ++ | |
| | Halonitromethanes | + | + | + | + |
| | Haloamides | + | | ++ | |
| | Chlorophenols | + | | | |
| | Haloanisols | + | | | |
| | Cyanogen chlorine | + | | + | ++ |
| | Unregulated HAA | + | | + | |
| | Unregulated THM | + | - | + | |
| | Tribromopyrrole | + | + | + | + |
| **Non-halogenated organics** | Aldehydes | + | + | | ++ |
| | NDMA and nitrosamines | + | | + | |
| **Inorganics** | Hydrazine | | | + | |
| | Chlorate | + | + | + | |

MX: 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone; HEX: Hexachlorocyclopentadiene; TEX: tetrachlrocyclopentadiene; THM: trihalomethanes; HAA: haloacetic acids; NDMA: N-Nitrosodimethylamine.

In addition to the studies about toxicological effects, great interest is about how DBP formation occurs. NOM type and contents, pH, temperatures and disinfectant doses are the major factors governing the formation of DBP (Amy, 2000). For example, raw water with high aromatic content, highly absorption of ultraviolet light (UVA), can lead to high presence of HAA than THM (Lin Liang and P. Singer, 2003). UVA is a qualitative parameter related to organic carbon contents by means of specific absorption of ultraviolet light parameter (SUVA), this is calculated dividing UVA per mg·L$^{-1}$ of organic carbon (Iriarte-Velazco et al., 2007). However, SUVA is not enough to characterise NOM in terms of DBP formation because NOM classification is a complex task (Chow et al., 2005).

An entire field of analytical chemistry has sprung up to support the study of DBP formation in potable water (Pressman, 2010; Richardson et al., 2012). Besides, more than 600 emerging DBPs have been reported in literature (Richardson et al., 2000) less than 100 have undergone quantitative occurrence or health effect studies.

USEPA regulates DBP formation by means of DBP Rule (DBPR) since 1979 in two stages. Stage 1 was developed in order to reduce the current maximum concentration level (MCL) for total THM, regulate additional DBP, set limits for the use of disinfectants and reduce the level of organic material as a DBP precursor in the source water (USEPA, 1998). Stage 2 was developed after the newest information were collected, providing a simple straightforward description of the rule, critical deadlines and requirements for drinking water systems in different states, together with information on monitoring needs. Currently, total sum of four THM is fixed to 80 $\mu g \cdot L^{-1}$, and 60 $\mu g \cdot L^{-1}$ for the sum of the five HAA.

European drinking water directive includes the standards for THM as the main DBP fixed at 100 $\mu g \cdot L^{-1}$, but HAA and other DBP are not regulated in this Directive (98/83/EC). However, legislation regarding emergent DBP and other organic compounds are currently under revision to redefine the list of dangerous priority substances (Gray, 2010a).

#### 1.2.2.2. Organic micropollutants

Drinking water often contains trace amounts of hundred of organic compounds, from natural and synthetic origins. Usually, natural organic compounds are considered quite benign, although can lead to possible aesthetic problems such as colour, odour and taste. They derive from a number of different sources and vary significantly in its toxicity, for example natural toxins from some blue-green algae (cyanobacteria) are complex organic compounds with high toxicity.

The WHO guidelines for drinking water are used universally and are the basis for both European and US legislation (WHO, 2004). Table 1.2 compares the standards for guidelines forehead mentioned regarding some priority dangerous substances, which are revised whenever required to reflect the most recent toxicological and scientific evidence (Gray, 2008).

Most of the manufactured or synthetic organic compounds arise from their use within catchments resulting in contamination of water resources downstream. These include pesticides, industrial solvents, plasticizers, pharmaceutical and personal care products

(PPCP), endocrine disrupting compounds (EDC), detergent by-products. In some cases they can come from the same water treatment installations (PAHs, plasticisers) (Gray, 2010c).

Table 1.2: Maximum concentration levels (MCL) regarding priority dangerous substances

| **($\mu g \cdot L^{-1}$)** | **Drinking water** | | **Freshwater** | |
|---|---|---|---|---|
| | **USEPA** | **WHO** | **European** | **Source** |
| Alachlor | 2 | 20 | 7 | Herbicide on corn and soybeans, under review of cancellation |
| Atrazine | 3 | 2 | 2 | Widely used herbicides on corn and on non-crop land |
| Benzene | 5 | 10 | 50 / 1 | leaking tanks of fuel; common solvent |
| Carbon tetrachloride | 5 | 4 | N.A. / 10 | Cleaning agents, waste in coolants manufacturing |
| Chloroalkanes ($C_{10}$ to $C_{13}$) | | | 1.4 | |
| Chlorpyrifos | *Banned in homes 2001* | 30 | 0.1 | Organophosphate insecticide |
| Chlorfenvinphos | *Banned in 1991* | | 0.3 | Organophosphate insecticide |
| Endrin | 0.2 | 0.6 | N.A. | Insecticide in cotton and small grains |
| 1.2-Dichloroethane | 5 | 30 | N.A. / 3 | Insecticides manufacturing, gasoline |
| DEHP | 8 | | Banning | Plasticiser |
| Diuron | | | 1.8 | Herbicide |
| Heptachlor | 0.4 | | | Insecticide on corn, banned except in termite control |
| Hexachlorobutadiene | | 0.6 | 0.6 | Solvent |
| Isoproturon | | 9 | 1 | Insecticide |
| Lindane | 0.2 | 2 | | |
| Pentachlorophenol | 1 | 9 | 1 | Wood preservative and herbicide, non-wood uses banned in 1987 |
| | | | | |
| Simazine | | 2 | 40 | Herbicide |
| Trichloroethylene | 5 | 70 | N.A. | Solvent |
| Vynil chloride | 2 | 3 | 0.5 | Polymer manufacturing |
| Trifluarin | | 20 | N.A. | Herbicide |

DEHP: Di(2-ethylhexyl)ftalate

From data in Table 1.2, it can be observed that legislated parameters in Europe have higher limits than USEPA and WHO guidelines because they are focused into protecting the water resource, not considering drinking water health effects (2000/60/EC). In United States, many states fix more stringent limits for certain parameters. Toxicological effects of dangerous priority substances are indicated in 0 (Gray, 2010a).

Table 1.3: Toxicological effects related to priority organic substances for US drinking water standards

| **Impact** | **Dangerous priority substance** |
|---|---|
| Probable cancer (kidney/ liver/ lung) | Alachlor , carbon tetrachloride, dichlorobenzene *p*-, dichloroethane (1,2-) , Dichloropropane (1,2-), epichlorohydrin, ethylene dibromide (EDB), heptachlor, pentachlorophenol, polychlorinated biphenyls (PCBs), tetrachloroethylene, toxaphene, trichloroethylene |
| in nervous system: | Acrylamide |
| Cancer | Vinyl chloride, benzene |
| Other health problems in nervous system or in kidney/ liver/ lungs: | Aldicarb, carbofuran, Dichlorobenzene *o*-, Dichloroethylene (*cis*-1,2-), Dichloroethylene (*trans*-1,2-), Endrin, ethylbenzene, Lindane, methoxychlor, monochlorobenzene, styrene, toluene, 2-4-5-TP (Silvex), trichloroethane (1,1,1), xylenes |
| reproductive and cardiac: | Altrazine |

For nearly 30 years the dangerous substances Directive has been developed into the current legislation in the European Community (2006/11/EC; 2008/105/EC), in order to ensure effective protection of the aquatic environment of the Community, particularly that caused by certain persistent, toxic and bioaccumulable substances. As part of these procedures community-wide emission controls and quality standards for all priority substances are being prepared to ensure good chemical surface water status by 2015 (Gray, 2010a).

### 1.2.2.3. Inorganic and trace element pollution

Inorganic composition in water is very influenced by the soil and rocks surrounding or previous to the water catchment, but industrial, agricultural and at less extent urban activities are also an important focus of inorganic pollution in water sources. Additionally to the main inorganic ions present in water, trace elements can be found at very low levels with potential health risks. In Table 1.4 several inorganic standards and guidelines values are indicated (Gray, 2010a).

Generally, trace elements may be classified into heavy metals, metalloids and micronutrients, between others. The presence of some trace elements is beneficial as essential elements, such as selenium, chromium, copper, molybdenum, nickel, sodium and zinc, which are naturally found in waters, especially in ground waters. However, their industrial uses in processes such as the manufacture of pesticides, polymers and electronic components increase their levels in the atmosphere, water or soil becoming possible pollutants.

Table 1.4: Standards and guideline values for inorganic substances and trace elements

| ($\mu g\cdot L^{-1}$) | Drinking water | | | |
|---|---|---|---|---|
| | 98/83/EEC | WHO | USEPA | Source |
| Aluminium | 200[a] | | | |
| Ammonium | 500[a] | | | |
| Antimony | 5.0 | 20 | | |
| Arsenic | 10 | 10[b] | 10 | Geological, pesticide, residues, industrial |
| Barium | | 700 | 2000 | Mineral, oil/gas drilling, paint, industry |
| Boro | 1.0 | 500[c] | | |
| Bromate | 10 | 10[c,d] | | Bromide oxidation during disinfection |
| Cadmium | 5.0 | 3.0 | 5 | Mineral, metal, corrosion |
| Chlorate | | 700[e] | | |
| Chloride | $2.5\cdot10^{5}$ [a] | | | |
| Chlorite | | 700[e] | | |
| Chromium | 50 | 50[b] | 100 | Mineral, metal, textile, tanning, leather |
| Copper | 2000 | 2000 | | Corrosion in building pipes |
| Cyanide | 50 | 70 | | Insecticide in cotton and small grains |
| Fluoride | 1500 | 1500 | 4000 | Geological, additive |
| Iron | 200[a] | | | |
| Lead | 10 | 10 | | Installations corrosion |
| Manganese | 50[a] | 400[f] | | |
| Mercury | 1.0 | 1.0 | 2.0 | Industrial/chemical; fungicide, mineral |
| Molibdenum | | 70 | | |
| Nickel | 20 | 20[b] | | |
| Nitrate | $0.5\cdot10^{5}$ | $0.5\cdot10^{5}$ | $0.1\cdot10^{5}$ | Fertilizers feedlots, sewage, mineral |
| Nitrite | 500 | 200-3000 | 1000 | unstable |
| Selenium | 10 | 10 | 50 | Mineral, by-product of copper mining |
| Sodium | $2.0\cdot10^{5}$ [a] | | | |
| Sulphate | $2.5\cdot10^{5}$ [a] | | | |
| Uranium | Tritium (100 $Bql^{-1}$) | 15[b,c,g] | 30 | Geological /natural |

[a] the indicator parameters in the new EC Drinking Water Directive (98/83/EC) used for check monitoring;

[b] provisional guideline value;

[c] provisional guideline value because calculated guideline value is below the level that can be achieved through practical treatment methods;

[d] provisional guideline value because calculated guideline value is below the achievable quantification level;

[e] provisional guideline value because disinfection is likely to result in guideline value being exceeded;

[f] concentrations of the substance at or below the health-based guideline values may affect the appearance, taste or odour of the water, leading consumer complaints;

[g] additionally 200 individual radionuclides for radiological pollution in drinking water

Things become worse with implications for human health when these elements are found at high concentrations. Arsenic, for example, is considered a very potent carcinogen causing primarily cancers of the skin but also increasing the risk of cancer of many of the vital organs

(100 million people are affected in China, India, Balngadesh and Taiwan) (Karim, 2000). Heavy metals as nickel, lead, mercury and cadmium, and its compounds, are also considered as priority dangerous substances and their levels are regulated under revision until 2015.

Usually, detected levels of major inorganic ions in water sources are not dangerous to human health. Nevertheless, in case of nitrogen substances in waters (nitrites, nitrates, ammonium and other organic forms), negative effects can be water eutrophication over the environment, and over human health could imply some risk in drinking water consumption (infantile methahemoglobinaemia or cancer from N-nitroso compounds). There is a specific legislation for nitrates in order to protect waters from agricultural sources pollution (91/676/EEC).

Regarding halogen elements, fluoride is added in some drinking water treatment installations to prevent dental caries. However, WHO suggested fluoride addition at levels of 0.5 to 1 $mg\cdot L^{-1}$, with a maximum of 1.5 $mg\cdot L^{-1}$ (WHO, 2004) because an excess can lead to skeletal fluorosis (10 million people are suffering fluorosis). Bromide and iodide intrusions in water sources may lead to high levels of halogenated DBP or bromate, accentuated in cases of chlorine use as disinfectant agent (Von Gunten, 2003). When bromide exists in source water and ozone is employed as disinfectant agent undesired concentration of bromated can be quantified in final drinking water. In general, inorganic ions (anions and cations) are measured as total dissolved solids (TDS) with a generally acceptable upper limit for drinking water of 500 $mg\cdot L^{-1}$. One of the major concerns regarding natural inorganic composition in water is the hardness, when the bivalent cations, calcium and magnesium, are found at levels superior to 300 $mg\cdot L^{-1}$ expressed in $CaCO_3$. This case is considered an aesthetic aspect, the same as high contents of iron and manganese, promoting bad tastes and stain laundry.

### 1.2.3. Advanced Processes to improve drinking water quality

The improvement in analytical methods providing lower detection limits, the emergence of new chemical constituents, high level of physicochemical phenomena in treatment processes and a more demanding legislation are the main driving factors to develop and implement other complementary unit processes in the conventional water treatments (Figure 1.7). However, actual challenges in DWTP are numerous and different in origin. For this reason the technical options have to be evaluated for each case, considering site specific costs (capital, operational costs) and even environmental impacts.

Higher sophistication in drinking water process is required as higher pollution in water bodies is present. The work presented in next chapters is partially dedicated to the main technologies able to remove DBP and organic pollutants, as major substances of concern in current DWTP of developed countries.

Changing chlorine for alternative disinfectants may reduce the formation of THM and HAA, but conversely can lead to worse compounds (nitrosamines, haloacetonitriles, haloamides) (Krasner et al., 2006). For this reason, technical options are mainly focused to eliminate the precursor material of DBP: natural organic matter (NOM).

The changes in NOM composition, highly influenced by seasonal variations, have significant influence in selection, design and operation of water treatment processes (Teixeira and Nunes, 2011). General parameters to assess quality controls over dissolved organic carbon are: carbon (DOC), chemical oxygen demand (COD), absorption of ultraviolet irradiation (UVA), pH, turbidity and colour. However these parameters do not give information about character of NOM, such as molecular weight or hydrophobic behaviour.

The different NOM fractions exhibit different properties in terms of treatability by advanced processes and reactivity in front disinfectant agents. For example coagulant demand or disinfectant agent doses are variable in function of the NOM to be treated, with consequences in DBP formation potential (DBPFP) (Sharp et al., 2006).

Is important to note that in most cases water has been disinfected at the beginning, and some DBP have been formed previously to the advanced process. In these cases, an adsorption technique (GAC) (Szlachta and Adamski, 2009) or aeration can be effective to reduce DBP and hydrophobic or volatile compounds, respectively. Another combination which has been effective in some cases, is a previous adsorption using magnetic ion exchange resins (MIEX) (Mergen et al., 2008).

If no further treatment is applied, the presence of undesirable substances can remain in the final drinking water: DBP, organic pollutants such as pesticides, pharmaceuticals, cosmetics, surfactants, algae and some responsible of bad tastes and odours (Jacangelo et al., 1995; Yeh et al., 2000). At large extent, enhanced coagulation or softening, oxidation processes, technologies as adsorption (granulated or powdered activated carbon, GAC or PAC), ion-exchange resins, and membrane processes are available to face up with some problematic water components, such as DBP, but are also useful for nitrates, pesticides and pathogens removal (Boussahel et al., 2002; Kosutic et al., 2005; Koyuncu et al., 2008; Murthy and Chaudhari, 2009; Yeh et al., 2000).

#### 1.2.3.1. Enhanced coagulation

Conventional coagulation reduces particulate matter in suspension although leaves part of the colloidal material, such as NOM (Matilainen et al., 2010; Volk et al., 2000). Further studies and developments in this step have elucidated that hydrophilic organic matter (polysaccharides, proteins, amino sugars) resists the clarification in coagulation-flocculation-settling step becoming part of the disinfection by product precursor material (Allpike et al., 2005).

#### 1.2.3.2. Advanced oxidation processes

Advanced oxidation processes (AOP) are also powerful techniques in disinfection and organic compounds degradation. Development in oxidation processes had as objective the reduction of the formation in DBP during pretreatment, but currently this technique is also applied as final disinfection in cases of high biostability in distribution systems. Ozone and ultraviolate (UV) radiation are main techniques employed, sometimes simultaneously in order to increase oxidation potential for microorganisms elimination and NOM degradation (Goslan et al., 2006).

Catalysts are usually added in some cases to promote high potential of oxidation more rapidly, being possible to reduce hydraulic times in specific points of water treatment. Photo-Fenton process makes use of irons species to enhance oxidation process. In this case, the catalyst can come from enhanced coagulation using iron salts (Murray and Parsons, 2004).

A negative effect can be obtained when ozonation is applied at high doses previous to coagulation because smaller organic molecules would be formed being more difficult to coagulate. Smaller doses of ozone reduce oxidation power during ozonation and large organic matter can be retained during pretreatment (Bose and Reckhow, 2007).

#### 1.2.3.3. Adsorption and ionic exchange resins techniques

Adsorption technologies are applied to remove DBP precursors but also are able to reduce contents of undesirable organic compounds (Delgado et al., 2012). In case of activated carbon (AC) filtration, different modes can be employed depending on the size particle, powdered (PAC) and granular (GAC), or considering biodegradation in addition to physical or chemical adsorption in active sites of carbon (Kim and Kang, 2008). Although biofilm can improve the removal of organic compounds of low molecular mass, the most part become recalcitrant to AC and consequently pass to next steps (Szlachta and Adamski, 2009; Uyak et al., 2007).

Ionic exchange resins (IEX), such as magnetic (MIEX) or also fluidised (FIX), are applied in water treatments as adsorption techniques, removing organic and inorganic contaminants like sulphate, nitrate or phosphate (Apell and Boyer, 2010; Morran et al., 2004). MIEX is more likely to adsorb hydrophilic fraction of NOM improving the coagulation-flocculation-settling step in terms of reducing coagulant doses and sludge residual (Sani et al., 2008).

#### 1.2.3.4. Membrane technology

In water treatment membrane technology is widely used, currently nanofiltration (NF) and reverse osmosis (RO) are the most used to produce drinking water of high quality. Other pressure driven membranes such as microfiltration (MF) and ultrafiltration (UF) are mostly applied as a pretreatment for NF and RO in order to reduce colloidal organic matter or particles. Recently, IEX has been used as a pretreatment of membrane technology, with the intention to reduce fouling in membranes (Cornelissen et al., 2012).

NF can be applied in drinking processes treating groundwater and freshwater with low salinity content, where the major concern usually are organic molecules (NOM and SOC) and divalent ions removal (TDS < 1000 $mg \cdot L^{-1}$) (AWWA, 2007).

In case of water treatments for drinking water proposals, NF technology allows to remove from drinking water DBP precursors in one step, in addition to their easy scale-up for different production capacity. Even though, membranes in immersed configuration can be combined with coagulation, improving organic matter separation (Humbert et al., 2007; Matilainen et al., 2010).

Other advantadges for NF as membrane technology are the specific separation capacity for a wide range of undesirable organic compounds and a partial salt rejection for inorganic salts (Van der Bruggen and Vandecasteele, 2003). Energetic costs are lower than in case of reverse osmosis (RO) membranes as a result of higher permeability in NF. However, membrane fouling is the major drawback in all membrane processes because reduce process yield, reducing membrane life-time or requiring further pretreatment as a preventive measure in front of chemical cleaning required to recover initial permeabilities. Following section 4 is dedicated to membrane technology.

## 1.3. WATER RECLAMATION AND REUSE

Water reclamation and reuse is the treatment or processing of wastewater to make it reusable with reliability and meeting water quality criteria. Reclaimed water (reclamation) is used synonymously as recycled water (recycling) in most cases (Asano et al., 2007). Reuse of reclaimed wastewater has become an important source for some applications, for example in urban landscaping, irrigation of gardens, agriculture or cleaning activities, at the same time that ecosystems water balance should be maintained.

In ancient Greece, 3000 years ago wastewater was already used for agricultural irrigation. In modern times, the beginnings of water reclamation and reuse are situated in the middle of 19 century with the introduction of wastewater systems for conducting household wastes away from urban dwellings, but into the nearest water courses. One of the oldest operating water reclamation systems was in early 1960s, when the city of Colorado implemented a dual distribution system to meet irrigation demands in addition to surface water from a nearby stream (Asano et al., 2007).

The social, economic, and environmental impacts on conventional water resources and the inevitable prospects of water scarcity are driving the shift to a new paradigm in water resources management. Traditional developments in water resources have focused on modifying water storage and flow patterns by constructing dams and reservoirs and designing systems for interbasin transfer. It is argued by some authors that the competition to develop new sources of water can be avoided by implementing measures for more efficient use of water (Gleick, 2003; Vickers, 2001).

Although water is constantly being recycled in a system (hydrological cycle), nowadays the quality and availability varies significantly. Figure 1.8 shows water quality changes during municipal uses considering the option of water reuse for regenerated water.

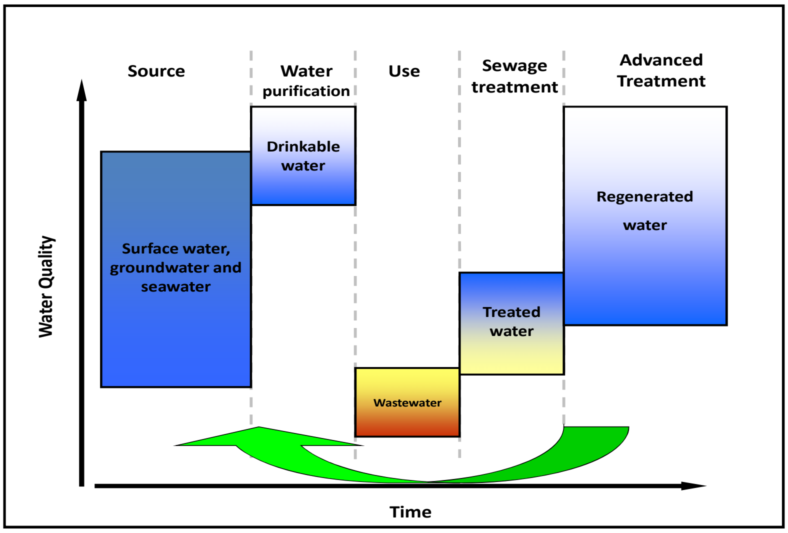


Figure 1.8: Water quality changes during municipal uses of water in a time sequence and the concept of water reclamation and reuse

Usually, water treatment technologies are applied to source water such as surface water, groundwater, seawater to produce drinking water under regulations and guidelines standards. Domestic and other water uses degrade water quality by absorbing and accumulating chemical or biological contaminants and other constituents, generating wastewater. In most cases, wastewater is treated in a plant before its emission to water bodies, but further treatment is required when exists a final reuse application. The implementation of advanced techniques in wastewater treatment process, such as adsorption techniques, advanced oxidation processes or membrane technologies, technically are able to regenerate reclaimed water until similar drinking water quality.

For a communities approaching to the limits of their available water supplies, water reclamation and reuse have become an attractive option to protect water sources. The main aspects for this preservation can be the substitution for reclaimed water in applications not requiring as quality as in potable water uses, the increase of alternative water sources as supply to meet present and future water demands, the reduction of nutrients and other toxic contaminants which enter into water bodies. In turn, these measures facilitate to accomplish with current and future environmental regulations (Balsells, 2011).

Implementation of water reuse depends on several factors, such as economic considerations, potential uses for the reclaimed water, public health protection, stringency of waste discharge requirements, stakeholder interests (including those representing environment) and public perception. Although the immediate drivers behind water reuse may differ in each case for urban and industrial wastewaters, a more closed hydrologic cycle is reach from a smaller or local scale. In this way, integration of reclaimed water and reuse into water resources planning can lead to promote and coordinate development and management of water (treatment process reliability), infrastructures, land and related resources (wastewater plant sitting, economic and financial analyses) to maximize the resultant economic and social benefits in an equitable and sustainable manner.

### 1.3.1. Reuse applications, health and environmental concerns

Water reuse is practised because other sources of water are not available due to physical, political or economic constraints and further attempts to reduce consumption are not feasible. Water reuse represents technical and economical challenges, implying the incorporation of extensive treatments, commonly applied to mitigate health concerns and hence convince public and responsible institutions (Hermanowicz, 2005).

A growing trend worldwide is to prioritise the preservation of the highest quality water sources for drinking water supply, this supposes to find an alternative source, such as reclaimed water, for applications that have less significant health risks. The most accepted reuse application around the world are shown in Table 1.5.

Table 1.5: Classification of water reuse applications in categories

| Category | Typical application |
|---|---|
| Agricultural irrigation | Crop irrigation<br>Commercial nurseries (greenhouse) |
| Landscape irrigation | Parks, school yards, freeway medians, golf courses, cemeteries, greenbelts, residential |
| Industrial recycling and reuse | Cooling water, boiler feed, process water, heavy construction |
| Groundwater recharge | Groundwater replenishment, salt water intrusion control, subsidence control |
| Recreational/environmental uses | Lakes and ponds, marsh enhancement, fisheries, snowpaking streamflow augmentation, |
| Nonpotable urban uses | Fire protection, air conditioning, toilet flushing |
| Potable reuse | Blending in water supply reservoirs (indirect), direct pipe to pipe water supply, blending in groundwater (indirect) |

Types of wastewater used for water reclamation are treated and untreated sewage effluent, storm water runoff, domestic greywater and industrial wastewater (Toze, 2006). For all these water types, quality has different levels and contaminant potential is variable, impacting in the degree of treatment which in turn depends on the quality required for the reuse application. The main advantage of water reuse is the augmentation of a water supply, especially when it is compared to an increasingly expensive and often environmental destructive development of some water resources. In many parts of the world, the success of water reclamation and reuse projects have emerged from the pressures associated to urgent water necessities coupled with the opportunity to develop water reuse systems.

In developed countries reclaimed water is treated using strict water quality control measures to ensure that it is nontoxic and free from microorganism causing disease, more important in domestic and food production uses. Regulations in Europe and Spain are generally based on World Health Organization guidelines and Pollution monitoring and research (UNEP, 2005; WHO, 2006). Table 1.6 shows different parameters legislated in case of Spain in comparison of California regulations (California, 2001; USEPA, 2004). The constituent limits for treated effluent or water to be reused could also be stated as not-to exceed values with some level of compliance. Conformance criteria in Spanish legislation require 90% of the analysed samples to accomplish with maximum admitted values (VMA), and in case of surpass the values never above the maximum deviation permitted (RD1620/2007).

A part of the standards indicated in the table above, additional considerations regarding specific constituents or dangerous substances have to be carried out in order to guaranty water reuse safety. For example, USEPA recommends criteria for constituents that have been associated with specific acute and chronic effects, fixed to not exceed limit of once in 3 years or at a 99.9% level of compliance.

Risk factors of using reclaimed water can vary in severity depending on the potential for human, animal or environmental contact, for example in case of microbial pathogens, while others have longer term impacts which increase with continued use of recycled water. In last case, an example would be saline effects on soils or toxics effects for some undesired compounds (DBP, pesticides, pharmaceuticals, personal care products) (Tangsubkul et al., 2005).

In this way, emerging dangerous substances, such as pathogens and trace organic compounds, have been extensively investigated with regards public water consumption and health risk associated (Köck-Schulmeyer et al., 2011). Water pollution control efforts have made a viable alternative the treated effluent from municipal wastewater treatment plants as a water source for less restrictive uses than drinking water.

On the other hand, freshwater sources for potable proposals are likely to contain recalcitrant compounds which conventional wastewater treatments are not able to remove. As a consequence, much of the research that addresses direct and indirect potable water reuse is becoming equally relevant to unplanned indirect potable reuse because compounds not removed by conventional treatments can be associated to human health risk.

Table 1.6: Reclaimed wastewater quality parameters regarding reuse application

| | Typical constituent concentration | | | |
|---|---|---|---|---|
| **Spain** (RD1620/2007) | TSS mg·L$^{-1}$ | Turbidity (NTU) | *Escherichia Coli* UFC/100mL | Nematodes eggs Huevo/10 L |
| Agricultural [a] | | | | |
| Nonfood crop | 35 | | 10000 | 1 |
| Food crop | 20 | 10 | 100 | 1 |
| Food crop post processed | 35 | | 1000 | 1 |
| Industrial [b] | | | | |
| Cleaning NO food industry | 35 | 15 | 10000 | |
| Cleaning in food industry | 35 | | 1000 | 1 |
| Cooling towers | 5 | 1 | 0 | 1 |
| Recreational and environmental [b] | | | | |
| Direct aquifer recharge [c] | 10 | 2 | 0 | 1 |
| Golf field irrigation [d] | 20 | 10 | 200 | 1 |
| Ponds, ornament | 35 | | 10000 | |
| Private gardens | 10 | 2 | 0 | 1 |
| Parks, sport fields | 20 | 10 | 200 | 1 |

| **California** (California, 2001) | BOD mg·L$^{-1}$ | TSS mg·L$^{-1}$ | Total N mg·L$^{-1}$ | Turbidity NTU | Total coliforms No./100 mL | Fecal coliforms No./100 mL |
|---|---|---|---|---|---|---|
| Agricultural [a] | | | | | | |
| Nonfood crop | ≤30 | ≤30 | | ≤2 | ≤23 | |
| Food crop | ≤10 | | | | ≤2 | |
| Lanscape irrigation | | | | | | |
| Restricted access | ≤30 | ≤30 | | | ≤23 | |
| Unrestricted access | ≤10 | | | ≤2 | ≤2.2 | |
| Industrial [b] | | | | | 23 | |
| Groundwater recharge | | | | ≤2 | ≤2 | |
| Recreational/environment | ≤10 | | | ≤2 | ≤2.2 | |
| Nonpotable water uses | ≤10 | | | ≤2 | ≤2.2 | |
| Indirect potable use | | | | ≤2 | ≤2.2 | |

[a] Agricultural uses may require of specific constituents analysis

[b] Industrial wastewater quality varies on the type of reuse and may require removal of specific constituents

[c] Total nitrogen is controlled in case of groundwater recharge

[d] Total phosphorous control for recreational uses (pools, water bodies, running watercourses)

### 1.3.2. Technological development for water reclamation and reuse

Reuse of treated effluents provides a regular supply to users and aids to assure the quality of wastewaters from a sanitary and environmental point of view. These aspects related to water reuse require carry out and study suitable technologies in order to plan general water reuse systems. Regulated parameters give the quality criteria to produce adequate water for reuse depending on the final application (see Table 1.6).

Other important factors in treatment train selection are the process flexibility, the operating and maintenance requirements, in addition to economical and environmental impacts also associated to conventional wastewater treatment processes.

### 1.3.2.1. Basics in wastewater treatment

A wastewater treatment plant is a combination of separate treatment processes or units designed to produce an effluent of specified quality from a wastewater (influent) of known composition and flow rate. Generally, wastewater effluents are discharged to surface waters, primarily rivers and lakes, because less demanding quality parameters are required in comparison for reclaimed wastewater or reuse (91/271/EEC).

A general scheme of wastewater composition is shown in Figure 1.9, where the main constituents are classified into two categories: organic and inorganic. Organic matter is susceptible to be degraded during conventional wastewater treatment, and inorganic substances can improve biodegradation rates or can impede microbial activity. On the other hand some substances can be recalcitrant, in most cases having negative effects in final quality of the effluent.

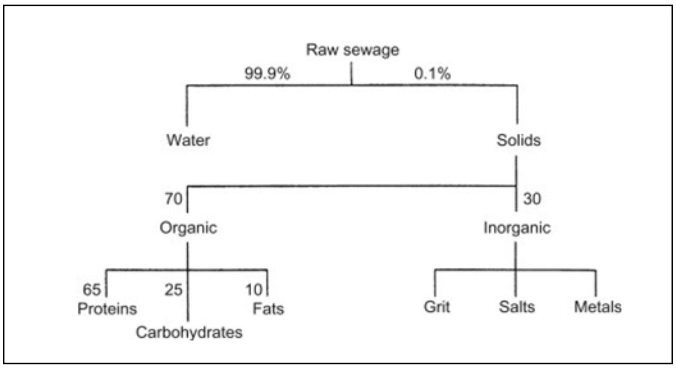


Figure 1.9: Composition (by volume) of the solid fraction in domestic wastewater (Gray, 2010d)

The aim of the wastewater treatment is to convert the solid portion present in sewage influent to a manageable sludge (2% dry solids) while leaving only a small portion in the final effluent (0.003% dry solids). Generally, carbohydrates (glucose, sucrose, lactose) are oxidised into carbon dioxide and water during the biological treatment, although in anaerobic conditions the presence of volatile acids increases. Protein is the major source of nitrogen along with urea, and together with detergents turn into the main source of phosphorous (orthophosphate, polyphosphate, organic complex). Fats substances are quite stable compounds and not readily degraded biologically into fatty acids (palmitic, stearic and oleic).

Biological treatment needs a suitable combination of nutrients, theoretically the carbon, nitrogen and phosphorous (C:N:P) ratio should be 100:5:1. However, in most cases nutrients are superior implying an excess of N and P in the final effluent with the negative consequences into receiving water bodies (eutrophication).

In terms of treatment plant design, unit processes are classified into five groups or functions:

- Preliminary treatment: screening and other techniques to remove and disintegrate gross solids, grit, oil, greases and the separation of storm water. Industrial wastewater may require pre-treatment before being rendered suitable to discharge to sewer.
- Primary treatment (sedimentation): involves the removal of settable solids, which are separated as sludge.
- Secondary treatment (biological): dissolved and colloidal organic matter is oxidised by microorganisms
- Tertiary treatment: biological treated effluent is further treated to remove remaining BOD, suspended solids, bacteria, specific toxic compounds or nutrients to enable the final effluent to comply with a standard more stringent that secondary treatment are able to reach.
- Sludge treatment: process in which sludge is dried and stabilised for its disposal

In most cases, synthetic organic compounds as emergent pollutants are difficult and costly to be removed by conventional wastewater treatments. Consequently, these recalcitrant compounds have been identified as causing major environmental problems in receiving waters, especially where this water is reused for supply purposes (2006/11/EC; 2455/2001/EC; Köck-Schulmeyer et al., 2011). Dilution factor influences the degree of treatment in WWTP plant dictaminating the composition of wastewater effluents, considering abstractions for public supply existing downstream.

Reclaimed water system design is approached in the same way as conventional drinking water plant design. However, special issues arise from the water quality, reliability, variation in supply and demand, and the quality required for the reuse application.

### 1.3.2.2. Technologies and systems for water reclamation and reuse

Advanced treatment technologies and their combination are investigated and developed to essentially assess the current water quality required in reuse applications. Currently, greater emphasis is given to technologies for wastewater reclamation that provides higher levels of removal of suspended, colloidal, and dissolved solids; pathogenic organisms, and trace constituents. On the other hand, cost-effective and reliable technologies for water are vital to successful implementation of water reuse projects (Asano et al., 2007). Previous pilot plant experimentation is highly recommended to evaluate process feasibility.

Although regulated standard parameters can vary depending on the country legislation, the selection of processes treatment in all cases begins to consider the concept of multiple barriers. This principle establishes a series of barriers to prevent the passage of pathogens and harmful organic and inorganic contaminants into the water system. General measures to implement new technologies can take form as control the source of pollution before entering into wastewater, as combination of treatments providing specific level of constituent reduction or as environmental buffer (storage ponds, soil aquifer treatment).

Taking into account the stages in wastewater treatment, reclaimed water quality for reuse can be obtained implementing the technologies in secondary, tertiary and even in advanced treatment processes. Table 1.7 lists unit operations and processes to remove undesired constituents in water reuse (Asano et al., 2007).

Table 1.7: Operational units and processes to remove different constituents

| | **Constituent class** | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Operational unit and processes** | **Suspended solids** | **Colloidal solids** | **Particulate** | **DOC** | **Nitrogen** | **Phosphorous** | **Traces** | **TDS** | **Bacteria** | **Protozoan cysts and oocysts** | **Viruses** |
| Secondary treatment | X | | | X | | | | | | | |
| Secondary with nutrient removal | | | | X | X | X | | | | | |
| Depth filtration | X | | | | | | | | X | X | |
| Surface filtration | X | | X | | | | | | X | X | |
| Microfiltration (MF) | X | X | X | | | | | | X | X | |
| Ultrafiltration (UF) | X | X | X | | | | | | X | X | X |
| Dissolved air flotation (DAF) | X | X | X | | | | | | | X | X |
| Nanofiltration (NF) | | | X | X | | | X | X | X | X | X |
| Reverse Osmosis (RO) | | | | X | X | X | X | X | X | X | X |
| Electrodialysis (ED) | | X | | | | | | X | | | |
| Carbon adsorption (CA) | | | | X | | | X | | | | |
| Ion exchange (IE) | | | | | X | | X | X | | | |
| Advanced oxidation (AO) | | | X | X | | | X | | X | X | X |
| Disinfection | | | | X | | | | | X | X | X |

Secondary treatment offers great versatility to remove the undesired constituents under different conditions: membrane bioreactor, activated sludge, trickling filters, rotating biological contactors in addition to consider partial or total nitrogen removal (nitrification, denitrification). Effective processes in case of total phosphorous removal are biological and precipitation techniques, in addition to RO membranes.

Filtration processes have been extensively developed; at the beginnings to separate particulate, colloidal matter and some microorganism, currently membrane technology presents great selective power in front of a wide range of possible constituent removal. From MF and UF to separate particulate matter and microorganisms, until NF or RO to reach partial or complete salt removal, respectively. Consequently, membrane hybrid systems can be designed including, for example, MF or UF as a pretreatment for final membrane step, typically NF or RO. These system provide some benefits in operational and maintenance costs although increasing capital ones.

Undesired organic pollutants, usually present in trace concentrations, can be effectively removed from final water using technologies as NF, RO, AO, IE and CA. However, emerging contaminants are not routinely monitored in reclaimed water in comparison with conventional physico-chemical and microbiological contaminants. In this sense further study will be required for emergent dangerous substances which can suppose human health risks with regards to the reuse application (Toze, 2006).

Reclaimed water provides the chance to reduce the amount of water extracted from the environment, but technologies employed usually have higher energy consumption than conventional wastewater treatments and should be evaluated in terms of an environmental cost benefit perspective. For example, Life cycle assessment (LCA) has been employed to evaluate the environmental impact for new processes in water reuse applications (Ortiz et al., 2007; Stokes and Horvath, 2009). However, some environmental benefits can be obtained, such as the promotion of water preservation, which in turn have beneficial aspects as energy and chemicals reduction from a global point of view in water treatments.

### 1.4. MEMBRANE TECHNOLOGY

Membranes are able to separate molecules from a solution as a result of their differences in size, shape, chemical structure or electric charge. This separation phenomenon decreases the systems entropy, consequently energy in form of heat or mechanical work is required. With high variety in membrane properties due to different materials and manufacturing processes, the number of applications increases in all industrial sectors: drinking water, urban wastewater, textile, tannery, paper, metal, electronic, pharmaceutical and food (Koltuniewicz and Drioli, 2008).

On the other hand, membrane technology carries a major limitation based on the separation concept, because substances removed in filtrate product are accumulated in membranes or in a concentrate flow, not being totally eliminated of the global system. Table 1.8 shows the main advantages and drawbacks for this technology.

Table 1.8: General advantages and drawbacks of membrane technology

| | |
|---|---|
| **Advantages** | Separation can be carried out continuously<br>Flexibility to be combined with other processes (hybrid processing)<br>Separation can be carried out under mild conditions<br>Easy up-scaling<br>Reduction of steps in some treatment processes<br>Variability in membrane properties to adjust correctly for each use<br>Chemical addition is not playing the main role |
| **Drawbacks** | Energy consumption<br>Membrane fouling<br>Membrane lifetime<br>Low selectivity |

The first recorded study of membrane phenomena and the discovery of osmosis process dates back to the middle of the 18th century when Nollet discovered semipermeable membrane and the osmotic pressure with a pig's bladder (Nollet, 1752). In 1867, Traube prepared the first inorganic semipermeable membrane from copper ferrocyanide film supported in a porous clay frit, which was used for the separation of electrolytes (Traube, 1867). The development of asymmetric membranes, as thin film composite membranes (TFC), became the trigger for industrial membrane applications in 1960s (Loeb and Sourirajan, 1962) because higher water fluxes were obtained as a result of the small thickness for the active barrier layer. This was the major advance toward the application of reverse osmosis (RO) membranes as an effective tool for the production of potable water from the sea (Mulder, 1996).

Separation capacity in membrane technology is possible because membrane acts as a semipermeable barrier by means of different separation mechanisms in function of membrane type. Nature of source water and operational conditions also influence the separation capacities of the membranes. Sieving or straining effects are the main separation mechanism for all membranes. In case of porous membranes, it is the only exclusion phenomena unless fouling appeared in one of its forms, for example in membrane processes were feed solution or water have high contents of colloidal and suspended solids, these can be retained in the membrane surface reducing water permeability (process yield) and contributing over the separation of other constituents by sieving effects (straining) or other phenomena, mainly adsorption (Yoon et al., 2006).

Membranes with low porosity and small pores generate significant resistance to water flow at the same time that minimizes permeability for feed solution constituents. Is the case of TFC membranes, where filtration occurs at the active layer which is a thin skin with low porosity and very small void spaces.

### 1.4.1. Membrane processes classification

A first classification can be considering the force that makes possible the transport for the components in the feed phase through the membrane (Annex 1). Driving forces can be gradients in pressure, concentration, electrical potential or temperature. In addition, membrane separation process is characterized for the membrane pore size employed, determining selectivity and flux.

The degree of substance selectivity depend on a major extent on the membrane pore size, categorizing membranes from the coarsest to the tightest in microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), as Figure 1.10 shows. Often is considered an effective pore diameter, normally in μm or using the molecular weight cut off (MWCO). MWCO is based on an empirical determination that consists in measuring the bigger solute that can pass through the membrane to the permeate side in a percentage of 90% (usually polyethileneglycols are used for this determination).

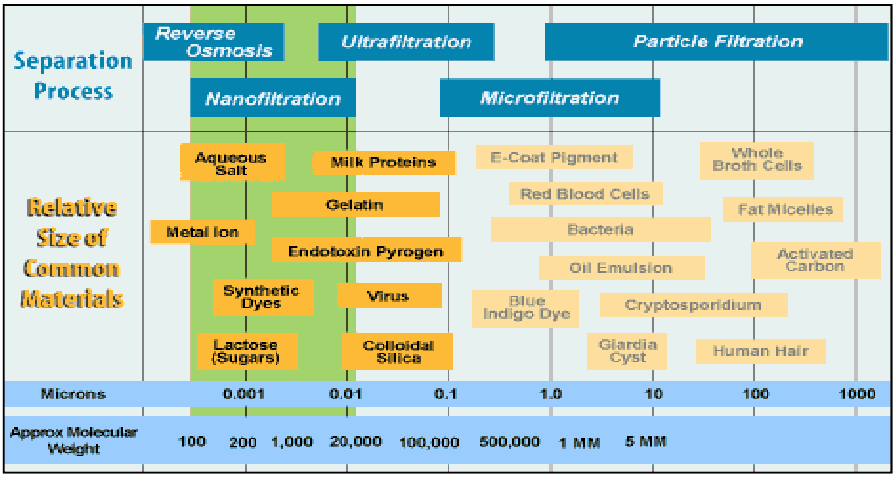


Figure 1.10: Membrane classification regarding selectivity range (ecoweb)

When particles of diameter >100 nm have to be retained, it is possible to use MF because has a rather open membrane structure. Hydrodinamic resistance in this case is low and small driving forces are sufficient to obtain high fluxes. In cases where highly pure water is required, RO membranes are the selected membrane because is able to reject monovalent ions as the smallest solute (less than 1 nm). As the size of constituents being retained decreases, hydrodynamic resistance increases and higher driving forces are needed to obtain product flux (permeability).

In pressure-driven membranes, the product flux obtained is determined by the applied pressure and the membrane resistance (or permeability). Gradient of pressure between both sides of the membrane is called transmembrane pressure (TMP). Usually membrane filtration as MF and UF operates at TMP between 0.2 and 1.5 bars, while NF usually operates between 3 and 15 bars, and RO at TMP values higher than 15 bars. Exact operational TMP not only depends on the quality of the feed stream but also the design conditions and membrane configurations.

It is important to note that membranes are used in a wide variety of fields and industries, and the distinction between membrane types as used in water treatment may be not appropriate in other sectors. In water processes, main differences in pressure driven membranes have been found between MF/UF and RO/NF, indicated in Table 1.9 (Crittenden et al., 2012).

Table 1.9: comparison between MF/UF and NF/RO in water treatment

| Process characteristic | MF/UF | RO/NF |
|---|---|---|
| Objectives | Particle and microorganism removal | Seawater and brackish water desalination, softening, NOM removal for DBP control, specific contaminant removal |
| Target contaminants | Particles | Dissolved solutes |
| Typical source water | Fresh surface water | Ocean, seawater, brackish or coloured groundwater and surface water with problematic contents of NOM or pesticides |
| Membrane structure | Homogenous and asymmetric | Asymmetric and thin-film composite (TFC) |
| Common configuration | Hollow fiber (HF) | Spiral wound (SW) |
| Dominant exclusion mechanism | Straining | Differences in diffusivity or solubility |
| Removal efficiency of impurities | 99 % | 50-90% depending on the objectives |
| Most common flow pattern | Dead end | Tangential |
| Operation includes backwashing | Yes | No |
| Typical membrane transpressure | 0.2-1 bar | 5-85 bar |
| Typical permeate flux | 30-170 $L \cdot m^{-2} \cdot h^{-1}$ | 1-50 $L \cdot m^{-2} \cdot h^{-1}$ |
| Typical recovery | 95% | 50% RO (seawater) / 90% NF |
| Competing filtration | Granular filtration | Distillation, ion exchange, carbon adsorption, precipitate softening |

### 1.4.2. Membrane materials and characterization

Membrane may be classified into various ways according to membrane materials, structure and shape. Synthetic membranes from both organic and inorganic materials are currently used in industrial applications where different mechanical and chemical resistances are required for a specific separation.

Form the structural point of view, the difference between symmetric and asymmetric is the existence or not of homogeneous structure throughout the membrane thickness. Asymmetric membranes consist of a dense skin layer (0.5 µm) supported by a microporous matrix (50-200 µm). Both layers can be of the same material (integrally skinned asymmetric and single layer) or with different materials which are called composite asymmetric membranes (TFC) (Koltuniewicz and Drioli, 2008).

The ideal material is one that can produce a high flux without clogging or fouling and is physically durable, nonbiodegradable, chemically stable in normal conditions and also resistant to punctual chemical agents and temperature, besides of having an acceptable price. Figure 1.10 shows the main polymers used in porous membranes (MF and UF) (Mulder, 1996).

Table 1.10: polymers employed in MF and UF manufacturing

| Polymer | MF | UF |
|---|---|---|
| Polycarbonate | x | |
| Poly/vinylidene-fluoride (PVDF) | x | x |
| Polytetrafluoroethylene (PTFE) | x | |
| Polypropylene (PP) | x | |
| Polysulfone (PS) | x | x |
| Polyamide (PA) (aliphatic) | x | x |
| Poly(ether-imide) | x | |
| Polyether ether ketona (PEEK) | x | x |
| Polyacrylonitrile (PAN) | | x |
| Polyimide/poly(ether imide) | | x |
| Cellulose-esters/acetates (CA) | x | x |

In the case of RO, cellulose acetate was the dominant material until the development of the interfacial-polymerised composite membranes (Cadotte, 1981). Evolution in membrane processing has been proliferated in the last decades. Instead of synthesizing new polymers, major efforts are focused in chemical and physical modifications on those polymers that are promising membrane separation materials, for example, aromatic polyamides present additional mechanical and hydrolytic stabilities giving permselective properties suitable for NF and RO (Ozaki and Li, 2002). This is the case of NF and RO membranes are TFC membranes with modified surface giving special characteristics (highly correlated to the material employed and its manufacturing process) associated to separation mechanisms (Kiso et al., 2001b).

Inorganic membranes are used in the pore size range of MF and UF when the application requires higher thermal and chemical resistances. Four different types frequently used: ceramic, glass, metallic (including carbon) and zeolitic.

Membrane providers consider the composition and manufacture processes of their membranes to be proprietary. As a result, possible consumers are not able to compare commercial membranes using intrinsic properties criteria and then, characterization methods result a useful tool to reach this goal (Makdissy et al., 2010). Most important membrane characteristics and methods for their determination are defined in Annex 2.

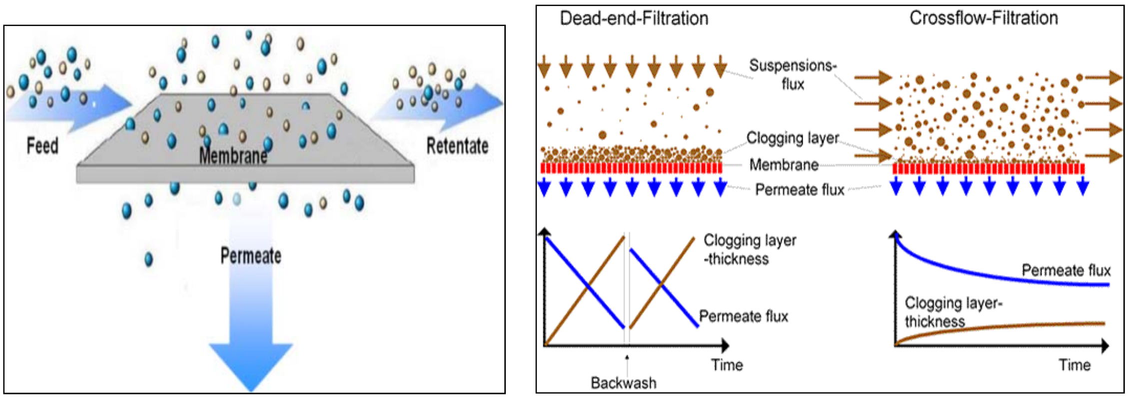
Characterization test for membranes usually are carried out before, during and after real applications in order to evaluate membrane modifications during the process (Hilal et al., 2004). Additionally, characterization methods are carried out for laboratory and pilot experiments also providing valuable information for manufacturers and users.

This is the case of NF and RO membranes are TFC membranes with modified surface giving special characteristics (highly correlated to the material employed and its manufacturing process) associated to separation mechanisms (Kiso et al., 2001b).

### 1.4.3. Process operation and membrane modules configurations

There are two modes of operation, cross-flow and dead-end. In the first case, the feed stream split into two flows, concentrate (or retentate) and permeate flows, as shown in Figure 1.11.a). In case of dead-end filtration mode, only exists feed and permeate flows. Main differences in flow directions and flux decline are observed in Figure 1.11.b for both modes of operation.

Cross-flow mode has beneficial effects reducing fouling tendencies because it varies flow regime and promotes turbulence happening in the membrane surface. Conversely, in dead-end mode substances are separated from permeate but still exist adsorbed into the membrane, consequently a high frequency of backwashings during the day is required, generating wastewater to be correctly disposed (Smith et al., 2006). In cross-flow mode less chemical cleaning is required, although existing a continuous concentrate stream.



a) b)

Figure 1.11: Representation of membrane process where the feed stream is divided into a retentate and permeate stream in a) cross-flow mode (Belstein-Institute) and b) compared to dead end mode (Membranes Modules Systems (memos))

Theoretically, feed water recovery is lower in cross-flow than in dead-end mode, for this reason the first case supposes more elevated operational cost in pumping feed water in large installations (electrical costs) than dead-end operation mode (Glucina et al., 1998). However, a suitable design in large scale membrane installations and the optimization of the process making pilot testing and following experts knowledge, can lead to increase plant recovery reducing operational costs in all membrane configurations (Van der Meer, 2003). In Annex 3 a summary about the main equations to consider in membrane processes are presented.

The membrane module geometry and the way that is mounted and oriented in relation to the flow of water give the configuration of the membrane and is a determining factor in overall process performance. Ideally the membrane should be configured to have some of the following characteristics, although some of them are mutually exclusive:

- High membrane area to module bulk volume ratio
- High degree of turbulence for mass transfer promotion on the feed side
- Low energy expenditure per unit product water volume
- Low cost per unit of membrane area
- Design that facilitates cleaning
- Design that permits modularization

In general, a system does not consist of just one single module but of a number of modules arranged together as a system. In fact, each technical application has its own system design based on specifications requirements. Some aspects to be considered are the type of separation problem, ease of cleaning, ease of maintenance, ease of operation, compactness of the system, scale and the possibility of membrane replacement.

There are six principal configurations currently employed in membrane processes which are based on planar or cylindrical geometry. Table 1.11 indicates the different configurations used in membrane technology with their practical benefits and limitations (Judd, 2006). Tubular or cylindrical geometries are different in function on the membrane tube diameter, thus tubular (MT), capillary (CT) and hollow fiber (HF) have respective diameters above 10.0 mm, between 0.5-10.0 mm and below 0.5 mm. In case of MF and UF where these configurations are generally applied, two flow directions can be considered: outside-in and inside-out.

Table 1.11: Membrane configurations

| Configuration | Cost | Turbulence | Backflush | Application |
|---|---|---|---|---|
| Flat sheet (FS) | High | Fair | No | ED, UF, RO |
| Pleated filter cartridge (FC) | Very low | Very poor | No | DEMF, low TSS waters |
| Spiral wound (SW) | Low | Poor | No | RO/NF, UF |
| Multitubular (MT) | High | Very good | No | CFMF/UF, high TSS waters, NF |
| Capillar tube (CT) | Low | Fair | Yes | UF[a] |
| Hollow fiber (HF) | Very low | Very poor | Yes | MF/UF, RO[b] |

[a] CT used in UF water flows from inside to outside the tubes
[b] HF used in MF and RO: water flows from outside to inside tubes
ED: electrodyalisis; DEMF: dead end microfiltration; CFMF: cross-flow microfiltration

The main criteria to choose the flow direction mode is based on the solid contents in feed solution (USEPA, 2005). In outside-in flow direction only dead-end mode is applied, and present advantages such as more feed solution recovery (higher areas than inside out) and less sensitivity to particulate clogging. Inside-out flow direction, can operate in dead-end and cross-flow modes, for the latter water fluxes can be increased as a result of turbulence in the inner channel which avoid particulate deposition.

In case of plate and frame configurations, flat-sheet (FS) and spiral-wound (SW), only operate in cross-flow. NF and RO technologies are usually applied in SW configuration, where backwashing is not possible, so cleaning episodes implies the same flow direction than normal filtration operation. Turbulence is generated in SW modules by mean of spacer in the feed/concentrate channel of the membrane (feed-spacer).

### 1.4.4. Membrane fouling

Fouling is the phenomena that imply a reduction of permeate flow at constant operational pressure, or increases of operational pressure when membranes are operating at constant permeate flow. This fact supposes one of the major drawbacks for membrane technology and has been widely studied and investigated in a big number of research papers (Chen et al., 2003; Hilal et al., 2005; Porcelli and Judd, 2010). The main objective of the research in this area is to find out with preventive measures and develop the corrective actions for each specific case.

Fouling has different origins depending on the constituents and solutes rejected: inorganic salts, organic matter and specific compounds, microorganisms (biofouling), colloidal and suspended particles (gel or cake layer formation). Scaling or inorganic precipitation is likely to happen in NF or RO rejecting high percentages of inorganic salts presented in surface and ground water, or brackish and sea water (Shirazi et al., 2010). Organic fouling, biofouling and gel or cake layer formation is likely to occur in all membrane types (Park et al., 2006).

In function of the type of fouling and the membrane employed for the separation, fouling may consist in particles deposition, pore blocking, physical and chemical interactions between compounds and membrane, or the development of a biofilm that can decrease membrane effectiveness (Vrouwenvelder et al., 2009b). A schematic process of fouling is represented in Figure 1.12.

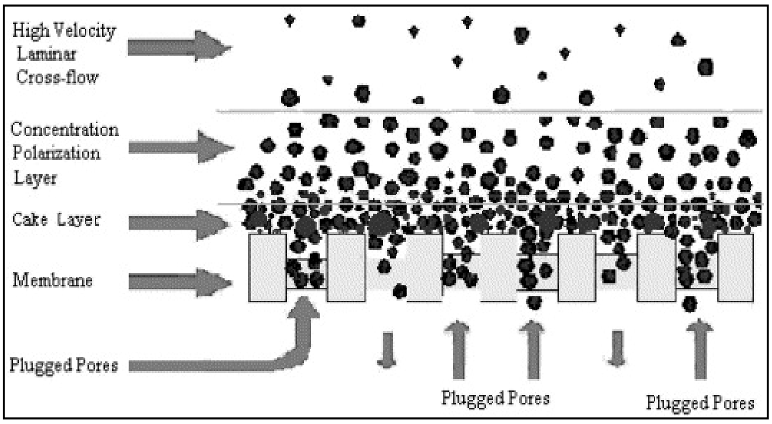


Figure 1.12: General representation of different steps in fouling formation (Zhan et al., 2004)

Operational conditions in large scale membrane processes greatly influence in membrane fouling and permeate flux declining (or the need to increase operational pressure to maintain permeate flux constant). Figure 1.13 shows a schematic representation of membrane transport to illustrate concentration of polarization (CP) phenomenon. Usually, in water treatments, NF and RO membranes experiment CP in their interface between the bulk solution and membrane surface, influencing solutes transport, and eventually membrane separation capacity.

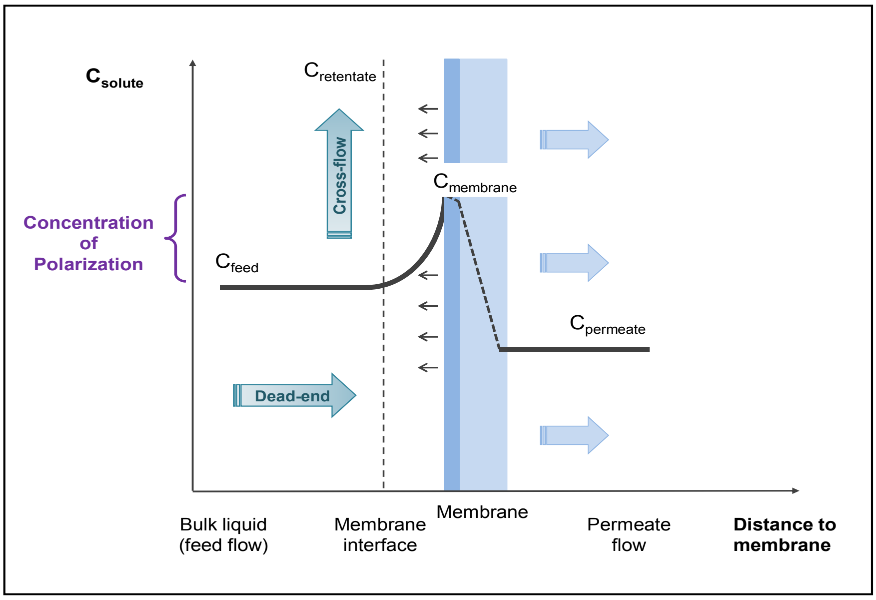


Figure 1.13: Schematic representation of membrane transport and concentration of polarization

In case of spiral modules, CP phenomenon is reduced with the use of a feed-spacer increasing turbulence in the membrane surface, also having positives effects to reduce biofouling (Vrouwenvelder et al., 2009a). In addition to hydraulic consideration and feed water composition, parameters related to initial interactions between water components and membrane surface (hydrophobic or electrostatic) are considered in models to predict fouling formation (Shetty and Chellam, 2003; Vrouwenvelder et al., 2006). Preventive measures are preferred to avoid the formation of irreversible fouling, because when important irreversible fouling takes place, chemical cleanings may be useless and even can damage the membrane.

Several methods or indices have been proposed to predict a colloidal fouling potential of feed waters, including turbidity, silt density index (SDI) and modified fouling index (MFI) (ASTM, 2002; Boerlage et al., 2004; Khirani et al., 2006). The SDI is the most used index and its measurement is recommended by suppliers in order to design the most appropriate pretreatment for NF and RO membranes (DOW, 1995- 2012). Preventive measures can consist in particle/colloidal filtration (UF) or scale inhibitors addition (like phosphonates and other commercial products).

Scaling or inorganic salts precipitation usually occurs in NF and RO membranes because in the concentrate stream ions concentration can be double feed water levels. The most common problematic salts are carbonates ($CaCO_3$), sulfates ($CaSO_4$, $BaSO_4$, $SrSO_4$) and phosphates ($Ca_3(PO_4)_2$), and even though $CaF_2$. In order to control inorganic and colloidal fouling in NF and RO installations, a previous characterization of water is required. Table 1.12 shows the most important parameters for a complete feed water analysis (DOW, 1995-2012).

Table 1.12: Analytical parameters and measurements for an initial characterization of the feed water in case of NF and RO process

| **Cations** | **Anions** | **Organic** | **Colloidal and particulate** | **Other** |
|---|---|---|---|---|
| $NH^{4+}$ | $HCO_3^-$ | TOC | Turbidity | TDS |
| $K^+$ | $CO_2^{-3}$ | BOD | SDI | Alkalinity |
| $Na^+$ | $Cl^-$ | COD | Fe (tot) | Hardness |
| $Mg^{2+}$ | $F^-$ | AOC | SiO2 (colloidal) | Bacteria |
| $Ca^{2+}$ | $NO^{3-}$ | BDOC | SiO2 (soluble) | Free chlorine |
| $Ba^{2+}$ | $SO_4^{2-}$ | | | Boron |
| $Sr^{2+}$ | $PO_4^{2-}$ | | | |
| $Fe^{2+}$ | $S^{2-}$ | | | |
| $Mn^{2+}$ | | | | |
| $Al^{3+}$ | | | | |
| Observations (colour, odour, biological activity): | | | | |

The cleaning procedure, cleaning chemicals, and frequency of cleaning need to be determined and optimized case by case. Correct cleaning sequence is of great importance, for this reason feed water characterization and wide knowledge about the global process is fundamental. For example in case of drinking water treatment from fresh surface water, NOM and colloidal constituents are considered the major foulants and plant design have to consider a suitable pretreatment to reduce these constituents (Al-Amoudi and Lovitt, 2007; Liikanen et al., 2002; Porcelli and Judd, 2010).

### 1.4.5. Nanofiltration in drinking water treatment processes

Membrane technology dependant on the water application may substitute a number of conventional unit processes (most of them involving several state phases) in only one robust separation method. This goal can be achieved with a suitable design, including pre and post treatment to obtain the desired quality in produced water at the best efficiencies for membrane technology.

In the lates 1970s, nanofiltration membranes (NF) were developed from RO membranes, which initially were used for seawater desalination in order to obtain drinking water (Loeb and Sourirajan, 1962). Partial salts removal and very low rejection for monovalent ions, such as chloride and sodium, reduce operational feed pressure in NF systems, lowering energy costs and make NF a very suitable technology for water softening and dissolved organic carbon (DOC) removal applications.

NF appears to be a competitive option in front of others treatments for drinking water processes, like GAC, advanced oxidation processes, enhanced coagulation or ionic exchange resins,  when total dissolved salts (TDS) removal is not a primary concern and DBP precursors need to be separated before final disinfection (see section 2.3).

Currently, NF is employed in real plants using spiral wound membranes because are less expensive than hollow fibres. On the other hand, spiral wound modules are prone to fouling and are more difficult to clean, being necessary a suitable pretreatment which will increase capital and operational costs (UF, enhanced filtration as GAC, ion exchange resins) (Chellam et al., 1997; Knops et al., 2007; Sethi and Wiesner, 2000). NF after conventional pretreatment in drinking water process can suppose an additional price of 0.11 €·m$^{-3}$ for NF plant capacity near to 20000 m$^{3}$·day$^{-1}$ (Gorenflo et al., 2003; Liikanen et al., 2006).

The reduction of costs in NF can be achieved by increasing water recovery, lowering energy consumption and improving clean efficiency, all of them related to environmental benefits (Costa and de Pinho, 2006; Liikanen et al., 2003; Sethi and Wiesner, 2000; Van der Bruggen et al., 2008).

In general, NF process implies a pretreatment of the feed water entering to the membranes system. Pretreatment usually requires the addition of acid, scale inhibitor, and in cases of prechlorination at the beginning of the drinking water process, it is also required a chemical agent to reduce free chlorine (typically sodium metabisulphite) in order to avoid the damage of TFC polyamide membranes. Security cartridges (1-20 µm) must be used to prevent NF membranes of higher particulate matter. In cases of water with high fouling potential, other steps may be needed, such as MF or UF. As the final step, water permeate may require a post-treatment in function of the specific application.

### 1.4.5.1. Physico-chemical characteristics of NF membranes and separation mechanisms

Spiral wound membranes are widely used in modern municipal water treatment applications for NF (or RO). NF has been considered leaky reverse osmosis where the separation mechanisms are achieved through a combination size exclusion (straining), charge rejection and solubility-diffusion through mesopores (hydrophobic character, hydrogen bonds, Van der Waals forces or solvation capacities). Depending on the physicochemical properties of the membrane materials and solutes in the solution media, separation can be reach for one or different mechanisms. Predictive models have been developed to approximate theory to real process providing quantitative values from physichochemical data and experimental results (Van der Bruggen et al., 1999; Van der Bruggen and Vandecasteele, 2002; Verliefde, 2008).

For example, the straining mechanism consist in a separation by sieving effect, molecules bigger than the pore size distribution of the membrane are rejected. Molecular weight (MW) is the simplest parameter that suppliers use to characterize membranes by means of molecular weight cut-off (MWCO) (section 1.4.1).

The models based only with size exclusion mechanism (Spiegler-Kedem, Stokes-Einstein) are very useful to define colloid and particles rejection, and in some extension for salts, considering the specific volume of the hydrated ion (Berg et al., 1997; Nakao and Kimura, 1982; Van der Bruggen and Vandecasteele, 2002). There are important limitations for this mechanism, for example the spheric shape considered in most cases (Braghetta et al., 1997; Park and Cho, 2008; Verliefde et al., 2009).

Minor part of organic compounds may be not retained by NF because their MW is lower than 300 Da (formaldehid, acetone, THM, piruvic and acetic acid) (Meylan et al., 2007). In contrast, desalination degree for membranes, using NaCl and $MgSO_4$, is also used to correlate rejection capabilities for NF membranes in front of some organic compounds, such as pesticides, alkylftalates, alcohols and polysaccharides (Kiso et al., 2001a; Kiso et al., 2001b). However, in some cases, desalination degree for membranes not always is a good predictor for hydrophobic compounds rejection (sterols) (Schafer et al., 2003).

However, when molecules are smaller than the MWCO, charge effects and polar character of the solute may interfere in their permeability through the membrane. Phenomena based on charge interactions are possible because NF membranes (like RO) have been superficially modified during their manufacture process with the intention to increase its superficial charge or hydrophilic character. Functional groups, such as Sulfonic and carboxylic functional groups give negative superficial charge at typical pH of operation in water treatment. The parameter to characterize membrane charge is called Z-potential and its measure in function of pH. This determination, also allow knowing the isoelectric point of membrane surface which represents the pH that functional groups have been neutralized and Z-potential is zero. Near to this conditions, anionic solutes are less rejected (Bellona and Drewes, 2005).

Charge effects play an important role in membrane separation process in NF membranes, because small negative charged solutes are rejected as a result of repulsion interactions (Kosutic et al., 2005). On the other hand, pore size can change in the membrane surface as a result of interactions between functional groups in the active layer (Childress and Elimelech, 2000).

A consequence of charge separation, electroneutrality balance can be altered and some unexpected results have been observed in accord to this principle. For example rejection of calcium was increased with higher sulfate concentrations in feed solutions (Chellam and Taylor, 2001), or rejection of some heavy metals decreased when feed solution presented higher hardness levels (Ozaki and Li, 2002). Another effect of calcium ions was observed for rejections of some neutral organic compounds (Boussahel et al., 2002; Childress and Elimelech, 2000). All these studies demonstrate the importance of ionic strength in the feed solution, in addition to operational pH (Freger et al., 2000; Schafer et al., 2002; Visvanathan et al., 1998).

On the other hand, most of organic molecules are neutral but their electronic distribution is not uniform and polar character are manifested. Hydrophilic and hydrophobic compounds classification takes into account the polar character of compounds. Compounds are characterized by means of partition coefficient of the molecule between octanol and water, $K_{ow}$ (or log $K_{ow}$), similar to Henry coefficient. Membranes are characterized regarding water drop angle, which measures drop spread in membrane surface (higher values of this angle indicate higher hydrophobic character of the membrane) (Kimura et al., 2003; Wintgens et al., 2003).

In these conditions different interactions can exist between molecules, membranes and solvent. For example polar compounds due to functional groups (hydroxyls, halogens) in their structure can form hydrogen bonds with water, acquiring big hydrated volumes and experimenting major rejection in NF separation (Braeken et al., 2005). Conversely, hydrophobic compounds can interact with membrane materials, at the beginning in the surface and later into the pores, experimenting adsorction-diffusion phenomena which implies lower rejection capacities (Nghiem, 2005; Verliefde, 2008). Furthermore, solutes with major interactions with membrane can result in observed negative rejections due to its diffusion through the membrane pores, apparently increasing its concentration in permeate side with regards to the feed solution. This has been observed for positive molecules with low hydrophobic character ($K_{ow}$) (Van der Bruggen and Vandecasteele, 2002).

Organic fouling and associated biofouling can occur as result of organic and microorganisms adsorption into hydrophobic membranes, for this reason more hydrophilic membranes are manufactured (Vrijenhoek et al., 2001).

### 1.4.5.2. Real cases of NF in drinking water production

The cheapest form to test membranes effectiveness is on laboratory scale, where feed solution can be the real water of concern and filtration tests can be carried out at various operational conditions (feed pressure, pH, temperature, cross-flow velocity). However some limitations exist in this scale, such as hydraulic differences between flat-sheet and spiral wound configurations that make difficult direct comparison from laboratory to full scale plants.

Initial studies from laboratory scale to pilot plant are recommended to evaluate NF efficiency, before the design for a real plant (Ventresque and Bablon, 1997). Among other aspects, these previous studies are fundamental to select the most appropriate membrane and to choice the pretreatment in function of the feed water quality, in addition to the rest of operational conditions for the global process (Cho et al., 1999; Koyuncu et al., 2006; Siddiqui et al., 2000).

The implementation of NF technology in DWTP took place with the objectives to reduce DBP formation, hardness or the presence of emergent pollutants in final drinking water. Table 1.13 indicates the most important plants installed around the world with the main design characteristics. Pretreatment for each case is indicated in remarks, cartridge filtration is generally applied in NF and RO plants as an indispensable security step.

A part of literature data, pilot plant experimentation offers the option to evaluate real fouling formation and its removla, or the effects of fouling on compounds separation at hydraulic conditions similar to real cases (feed flow recovery, permeate flux).

Analythical results and technical data from pilot studies with the help of supplier's recommendations lead to suitable preliminary design for real plants. In addition these data can be used to evaluate environmental and human heaths impacts. Next section describes these assessment tools because may be useful as a complementary points of view a part of economical and technical criteria.

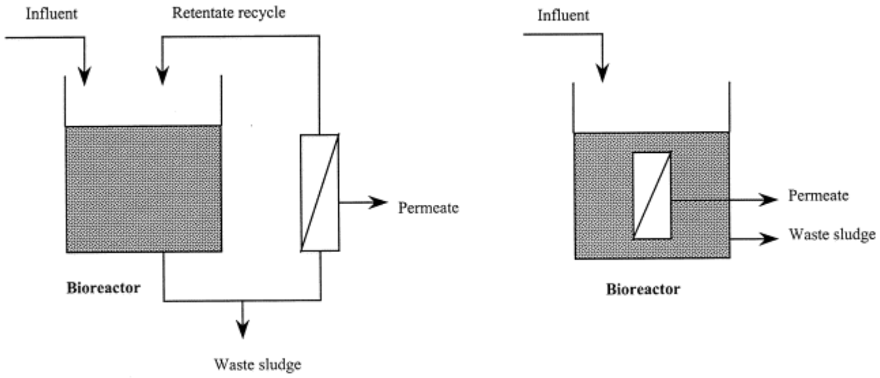
Table 1.13: Characteristics of the major NF real plants around the world

| Plant | Design | Rejection | Capacity | Membrane | Remarks |
|---|---|---|---|---|---|
| **Méry-Oise Prototip (Ventresque and Bablon, 1997)** | 2 trains in parallel, with 3 stages 8:4:2 PV<br>6 module/PV | 90% DOC | $120\cdot10^3$ l·day$^{-1}$ | NF70<br>NF200 | -pretreatment: storage, ozonation, double layer filtration,<br>- 75-85 % of feed water recovery |
| **Méry-Oise Planta real (Paris) (Cyna et al., 2002)** | 8 trains in parallel, with 3 stages; disposition of 190 PV in 54,54:54:28<br>6 module/PV | 65-80% DOC – BDOC;<br>>93% Atrazine;<br>50-70% $Ca^{2+}$ | $30\cdot10^6$ to $140\cdot10^6$ l·day$^{-1}$ | NF200B-400 | - 85 % of feed water recovery<br>- coagulation with PAC; flocculation with anionic polyelectrolit; pH at 6.9 with $H_2SO_4$; ozonation and double layer filtration |
| **Boca Ratón (Florida) (Escobar et al., 2000)** | 10 trains with two stages; PV disposed in 72:36<br>7 module /PV | 95% hardness;<br>85% chloride;<br>>90% TOC | $40\cdot10^6$ l·day$^{-1}$ with 12 trains<br>$36.7\cdot10^6$ l·day$^{-1}$ with 10 trains | TFCS spiral | -Multimedia filtration<br>-$H_2SO_4$ addition (140 mg/l)<br>-Antiscalant 2 mg/l<br>-Disinfection with 4 mg/l $Cl_2$ and 1.3 mg/l ammonia<br>-post-treatment aeration plus 45 mg/l NaOH to adjust pH<br>- 85 % of feed water recovery |
| **Debden Road (UK) (Wittmann et al., 1998)** | 1 train with 14:7:4 *PV*<br>6 module /PV | 40-50% hardness;<br>30-40 % conductivity<br>Pesticides levels < 0.3 µg/L | $3\cdot10^6$ l·day$^{-1}$ | NF200B-400 | - antiscalant; possible $H_2SO_4$ addition<br>-final hardness between 150-180 mg/l.<br>-85 % of feed water recovery<br>-No remineralization |
| **Jarny Metz (East of France) (Bertrand et al., 1997)** | 2 trains<br>9:5 PV<br>6 module/PV | 98.7 % hardness;<br>96.3% conductivity | $2.7\cdot10^6$ l·day$^{-1}$ | NF70-345 | -Flocculation, reduction of $CaCO_3$ with CaO 250 mg/l<br>- $H_2SO_4$ acidification<br>- antiscalant<br>- 65 % of feed water recovery |
| **Bajo Almanzora (Spain) (Redondo and Lanari, 1997)** | 4 trains in parallel; 2 stages with 44-22 PV<br>6 module/PV | 98.5 % hardness;<br>95.5 % conductivity | $30\cdot10^6$ l·day$^{-1}$ | NF70-345 | -ozonation, coagulation,sand filtration, HCl, antiscalant, sodium metabisulfite<br>- 70 % of recovery |

### 1.4.6. Membrane bioreactors

A classical membrane bioreactor (MBR) comprises conventional activated sludge process coupled with membrane separation to retain the biomass. Permselectivity depends on the pore size of the membrane (with effective pore < 0.1 μm) selected for the the MBR application, typically with the intention to obtain clarified and substantially disinfected effluent.

In addition, MBR in wastewater treatment concentrates up the biomass and reduces the necessary tank size, in doing so can also increases the efficiency of the biotreatment process. These systems have two main modes, sidestream (sMBR) or immersed (iMBR), in function of the membrane location, outside or inside the bioreactor which contains activated sludge (Figure 1.14). At the same time, depending on the membrane used, MBR can vary between different membranes (MF, UF, NF or RO) and their implementation can also be considered as a membrane train using sMBR or iMBR modes. The design of global membrane process depends on the quality of influent and the effluent fate (reuse or discharge).



a) b)

Figure 1.14: Configuration of MBR systems a) sMBR, b) iMBR (Gander et al., 2000)

The first membrane bioreactors were developed commercially by Dorr-Oliver in the late 1960s with the application to ship-board sewage treatment in Japan. In USA Thetford Systems was developed another sidestream process for wastewater recycling duties (from the late 1980s to early 1990s). Initially, flat-sheet (FS)-MF iMBR was developed by Kubota and by the end of 1996 and Weir Envig in South Africa developed an anaerobic digester UF (ADUF) MBR, for use in high-strength industrial wastewaters. (Judd, 2006). In the last years, the number of MBR installations has increased and can be divided separately for domestic and industrial applications, showing different tendencies as is indicated in Figure 1.15.

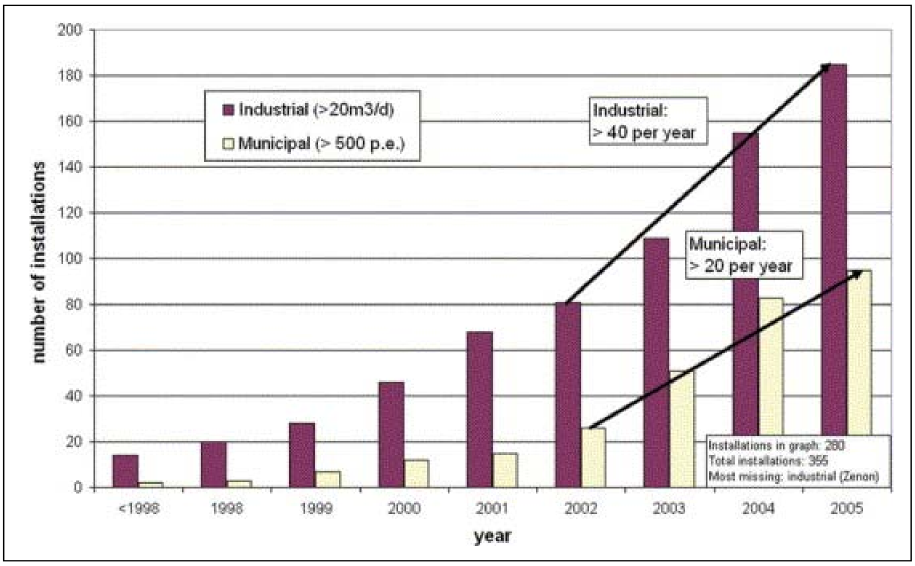


Figure 1.15: Development of industrial and municipal MBR markets (Lesjean et al., 2006)

Costs of membranes have decreased over the past 15 years together with operational ones, reducing unit costs by up to 30-fold since 1990 (Kennedy and Churchouse, 2005). This is result of the improvements in design and/or operation and maintenance activities, which increase membrane life. (Cote et al., 2012).

Future reductions in price are expected in case of membrane modules standardization is likely to happen, as it happens in RO technology (Kraume and Drews, 2010; Santos and Judd, 2010). In this sense, MBR market in membrane technologies is expected to increase faster than market for advanced wastewater treatment equipment and more rapidly than the markets for other types of membrane systems. The key for this optimistic tendency for MBR markets, during the current and future decade, consists in greater legislative requirements regarding water quality. Legislation development takes into account different aspects with regard to the sensitivity of the receiving water body and for reuse and recycling initiatives. Incentives and funding are also necessary because MBR is considered high costly compared with the more established conventional technologies (Frost and Sullivan, 2003), for this reason is useful to make previous experiments in a pilot plant.

### 1.4.6.2. Biotreatment

Biotreatment or biological treatment processes are those involved in dissolved and suspended organic matter degradation by microorganisms, which turn into the formation of two phases. Viability of the biological process requires maintaining suitable levels of microorganisms (biomass) with organic and nutrients levels.

Organic matter contents can be indirectly measured by means of oxidation reactions, being called chemically (COD) or biologically (BOD) oxidation demands. Microorganisms generate their cellular material and obtain energy from organic substrates with oxygen (aerobic) or independently of the oxygen concentration (anaerobic). The high effectiveness of aerobic process converts organic molecules into carbon dioxide ($CO_2$), water ($H_2O$) and inorganic nitrogen without severe byproduct formation. At the same time, biomass release extracellular polymeric substances (EPS), considered as a variety of materials that depends on not only of the feed characteristics but also of the operational facets of the systems, such as microbial speciation (Sofia et al., 2004). The conversion implies the formation of a solid phase with settling abilities to separate from the clarified effluent.

Microorganisms degrade mostly organic components by means of oxidation and reduction reactions, in this sense, redox conditions are divided into three types: aerobic, anaerobic and anoxic (oxygen for bioactivity comes from another compound). In each case, different communities of microorganisms are favored in front of the concerning type of treatment. Aerobic treatments remove organic compounds (COD and BOD) and oxidize ammonia to nitrate. Aerobic tanks may be combined with anoxic and anaerobic tanks to provide biological nutrient removal (BNR), nitrogen and phosphorus (Metcalf, 2003). In Annex 4 there is a table indicating the different classes of biodegradation processes.

Biotreatment processes are slow and variable to organic load. Hydraulic retention time (HRT) defines the optimum times that wastewater needs spending in the biological tank to reduce organic levels to desired levels. On the other hand, sludge retention time (SRT) also called sludge age ($day^{-1}$), is an important design parameter used for suspended growth systems (Cicek et al., 2001; Ouyang and Liu, 2009). SRT is the time of residence for the active sludge into the bioreactor.

The correct adjustment of HRT and SRT must allow microbial growing, relying on appropriate conditions of total dissolved solids (TDS) concentration, pH and temperature.

### 1.4.6.3. Operational process and configurations for MBR

MBR are typically employed in wastewater treatments in order to increase water purity and to recover some particles or suspended matter with certain interest in the biological process. The degree of selectivity depends on the membrane pore size, the coarsest membrane, associated with MF often in immersed MBR, can reject particulate matter, instead of RO technology which can reject monovalent ions in side stream mode of operation. Figure 1.16

shows the concepts in MBR process regarding their mode, process and membrane configurations.

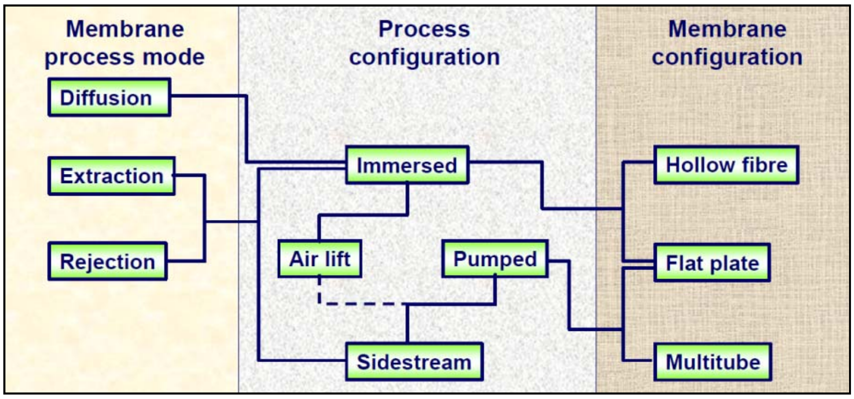


Figure 1.16: Membrane and process configurations (Judd, 2006)

Extractive (eMBR) and diffusive (dMBR) modes for MBR are employed for other proposals than separate the biomass from the treated water. On the other hand, hydraulic operation can be carried out using pumping or airlifting.

Immersed MBR are preferred in medium to large-scale domestic wastewater treatment, aeration in the same bioreactor generate shearing the membrane and reducing fouling tendencies. HF presents more complex hydrodynamics but at the same time, fouling detected was lower than FS (Hai et al., 2005).

The pore size of commercial MBR materials tends to be in the coarse MF to fine UF region, offering sufficient rejection and reasonable fouling control under the conditions employed. Membrane material (PVDF, mixed cellulose esters MCE and PES) and manufacturing can give different surface roughness and porosity to the membrane, which in turn modifies fouling behavior (Meng et al., 2009).

Biofouling can be developed when soluble microbial products (SMP) block pore membranes, forming a gel structure on the surface where biofilm find a nutrient source (Rosenberger et al., 2005; Wang et al., 2007). The most influent parameter in fouling formation is the interaction between the membrane and the biological suspension, consequently adsorption of EPS and filamentous bacteria on the membrane surface are highly dependant of membrane hydrophobicity and charge (Bae and Tak, 2005).

One of the advantages of an MBR system is longer SRT because biomass is retained in the tank, having a major control over its settling and recycling (Stephenson et al., 2000). This fact is beneficial for MBR because is possible to reduce HRT although the slow rate of microbial growth demands (compared with chemical processes), and hence, small volume reactors can be effective. Mixed liquor suspended solids (MLSS), temperature, particle size, air bubble size and composition of the water problem (salinity, viscosity) also influence in the global biological yield and this parameter is applied in some equation to predict or design a MBR (Henkel et al., 2009; Judd, 2006).

The relation between food and microorganism (F:M ratio) defines the rate at which substrate is fed into the tank, becoming an empirical design parameter (Ghyoot and Verstraete, 2000). Regarding nitrogen degradation, this is slower than carbon degradation, then nitrification in aerated systems requires of higher HRT to reach perfect conversion to $NO_3^-$ in MBR (Fan et al., 1996; Huang et al., 2001).

In MBR systems, major operational parameters contributing to operating costs are liquid pumping, membrane maintenance and aeration. The latter is the most important in case of iMBR, where oxygen is required for maintaining a viable suspended biomass at the same time that aeration is scouring membrane to prevent flogs clogging. This design parameter has high influence in energy consumption, which can be theoretically determined by:

- Oxygen requirements for the biomass
- Oxygen transfer coefficient from the aerator characteristics
- Alpha factor from empirical correlations with MLSS
- Specific aeration demand from the aeration rate and the next flux
- Air flow rate through the blower
- Blower power requirement
- Pumping energy for both permeate extraction and recirculation

Design is thus critically dependant on the selected operating parameters, such as permeate flux and the aeration demand required to maintain this flux, considering physical and chemical cleanings required and employed (Judd, 2006).

### 1.4.6.4. Real applications

Submerged or immersed MBR (iMBR) represent the most widely employed of all MBR configurations, since they incur the lowest specific energy demand and therefore become the most economically viable for large-scale applications. Summarizing there are five key points to design and operate an iMBR:

- The membrane, its design and the sustaining of permeability

- Feedwater, its characteristics and its pretreatment
- Aeration of both membrane and the bulk biomass
- Sludge withdrawal and residence time
- Bioactivity and nature of biomass

From Figure 1.16, typical membrane configurations for MBR are limited to plate-and-frame/flat sheet (FS), hollow fiber (HF) and (multi)tubular (MT). For all membrane configurations, cleaning is fundamental in MBR processes because solids and foulant loadings from the bioreactor liquor are very high on the membrane.

Since MBR performance is highly dependant upon feed water quality and final use of wastewater effluent, pilot plant studies are highly recommended before the design of full.plant (Artiga et al., 2005; Valderrama et al., 2012; Van der Roest et al., 2002). Pilot experimentation allows determining specific design considerations, such as operation fluxes, plant retrofitting, presence of primary clarification or the design of filtration systems inside or outside the biological reactor. Once operational conditions are correctly stablished, effluent quality can be analysed in order to accomplish for wastewater emissions to water bodies or for reuse applications.

A number of case studies have been summarized in Judd's book from different commercial suppliers and configurations available, Table 1.14 shows some of them.

MBR are generally regarded by the water industry as a whole as being a novel technology, although submerged systems are now 20 years old. In addition, MBR technology is more expensive taking into account the need of membrane replacement and the supplementary membrane aeration requirements. However MBR can provides an interesting effluent quality with reasonable process for wastewater reuse applications (irrigation, aquifers recharge) in regions with water scarcity problems.

By the end of 2008 there were 37 large plants distributed throughout European countries. Submerged MBR are preferred in large plants due to the low energetic costs in front of side-stream MBR. This fact may have important consequences in the environmental impact for MBR technology, not only considering energy demands but also taking into account wastewater reuse applications. Intensive treatment using high energy cost membranes can lead to better water qualities increasing the range of wastewater reclamation.

Table 1.14: Some real MBR installations around the world and main characteristic operational parameters

| Plant | Tanks and panels | Operational parameters | Cleaning |
|---|---|---|---|
| Porlock (UK), 1998<br>*effluent quality for recreational<br>*small foot-print | 4 aeration tanks with 89 $m^3$ liquid volumes;<br>6 membrane units per tank;<br>150 panels/unit;<br>2880 $m^2$ membrane surface<br>Kubota iMBR-FS | 1900 $m^3 \cdot day^{-1}$<br>FTM: 27 lmh<br>0.02-0.11 bars<br>$SAD_p$=32 $Nm^3$ air;<br>SRT=30-60 days;<br>12-18 $g \cdot L^{-1}$ MLSS<br>0.3-0.5 kg sludge per kg of BOD (3-6.5 $m^3 \cdot day^{-1}$ DS 2%) | Relaxation each 30-60 min;<br>0.5% NaOCl each 8-9 months;<br>Membrane replacements 1-3% annually |
| Taiwan (ITRI) (Chang et al., 2001)<br>*Technical cheap membranes | 270 $m^2$ total filtration area<br>MBr is retrofitted into 75 $m^3$ square-sided SBR tank<br>*FS with PP non woven fabric (NWF) | 4.5 lmh<br>34 $g \cdot L^{-1}$ of fats, oils and grease<br>95% COD removal<br>($COD_{influent}$= 2600 $mg \cdot L^{-1}$) | 8 min operation and 2 min of relaxation;<br>Cleaning: 6 $g \cdot L^{-1}$ NaOCl each 4 h |
| Tilburg (Netherlands) 1999<br>(Fuji Photo Film, 2006) | 12 stacks with 100 panels; 1620 $m^2$ membrane area<br>*silver recovery from 20-24% dewatered sludge<br>Toray FS iMBR-RO | 840 $m^3 \cdot day^{-1}$<br>21.6 lmh (peak at 27.8 lmh)<br>0.15 bars; SRT=24 days<br>15 $g \cdot L^{-1}$ MLSS which 12 $g \cdot L^{-1}$ is estimated to be biomass<br>$SAD_p$= 18.5 $Nm^3$ air; | |
| Ontario (Canada) 2000<br>*industrial WWT before sewage<br>*reduce costs sludge disposal | Zeeweed tank 500c cassettes<br>557 $m^2$ total membrane area<br>Zeeweed HF iMBR | 150 $m^3 \cdot day^{-1}$; 12 lmh<br>0.14- 0.44 bars (0.17 bars)<br>10- 15 $g \cdot L^{-1}$ MLSS<br>Membrane aeration: 360 $m^3 \cdot h^{-1}$ (0.33 bars);<br>Bioreactors blowers: 940 $m^3 \cdot h^{-1}$; (0,88 bars) | Backpulsing 30 s every 10 min;<br>Cleaning: NaOCl and citric acid; twice a week (1 h of 200 $mg \cdot L^{-1}$ NaOCL solution) |
| Bilbao (Spain) 2004<br>*leachate treatment at the landfill | BIOMEMBRAT® with a pressurized bioreactor tank (denitrification plus two nitrification tanks)<br>Wehrle Unwelt GMBH UF sMBR | 1800- 2200 $m^3 \cdot day^{-1}$<br>120 lmh<br>3 bars<br>SRT: 53 days; HRT: 15 h<br>3 UF trains (PV) for each line with 6 modules per PV<br>Aeration rate at 4000 $Nm^3 \cdot h^{-1}$ | |

$SAD_p$= aeration rate for 1 $m^3$ of product water; DS: Dried Sludge
ITRI: Industrial Technology Research Institute

## 1.5. ENVIRONMENTAL IMPACT AND BENEFITS OF MEMBRANE TECHNOLOGIES

Additionally to economical and political criteria in order to select advanced technologies implementation in water treatments, life cycle assessment (LCA) and human health risk (HHR) evaluation are useful tools when environmental concerns and impacts on public health are considered.

### 1.5.1. Life cycle assessment LCA

Life cycle assessment (LCA) is the methodology used to study environmental impacts of a product, process or service. In this work, LCA has been applied to conventional and advanced water processes in order to have additional criteria a part of its technical reliability:

- identification of changes to improve product manufacturing or processes from an environmental point of view,
- provision of additional information to decision makers in industry or government,
- selection of environmental indicators, including measurement techniques,
- marketing (products labeling as more environmental friendly.

LCA method is a valuable tool to support decision making in water treatment in terms of comparison and selection of suitable technology and to identify opportunities to enhance environmental performance of the global process.

The methodology used in LCA studies has been standardized by International Standardization Organization in ISO 14040 and 14044 (ISO, 2006a; b). Acording to above standards, LCA studies can be divided in four phases: goal and scope, data collection for inventory construction, environmental impact evaluation and final interpretation.

Initially, in goal and objectives steps, the appropriate boundaries, functional unit and limitations are defined for the system under study (product, service, process). Once the first step is clear, a recollection of primary and secondary data is performed in order to build the inventory regarding materials and energy flows during the different stages of the system considered (raw materials adquisition, manufacturing, operation, end-of-life including dismantling). Finally, validation and interpretation of the results obtained are the last steps to finish a LCA study, and in most cases are iterative steps in order to improve and present the final LCA results.

In general, literature review about LCA provides studies with different objectives and scopes, making difficult the comparison of their results. In addition, different regional situation is a limitation to compare LCA results in a global sustainable framework (Comandaru et al., 2012; Godskesen et al., 2011; Mohapatra et al., 2002).

Environmental impacts in LCA are determined for different impact categories like climate change, ozone depletion, photochemical compounds and particulate formation, toxicity effects to human, water and soils, water or metal and fossil depetion resources. All these impact categories can be grouped in three main topics: environmental effects, human effects and resources depletion. The number and importance of each impact category depends on the region of the study as well as the contribution on the environmental impact of the processes and materials involved in each case (Reap et al., 2008).

Last phases within Life Cycle Impact Assesment (LCIA) step are the, normalization and weighting phases. They are optional due to lack of scientific consensus as their determination could involve subjective and regional assumptions used for specific interpretations demanded for some sectors. Normalization factors application give results as the contribution degree for each environmental category over the local environmental problem. Weighting step provides only one value expressed in a common unit to obtain the total environmental impact of the system. However, these calculation phases are used for specific interpretations demanded for some sectors. Figure 1.17 shows an example of structure to understand methodology in environmental impact calculation during LCA studies.

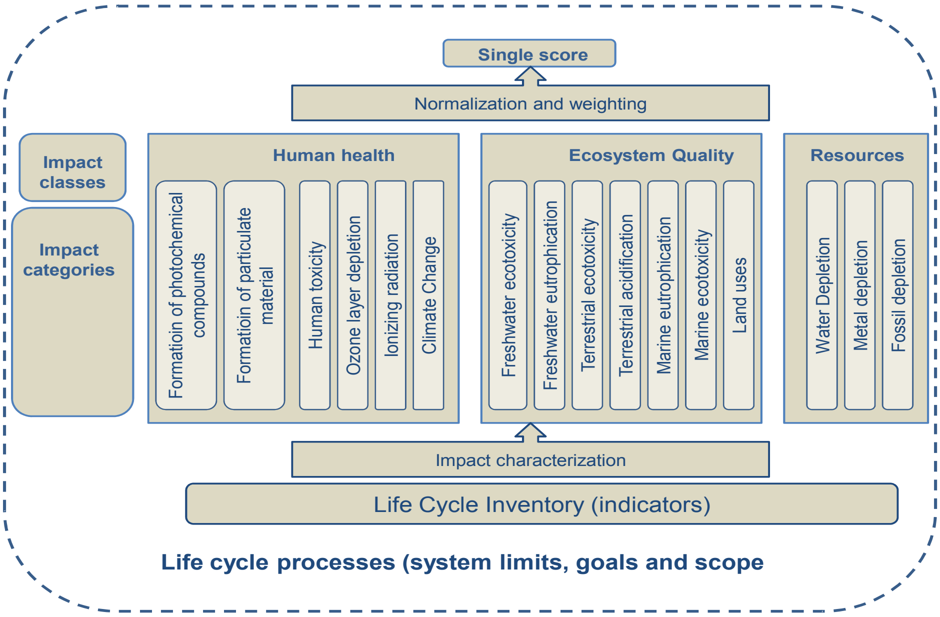


Figure 1.17: Example of structure for LCA methodology to give results of environmental impacts

Until the date most attention has been paid to climate change, but currently scientific community and other organizations remark the importance of other concerns involved in a sustainable framework, such is quality and quantity of water as a natural resource (Comandaru et al., 2012; Godskesen et al., 2011; Tangsubkul et al., 2005).

### 1.5.1.1. LCA studies related to drinking water

Main motivations to carry out LCA and sustainability studies can be: reducing negative impacts over the environment, improving health and hygiene, conserving natural resources and saving human and financial resources (Hellström et al., 2000).

Past and current LCA studies in drinking water treatment processes demonstrate operational stage as the major contribution to environmental impact, more significant than construction and dismantling stages (Hernández-Sancho et al., 2011; Tangsubkul et al., 2006). System boundaries for global urban water management include water pumping from abstraction, drinking water treatment and distribution. In some cases, focusing on the energy resources for electricity production or even to compare different options for future infrastructures (Friedrich et al., 2009; Lassaux et al., 2007; Lundie et al., 2004; Lundin and Morrison, 2002; Norström et al., 2008; Stokes and Horvath, 2009). However the lack to the regional uniformity in water related problems makes difficult to find a consensus to select a unique technology suitable to any place.

In Europe a big number of LCA dedicated to drinking water treatment processes have been published, for example evaluating reverse osmosis (RO) for treating freshwaters and brackish waters (Mohapatra et al., 2002) or seawater (Tarnacki et al., 2012), and also relating water technology to the quality obtained and operational costs (Barrios et al., 2008; Tapia et al., 2008).

LCA has been employed to compare environmental impacts of advanced technologies, such as membranes, in front of conventional treatments to produce drinking water (Bonton et al., 2012; Friedrich, 2001). Friedrich improved LCA by evaluating impacts of the construction and decommissioning stages for a conventional process or for UF membranes implementation in a DWTP, concluding a minor contribution of these stages in comparison to operational stage. The recent LCA study of Bonton and others provides the most detailed inventory for capital materials employed in NF technology.

Energy consumption during the process is the most negative factor when new technologies are analysed by LCA tool, however some advantadges could be the improvement of water quality and the benefits related to human health (Beavis and Lundie, 2003; Mo et al., 2011).

Typical approximation trying to improve environmental impacts for high-energy cost technologies consist in changing the energy source (from fossil to renewable) (Raluy et al., 2005a; Stokes and Horvath, 2006). In this way, some works have evaluated seawater desalination technologies in front of river diversion, as alternative sources for drinking supply (Raluy et al., 2005a; Raluy et al., 2005b; Raluy et al., 2005c; Vince et al., 2008).

As the number of plants for water desalination increases, most attention was paid to environmental concerns associated to concentrate disposal (Lattemann and Höpner, 2008; Nederlof et al., 2005). However, LCA works in this area typically define system boundaries in a way that total effects of concentrate disposal are out of study due to the difficulty to calculate them (Peters and Rouse, 2005; Tarnacki et al., 2012). Additionally to energy consumption, chemical products addition during drinking water process also plays an important role in some environmental impact categories such as ozone depletion, water and terrestrial ecotoxicity (Mavredaki et al., 2007).

### 1.5.1.2. LCA studies in wastewater treatment and reclamation processes

First LCA studies of wastewater treatment process dates around 1998 in Sweden (Lundin et al., 2000; Tillman et al., 1998). These studies used LCA as environmental management tool to evaluate and compare different scenarios for WWTP in specific locations, for example alternative systems treating separately grey water and black water, in large or small scale plants.

From an environmental point of view, wastewater treatment plant (WWTP) processes upgrade the quality of its influent reducing the impact of its effluent discharge in water bodies. In this context, implementation of advanced technologies to upgrade wastewater quality can move the problem among environmental vectors, from water to gas and solid phases, being necessary environmental criteria which contemplate the impacts on water, air and soils when alternative processes are under study (Zambrano, 2007).

Today, the most important factor in developing and implementing new technologies in WWTP is the existence of more restrictive legislations than in the past regarding environmental concerns, in addition to other aspects such as land occupation of installations (Balsells, 2011; Hoibye et al., 2008; Muga and Mihelcic, 2008; Yang et al., 2010; Zambrano, 2007). At the same time that water bodies may be preserved (freshwater eutrophication), new technologies usually demand more energy and probably, more materials resources resulting in an increase of some impact categories (Remy and Jekel, 2012; Vidal et al., 2002; Wang et al., 2012).

As example, LCA studies focused in urban water management have compared economical and environmental costs from a MBR system treating wastewater and from a desalination plant, obtaining expensive costs and higher environmental impacts for seawater desalination although final quality of water may be not comparable (Cote et al., 2005; Stokes and Horvath, 2009). Results from LCA studies can vary enormously considering system boundaries (Hospido et al., 2008), additionally when the objective of LCA is the comparison between water processes, the degree of quality for raw and final water also plays an important role and often is misconsidered.

On the other hand, new technologies offer the challenge for water reclamation and reuse (Tangsubkul et al., 2005). MBR implementation and other membrane technologies able to upgrade wastewater quality for reuse proposals have been evaluated in last years regarding economic costs and environmental impacts using LCA tool (Ortiz et al., 2007; Tangsubkul et al., 2006). However, environmental consequences for wastewater reuse are not completely understood and require further research to be included in LCA studies (Comandaru et al., 2012; Toze, 2006).

Although some effects of water reuse application in agriculture have been recently studied (Laurenson et al., 2011; Mosse et al., 2012; Simate et al., 2011), there is a lack about real environmental impacts to be included in LCA studies (Petti, 2010). For example, in case of beverage and agro-food industries, like winery or brewery, LCA studies not consider wastewater treatment and possible reuse although it is an important part to take into account in environmental and sustainable studies for these industries (Fillaudeau et al., 2006; Valderrama et al., 2012; Vazquez-Rowe et al., 2012).

A part of better effluent quality produced by MBR taking into account microorganism and suspended solids removal, volumes of sludge as a residue can be reduced which suppose some environmental benefits (Cote et al., 2012; Valderrama et al., 2012; Yang et al., 2006). In this sense, the conversion and use of the sludge generated during the treatment process as a solid waste, have been considered into system burdens at the beginnings of LCA studies for sewage treatment plants. However, in other studies, the stages associated to the sludge line process were not included, neither its application as compost or fertilizer in soils (Gaterell et al., 2005). This is a consequence of a lack of information about the drawbacks for real sludge application, as for example probable contents of recalcitrant and bioacumulable substances, such as heavy metals (Foley et al., 2010; Hospido et al., 2008; Lundie et al., 2004).

With development of processes in WWTP to improve process efficiency and sustainability, some studies have considered the inclusion of an energy production line with the biogas from the sludge digester. This feasible option, especially for large plant, resulted in a reduction of greenhouses gases emissions. (Hospido et al., 2008; Hospido et al., 2004; Shahabadi et al., 2009).

Another limitation in LCA studies regarding water processes is that for specific cases, environmental impacts regarding freshwater scarcity and ecological sustainability are not contemplated (Godskesen et al., 2011). In this framework further research is required to include water recycling and reuse LCA studies with regards to quantity and quality of this natural resource.

As a conclusion of all references cited before, LCA studies can be applied to evaluate and compare current or alternative water treatment processes and alternatives, moreover to study possible improvements to optimize water management in key steps such as energy and chemicals consumption.

### 1.5.2. Human Health Risk Assessment

Human health risk (HHR) assessment is the process to evaluate possible health effects in humans as a result of chemicals present in polluted media, now or in the future. In this way HHR, provides a tool to identify risk and assess and validate the effectiveness of new technologies to guarantee drinking water safety for the consumers.

In general, the HHR procedure consists in the following steps: data collection and evaluation, exposure assessment, toxicity assessment, and risk characterization. Figure 1.18 shows a scheme for these steps indicating its relation and the main question related to.

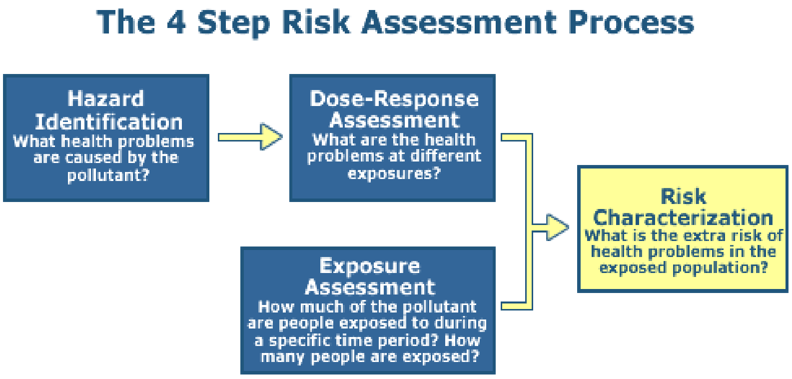


Figure 1.18: Conceptual scheme proposed for HHR assessment studies (USEPA, 2012)

Arguably, there are important implications to define the factors involved in a case study. The exact definition of what a “risk factor” is and the interpretation of HHR assessment require careful attention because interrelationships exist among diet, exercise and physiological risks on the one hand, or among water, sanitation and personal hygiene on the other.

The content of chemicals in an environmental medium (soil, water and air), the contact exposure between a person with contaminated environmental medium, and the inherent toxicity of the chemical are factors that mainly influence human health risk assessment. The first and second step examine whether a stressor has the potential to cause harm to humans and the numerical relationship between exposure and effects. Is important to note that some values are based in animal studies and the effects in humans have not been elucidated.

Exposure assessment as the step 3 examines what is known about frequency, timing and levels of contact with the stressor to finally summarizes and integrate information from the proceeding steps of the risk assessment to synthesize an overall conclusion about risk. The source of exposure, exposure pathways, potentially exposed population, the magnitude, duration, and frequency of exposure to site contaminants for each receptor group have to be identified based on the typical lifestyle of inhabitants.

A clear understanding of the role and relative magnitude of diseases, injuries and their underlaying causes should guide policies and programs for health development, together with effective and affordable interventions to reduce them. While the monitoring and analysis of diseases and mortality in populations has been largely undertaken by actuaries and demographers, much of the work on causes of disease has emanated from research in fields such as epidemiology, toxicology and physiology, which focus on chemical micro-level analysis.

The reduction of toxic compounds concentrations in water has important benefit in human health, for this reason HHR become valuable in order to establish a criteria between new technologies costs and regulated standards for the compounds of concern taking care of public safety.

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# Chapter 2: Objectives

The global purpose of this thesis is to evaluate the technical feasibility and the environmental impact of membrane technology to improve water quality in two selected applications: drinking water treatment and winery wastewater treatment for possible reuse.

Membrane technologies as nanofiltration (NF) and membrane bioreactor (MBR) are employed in different sectors, being the most important in water treatment processes.

Under the hypothesis that NF is an efficient technology to obtain drinking water of excellent quality, specific objectives are:

- Compare different commercial NF membranes at lab-scale regarding its permeability and water quality, specifically in their ability to remove trihalomethane (THM) precursor material.
- Compare the performance of two selected NF membranes in a pilot plant installation, regarding permeability, permeate water quality, specifically in their ability to remove THM precursor material, and fouling formation.
- Study the ability of NF membranes to remove specific organic pollutants.
- Validate if NF performance in laboratory set-up (flat-sheet) and design software provide results useful to predict the performance of NF in full-scale processes (spiral-wound).
- Study the initial flux decline in real NF membranes processes in laboratory and pilot experiments.
- Evaluate the environmental impact of a real NF installation scale-up to produce drinking water and compare it to that calculated for conventional treatment process.
- Evaluate the reduction of HHR resulting from decreasing THMFP by NF in a drinking water treatment plant.

Under the hypothesis that MBR is capable to treat the wastewater from a winery industry and provide water of enough quality for reuse applications, specific objectives are:

- Evaluate technical feasibility of MBR to treat winery wastewater for possible reuse applications.

- Study fouling tendencies of MF membranes submerged into MBR.

- Compare the environmental impact from the conventional activated sludge (CAS) process in the current wastewater treatment plant in front of an alternative plant using MBR technology.

- Compare environmental impact for two models of MF membranes with different aeration requirements to prevent fouling formation during its operation.

# Chapter 3: Overall results

This chapter is dedicated to give an overview of the obtained results in this thesis. The experimental work is organized in chapters, presenting here an abstract for each one.

### Chapter 4: NF membrane selection for drinking water purposes: Laboratory studies

Nanofiltration, as a membrane technology with separation abilities between ultrafiltration (UF) and reverse osmosis (RO), has been widely studied in the last decade with the increase of membrane applications in different sectors. However, some previous testing is recommendable before NF implementation in a full-scale plant.

A wide range of commercial membranes were tested and compared at laboratory scale in order to select the most appropriate to improve water quality produced in a real drinking water treatment plant (DWTP). Most of the membranes tested showed a reduction of trihalomethanes formation potential (THMFP) higher than 95% with partial rejection for inorganic ions and variable productivity. Additionally, the evolution of THMFP through a selected hydric system was evaluated in five sampling points, together with THMFP reduction in all these points when three selected NF membranes were used (SR100, NF270, ESNA1LF2).

Previous testing in laboratory set-up indicated the main differences between membranes: water permeability and separation capacities in front of organic and inorganic feed water components. NF demonstrated their ability to remove trihalomethane (THM) precursor material in all campaigns contemplating different feed water qualities (seasonal variations and different raw water intakes).

### Chapter 5: Pilot plant comparison study of two commercial nanofiltration membranes in a drinking water treatment plant

In case of groundwater and surface water treatment, pilot studies and full-scale plants have shown the effectiveness of NF to produce constant water quality removing a wide range of components. In this work, NF270 (Dow Chemical) and ESNA1LF2 (Hydranautics) were tested parallelly in a pilot scale. The comparison of both membranes was carried out simultaneously in the pilot plant installed in the DWTP of Manresa. In the spiral wound configuration, both membranes also showed effective separation of THM precursors, reducing THMFP in treated water at values of approximately 90%, depending on the season. Main difference between both membrane performances was the lowest salt passage for ESNA1LF2 which could result in higher operational costs for a real plant installation than NF270, important to select one or another membrane.

Chemical cleanings were applied in situ, during pilot plant experimentation, when initial flux decline was higher than 12%. However, membrane's autopsy over spiral-wound used during the experimentation did not show evident fouling. Other chemical solutions for cleaning proposals were tested in the laboratory scale (flat-sheet) using pieces of the used spiral-wound membranes. Results from this part showed differences among the cleaning agents, but not clear evidences about possible foulants type (organic, inorganic, colloidal) were elucidated.

### Chapter 6: Organic pollutants rejection in a pilot plant simultaneously comparing two different nanofiltration commercial membranes

A remarkable increase of water scarcity in some regions and a common use of synthetic products is affecting qualities of water sources, giving importance to removal of organic contaminants. Nanofiltration (NF) technology has been proved as an effective separation process to remove some organic pollutants in drinking water. A pilot plant was operated using the same water source and similar hydrodynamic conditions as an industrial full-scale drinking water treatment plant. The main goal of this study was the simultaneous comparison of two commercial NF to elucidate which one are the most effective removing organic pollutants with different hydrophobic character. Real pre-treated water was spiked with surrogates for target organic pollutants. Membranes ability to reject them was evaluated and interesting differences in their capacity to remove caffeine and linear alkyl sulphonate (LAS) were found.

### Chapter 7: NF performance in flat sheet and spiral wound modules: prediction of full-scale performance and initial flux decline evaluation

One of the most important applications of NF is in water processes, where two main configurations are used: flat sheet and spiral wound module. The cross-flow module using flat sheet membranes is the simplest option to test a NF membrane in a laboratory set-up, but at the industrial scale, NF is basically used in the spiral wound configuration. The objective of this work was to compare the NF performance at different scales and using design software from suppliers, to be able to predict NF performance in real plants because no studies were found in literature. Good prediction were obtained for both membranes (NF270 and ESNA1LF2) from laboratory experiments and from software calculations when operation parameters were stablished as the same that in pilot plant (similar to real applications).

In addition, the initial flux decline detected in real plants was studied, in laboratory and pilot scales, to elucidate possible causes associated to: membrane compaction, effects of preservative liquid, ionic strength in feed solution or the presence of humic acid. These results lead to think that flux decline may occur because initial fouling formation takes place in membrane when a correct process start-up is scripted.

### Chapter 8: Environmental impact and human health risk study of nanofiltration in drinking water treatment

Life cycle assessment (LCA) methodology was applied to a drinking water process in order to evaluate the environmental impact increases in front of the reduction of human health risk (HHR) when nanofiltration (NF) technology is implemented.

In this case study, NF was the advanced treatment considered to improve drinking water quality in a plant treating 23000 $m^3 \cdot day^{-1}$. Results from previous chapters demonstrated the NF capacity to reduce trihalomethanes formation potential (THMFP) as a risk for the human health associated with drinking water consumption. From an environmental point of view, NF represents an increase in energy consumption and environmental impacts have been nearly doubled in comparison to those calculated for conventional drinking water treatment. On the other hand, the carcinogenic risk associated to THM presence in drinking water decreases when higher percentages of NF permeate are mixed with water from the outlet of conventional treatment (25, 50, 75, 100% of NF water). Results showed a reduction of one order of magnitude for the carcinogenic index when 100% of drinking water is nanofiltered.

### Chapter 9: Winery wastewater treatment for water reuse purpose: Conventional activated sludge bersus membrane bioreactor (MBR)

Wastewater from a winery industry presents fluctuations in its organic loads during the year, making the disposal of this effluent a major environmental problem for this sector. In this way, membrane bioreactor (MBR) has been evaluated with additional interest to produce reclaimed water for reuse proposals.

A comparative study was carried out in order to evaluate the winery wastewater treatment by a MBR pilot plant and compare to a full-scale conventional activated sludge system. The influent and effluents were monitored and controlled in order to reach the quality determined by Spanish legislation as well as the international guidelines and regulations for wastewater reuse and reclamation. After 6 months of continuous operations, the physico-chemical and microbial parameters for the MBR permeate, achieved the specifications defined for urban service, agricultural and recreational uses. The MBR plant showed a quite stable and flexible operation during the experiment. A significant correlation between EPSc and permeability confirmed the influence of the hydrophilic fraction on the membrane fouling potential.

### Chapter 10: Environmental evaluation of membrane bioreactor technology in front of conventional activated sludge for winery wastewater treatment

Life cycle assessment (LCA) was performed in order to evaluate the environmental impact of the MBR technology implementation at full scale in the winery wastewater treatment plant (WWTP, in previous chapter). In this context, LCA results from a MBR system and the actual CAS bioreactor were compared.

Inventory data required for LCA evaluation has been constructed taking into account construction and operational data for the wastewater processes considered. In this work, impacts on different environmental impacts were evaluated for both systems.

Results showed that MBR presented higher impacts because more energy is required than in case of CAS bioreactor. This additional energetic demand is due to high aeration requirements to prevent membrane fouling in membrane surface and to degrade organic loads into the MBR bioreactor. Advantadges in MBR system are the achievement of the required standards for water reuse applicantions and the supposed reduction in sludge volumes formation during the process.

# Chapter 4: NF membrane selection for drinking water purposes: Laboratory studies

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Parts of this chapter were based on:

Ribera, G., Llenas, L., Martínez-Lladó, X., Rovira, M., De Pablo, J.; Trihalomethane formation potential along an hydric system: Nanofiltation in drinking water treatment IWA Conference poster 2010, Montréal, Canadà 19-24 setembre 2010.

Ribera, G., Llenas, L., Rovira, M., De Pablo, J., Martínez-Lladó, X.; Pilot plant comparison study of two commercial nanofiltration membranes in a drinking water treatment plant (2013) Desalination and Water Treatment 51 (1-3), 448-457.

## 4.1. INTRODUCTION

Nanofiltration, as a membrane technology with separation abilities between ultrafiltration (UF) and reverse osmosis (RO) (Hilal et al., 2004), has been widely studied in the last decade with the increase of membrane applications in different sectors, for example in water processes. In case of groundwater and surface water treatment, pilot studies and full-scale plants have shown the effectiveness of NF to produce constant water quality removing undesired organic (pesticides, pharmaceuticals, surfactants) or inorganic (nitrates, sulphates, arsenic) components (Cyna et al., 2002; Duran and Dunkelberger, 1995; Gaid et al., 1998; Gorenflo et al., 2003; Kosutic et al., 2005; Majamaa et al., 2011; Ventresque et al., 2000).

Membrane modifications, for example in superficial characteristics, play an important role in separation mechanism and thus giving different properties among all commercial membranes (Koyuncu et al., 2008; Lee and Lee, 2007; Verliefde, 2008). In recent years, innovation in membrane technology has been addressed to reduce fouling tendencies during the process, with the intention to reduce operational costs (Costa and de Pinho, 2006; Liikanen et al., 2006). Unfortunately, information specified for membrane manufacturers is limited and operational factors and feed solution characteristics influence in a different degree NF performance (Arsuaga et al., 2008).

Previous testing before the installation of a real NF plant is recommendable because a wide range of commercial membranes have been developed in last years., firstly to select the most suitable commercial membrane and secondly to find out which are the most appropriate operational conditions for the global drinking process.

In case of NF technology major challenges to face up in drinking water treatment plants (DWTP) have been the reduction of disinfection by products (DBP) or hardness. Separation mechanisms in NF mainly include size exclusion and electrostatic repulsion which allow compounds and ions removal from water (Childress et al., 2000; Hilal et al., 2004; Schäfer et al., 2005; Van der Bruggen et al., 1999). Consequently, inorganic ions and charged compounds may be partially removed depending on their concentration, electric charge and molecular weight. From this point of view, groundwater and some brackish waters have been treated by NF technology in order to reduce hardness or remove heavy metals or other inorganic contaminants, such as sulphates or nitrates (Kosutic et al., 2005; Murthy et al., 2009; Redondo et al., 1997). In case of neutral organic compounds, hydrophobic character of the molecules and membranes influences their specific separation (Verliefde et al., 2009).

On the other hand, weather variations during the year, such as insulation, dried and warm periods, and vegetal and algae activity influence NOM composition in water (DBP precursors), altering water quality (Hruska et al., 2009). As the name indicates, DBP are formed in the disinfection processes where natural organic matter (NOM) reacts with disinfectant agent (generally chlorine or its derivates) added to assure biological stability of water during the distribution system until point of consumption. Although NOM is not recognized as a pollutant or dangerous substance, it acts as a precursor for DBP, which may present intrinsic toxicity (Richardson et al., 2007). Consequently, a large number of studies regarding DBP formation have been focused to analyze the main reactivity factors such as raw water composition, temperature and pH conditions during disinfection, concentration and type of disinfectant agent (Hua and Reckhow, 2008; Matamoros et al., 2007; Singer, 1999; Yang et al., 2007).

Special attention is paid to trihalomethanes (THM) as the main DBP regulated in many countries around the world as a consequence of their effects in humand health (98/83/EC; USEPA, 1998; WHO, 2004). Determination of THM formation potential (THMFP) is a method used in many studies in order to estimate the content of NOM as a precursor material for THM formation, representing DBP (AWWA, 1998).

This work has been focused on the comparison of the separation capacity in front inorganic and organic substances from water for 10 different NF commercially available membranes in order to select the most appropriate ones for two real case scenarios. Experimental work took place using flat sheet membranes in a bench scale set-up with adjustable elements to operate at same process conditions in a wide range of feed pressure in each membrane test. Real pretreated water from a DWTP was employed for NF membranes comparison in three different sampling campaigns in order to observe the effects of seasonal variation on raw water, permeates and global performance of NF filtration. In addition, different water qualities of raw water collected in five sampling points of a hydric system demonstrated the evolution of THMFP and NF tests carried out with these different feed water qualities showed the effectiveness of NF to reduce THMFP (Ribera et al., 2010).

## 4.2. MATERIALS AND METHODS

### 4.2.1. Water samples

The first part of the study is focused on NF experiments using water collected in the drinking water treatment plant of Manresa, and in the second part, experimentation was focused on water coming from five different points of the Llobregat River hydric system, which feeds the DWTP.

Llobregat is the second longest river in Catalonia with 170 km of length. It originates in on the southern slopes of Pyrenees (Berguedà region), and ends in the Mediterranean Sea (in the municipality of El Prat del Llobregat, near Barcelona). NF experiments were carried out to evaluate the ability of nanofiltration to improve the drinking water quality in the middle zone of this River.

#### 4.2.1.1. Testing different NF membranes to improve drinking water quality

Quality of raw water presents high influence in drinking water. The case under study has been centered to evaluate the improvement in drinking water quality when NF is employed at laboratory scale. Raw water from the DWTP comes from Parc de l'Agulla, where an artificial reservoir of 0.2 $Hm^3$ is fed with water from Llobregat River through Canal de la Sequia. The Sequia channel was constructed in the middle of the XIV century when Manresa and its surrounding were suffering severe drought. This hydraulic infrastructure is still considered an important architectural work to provide water to the city in addition to prevent some alterations in the freshwater composition from the Llobregat River resource.

Once water from Parc de l'Agulla reaches the DWTP, predisinfection is applied in order to remove some microorganisms and guarantee the effectiveness of the next steps. Almost simultaneously, coagulation step adding polyaluminum chloride (PAC) is performed with the intention to reduce particulate and colloidal matter present in natural surface waters. Next step is based on slow filtration through sand beds where suspended substances are retained before the final disinfection step. Chlorine gas is the disinfectant and oxidant agent employed for pre and final disinfection steps.

Pretreated water for laboratory experiments was collected after sand filtration, just before final disinfection where major formation of THM takes place. It is important to consider the presence of free chlorine in water samples, which was removed adding sodium metabisulphite after sample collection avoiding dameges in NF membrane during filtration experiments.

An extensive evaluation for NF membranes performance in the laboratory set-up was carried out in three campaigns of 15 days of duration each one, considering the seasonal variation of the raw water under study (July 2009, November 2009 and March 2010). Conventional pretreated water collected from the DWTP plant was analyzed in order to characterize main quality parameters of the feed water. Mean values for each experimental campaign are shown in Table 4.1.

Table 4.1: Averaged values determining the main feed water composition for NF system in the three campaigns performed

| Parameter | Units | July 2009 | November 2009 | March 2010 |
|---|---|---|---|---|
| $Ca^{2+}$ | ($mg \cdot L^{-1}$) | 75.1 ± 2.8 | 89.3 ± 5.0 | 91.3 ± 2.4 |
| $Mg^{2+}$ | ($mg \cdot L^{-1}$) | 12.1 ± 0.3 | 11.0 ± 0.2 | 17.2 ± 0.8 |
| $Na^{+}$ | ($mg \cdot L^{-1}$) | 20.5 ± 5.0 | 33.3 ± 0.7 | 31.8 ± 1.8 |
| $K^{+}$ | ($mg \cdot L^{-1}$) | 2.10 ± 0.2 | 1.64 ± 0.1 | 2.41 ± 0.2 |
| $F^{-}$ | ($mg \cdot L^{-1}$) | 0.25 ± 0.08 | 0.12 ± 0.00 | 0.15 ± 0.02 |
| $NO_3^{-}$ | ($mg \cdot L^{-1}$) | 0.82 ± 0.2 | 3.81 ± 0.4 | 7.09 ± 1.6 |
| $Cl^{-}$ | ($mg \cdot L^{-1}$) | 34.1 ± 2.4 | 45.9 ± 2.9 | 41.4 ± 4.2 |
| $SO_4^{2-}$ | ($mg \cdot L^{-1}$) | 104 ± 10 | 94.5 ± 3.7 | 98.4 ± 4.0 |
| $HCO_3^{-}$ | ($mg \cdot L^{-1}$) | 186 ± 4 | 177 ± 2 | 177 ± 1 |
| NPOC | ($mg \cdot L^{-1}$) | 3.9 ± 0.9 | 1.9 ± 0.4 | 3.1 ± 0.4 |
| Conductivity | ($\mu S \cdot cm^{-1}$) | 536 ± 41 | 543 ± 10 | 616 ± 32 |
| UVA | | 0.071 ± 0.013 | 0.046 ± 0.008 | 0.071 ± 0.007 |
| pH | | 7.78 ± 0.12 | 7.82 ± 0.16 | ± 0.10 |

### 4.2.1.2. Evaluation of THMFP reduction in Llobregat River system

The experimental campaign in the Llobregat's hydric system was performed during ten days in May 2010. Five water samples were collected in different points indicated in Figure 4.1.

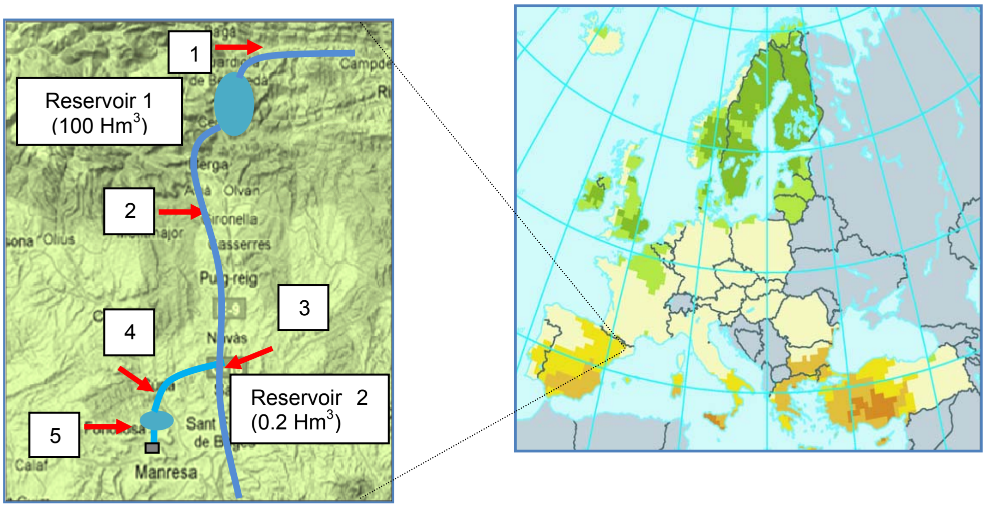


Figure 4.1: Selected hydric system in the NE of Spain (European map in Chapter 1). Sampling points in the hydric system selected: 1) Pobla de Lillet; 2) Gironella; 3) Balsareny; 4) Parc de l'Agulla; 5) DWTP in Manresa

The first three points are part of Llobregat River. On the other side, point 4 and point 5 are located in the inlet to the reservoir in Parc de l'Agulla and after the sand filtration in the

DWTP, respectively. Table 4.2 indicates the main composition for raw water samples collected in each point.

Table 4.2: Punctual water composition analyzed in the five sampling points selected

| Parameters | Units | Point 1 | Point 2 | Point 3 | Point 4 | Point 5 |
|---|---|---|---|---|---|---|
| $Ca^{2+}$ | $(mg \cdot L^{-1})$ | 59 | 98 | 93 | 78 | 85 |
| $Mg^{2+}$ | $(mg \cdot L^{-1})$ | 2.2 | 12 | 13 | 13 | 13 |
| $Na^{+}$ | $(mg \cdot L^{-1})$ | 2.9 | 20 | 20 | 21 | 21 |
| $K^{+}$ | $(mg \cdot L^{-1})$ | 0.4 | 1.5 | 1.7 | 1.7 | 1.6 |
| $NO_3^{-}$ | $(mg \cdot L^{-1})$ | 2.4 | 2.6 | 3.8 | 2.6 | 1.9 |
| $Cl^{-}$ | $(mg \cdot L^{-1})$ | 6.2 | 29 | 29 | 25 | 30 |
| $SO_4^{2-}$ | $(mg \cdot L^{-1})$ | 4.7 | 109 | 101 | 78 | 103 |
| $HCO_3^{-}$ | $(mg \cdot L^{-1})$ | 152 | 179 | 182 | 176 | 162 |
| NPOC | $(mg \cdot L^{-1})$ | 0.69 | 1.8 | 2.1 | 2.2 | 2.5 |
| Conductivity | $(\mu S \cdot cm^{-1})$ | 323 | 626 | 557 | 581 | 554 |
| pH | | 8.21 | 8.26 | 8.34 | 8.22 | 8.05 |

Point 1 is very close to the Llobregat River spring, consequently its salt content is lower than in the rest of the studied points, as it is observed from their conductivity values. Approximately 50 km downstream of the River spring, water has dissolved the maximum of mineral salts present in soils and rocks surrounding the riverbed. However, none of the sample points present bromide anion because among other reasons (geological) the hydric system selected avoid passing through the potash exploitation (Valero and Arbós, 2010).

Organic contents increase through the river course indicating possible vegetal and algae growth downstream. The first noticeable increase takes place after the first reservoir (La Baells). Second increase is observed between point 4 and point 5 as a result of the second but small reservoir considered in this study. To avoid severe clogging of NF membranes using directly the raw water collected, water samples were previously filtered through glass-fiber filters 0.45 µm (Millipore).

### 4.2.2. Membrane laboratory set-up (flat sheet)

Experiments in laboratory were carried out using a SEPA CFII module (GE-Osmonics), where one flat sheet membrane was disposed in the cell for each daily test. Figure 4.2 shows a picture of the experimental set-up employed in the laboratory and the flow diagram in order to indicate the main elements and streams entering and leaving the module. Experimental comparison tests require the same operational conditions for each membrane in order to obtain reproducible results.

Operational conditions were fixed as close as possible to real conditions for NF processes in drinking water applications. Feed pressure was established in a range from 3 to 15 bars, samples of NF permeates were collected every 3 bars of pressure. Initial and final samples of feed solution were also collected before and after the experiments for all tests. Apart of samples collected for analytical determinations, permeate flow was measured for each feed pressure to calculate the permeability of membranes, by dividing flow values per membrane area and trans-membrane pressure (TMP). Permeability will be related to NF production capacity for a real plant.

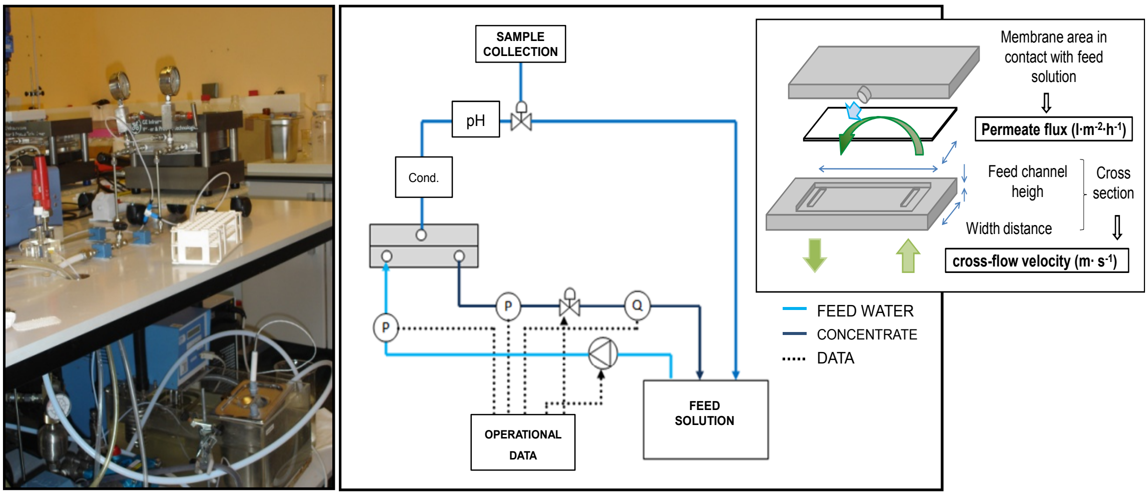


Figure 4.2: Images of the laboratory experimental set-up using SEPA CFII module for flat sheet membrane configuration

Another hydraulic factor to consider during operation in membrane filtration working at cross-flow mode, is the superficial velocity of water passing over the surface of membrane. For these laboratory experiments cross-flow velocity was fixed near to 1 $m \cdot s^{-1}$ with a feed flow of 250 $l \cdot h^{-1}$. Temperature was maintained nearly constant at 25 ± 2 °C during the filtration experiments.

The experiments to evaluate NF effectiveness in different points through the selected hydric system were carried out at three pressures of 2, 4 and 6 bars. The rest of operational conditions were maintained at the same values as mentioned before.

Determinations of THMFP in laboratory scale were carried out for feed water and permeate samples, these obtained at the median pressure of the range, at 4 bars.

### 4.2.3. Commercial NF membranes tested and pretreatment

All membranes employed in this part were supplied in flat sheet form by their manufacturers. Table 4.3 presents the commercial NF membranes during the laboratory experimentation and their respective manufacturer. Preconditioning of flat sheet membranes was always the same, at least 12 hour soaking in deionized water. Once the membrane is in the cell, pressure was slowly increased until the maximum value of the experiment, and then running at this value during 1 hour.

Table 4.3: Commercial NF membranes tested in laboratory experimentation

| Supplier | model | Supplier | model |
|---|---|---|---|
| Dow Chemical | NF 270 | Hydranautics | ESNA1 LF2 |
| Dow Chemical | NF 200 | Koch | TFCS-SR3/100 [a] |
| Alfa Laval | NF 99 | Koch | TFCS |
| Osmonics | DK | Koch | TFCS-SR2 [b] |
| Osmonics | DL | Iberlact | PC D400 |

[a] TFC-SR3 from Koch is the current TFC-SR100
[b] Koch stop producing TFC-SR2

All the membranes indicated above were used for comparison in the first part of the laboratory test comparison, but in the second experimental part, only TFC-SR100, NF270 and ESNA1LF2 were the membranes selected due to the performance results in the first part. NF270 and ESNA1LF2 were also compared in front of trace elements rejections, such as arsenium, chromium, molybdenyum between others.

### 4.2.4. Analytical methods

Results from experimentation are expressed as a rejection for different inorganic and organic parameters. To calculate solutes rejection, feed water and permeate samples are analyzed in order to obtain the value from the following equation:

$$R\,(\%) = \left(1 - \frac{C_{p,i}}{C_f}\right) \cdot 100$$

Where $C_{p,i}$ and $C_f$ are the concentration of the solute in permeate and feed water samples, respectively.

Conductivity was measured at the start and the end of each experiment, to have the average value for this parameter representing the total salts dissolved in feed solution. For permeate samples, conductivity was determined on-line using a conductivity cell (Crison 53 92). For pH determinations the procedure was the same using a pH electrode (Crison 53 03).

Specific inorganic solutes were determined as major inorganic ions detected: $Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, $K^{+}$, $SO_4^{2-}$, $NO_3^{-}$, $Cl^{-}$ and $F^{-}$ by ionic chromatography analysis (Dionex ICS-2100). The columns used for cations and anions were CS16 and AS19 from Dionex, respectively. Mobile phase for the former contained 30 mM of methanosulphonic acid and for the latter was 10 and 45 mM of KOH. Inductively coupled plasma mass spectrometry (ICP-MS), Agilent 7500cx was used to analize trace elements in feed and permeates samples from NF270 and ESNA1LF2 membranes.

Inorganic carbon (IC) was analyzed by Total Carbon (TC) Analyser. Shimadzu 5050A was the instrument used in July and November campaigns (2009), but in campaigns performed in March and May 2010, a new TC analyser Analytikjena Multi N/C 3100 was employed. The same instruments were used to determine organic carbon as non purgable organic carbon (NPOC) presenting noticeable limits of detection (LOD), specified at 100 and 50 $\mu g \cdot L^{-1}$ for the former and the latter instrument, respectively.

Ultraviolet light absorbance (UVA) was measured using a spectrophotometer (Shimadzu UV_1603).

THMFP was determined applying the 5710B standard method and THM concentrations were analysed by head space gas chromatography coupled to electron capture detector (AWWA, 1998), HS-GC/ECD (Agilent 7694E- Hewlett Packard 6890 series). THM concentrations takes into account the quantified levels in $\mu g \cdot L^{-1}$ of TCM, BDCM, DBCM and TBM. The column employed was DB624 from Agilent.

## 4.3. RESULTS AND DISCUSSION

### 4.3.1. Testing different NF membranes to improve drinking water quality

Rejection capacity for different commercial NF membranes was evaluated in three campaigns considering inorganic and organic parameters rejection in front of membrane productivity.

#### 4.3.1.1. Major inorganic ions rejection

Conductivity measurements give an idea of the dissolved salt content in water. Figure 4.3 shows percentage of conductivity reduction in permeate side for each tested membrane in front of the permeate flux for July 2009, November 2009 and March 2010.

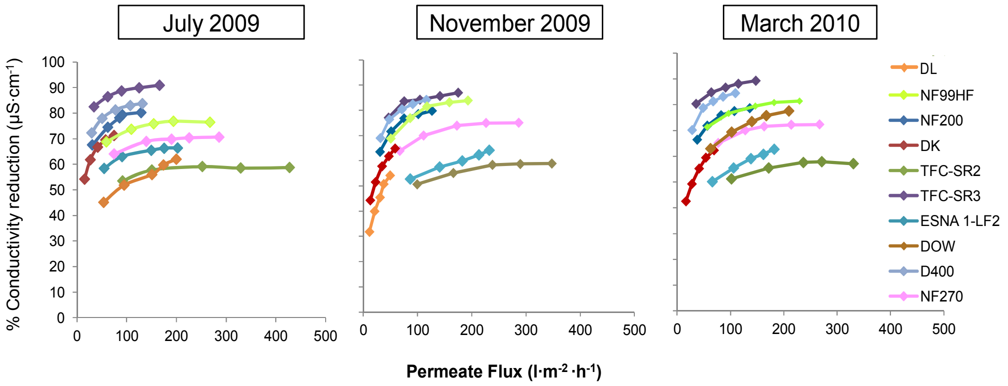


Figure 4.3: Capacity for each tested NF membrane to reduce conductivity in front of permeate flux

Permeate flux obtained for each membrane at different feed pressures give an idea of NF productivity treating the feed solution, in this case, real pretreated water from a DWTP. TFC-SR2 and NF270 are the most permeable commercial membranes in front of the feed water of concern, in spite of DK and DL membranes that showed the lowest permeate fluxes.

In case of requiring higher conductivity reductions in permeate flow, the most suitable membranes would be TFC-SR3, D400 and 99HF as shown in Figure 4.3. However conductivity represents the sum of al cation and anions in solution, for this reason is also important to distinguish NF membrane separation for main inorganic ions.

In Figure 4.4 is represented total inorganic carbon, where at the pH between 7 and 8 of the solution, bicarbonate ($HCO_3^-$) is the main important chemical form.

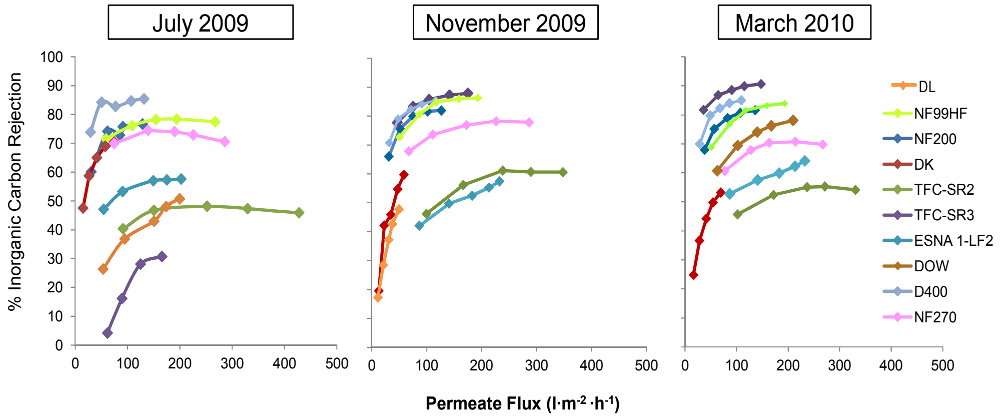


Figure 4.4: Rejection of inorganic carbon (IC), mainly as bicarbonate form ($HCO_3^-$), in front of permeate flux for each tested NF membrane

As in case for conductivity reduction, TFC-SR3, D400, 99HF and NF200 are the most impermeable to $HCO_3^-$ ions. In this case, higher contents of bicarbonate in permeate side may prevent post-treatment requirements to maintain corrosion under control. Consequently, membranes with lower rejection in front of inorganic carbon have a special interest in freshwater treatment for drinking water proposals, providing higher water permeate fluxes at lower feed pressures, such as TFC-SR2, NF270 and ESNA1LF2.

Another major inorganic anion with a relevant importance is sulphate, although in this case levels in raw water are not problematic, in some regions sulphate content have reached levels close to legislated standards (Bertrand et al., 1997). Generally, Figure 4.5 indicates a high rejection for this divalent anion for tested NF membranes.

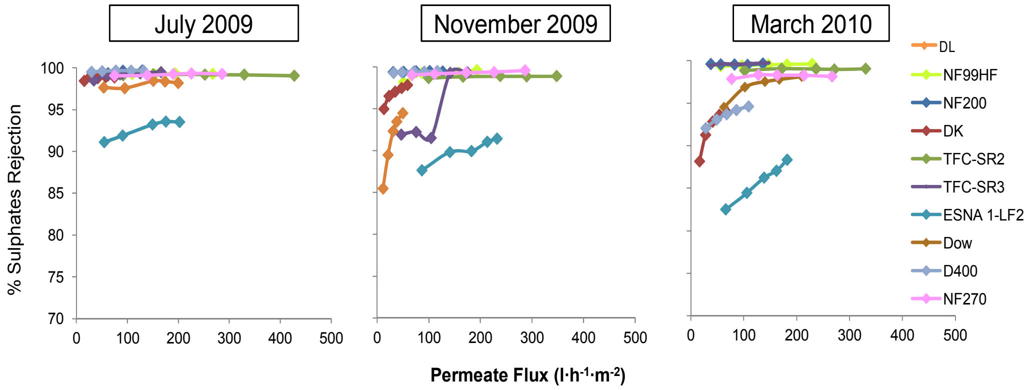


Figure 4.5: Sulfates rejection ($SO_4^{2-}$) in front of permeate flux for each tested NF membrane

From results regarding sulfates in permeate side, all membranes presented rejections higher than 70%. In order to differentiate between tested membranes, y-axis in Figure 4.5 has been augmented. NF membranes are characterized with negative charge in the surface side in contact with the feed water, then is seems obvious that divalent anion are more rejected than monovalents, such as the case of $HCO_3^-$. ESNA1LF2 present a different behavior compared with the rest of NF membranes than reject sulfate at higher values than 95%. This fact is strange because, usually NF membranes are designed to have this high capacity of rejection.

Results indicated above show different rejection capacities between monovalent and divalent anions. Chloride, nitrate and fluoride were also evaluated in this laboratory experiments using flat sheet configuration (Figure 4.6, Figure 4.7 and Figure 4.8).

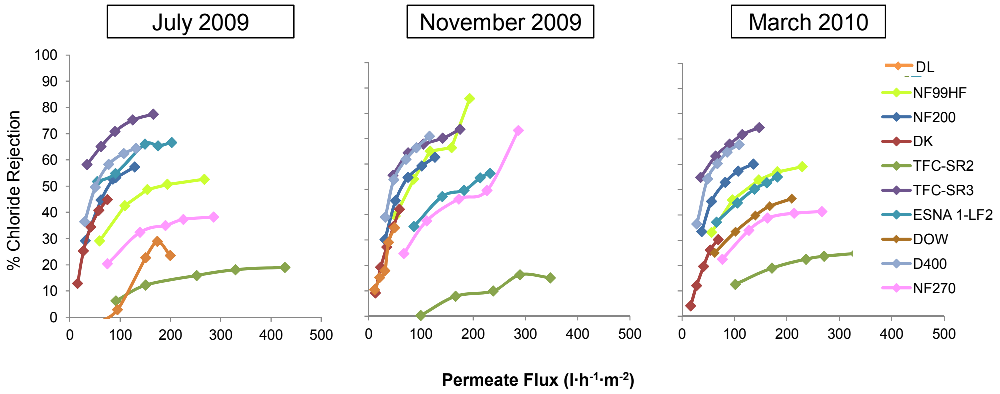


Figure 4.6: Chloride rejection ($Cl^-$) in front of permeate flux for each tested membrane

Chloride separation using NF membranes is not as effective as in the case of sulfates (Figure 4.5), rejection for $Cl^-$ anion is observed between a wide range, from 0% in the worst case to 70% in the best one using TFC-SR3. This NF membrane from Koch seems the most impermeable to all kind of anions, associated with expected lower flux permeates probably because pore size distribution is smaller. These characteristics also are observed for D400 and NF200 from Interlact and DOW Chemical, respectively.

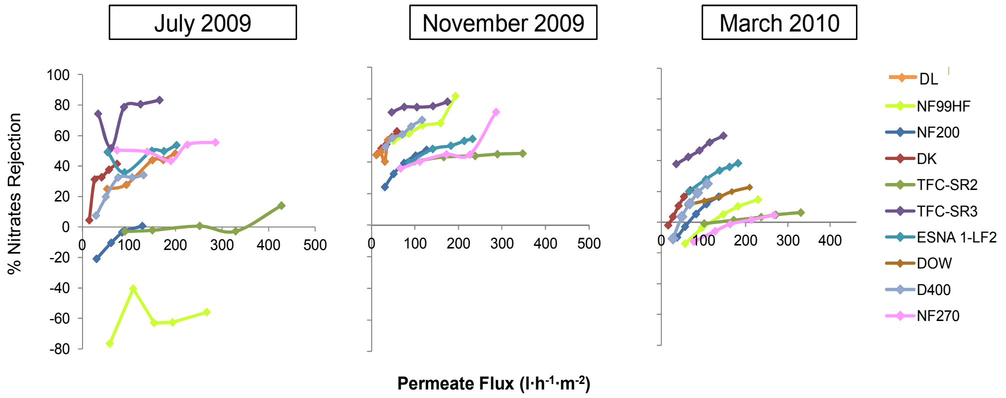


Figure 4.7: Nitrates rejection ($NO_3^-$) in front of permeate flux for each tested NF membrane

Rejection for nitrates is variable for all membranes finding rejection values from 0% to 70%, the same behavior for than in the case of chloride. From results obtained in July 2009, it is important to notice that nitrates in permeate were measured near to limit of quantification.

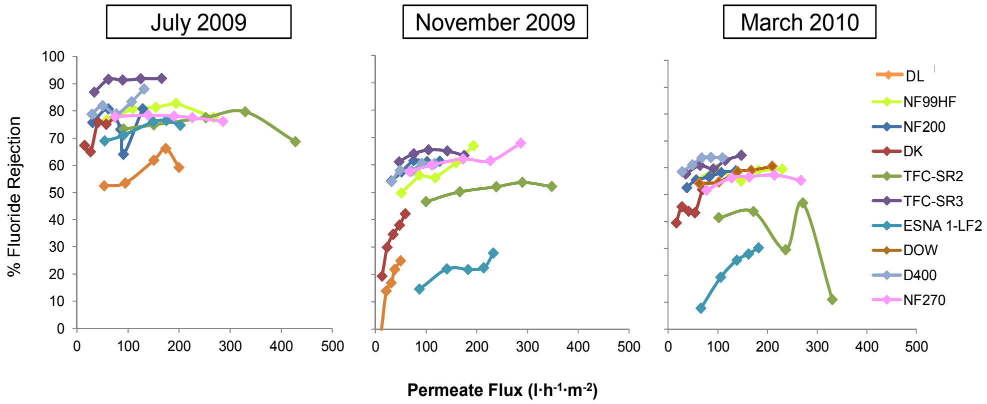


Figure 4.8: Fluoride rejection ($F^-$) in front of permeate flux for each tested NF membrane

Fluoride levels were higher in feed water for July 2009 campaign (Table 4.1) and this may lead to higher rejection during this period. However, it seems interesting than although the concentrations detected in feed water and permeate are lower than those obtained for nitrates, rejection values for $F^-$ can be slightly higher, between 40% and 80%, for most of membranes. Unfortunately, these differences can be a consequence of analytical limitation, associated to detection and quantification levels for these monovalent anions in feed and permeate sides.

Results for major anions have been compared with those obtained for major cations in order to compare separation capacities of the tested membranes. A part of the influence of charge effects in solutes separation, hindrance effects regarding solutes size is another important separation mechanism in NF process. Figure 4.9 and Figure 4.10 show rejection for calcium and magnesium as major divalent cations present in feed water ($Ca^{2+}$). These cations also have a special interest because are responsible of water hardness.

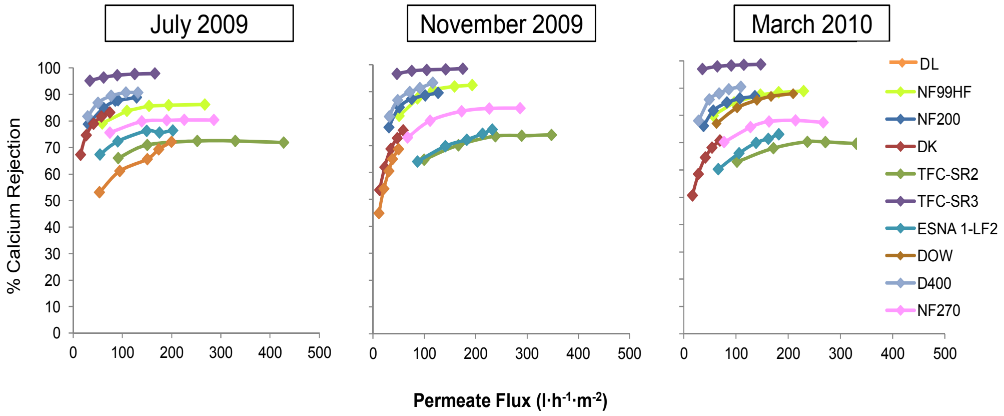


Figure 4.9: Calcium rejection ($Ca^{2+}$) in front of permeate flux for each tested NF membrane

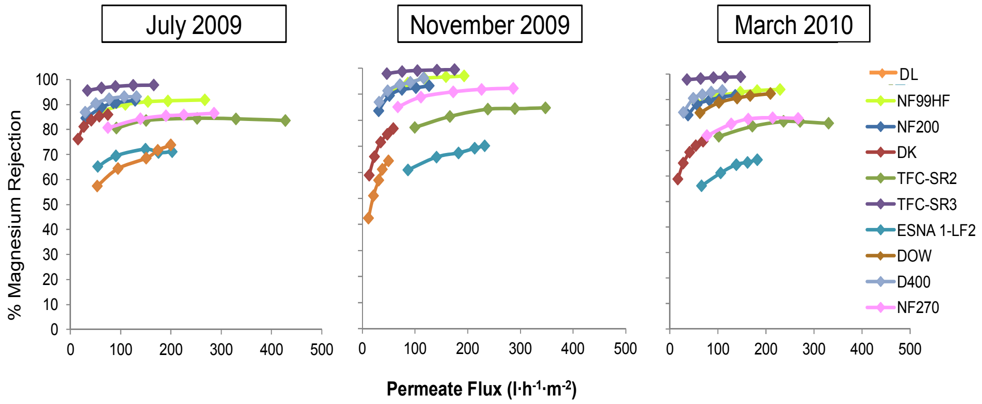


Figure 4.10: Magnesium rejection ($Mg^{2+}$) in front of permeate flux for each tested NF membrane

Similar rejections are obtained for magnesium and calcium cations, their size is bigger than other cations presenting sieving effect as a major separation mechanism involved in their rejection. For more permeable membranes TFC-SR2 and NF270, rejections are around 75% instead of the higher values around 90% obtained for less permeable membranes (TFC-SR3, D400, NF200 or 99HF). Partial reduction of $Ca^{2+}$ and $Mg^{2+}$ has beneficial effects in potable water quality because associated precipitations of $CaCO_3$ or $MgCO_3$ (in the installations or household appliances) can be diminished. The content of salts in the permeate side also avoids corrosion of metallic infrastructures (pipes) which can be controlled with Langelier saturation index (LSI).

Figure 4.11 and Figure 4.12 show the case of sodium and potassium as monovalent cations.

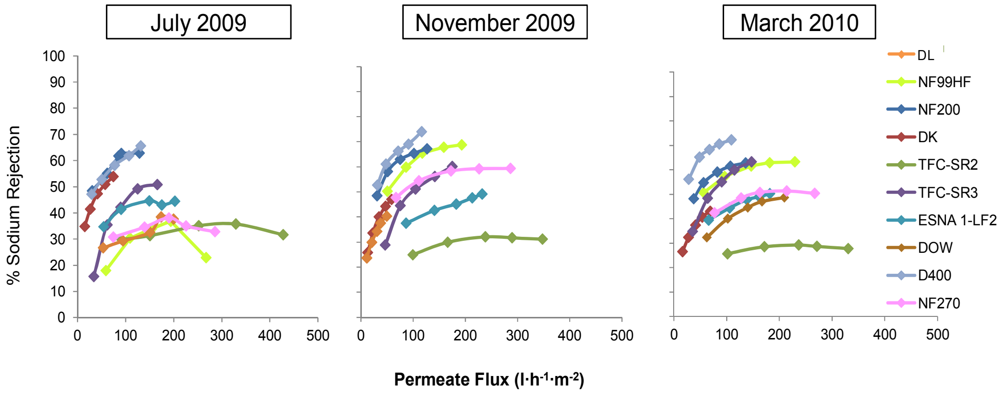


Figure 4.11: Sodium rejection ($Na^{+}$) in front of permeate flux for each tested NF membrane

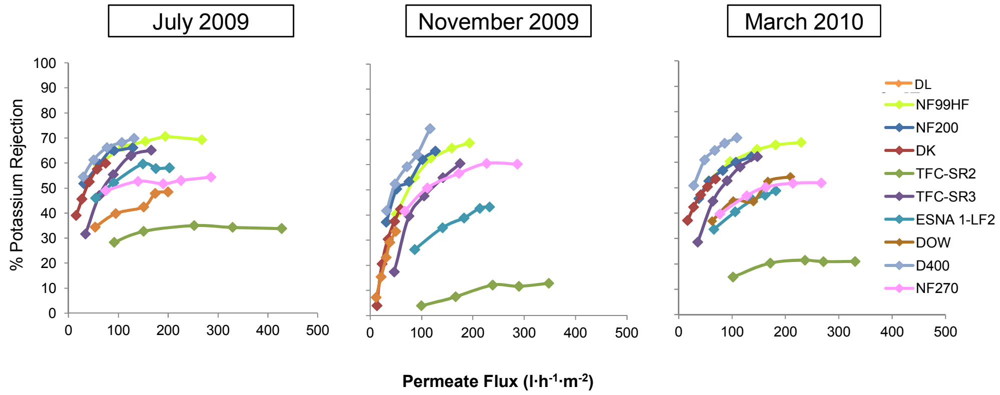


Figure 4.12: Potassium rejection ($K^+$) in front of permeate flux for each tested NF membrane

Similar rejection is obtained in case of sodium and potassium rejection. Behavior of different membranes follow the same tendencies for both cations in all campaigns although its initial concentration in feed water is different, between 20 and 30 mg·L$^{-1}$ for $Na^+$ and around 2 mg·L$^{-1}$ for $K^+$. This fact indicates again the opposite relation between permeate flux and monovalent and small solutes rejection, being TFC-SR2 the most permeable water at the same time that is unable in most of cases to reduce monovalent ions at higher percentages of 40% (also see Figure 4.6, Figure 4.7 and Figure 4.8 for monovalent anions rejection).

#### 4.3.1.2. Organic parameters rejection

NF membranes have been applied in a high number of applications in order to decrease organic matter and specific organic compounds. Results in this part show typical parameters regarding organic contents, for example the absorbance of ultraviolet (UVA) light is reduced in the permeate samples, having important implications in the reduction of precursor material for DBP formation. Figure 4.13 demonstrates the capacity of UVA reduction for each NF membrane in all campaigns.

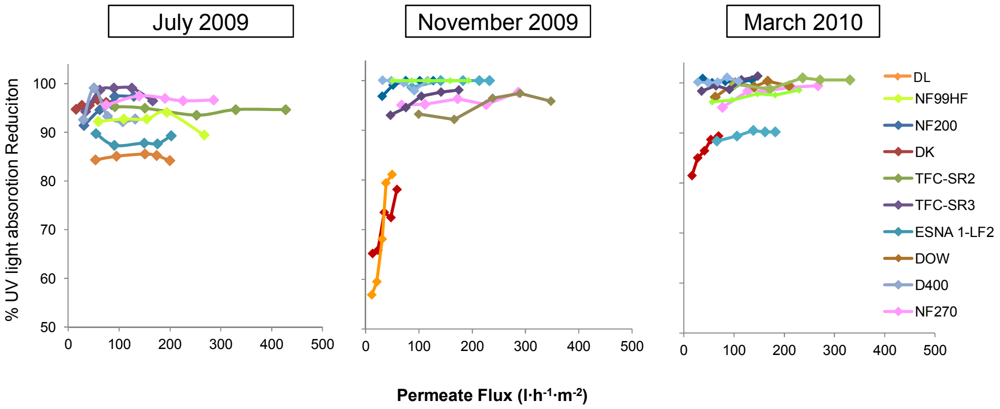


Figure 4.13: Percentage of reduction of ultraviolet absorbance (UVA) using different NF commercial membranes in the laboratory scale

The reduction of organic part which absorbs ultraviolet light is effectively removed from drinking water by NF membranes, generally over 90%, although UVA variability in raw water as a result of seasonal variations (Table 4.1). Some exceptions were observed for DL and DK, and punctually for ESNA1LF2 with rejections lower than 90%.

Content of organic carbon is coincident with higher values of UVA in the feed water studied (Table 4.1). Rejection values for NPOC contents are shown in Figure 4.14 only for the experimental campaign carried out in March 2010. In July and November 2009, analytical instrument has a higher limit of quantification for NPOC, consequently concentration in permeate samples was not quantified.

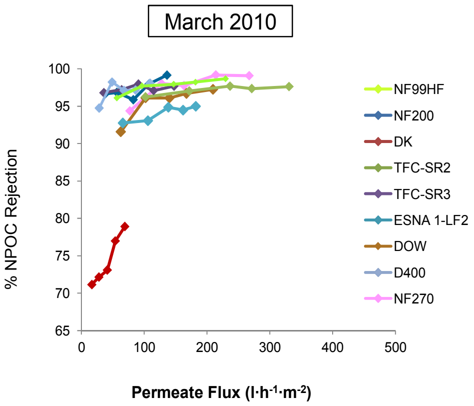


Figure 4.14: NPOC rejection in front of permeate flux for each tested membrane in March 2010

All NF membranes are able to reject NPOC contents in feed water at percentages higher than 90%, in exception of DK membrane which NPOC rejection was found between 70 and 80%. From these results is obvious the high effectiveness of NF to eliminate DBP precursor material in produced water. In this case, more permeable membranes as NF270 and TFC-SR2 have similar organic rejection than less permeable membranes (Figure 4.13).

#### 4.3.1.3. Reduction in trihalomethanes formation

Trihalomethanes formation potential (THMFP) was determined for experimental campaigns carried out in November 2009 and March 2010. Figure 4.15 shows the results obtained for each commercial NF membrane tested in the flat sheet module.

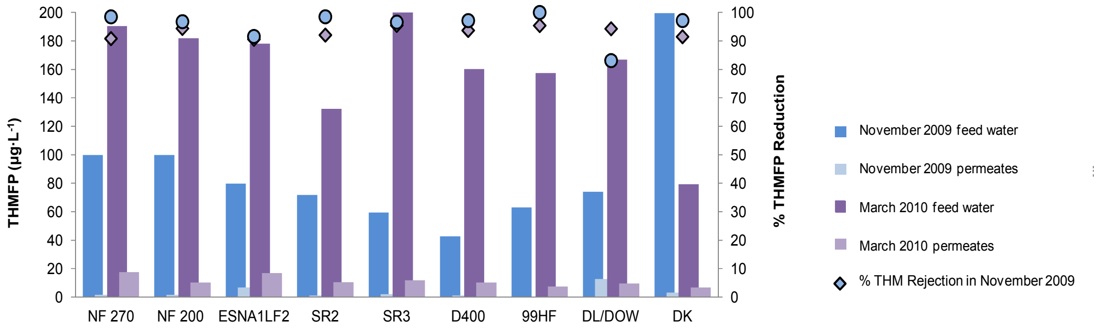


Figure 4.15: Determination of THMFP for feed water and permeates for membranes tested in November 2009 and March 2010 campaigns with the obtained reduction

In feed water, high values of THMFP were obtained as a result of high precursor material content in the water samples. It can be observed that in March 2010 existed higher possible formation for THM than in November 2009, indicating the existence of seasonal effects on raw water quality. In both experimental campaigns, strong disinfection conditions were employed in laboratory scale in accordance to standard method 5710B (AWWA, 1998) for feed water and permeate samples. NF membranes showed reduction of THMFP higher than 90% in most cases, whatever is THMFP value in feed water. It is important to notice that more permeable membranes also offer high effectiveness in the reduction of THM for final water produced by NF (TFC SR2 and NF270).

Feed water employed presented levels of chlorine, thus THM were previously formed before NF experiments in the laboratory set-up. The THM concentrations quantified in the pretreated water were required to calculate THMFP for prechlorinated waters, and at the same time they were useful to compare rejection capacity of NF membranes in front of THM formed in the pre-treatment, as Figure 4.16 indicates.

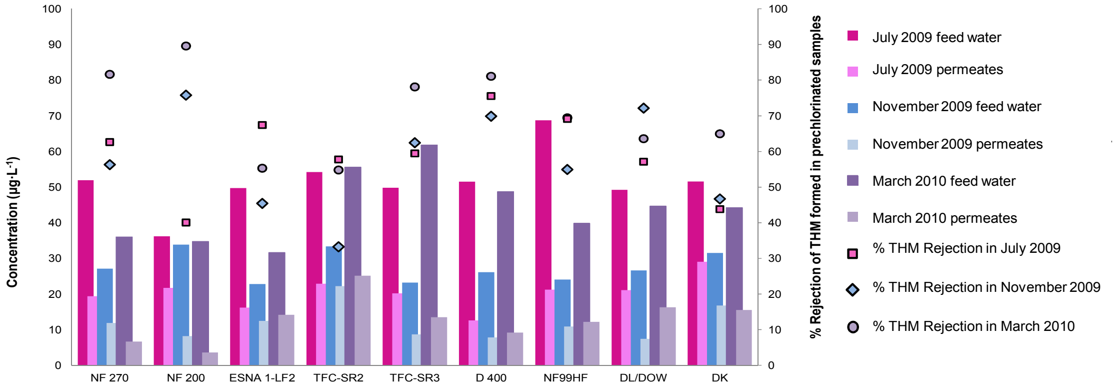


Figure 4.16: THM concentrations in feed and permeate samples in the July 2009, November 2009 and March 2010 and rejection of these compounds by the tested NF membranes

THM are small and neutral compounds able to pass through NF membranes, consequently partial rejection was observed for all membranes tested (between 40% and 80%). It is difficult to predict the best membrane in order to reject these small, neutral but polar compounds because no tendency seems observable along to the three experimental campaigns.

The highest levels of THM were detected during the experimental campaign of July 2009, according to the hottest and sunniest period. This climate conditions lead to increase THM precursor material in waters (Baytak et al., 2008; Teixeira and Nunes, 2011). In this case, THM formed during prechlorination are more permeable than their precursors and lower and variable rejections are observed for NF membranes, from 30% to 90%. These results are in accordance to the small size and polar character for THM (Meylan et al., 2007).

### 4.3.2. Results about THMFP reduction through a selected hydric system

Determination of THMFP was carried out in several points of the Llobregat's hydric system. Figure 4.17 shows the results obtained for this parameter and the respective reduction using ESNA1LF2, NF270 and SR100 (TFC SR3) membranes in the laboratory with the NF set-up.

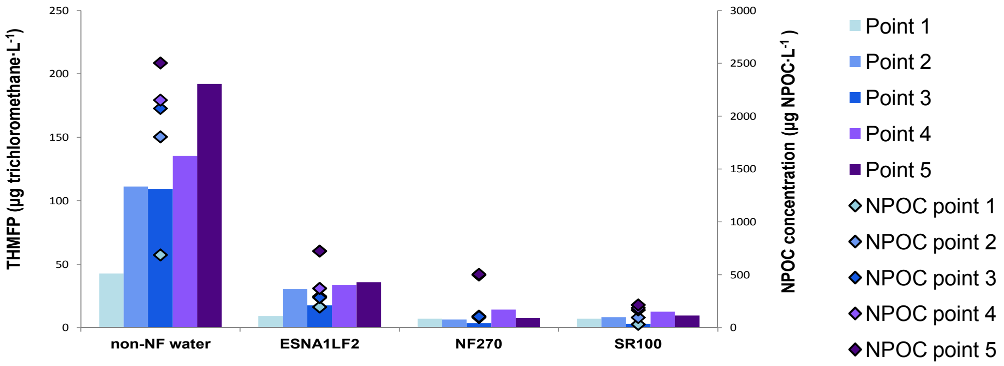


Figure 4.17: THMFP and NPOC reduction through the selected hydric system by three NF membranes. Point 1: Pobla de Lillet; Point 2: Gironella; Point 3: Balsareny; Point 4: Parc de l'agulla; Point 5: DWTP Manresa

THMFP has been related to organic carbon contents of water by analyzing NPOC. As it has been mentioned before, organic matter is a precursor material to form DBP, as in case of THM when chlorine or other halogenated disinfectant agents are employed, and results from Figure 4.17 confirm this fact. As a precursor material, higher NPOC contents in non-NF water lead to higher values for THMFP.

The map in Figure 4.1 indicates the presence of two water reservoirs for the selected hydric system. La Baells (100 $Hm^3$) is the first, between point 1 and point 2, and the small lake (0.2 $Hm^3$) in Parc de l'Agulla is the second, between point 4 and point 5. Although its difference in the volume storage of water, both contribute to nearly double the THMFP of freshwater through the selected hydric system in part of Llobregat River (Chellam et al., 2008; Chen et al., 2008; Yeh et al., 2000).

However, NF membranes tested in this study also show the high capacity to reduce THM concentrations in permeates. Results obtained indicate that NF270 and SR100 have higher capacity to decrease THMFP than ESNA1LF2, but SR100 showed lower water permeability (equivalent to TFC-SR3 in Figure 4.3 to 4.14).

### 4.3.3. Trace element rejection for selected membranes

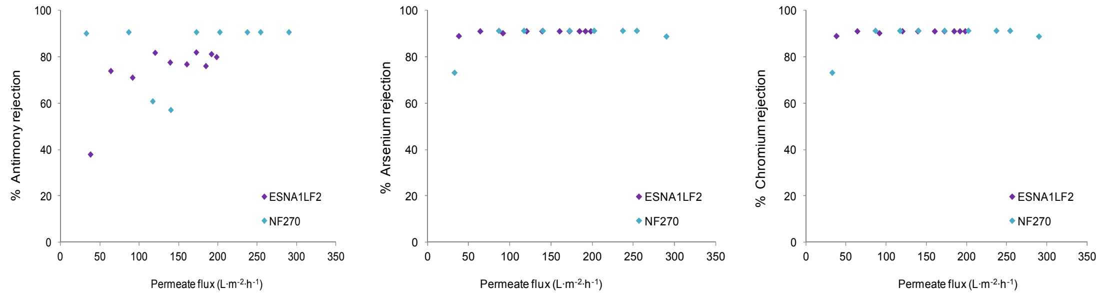
The additional experimentation carried out in order to elucidate NF capacity rejection in front of trace elements was evaluated for NF270 and ESNA1LF2. Trace elements analyzed are shown in Table 4.4, however not all have been detected in feed water, such as Be, Cd, Sn, Pb and Tl.

Table 4.4: Inorganic trace elements analyzed in order to compare NF270 and ESNA1LF membranes

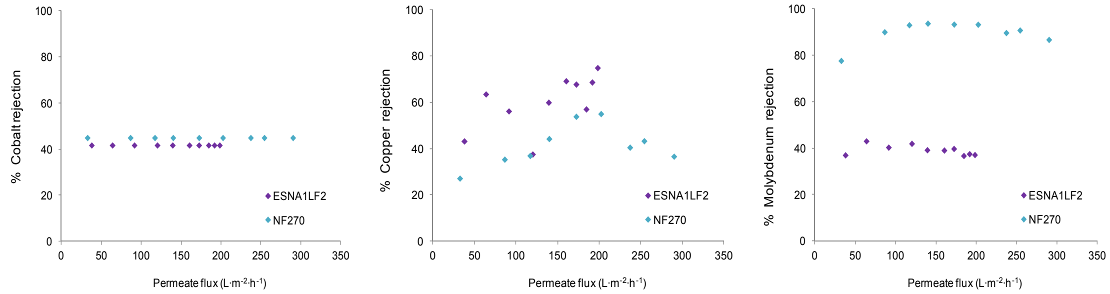
| Trace element | Feed concentration | LOD | Trace element | Feed concentration | LOD |
|---|---|---|---|---|---|
| Beryllium (Be) | < 0.1 $\mu g \cdot dm^{-3}$ | 0.1 | Selenium (Se) | 0.27 $\mu g \cdot dm^{-3}$ | 0.1 |
| Vanadium (V) | 0.45 $\mu g \cdot dm^{-3}$ | 0.1 | Molybdenum (Mo) | 1.41 $\mu g \cdot dm^{-3}$ | 0.05 |
| Chromium (Cr) | 0.97 $\mu g \cdot dm^{-3}$ | 0.3 | Cadmium (Cd) | < 0.05 $\mu g \cdot dm^{-3}$ | 0.1 |
| Cobalt (Co) | 0.18 $\mu g \cdot dm^{-3}$ | 0.1 | Tin (Sn) | < 0.1 $\mu g \cdot dm^{-3}$ | 0.1 |
| Nickel (Ni) | 0.69 $\mu g \cdot dm^{-3}$ | 0.3 | Antimony (Sb) | 0.55 $\mu g \cdot dm^{-3}$ | 0.05 |
| Copper (Cu) | 0.75 $\mu g \cdot dm^{-3}$ | 0.3 | Lead (Pb) | < 0.1 $\mu g \cdot dm^{-3}$ | 0.1 |
| Zinc (Zn) | 5.59 $\mu g \cdot dm^{-3}$ | 3 | Uranium (U) | 1.42 $\mu g \cdot dm^{-3}$ | 0.1 |
| Arsenic (As) | 0.50 $\mu g \cdot dm^{-3}$ | 0.05 | Thallium (Tl) | < 0.1 $\mu g \cdot dm^{-3}$ | 0.1 |

LOD: Limit of detection

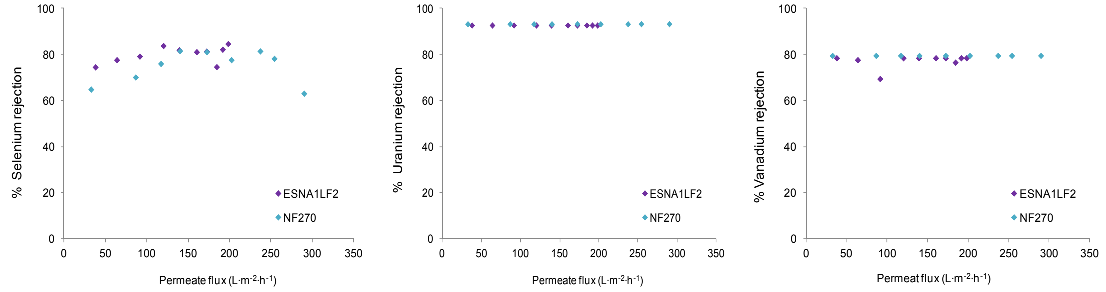
Figure 4.18 shows the rejection for some trace elements using both membranes for the punctual laboratory experiment operating in a range of feed pressure from 2 to 20 bars. Permeate sample was collected every 2 bars for ICP-MS analysis, at the same time of collection, permeate flow for each feed pressure was measured.



a) Sb b) As c) Cr



d) Co e) Cu f) Mo



g) Se h) U i) V

Figure 4.18: Trace elements rejection

In cases where concentration detected in permeate samples was lower than LOD, calculation for rejection was done considering LOD values (Co, As and U). As a result partial rejection can be obtained, making results interpretation complex for further prediction of separation capacities of NF in front of these elements.

From Figure 18 can be observed a common high rejections (>80%) for both NF membranes in case of As, Cr, U and V, although a clear difference was observed for molybdenum rejection, 90% for NF270 and 40% for ESNA1LF2. This could be explained if $MoO_4^{2-}$ is the predominant form for Mo, because NF270 has higher negative charge in its surface than

ESNA1LF2 and consequently higher repulsive forces and consequent higher rejections (see Chapter 5 and 6).

## 4.4. CONCLUSIONS

The experimentation performed in laboratory scale has been useful to compare different commercial NF membranes in terms of rejection capacities for a large number of parameters, such as major inorganic salts, organic carbon (NPOC and UVA) and trihalomethane formation potential (THMFP).

In addition, permeability measured for the wide range of commercial membranes showed great differences that can have important consequences in operational costs for real installations. In this sense, most of membranes with low permeability presented higher salts rejection, with implications in salt precipitation in the concentrate stream or requiring possible post-treatment for permeate stream. All this factors impact on energy and chemicals consumption during drinking processes and are important to consider when real NF process is planned to be implemented.

All membranes have reduced the content of THM precursors, expressed in this work as a reduction in ultraviolet light absorbance and THMFP. Both parameters have been rejected at higher percentages than 90% for all membranes.

From experimentation carried out in Llobregat River, the influence of water reservoirs is clearly evident increasing THMFP. Vegetal and algae growth specially takes place in stagnant waters where insulation is elevated, incrementing NOM contents as precursor material for THM. However, this study has demonstrated NF as an effective way to reduce DBP formation in these adverse conditions, when disinfection using chlorine under extreme conditions is employed in several points of a selected hydric system.

To finish with a first membrane screening in front of different constituents for a real water, NF270 and ESNA1LF2 were tested to observe their separation capacities in front of trace elements, indicating the apparent effectiveness of NF to remove heavy metals in case of water pollution. Under the experimental conditions carried out in this laboratory test (low concentrations in real water, metallic components in the set-up such as pump, pipes or valves) is difficult to predict the most effective membrane for trace elements rejection, however, NF270 showed better results for antimonium and molebdinum species rejection (> 80%) than ESNA1LF2 (40-80%).

In conclusion, TFC-SR2 and NF270 showed higher permeability and separation potentials, although the former currently is not produced by Koch. For further experimentation in pilot plant, NF270 and ESNA1LF2 were the selected membranes to be compared simultaneously.

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# Chapter 5: Pilot plant comparison study of two commercial nanofiltration membranes in a drinking water treatment plant

Parts of this chapter were based on:

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## 5.1. INTRODUCTION

Quality and quantity of freshwater resources in current world have been decreased in the last years. This fact has dramatic consequences in regions with water scarcity problems, such as the negative effects on the environment and the associated degradation of water resources for drinking supply. In some Mediterranean regions droughts often occur in cyclic periods endangering drinking water quality, furthermore water quality is usually deteriorated as a result of different pollution sources (industrial, agricultural, urban). Concurrently, increasing population get worsen the global water situation, requiring the implementation and development of new technologies into conventional processes for drinking water production.

Conventional treatments for drinking water are usually based in four main steps: predisinfection, coagulation, filtration and final disinfection. Variations of these processes are frequent due to the high variability of the water source quality and the different requirements of each country in the final drinking water quality. Disinfection is essential to control biological parameters in order to not endanger human health (Castro-Hermida et al., 2009). This key step could result into disinfection by-products (DBP) formation, for example trihalomethanes (THM) as the most well known DBP for its carcinogenic potential (Richardson et al., 2007; Wang et al., 2007).

When reduction of THM or other DBP is the main challenge in DWTP, different alternatives can be considered to lower NOM contents before disinfection. The enhancement of coagulation step can improve better settling of colloidal and diluted organic matter, hence reducing precursor material for DBP (Jacangelo et al., 1995). Later, other separation techniques were also applied in DWTP to reach the same goal, as the case of activated carbon mainly in granulated (GAC) form, or membrane technology to increase selectivity in filtration steps (Jacangelo et al., 1995; Kim and Kang, 2008). In this way, nanofiltration (NF) was also evaluated in drinking water process in order to reduce disinfection by-products formation (Agbekodo, 1994; Amy et al., 1990; Bellona et al., 2004; Chellam et al., 2008; Liikanen et al., 2003; De la Rubia et al., 2008; Visvanathan et al., 1998; Yeh et al., 2000).

One of the major advantage of NF consists in providing a compact barrier able to maintain constant the permeate quality independently of variations in feed water (Yeh et al., 2000). When moderate to high contents of inorganic salts are present in raw water, NF can be more efficient to obtain the desired quality because lower energetic cost is required than reverse osmosis (RO), for example for brackish water (Duran and Dunkelberger, 1995).

Furthermore, NF and RO membranes present similar separation capacity for natural and some synthetic organic compounds including pesticides, pharmaceuticals, personal care products (Kimura et al., 2003; Koyuncu et al., 2008; Radjenovic et al., 2008; Verliefde, 2008), and inorganic solutes, such as nitrates (Bertrand et al, 1997; Santafé-Moros et al., 2007), fluoride (Tahaikt et al., 2008) or heavy metals (Murthy et al, 2009; Plakas and Karabelas, 2012; Van der Bruggen et al., 2001).

In 2001 one of the largest nanofiltration plant was built in the city of Boca Raton (Florida), to treat underground water for drinking water purposes (Duran et al., 1995; Escobar et al., 2000). In Paris, Mery-sur-Oise DWTP treats freshwater through NF process using NF200 membranes to remove pesticides and reduce DBP formation (Cyna et al., 2002; Ventresque et al, 2000). The main problems of NF technology are the high energy requirements in comparison to conventional processes and the fouling tendency of membranes which increase flux decline, decreasing membrane performance (Costa and the Pinho, 2006; Van der Bruggen et al., 2008).

Laboratory and pilot plant studies are recommended to investigate flux decline, fouling type and availability to remove undesirable compounds in NF processes for different types of water composition and operational parameters (Boussahel et al., 2002; Cho et al., 1999; Jarusutthirak et al., 2007; Van der Bruggen et al., 2003). For example, productivity and selective rejection of water components can vary from one commercial NF membrane to another, having direct consequences on the drinking water price or final quality and requiring correct selection of the membrane for a concrete application (Her et al, 2000; Her et al., 2007; Sentana et al., 2010; Uyak et al., 2008).

Preliminary pilot plant study is useful in addition to suppliers' specifications to design, operate and monitored correctly to maintain quality and flow permeate (Liikanen et al., 2003). Membrane process efficiency and life time is highly influenced by the pretreatment, which can reduce fouling phenomena in membranes (Escobar et al., 2000; Her et al., 2000). Microfiltration (MF) or ultrafiltration (UF), adsorption techniques (GAG, ionic exchange resins) (Hilal et al., 2004; Kim et al., 2007; Wend et al., 2003; Boyer et al., 2005) are used individually or as a combination to prevent fouling. Chemical cleaning should be able to recover initial membrane productivity (Al-Amoudi and Lovitt, 2007). In this sense the effectiveness of some cleaning practices were checked in the present work at pilot plant and laboratory scale (Bernat et al., 2011).

The objective of this work is study the performance in a pilot plant for two commercial NF membranes selected from laboratory experimentation: NF270 (DOW Chemical) and ESNA1LF2 (Hydranautics) (Ribera et al, 2013). Their differences regarding operational parameters and rejection capabilities (inorganic and organic components) are evaluated during 6 months in order to select the most suitable membrane for a real installation. A two-stage pilot plant was designed and installed in the DWTP of Manresa, where approximately 23000 m$^3$/day of drinking water are produced from a concrete freshwater source located in this area. Furthermore, an UF step was installed as a pretreatment to provide the desired water quality to feed NF membranes. Daily monitoring was performed in order to control NF process in terms of transmembrane pressure, feed water recovery or conductivity reduction in permeate side.

## 5.2. MATERIALS AND METHODS

### 5.2.1. Feed water quality

Water from drinking water treatment plant (DWTP) in Manresa (NE of Spain) was used in this study and it was extensively described in Chapter 4. The average composition of water which feed the pilot plant is shown in Table 5.1 and comes from the output of sand filtration step, before final disinfection for distribution.

Table 5.1: Average composition of the conventional pretreated water used to feed the pilot plant

| Parameter | Average value | Standard deviation | Parameter | Average value | Standard deviation |
|---|---|---|---|---|---|
| Conductivity (µS·cm$^{-1}$) | 570 | 30 | NPOC (µg·L$^{-1}$) | 2560 | 540 |
| pH | 7.8 | 0.2 | $Ca^{2+}$ (mg·L$^{-1}$) | 82 | 9 |
| NPOC (µg·L$^{-1}$) | 2560 | 540 | $Mg^{2+}$ (mg·L$^{-1}$) | 12 | 2 |
| UVA (254 nm) | 0.039 | 0.015 | $Na^{+}$ (mg·L$^{-1}$) | 20 | 6 |
| THMPF (µg·L$^{-1}$) | 120 | 40 | $K^{+}$ (mg·L$^{-1}$) | 2.0 | 0.5 |
| SDI | 5.2 | 1.7 | Sr (mg·L$^{-1}$) | 1.05 | 0.05 |
| Al (µg·L$^{-1}$) | 51 | 13 | Si (mg·L$^{-1}$) | 0.91 | 0.93 |
| Ba (µg·L$^{-1}$) | 43 | 10 | $HCO_3^{-}$ (mg·L$^{-1}$) | 175 | 8 |
| $Fe_{total}$ (µg·L$^{-1}$) | 7.5 | | $SO_4^{2-}$ (mg·L$^{-1}$) | 100 | 23 |
| B (µg·L$^{-1}$) | 27 | 2 | $Cl^{-}$ (mg·L$^{-1}$) | 35 | 7 |
| U (µg·L$^{-1}$) | 0.4 | 0.1 | $NO_3^{-}$ (mg·L$^{-1}$) | 2.7 | 1.6 |
| Mn (µg·L$^{-1}$) | 0.14 | 0.17 | $F^{-}$ (mg·L$^{-1}$) | 0.16 | 0.04 |

Conventional pretreated water use chlorine for pre-disinfection and polyaluminum chloride (PAC) for coagulation, then water passes through sand filters. In order to avoid considerable fouling for the NF membranes, an ultrafiltration (UF) step was implemented after sand filtration to treat feed water before NF spiral wound modules.Inorganic water composition was considered practically constant during the experimental period. Trace elements detected in feed water were evaluated in different points of the pilot plant in order to study their separation and elucidate some differences between NF270 and ESNA1LF2.

### 5.2.2. Nanofiltration pilot process

From the results obtained from laboratory two NF membranes were selected for the pilot plant study, NF270 and ESNA1LF2. The aim of this study was to compare simultaneously both membranes in terms of their performance and trihalomethane formation potential (THMFP) reduction ability in a period of six months.

One of the rejection mechanisms of NF membranes is the steric exclusion, which is directly related with the membrane pore size. Other structural characteristics of NF membranes as electrical charge, hydrophobicity or roughness have been evaluated in previous studies for NF270 (Mänttari et al., 2004), although a lack of information exists for ESNA1LF2 and other commercial membranes. Table 5.2 shows some membrane specifications provided by suppliers and some characteristics found in the literature.

Table 5.2: UF and NF membrane specifications from suppliers per module

| | **Tripure UF** | **ESNA1LF2-4040** | **NF270-4040** |
|---|---|---|---|
| Supplier | Berghoff | Hydranautics | DOW-Filmtec |
| Configuration | Dead-end<br>(In-out)<br>Hollow fiber | Cross-flow<br>Spiral-wound | Cross-flow<br>Spiral-wound |
| Operation TMP (bar) | 1-1.5 | 21 max. | 41 max. |
| Design flux (l/m$^2$h) | 60-100 | | 22-29 |
| Pretreatment | Sand filtered | UF (SDI<3) | UF (SDI<3) |
| Water recovery | 95-100 % | 15 % | 17 % |
| Material | Polysulphone (modified PS) | Composite polyamide | Polyamide (polypiperazine) |
| Membrane Area (m$^2$) | 41.5 | 7.9 | 7.6 |
| Pressure drop per module (bar) | | 0.7 | 1.0 |
| MWCO | | 175[a] | 200[b] (270) |
| Clean water permeability (m$^3$/(m$^2$·day·kPa)) | | 3.3[c]<br>3.19[d] | 1.84[b,d] |

[a] (Klüpfel and Frimmel, 2010); [b] (Amy, 2001b); [c] (Sentana et al., 2010);
[d] (Park et al., 2005)

A general view of the NF pilot plant and a basic scheme of the process are presented in Figure 5.1 and was designed for a production capacity of approximately 3.6 m$^3$·h$^{-1}$. The two-staged pilot plant used has three arrays of pressure vessels (PV) placed in a 2:1 configuration. The first stage has two rows of six NF elements each one, with ESNA1LF2 4040 and NF270 4040 membranes in each separate row (stage 1.1 and stage 1.2). The second stage contained a combination of both membranes in a single row in order to increase global pilot plant recovery (stage 2).

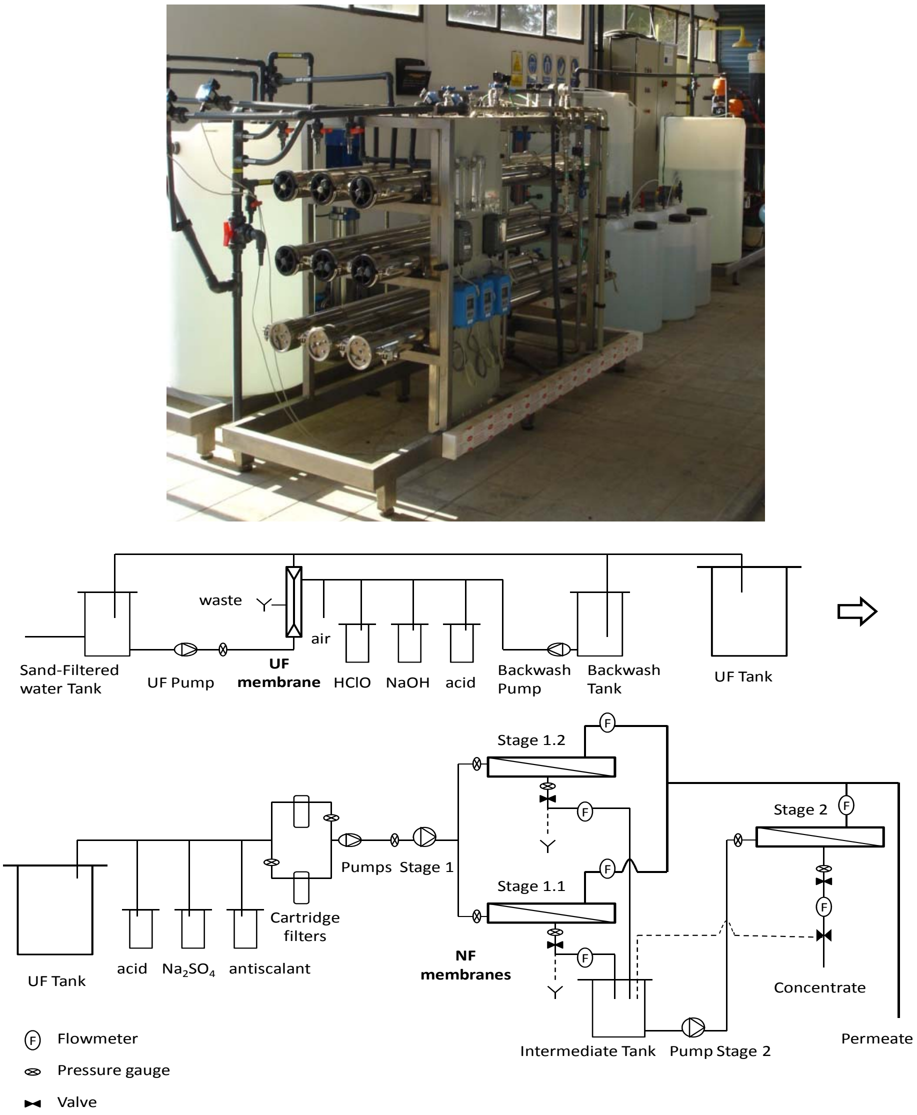


Figure 5.1: General view and basic scheme of the process for the pilot plant

Due to the high silt density values (SDI) observed in the feed water an UF step was added to improve the quality of NF feed water. Metabisulphite and antiscalant (Genesys LF) addition was required to remove free chlorine and to avoid inorganic and colloidal scaling. NPOC, inorganic carbon (IC), major inorganic anions (sulphates, nitrates, chloride) and cations (calcium, magnesium, sodium and potassium), conductivity, pH and UV absorbance were monitored weekly in feed and permeate water from stages 1.1, 1.2 and 2.

THMFP analyses were monitored monthly in feed (0% NF water) and permeate samples of stage 1.1 and 1.2 (100% NF water). Additionally, THMFP was determined in different samples obtained blending percentages of NF water permeate from both membranes, separately (at 25, 50 and 75 %), with conventionally pretreated water to produce final drinking water.

The pilot process was run six months applying chemical cleanings when normalised permeate flow decline was higher than 10%. During the first four months the global recovery of the plant (including both stages) was 75%. In the last two months, the pilot plant was operated in a recirculation mode of approximately 10 $l\cdot min^{-1}$ of concentrate flow to reach a global recovery of 90%. Transmembrane flux (TMF) was varied from 20 to 32 lmh in order to study its influence in permeability and the final water quality.

### 5.2.3. Evaluation of chemical cleaning agents

At the end of final pilot plant experimentation four spiral wound membranes were sacrificed in order to evaluate more deptly possible fouling formation, two of each type of membrane from first and second stage. All four modules were visually observed and some tests using laboratory experimental set-up were carried out to evaluate effectiveness of some chemical cleaning agents (ChC) recommended by NF membrane suppliers (DOW Water & Process Solutions technical manual, Nitto Denko- Hydranautics, 2011). Chemical solutions are described in Table 5.3.

Table 5.3: Selection of chemical solution conditions for NF membrane cleaning

| Type of ChC | Fouling type | Solution conditions |
|---|---|---|
| ChC 1:<br>NaOH+NaSDS | Organic, biofouling, silica, inorganic colloids | DOW: 0.1%NaOH+0.025%NaDSS, T<sup>a</sup> max 35 ºC pH max=12<br>Hydranautics: 0.1%+0.03%<br>pH max = 12 → T<sup>a</sup> at25ºC<br>T<sup>a</sup> max 35ºC → pH = 11 |
| ChC 2:<br>HCl | Inorganic: $CaCO_3$, $CaSO_4$, $BaSO_4$, $SrSO_4$, metallic hydroxides/oxides, inorganic colloids | DOW: 0.2%; pH 1-2 (25-35 ºC)<br>Hydranautics: 0.5% pH 1-2; (35ºC) |
| ChC 3:<br>$Na_2S_2O_4$ | metallic hydroxides/oxides and inorganic | DOW: 1.0 %; pH 5; (25-30 ºC)<br>Hydranautics: 1.0 % ( 35ºC) |
| ChC 4:<br>Citric Acid | carbonates, metallic hydroxides/oxides, inorganic colloids | DOW: 2.0 %<br>Hydranautics: 2.0 % (40 ºC) |
| ChC 5: in 2 steps<br>(1)NaEDTA<br>(2)HCl | 1. Sulfates, organic fouling, silica, biofouling, organic and inorganic colloids; 2. (same as ChC 2) | 1. DOW: 1.0 %; pH 12; (35 ºC)<br>Hydranautics: 1.0 %;pH 10 (40ºC)<br>2. (same as ChC 2) |

The experimental set-up and basic procedure in the laboratory scale is similar to that employed in Chapter 4). The most important difference is the use of two cells SEPA CFII in parallel to evaluate simultaneously the effectiveness of chemical cleaning for the dirty flat-sheet pieces of NF270 and ESNA1LF2 membranes (See Figure 5.2). Except of the different concentrations, the procedure was the same for all five types of ChC: first measuring the permeate flux before cleaning, then running one hour the solution at approximately 30 ºC at the recommended pH indicated in Table 5.3. Once performed the cleaning membrane were soaked with deionised water to neutralize and remove impurities before final permeate flux measurement (after the cleaning).

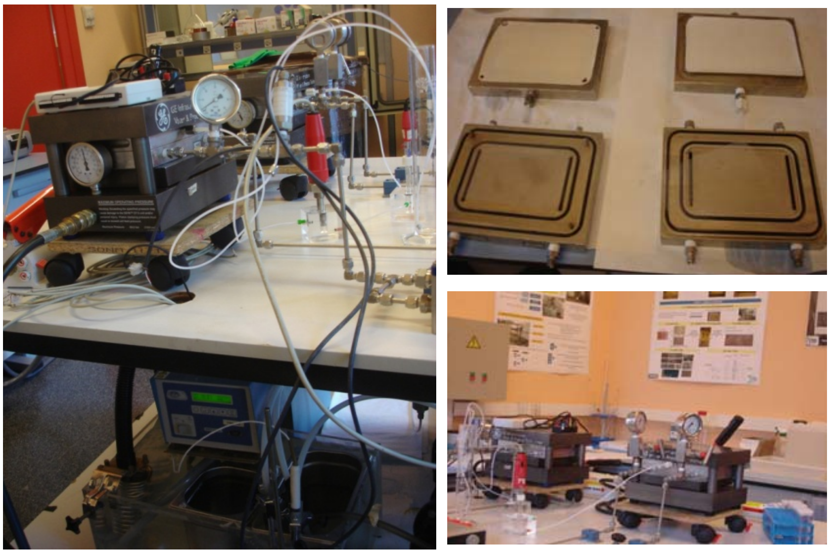


Figure 5.2: Laboratory experimental system to study two flat sheet membranes in parallel

Permeate flux before and after membrane cleaning was measured with real water collected in the point before the inlet to the NF membranes. Differences in permeability were calculated in order to compare chemical cleaning effectiveness with regard membrane productivity. In addition, scanning electronic microscopy (SEM) images and infrared spectroscopy (FTIR-ATR) were qualitative techniques to observe morphology and even some chemical characteristics of membrane surface (Her et al., 2007; Hilal et al., 2004) for dirty and cleaned membranes. Cleaning experiments were expected to give some clues in possible fouling formation for this case of NF process in drinking water treatment.

### 5.2.4. Analytical Methods

In order to determine the rejection of the studied components in the feed water, several analytical methods have been used for the analysis of the feed water and permeate samples, being previously described in Chapter 4 for laboratory studies for NF membrane selection. In this study, THM quantification in order to determine THMFP was carried out in Aigües de Manresa using head space gas chromatography technique with a new apparatus

(Agilent G1888- GC6850) and a methodology detecting THM above 10 ppb (RD140/2003). The column was the same than in Chapter 4 (DB624 from Agilent).

Infrared spectroscopy (FTIR) was used as a technique to evaluate differences before and after cleaning with regards functionalized groups in membrane surface. The apparatus used was Perkin-Elmer Spectrum VX. In addition some pictures were captured by scanning electronic coupled to electron ray X difraction microscopy (SUPRA$^{TM}$ Field Emission SEM, Carl Zeiss, with a Microanalysis X-Max EDX, Oxford Instruments).

## 5.3. RESULTS AND DISCUSSION

### 5.3.1. Simultaneous evaluation of NF270 and ESNA1LF2 in a pilot plant

Both membranes were tested in parallel at the same operational recovery and transmembrane flux (TMF) during the pilot plant experimentation. Feed pressure was the only operational parameter different between membranes, NF270 required 3-4 bars while ESNA1LF2 needed 4-5 bars. Figure 5.3 shows the normalized permeate flow individually for both membranes, in the stage 1 (S1.1 and S1.2) and in combination in stage 2 (S2) during the whole study.

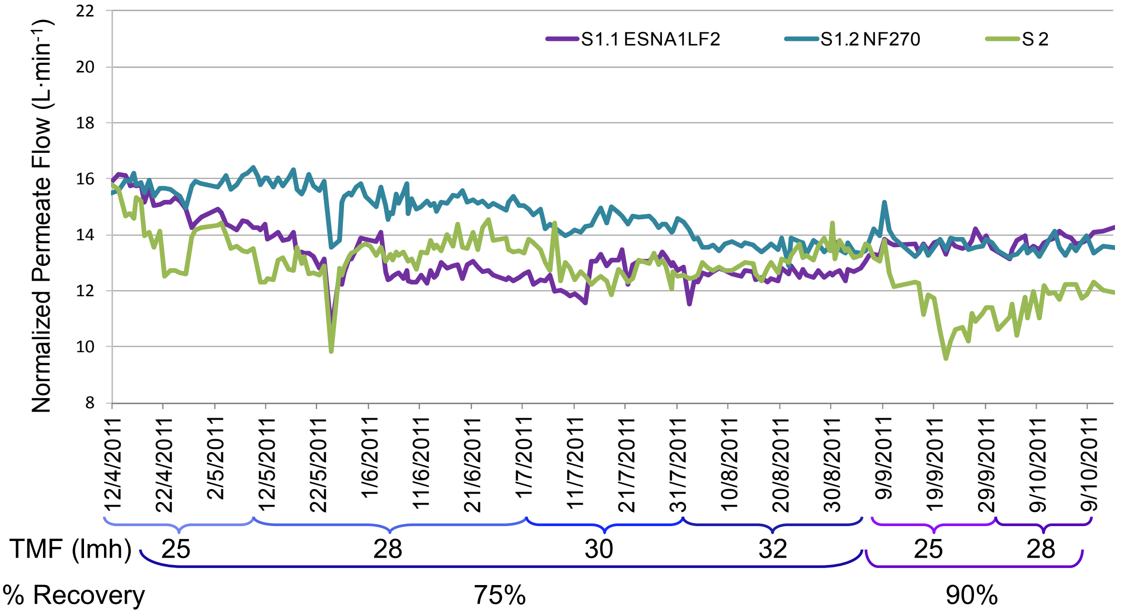


Figure 5.3: Normalized Permeate Flow of ESNA1LF2 and NF270 membranes

Three chemical cleanings using sodium hydroxide (NaOH) and sodium dodecylsulfate (SDS) were applied in order to recover the permeate flow (25/5/2011, 12/7/2011 and 01/8/2011). Total flux decline during pilot experimentation is higher in stage 2 (25%) than in stage 1 (12%). In addition, when feed water recovery was increased at 90%, stage 2 suffered dramatic decrease in its productivity (35%), as a result of increasing solutes concentrations in its membrane surface.

At the final of the pilot plant experimentation, four modules were sacrified in order to analyze the cause of permeability decrease. Membrane compaction was believed to explain initial flux decline because no evidences of important fouling deposition were detected in membrane autopsy (Visvanathan et al., 1998). Moreover, membrane compaction could take place because NF membranes were not feed continuously by UF, which resulted in intermittent operation of the pilot plant. However, laboratory scale tests were performed in order to evaluate effectiveness of some cleaning agents recommended by suppliers and be able to elucidate possible depositions on membranes (see section 5.3.2).

With the intention to compare separately both membranes in stage 1, Table 5.4 shows the average rejection values for major feed water components.

Table 5.4: Average component rejection during NF process at pilot plant experimentation

| | **NF270** | | **ESNA1LF2** | |
|---|---|---|---|---|
| **Parameter** | **Average Rejection (%)** | **Standard Deviation (%)** | **Average Rejection (%)** | **Standard Deviation (%)** |
| $Ca^{2+}$ | 63 | 4 | 90 | 2 |
| $Mg^{2+}$ | 71 | 4 | 89 | 2 |
| $Na^{+}$ | 32 | 4 | 56 | 9 |
| $K^{+}$ | 36 | 6 | 63 | 7 |
| $HCO_3^{-}$ | 43 | 4 | 74 | 5 |
| $SO_4^{-2}$ | 98 | 1 | 99 | 0.4 |
| $Cl^{-}$ | 7 | 4 | 71 | 5 |
| Conductivity | 57 | 4 | 83 | 5 |
| NPOC | 96 | 2 | 97 | 2 |
| UVA 254 | 99 | 2 | 99 | 2 |

Lower salt rejection for NF270 has some beneficial implications for drinking water treatment plants where the goal is to decrease THMFP (AWWA, 1998). Salt rejection is related to the membrane permeability. Higher salt rejection results in higher osmotic pressure differences in both membrane sides which imply higher feed pressures and energy requirements. Furthermore, lower salt rejection will result in lower corrosive potential in treated water which will decrease the post treatment costs.

Figure 5.4 represents the NF270 and the ESNA1LF2 ability to decrease THMFP in feed water.

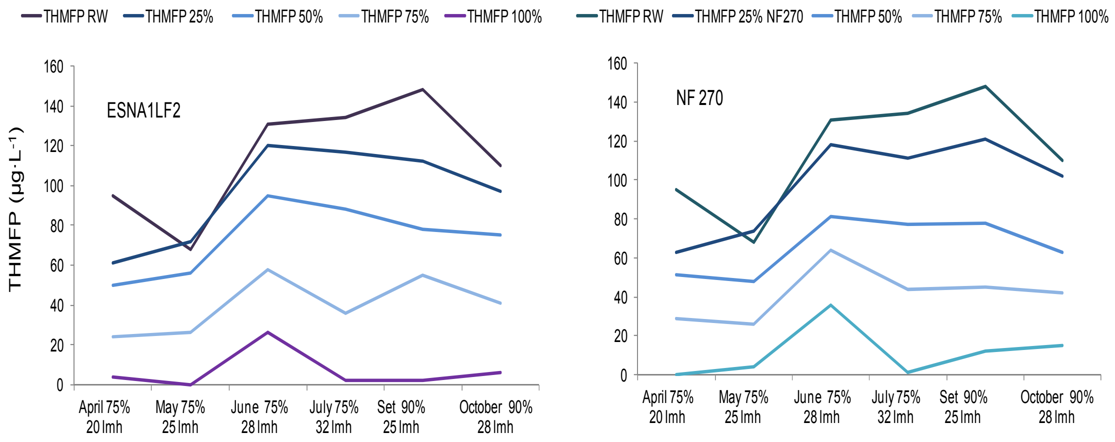


Figure 5.4: THMFP reduction in blended water samples. Blending ratio 25, 50, 75 and 100% indicates the percentage of filtered water blended with conventional pretreated water. In x-axis, 75% and 90% are the feed water recovery for NF process

THMFP reduction was nearly proportional to the percentage of permeate water in both membranes tested. A minimum of 50% of permeate water ensures a THMFP lower than 100 μg THM·$l^{-1}$ in all the experimental period. Even in the warm period between June and September, when the highest THMFP in the feed water was observed and membranes run at the highest TMF and recovery, both membranes demonstrated their ability to significantly reduce the THMFP.

Variability in temperature, NOM composition and biological activity could affect THMFP. SUVA (UVA/NPOC ratio, expressed as L·μg$^{-1}$·cm$^{-1}$) could act as indicator of the THMFP surface waters (Chen et al., 2008; Her et al., 2000; Hoehn et al., 1980). Figure 5.5 shows the relationship between THMFP of the feed and filtered water and its SUVA values.

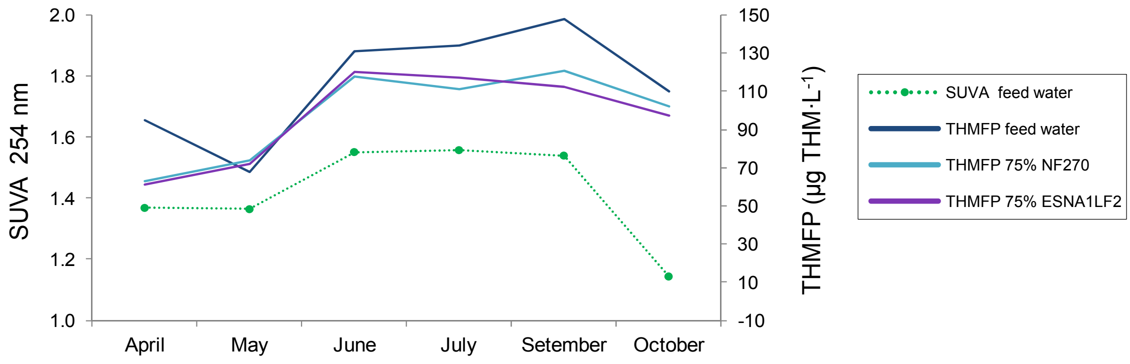
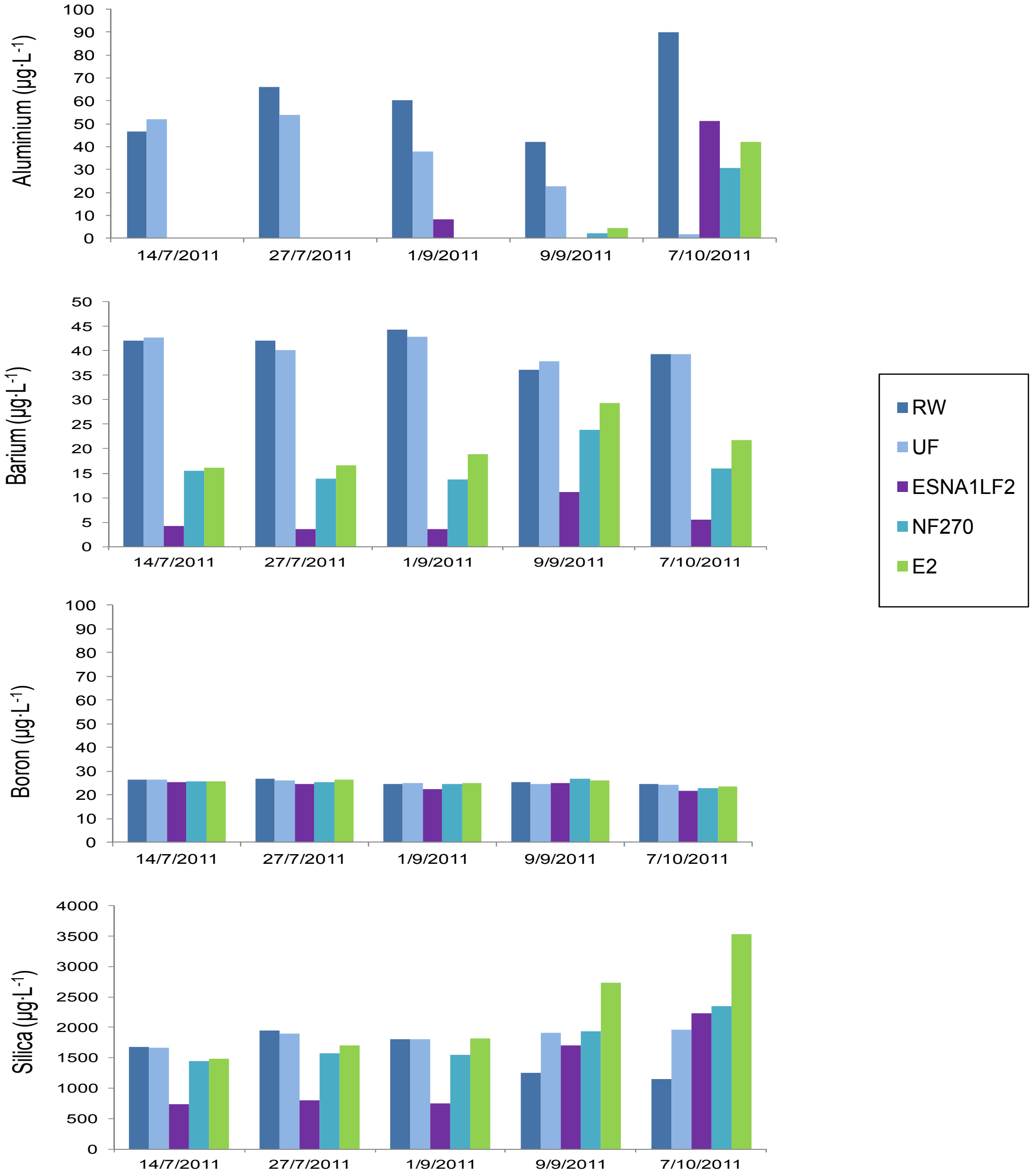


Figure 5.5: Relation between SUVA ratio and THMFP in feed and permate water samples

This results show that SUVA is closely related to the THMFP of the studied water in agreement with other studies (Ates et al., 2009; Li et al., 1996). Results obtained show that THMFP of the filtered water is mainly related to the NOM concentration and composition of the feed water and not to the TMF, recovery or feed water temperature at which membranes are operated. This means that low molecular weight fraction of the NOM is permeable to both membranes studied, resulting in a residual THMFP in the permeate water (Agbekodo et al., 1996; Meylan et al., 2007).

Trace elements separation capacity was also evaluated. Figure 5.6 indicates the removal profile for aluminum, barium, boron, silica, strontium and uranium as trace elements detected in feed water (seeTable 5.1) and quantified in permeate side.



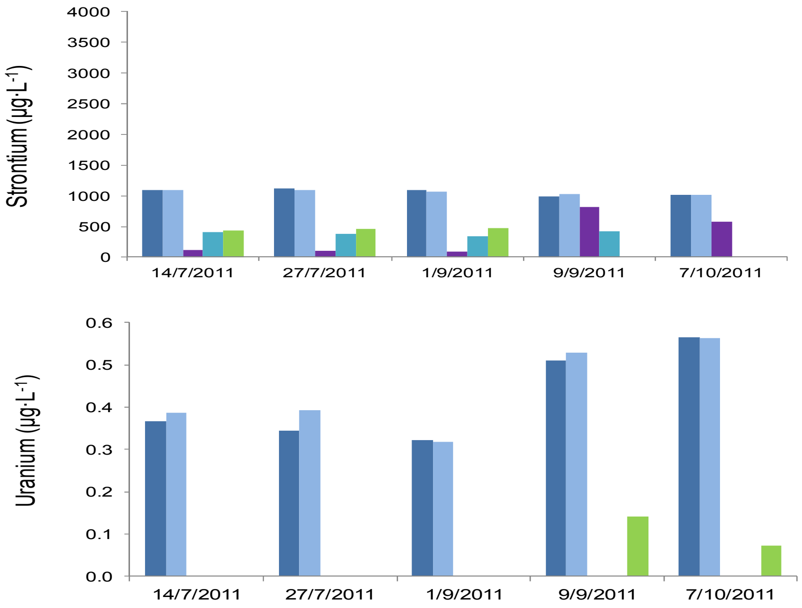


Figure 5.6: Concentration of trace elements through the pilot plant with UF and NF membranes

As it was expected, poor rejection was obtained for trace elements during UF step, because these components are small, thus passing through the pores of UF membranes. However, it is important to mention that some cations can be absorbed in NOM or the particles in the water (Comerton et al., 2009, Nowostawska et al., 2005).

NF membranes present variable rejection capacities for trace elements. In case of aluminum and uranium, NF270 and ESNA1LF2 showed rejections than 95% in most days, except when global recovery of the NF plant in increases near to 90% (9/09/2011 and 7/10/2011). In case of barium, silica and strontium, ESNA1LF2 present higher rejections than NF270 as it was observed for inorganic major ions (Table 5.4). Surpridingly, boron showed no rejection and the explanation can be its presence as borates which show similar behaviour as nitrates (Figure 4.7 in Chapter 4).

### 5.3.2. Study of chemical cleaning effectiveness in laboratory experimentation

In function of the results obtained from chemical cleaning experimentation carried out in the laboratory with membranes used in the pilot plant, some differences in cleaning effectiveness and type of membrane were observed. Figure 5.7 summarizes results in function of the ratio between permeate flux before and after chemical cleaning.

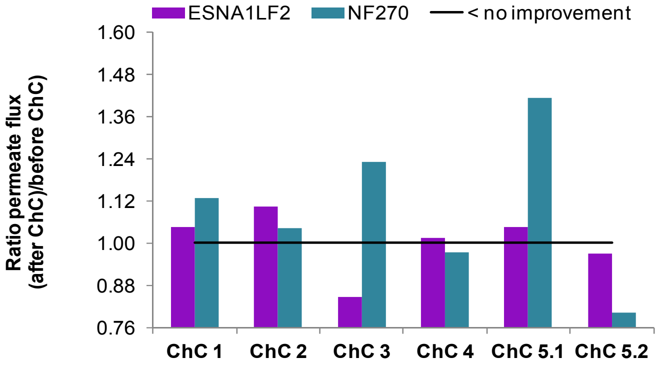


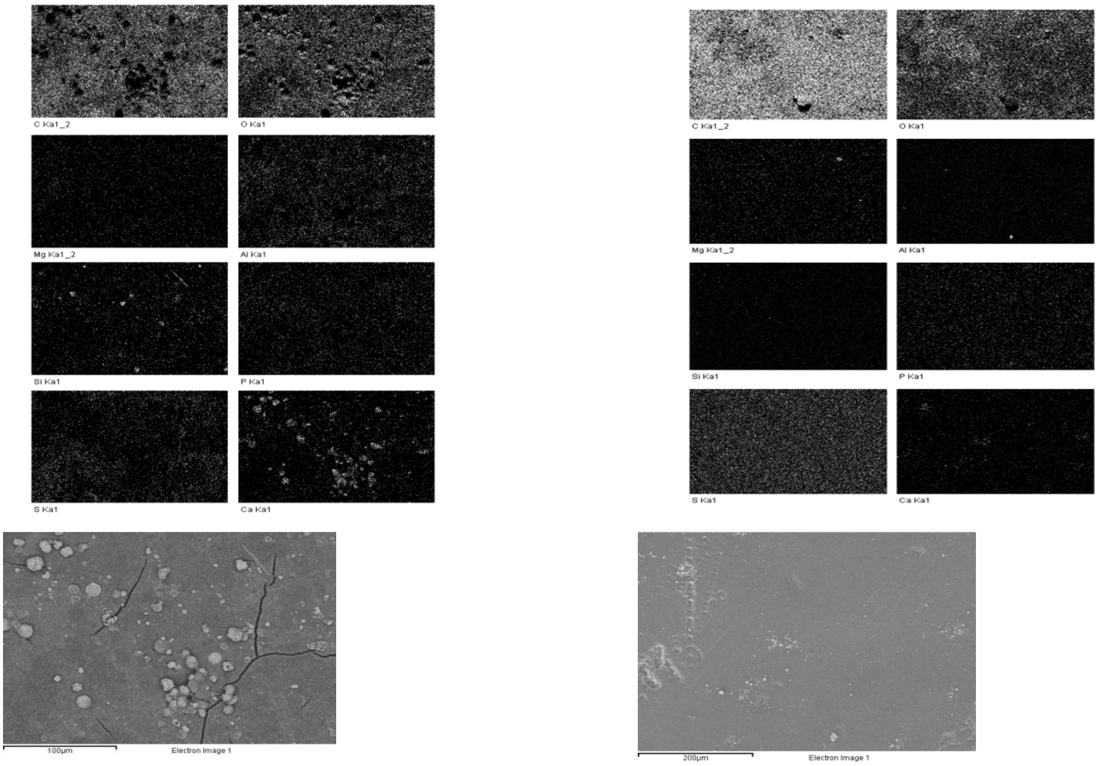
Figure 5.7: Permeate flux ratio before and after each chemical cleaning

NF270 experimented an important improvement on permeability before ChC 5 (NaEDTA), ChC 3 (sodium hydrosulfite) and even ChC 1 (NaOH), instead of the slightly increase of permeate flux for ESNA1LF2 (5%) when ChC2 is used (hydrochloric acid). In most cases, increase on permeate flux after chemical cleaning performed in laboratory test did not show a noticeable improvement, consequently low level of fouling formation could be considered.

The first step in ChC 5 consists in basic media with complexant agent, suitable conditions to remove organic fouling. In this case NF270 showed the better results after this cleaning, with an increase of permeate flux of nearly 35%. In accordance to information indicated in Table 5.3, possible fouling in membrane NF270 could be organic, biological, and inorganic (sulphates). Second step using chlorhidric acid showed a negative effect in permeate flux with regard the first step of ChC 5, although no further investigation was carried out.

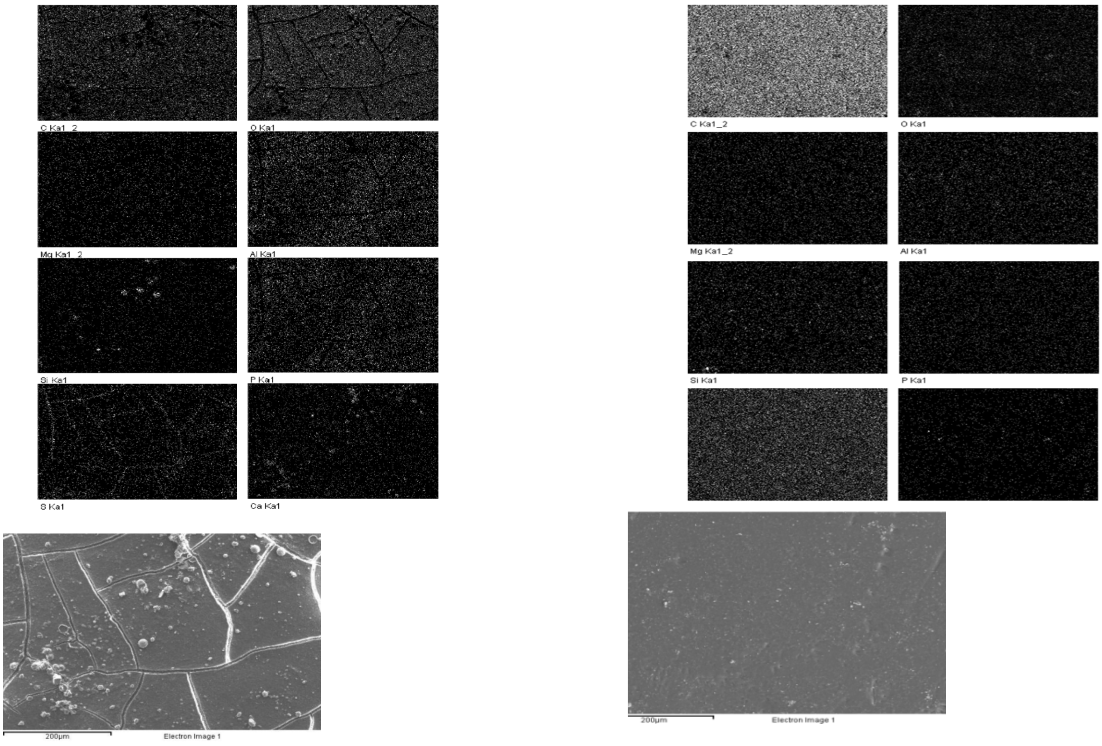
Following Figure 5.8 and Figure 5.9 are SEM-EDX pictures for ESNA1LF2 and NF270 membranes, respectively, indicating qualitative atomic composition before and after ChC 2 (acid) for the former, and ChC 5 (basic) for the latter.

From images obtained and suppliers information about membrane material, carbon (C), oxygen (O), nitrogen (N) and sulfur (S) are constituent elements in polymeric material for membrane manufacturing. An increase of the intensity for EDX signal responses is observed after chemical cleaning in both membranes.



a) Dirty piece of membrane b) Piece of membrane after ChC2

Figure 5.8: SEM-EDX images for ESNA1LF2

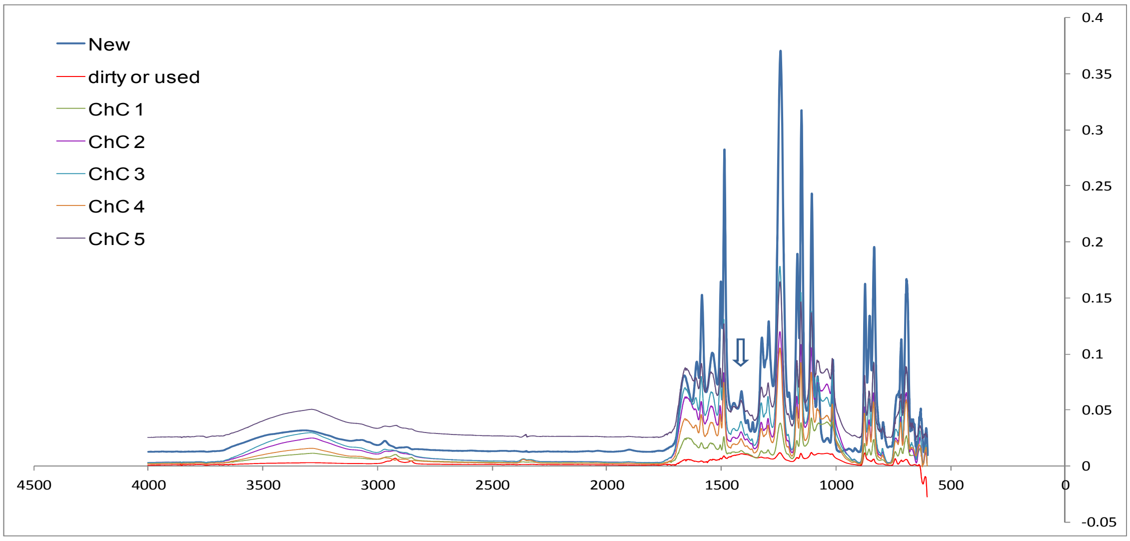


a) Dirty piece of NF270 membrane b) Piece of membrane after ChC 5

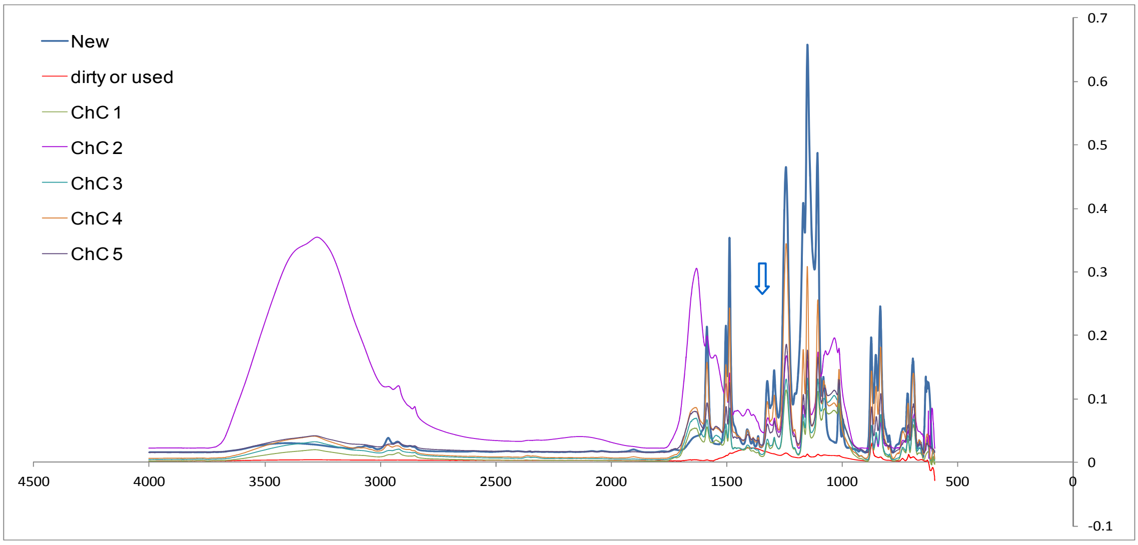
Figure 5.9: SEM-EDX images for NF270

Other elements were detected in less extent such as calcium (Ca), aluminum (Al), phosphorous (P), silica (Si) and magnesium (Mg), some of them reduced after chemical cleaning what can indicate some inorganic depositions. In each case, results from EDX images would be useful to detect inorganic fouling more than organic because elementel composition of organic compounds are the same that membrane materials.

Results in Figure 5.10 is interesting because allow observing differences in membrane types surface and different chemical cleaning applications, contrasted with a piece of new membrane.



a) ESNA1LF2



b) NF270

Figure 5.10: Infrared spectrums for new, dirty and cleaned pieces of membranes

To observe chemical cleaning effects from infrared spectrums one option is to compare recovery degree for original absorption band intensity (from new piece of membrane), for example at 1400 $cm^{-1}$, then decreasing order in chemical cleaning efficiencies is the following for each membrane:

ESNA1LF2: (new) > ChC 5 > ChC 3 > ChC 2 > ChC 4 > ChC 1
NF270: (new) > ChC 4 > ChC 2 > ChC 5 > ChC 3 > ChC 1

Comparing the type of fouling that each cleaning is able to remove, for all results obtained, NF270 seems to experience higher organic fouling that ESNA1LF2. On the other hand ESNA1LF2 seem to suffer major inorganic fouling according to major inorganic salts rejection and consequent precipitation in the feed/concentrate channel for the spiral-wound modules.

## 5.4. CONCLUSIONS

NF270 and ESNA1LF2 were selected for testing in equal operational conditions at pilot scale after results in the laboratory experimentation with 10 commercial membranes (Chapter 4). The main difference between both membranes was salt rejection. ESNA1LF2 showed the highest rejection of inorganic ions resulting in higher feed pressure requirements to maintain the same permeate flow than NF270. Furthermore, permeate water from ESNA1LF2 showed the lowest bicarbonate content which increases its corrosive power and further requirement should be considered.

Both membranes showed high rejections of THM precursor material, which resulted in very low THMFP in the permeate water. A blending ratio of 0.5 between filtered and feed water ensured a THMFP lower than 100 $\mu g\ THM \cdot l^{-1}$ in all cases regardless the seasonal and operational conditions variation (TMF and total water recovery). Feed water showed higher THMFP in the period between June and September. Seasonal variation considering higher temperature, biological activity and NOM concentration in the warm period could explain this increase. SUVA values were closely related to the THMFP of the feed water, which demonstrated the ability of this parameter to indicate the THMFP of the studied water.

Differences in trace elements rejection can be observed for both membranes, although similar results are obtained in accordance to separation capacities for major inorganic ions (barium, silica and strontium). Uranium and aluminum rejections are high for both membranes indicating interesting abilities for NF. However, trace element speciation in the problem feed solution play an important role, because some forms can be negatively or positively charged with different sizes. In this pilot study, ESNA1LF2 showed little higher rejections for trace elements at least for barium and strontium. This result is in accordance to higher salt rejections for this membrane.

Chemical cleaning applied were selected following suppliers recommendations to remove possible fouling of different origins (organic, inorganic, colloidal, biofouling). During six-month experimentation fouling formation was under control using UF as a pretreatment and chemical cleaning in situ. However, experimental test in laboratory scale (using dirty pieces of the used spiral-wound membrane) and respective membrane autopsies by SEM-EDX images and IR spectrum, demonstrated some transformations after chemical cleanings: permeate flux increases, possible recovering of original membrane material or changes in functional groups in the membranes surface. These results require more experimentation to elucidate exactly the type of depositions during real processes in order to find out with the better chemical cleaning for a concrete membrane.

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# Chapter 6: Organic pollutants removal by membrane technologies in drinking water treatment: pilot plant study of ultrafiltration and two nanofiltration commercial membranes

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## 6.1. INTRODUCTION

The presence of organic pollutants in water has become an important challenge for water technologies since the difficulties found during conventional water processes to remove them in final product water. Different types of these compounds have been detected in water bodies all over the world as a result of their wide use in many applications and the improvement of analytical techniques (Loos et al., 2009). Consequently, some of them have become emergent and undesirable contaminants due to their potential health risks, identified in human and animals by means of epidemiological and toxicological studies (Agency for Toxic Substances and Disease Registry ATSDR, 2009; USEPA, 2009). For this reason, concentrations of some of these compounds, such as pesticides or some chlorinated products, are limited in drinking water in many countries (Karabelas et al., 2009; RD140/2003).

Different physicochemical properties for this recalcitrant compounds, as for example the small size and the stable structure of these molecules make impossible its removal from the water matrix solution by typical separation techniques, such as coagulation and sand filtration. Biological degradation, activated carbon adsorption and advanced oxidation processes allow degrading some of these compounds, but not to all its extent (Jones et al., 2005; Van Dijk and Van Der Kooij, 2004). Ultrafiltration membranes (UF), due to their pore size, are effective for colloidal and particulate matter removal, but not for small substances. Instead, reverse osmosis and nanofiltration (RO and NF) allow to separate in a variable degree inorganic ions and small organic molecules, making them useful to be applied in many applications such as water, pharmaceutical and food industries (Schäfer et al., 2005; Van der Bruggen et al., 2008).

RO and NF membranes are able to effectively remove organic pollutants from drinking water as a result of different separation mechanisms, such as sieving effect, charge repulsion or hydrophobic interactions (Plakas and Karabelas, 2012). Molecular weight cut-off (MWCO), porosity, hydrophobic behavior or superficial charge, are membrane parameters depending in great extent on the membrane material and confidential manufacturing processes (Berg et al., 1997; Kosutic et al., 2006). Determining the influence of different factors affecting organic pollutants separation is a complex task that has been studied in many works (Bellona et al., 2004; Plakas and Karabelas, 2012; Verliefde, 2008).

Separation mechanisms of trace organic compounds by NF have been investigated under controlled conditions in laboratory experiments, such as operational pressure, organic matter content (NOM), pH and salinity (Berg et al., 1997; Hajibabania et al., 2012; Koyuncu et al., 2006; Yoon et al., 2006), and in less extent in pilot (Boussahel et al., 2000) and real plants (Radjenovic et al., 2008; Verliefde et al., 2009a).

Hydrophobic organic compounds, for example some pesticides and pharmaceuticals, usually present adsorption on and into membranes as a result of a mix of attractive interactions (van der Waals, hydrogen bonds), which could depend on the solution chemistry (Kiso et al., 2001; Zhang et al., 2004). This phenomenon can lead to an overestimation of NF rejection when no steady-state is occurring in case of uncharged and hydrophobic organic compounds (high values of partition coefficient in octanol-water, log $K_{ow}$) with molecular weight (MW) similar to MWCO of membranes (Koyuncu et al., 2006; Yoon et al., 2006). Verliefde et al. (Verliefde et al., 2009a; Verliefde et al., 2009b) developed mathematical models including hydrophobic interactions between solutes and membrane surface to predict a wide range of organic compounds removal in real plants. The degree of organic compounds removal in drinking water also depends on operational factors, including commercial membrane used, and initial raw quality.

Additionally, various authors have studied the influence of membrane fouling in organic compounds rejection (Nghiem and Hawkes, 2009; Verliefde et al., 2009c; Vogel et al., 2010), increase of rejection for these compounds was observed when only organic fouling is considered (Nghiem and Hawkes, 2009), instead of an apparent decrease of organic separation capacity for NF membranes when calcium carbonate contribute to fouling phenomena (Vogel et al., 2010).

In this study, two NF membranes (NF270 and ESNA1LF2) were evaluated simultaneously in a pilot plant to determine the ability of this technology to remove organic pollutants. After organic compounds characterization of the real pretreated water, cholesterol, caffeine, tert-buthylazine and linear alkylbenzenesulfonate (LAS) were selected as representative of the big range of organic pollutants (biomolecules, hydrophilic pharmacs, hydrophobic pesticides, negative-charged surfactants) in order to study the main separation mechanisms and its complexity in a real NF process. Differences in organic compounds rejection could be a key point to select one membrane for an industrial full-scale drinking water treatment plant in case of requiring further removal of some organic pollutants present in raw water of concern.

## 6.2. MATERIALS AND METHODS

### 6.2.1. Feed water type and initial organic traces characterization

In order to represent the behaviour of a full scale NF process, water used in present study came from the output of the sand filtration stage, previously to final chlorination, as it has been described in 0, considering conventional pre-treated water feeding the pilot plant .

Inorganic composition, ultraviolet light adsorption (UVA), silt density index (SDI), non-purgable organic carbon (NPOC) and trihalomethane formation potential (THMFP) were determined regularly during the six-months operation of the pilot plant (see Table 5.1)

Characterisation of organic compound traces was carried out preliminarily to this study analysing priority substances in two samples of the pretreated water (June and September 2011). Table 6.1 summarizes the organic compounds found in the pretreated water of concern and their partition coefficient in octanol/water in order to indicate the hydrophobic character for each organic compound. Hydrophobicity is often used to characterize organic matter composition with the intention to simplify the complex task of organic compounds classification (natural and synthetic) (Chow et al., 2005).

As it could be expected no pollutants were identified over the legislated levels in European and Spanish legislation. Although they are undesirable in drinking water, most of the compounds found in this study are not considered in these legislations (2008/105/EC; 98/83/EC; RD140/2003).

Generally, analytical results from September showed higher concentrations and presence of more organic pollutants than in June, as a result of seasonal variations that affect water composition, such as warm and drought periods, insulation time on water reservoirs or the consumption increase for some products (pesticides, insecticides, body care products) (Her at al., 2000).

Four target organic compounds were selected in order to represent organic pollutants. Their hydrophobicity was the criteria for its selection: caffeine, linear alkylbenzenesulfonate (LAS), terbuthylazine and cholesterol.

Table 6.1: Organic compounds characterization in the pretreated water and partition coefficient in octanol/water (Log $K_{ow}$)

| | | June 2011 | Sept 2011 | MDL | Log Kow |
|---|---|---|---|---|---|
| **Pesticides** | | | | | |
| Isoproturon | $ng\cdot L^{-1}$ | < MDL | 0.24 | 0.20 | 2.8 |
| Diuron | $ng\cdot L^{-1}$ | 1.09 | 1.76 | 1.00 | 2.7 |
| Desethylatrazine | $ng\cdot L^{-1}$ | < MDL | 0.60 | 0.38 | 1.8 |
| Simazine | $ng\cdot L^{-1}$ | 0.57 | < MDL | 0.10 | 2.2 |
| Atrazine | $ng\cdot L^{-1}$ | < MDL | 0.43 | 0.10 | 2.5 |
| Terbuthylazine | $ng\cdot L^{-1}$ | 1.65 | 0.10 | 0.03 | 3.2 |
| Lindane (γ-HCH) | $ng\cdot L^{-1}$ | < MDL | 1.17 | 0.06 | 3.7 |
| Diazinon | $ng\cdot L^{-1}$ | < MDL | 0.14 | 0.03 | 3.8 |
| Fenitrothion | $ng\cdot L^{-1}$ | < MDL | 0.13 | 0.01 | 3.3 |
| Metholachlor | $ng\cdot L^{-1}$ | 0.07 | 0.02 | 0.01 | 3.1 |
| Chlorpiriphos | $ng\cdot L^{-1}$ | < MDL | 0.22 | 0.10 | 5.0 |
| Chlorfenvinphos | $ng\cdot L^{-1}$ | < MDL | 0.02 | 0.01 | 3.8 |
| Endosulfan sulphate | $ng\cdot L^{-1}$ | < MDL | 0.02 | 0.01 | 3.1 |
| **Semivolatiles** | | | | | |
| Caffeine | $ng\cdot L^{-1}$ | 144 | 14.1 | 5.0 | -0.7 |
| Carbamazepine | $ng\cdot L^{-1}$ | < MDL | 2.3 | 2.0 | 2.6 |
| Galaxolide | $ng\cdot L^{-1}$ | 11.8 | 8.8 | 1.5 | 5.4 |
| Tonalide | $ng\cdot L^{-1}$ | 3.3 | 4.2 | 1.9 | 5.8 |
| NBBS | $ng\cdot L^{-1}$ | < MDL | 57.0 | 22 | 2.3 |
| NNDMT | $ng\cdot L^{-1}$ | < MDL | 15.7 | 1.0 | 2.2 |
| Colesterol | $ng\cdot L^{-1}$ | 3.5 | 10.2 | 1.5 | 8.5 |
| β-Sitosterol | $ng\cdot L^{-1}$ | 4.0 | 13.1 | 1.4 | 9.6 |
| **LAS** | $\mu g\cdot L^{-1}$ | 2.07 | 4.91 | 0.28 | 1.6 |
| **DBPs** | | | | | |
| Bromoform | $ng\cdot L^{-1}$ | 62.5 | 15 | 1.00 | 2.4 |
| Hexachloroethane | $ng\cdot L^{-1}$ | 5.8 | 0.68 | 0.10 | 4.1 |
| HCCPD | $ng\cdot L^{-1}$ | 1.7 | 0.90 | 0.10 | 5.0 |
| DCAN | $ng\cdot L^{-1}$ | 5.0 | 18.30 | 1.00 | 1.1 |
| DBAN | $ng\cdot L^{-1}$ | 0.03 | 1.10 | 0.01 | 1.6 |
| BCAN | $ng\cdot L^{-1}$ | < MDL | 7.80 | 1.00 | 1.2 |
| TCAN | $ng\cdot L^{-1}$ | < MDL | < MDL | 1.00 | 2.1 |
| Perchloroethylene | $ng\cdot L^{-1}$ | 3.5 | 2.60 | 1.00 | 3.4 |
| Benzoacetonitrile | $ng\cdot L^{-1}$ | 24.0 | 7.00 | 1.00 | 1.7 |
| Chloropicrin | $ng\cdot L^{-1}$ | 13.0 | 34.40 | 1.00 | 2.2 |
| 1,1-dichloropropanone | $ng\cdot L^{-1}$ | 2.0 | < MDL | 1.00 | 1.4 |
| 1,1,1-trichloropropanone | $ng\cdot L^{-1}$ | 33.8 | 44 | 1.00 | 0.2 |

<MDL: below the method detection limit; NBBS: N-Butylbenzenesulphonamide; NNDMT: N,N-Diethyl-meta-toluamide; HCCPD: 1,2,3,4,5,5-hexachloro 1,3-Cyclopentadiene; DCAN: Dibromoacetonitrile; DBAN: Dichloroacetonitrile; BCAN: bromochloroacetonitrile; TCAN: trichloroacetonitrile.

Caffeine is a small and neutral compound at pH conditions of this case. This molecule acts as a surrogate for some pharmaceuticals compounds, usually with hydrophilic character (log $K_{ow}$ < 1). Terbuthylazine represents some aromatic pesticides with high hydrophobicity (log $K_{ow}$ > 3) and with similar MW to the MWCO of the NF membranes. LAS is greatly employed and highly soluble anionic surfactant (Duarte et al. 2010) with linear hydrophobic chains, presenting intermediate hydrophobic behaviour (1 < log $K_{ow}$ < 3) and with slightly higher MW than NF membrane MWCO. Finally, cholesterol with high MW (387 $g{\cdot}mol^{-1}$) acts as an essential biomolecule, indicating the activity of organisms (Stackelberg et al., 2004).

Table 6.2 shows MW and log $K_{ow}$, as the important physicochemical characteristic which could affect the NF performance (regarding sieving effect and hydrophobic interactions) in front of these selected compounds (RSC 2012; Verliefde, 2008). In addition, right column indicates the represented compounds classified from hydrophobic point of view.

Table 6.2: Selected organic compounds in function of their molecular weight (MW), hydrophobic character (Log $K_{ow}$) and represented compounds.

| | MW ($g{\cdot}mol^{-1}$) | Log $K_{ow}$ | Hydrophobic categories / represented compounds | |
|---|---|---|---|---|
| **Caffeine** | 194.2 | -0.07 | Log $K_{ow}$< 1: | 1,1,1-trichloropropanone |
| **LAS** | 288.4 | 1.60 | 1<log$K_{ow}$< 3: | atrazine, simazine, desethylatrazine, diuron, isoproturon, 1,1-dichloropropanone, acetonitriles (DBAN, DCAN, BCAN, TCAN), Chloropicrin, bromoform, NBBT, NNDMT, Carbamazepine, |
| **Terbuthylazine** | 229.7 | 3.21 | Log $K_{ow}$ >3: | lindane, diazinon, fenitrothion, metholachlor, chlorpyriphos, chlorfenviphos, endosulfansulfate, galaxolidde, tonalide, Hexachloroethane, HCCPD, Perchloroethylene |
| **Cholesterol** | 386.65 | 8.74 | Log $K_{ow}$ >3: | β-Sitosterol |

DBAN: Dibromoacetonitrile; DCAN: Dichloroacetonitrile; BCAN: bromochloroacetonitrile; TCAN: trichloroacetonitrile; NBBS: N-Butylbenzenesulphonamide; NNDMT: N,N-Diethyl-meta-toluamide; HCCPD: 1,2,3,4,5,5-hexachloro 1,3-Cyclopentadiene.

However, it is important to notice that molecular weight and electric charge for each represented compound could play an important role in the separation ability of the membranes selected. To predict separation of other molecules with similar hydrophobicity to that corresponding to the four target compounds used, information about molecular volume (or molecular weight) and charge (at the operational pH conditions) should be considered for further interpretation.

### 6.2.2. Pilot plant set-up and membranes used

The nanofiltration pilot plant used in this experimental part is the same that in the previous chapter, however Figure 6.1 indicates the specific points for sampling collection. Pilot plant design was described in 5.2.2 together with the main operational conditions.

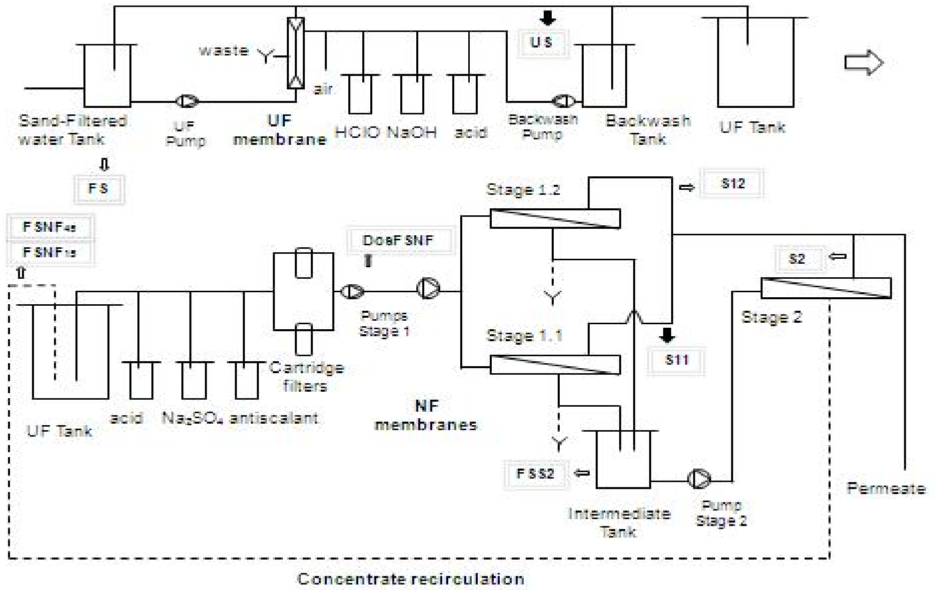

Figure 6.1: Schematic diagram of the NF pilot plant and sampling points shown in boxes

It is important to highlight that this design allowed the simultaneous comparison for two NF membranes, which can operate at the same recovery and permeate flux. These parameters were fixed at similar operational conditions as a full scale nanofiltration plant for the production of drinking water. Then variation in trans-membrane pressure (TMP) is the parameter able to distinguish operation requirements between both membranes.

Table 6.3 indicates some additional membrane characteristics that have been evaluated experimentally or collected from bibliographic data.

Table 6.3: Specific properties of NF membranes

| Propiety/ specification | NF270-4040 | ESNA1LF2-4040 |
|---|---|---|
| MWCO | 175<br>(Klüpfel and Frimmel, 2010) | 200<br>(Amy, 2001a) |
| Clean water permeability ($m^3/(m^2 \cdot day \cdot kPa)$) | 3.3 (Sentana et al., 2010a)<br>3.19 (Park et al., 2005) | 1.84 (Amy, 2001a; Park et al., 2005) |
| % conductivity rejection | 55 (Ribera et al., 2013) | 80 (Ribera et al., 2013) |
| Contact angle | 28.5<br>(Klüpfel and Frimmel, 2010) | 60 [b] (Yoon et al., 2005)<br>23-40 [c] (Childress, 2012) |
| Z-potential | -19.7 (Norberg et al., 2007)<br>-32 (Oatley et al., 2012) | - 12[b] (Norberg et al., 2007)<br>- 7 (Oatley, 2012) |
| Porosity AFM (nm) | 0.50 (Llenas et al., 2011) | 0.49 (Llenas et al., 2011) |
| Roughness AFM (nm) | 5.35 (Llenas et al., 2011) | 49.7 (Llenas et al., 2011) |
| Isoelectric point | 3.5 (Oatley, 2012) | 2-3 (Oatley, 2012) |

[b] Value for ESNA1 membrane

[c] Value for ESNA1LF membranes

One of the rejection mechanisms of nanofiltration membranes is the steric exclusion, which is directly related with the membrane pore size. That is why this is one of the main parameters in membrane characterisation. On the other hand, the membrane surface roughness is one of the most important surface properties as it has a strong influence on membrane fouling (Bowen and Doneva, 2000). Vrijenhoek and co-workers demonstrated through use of Atomic Force Microscopy analysis that the deposit of particles is higher for rough membranes than for smooth membranes when all test conditions are held constant (Vrijenhoek et al., 2001).

### 6.2.3. Pollution scenario to study NF separation capacities

A pollution scenario was simulated using batch recirculation mode in the pilot plant, minimising the dosage of organic pollutants. This mode required total recirculation of water in the plant, by means of directing first and second stage permeates and concentrates streams to the feed tank (1000 L). Chemical doses of sodium metabisulphite and scale inhibitor were added in the first 10 min of NF operation in these conditions (batch mode operation).

The semi-synthetic polluted water was prepared using real pretreated water from the DWTP and spiking the selected organic compounds into the 500L tank. A mix containing caffeine (high-performance liquid chromatography-grade, Sigma-Aldrich, Germany), terbuthylazine (100ng/uL in Acetone, Dr. Ehrenstofer, Germany), LAS (technical preparation 46.6% purum, Petresa, Canada) and cholesterol (sigma grade >99%, Sigma-Aldrich, Germany) was prepared in methanol and added to the 500L reservoir.
As UF step operates in a dead-end filtration mode, samples were collected in:

- Initial mix solution (FS) or pretreated water
- Ultrafiltered sample (UFS), when half part of the initial volume was filtrated

In order to study the separation phenomena during NF process, sampling points were established in the following sites and times:

- Stage 1 feed sample after the first 15 min of operation ($FSNF_{15}$)
- Stage 1 feed sample after 45 min of operation ($FSNF_{45}$)
- Permeate samples from S1.1, S1.2 and S2

$FSNF_{15}$ was collected 15 minutes after the start of the NF process in order to allow the homogenization of the spiked water with remaining water in the dead volume of the pilot plant. $FSNF_{45}$, was collected 45 minutes after in order to study the existence of phenomena such as absorption and volatilization of the compounds added.

### 6.2.4. Analytical methods

Gas chromatography coupled to mass spectrometry (GC/MS) was the analytical technique used to determine volatile and semivolatile organic compounds (disinfection by-products, neutral bases, pesticides). The methodology used for the analysis was based on methodologies described elsewhere (Planas et al., 2006; AWWA, 1998). The mass spectrometer employed was a GC/MS Trace MS Plus (Thermo Scientific).

Furthermore, the presence and quantification of surfactants was analysed using liquid chromatography coupled to mass spectrometry (LC/MS) (Barco et al., 2003).

Trihalomethanes (THM) analysis to determine of trihalomethanes formation potential (THMFP), non purgable organic carbon (NPOC) and ultraviolet light absorption (UVA) were carried out during experimentation in pilot plant (0).

## 6.3. RESULTS AND DISCUSSION

In order to evaluate the rejection of the selected representative organic molecules, results from the simulated pollution scenario performed in the pilot plant are shown in Figure 6.2 and Figure 6.3.

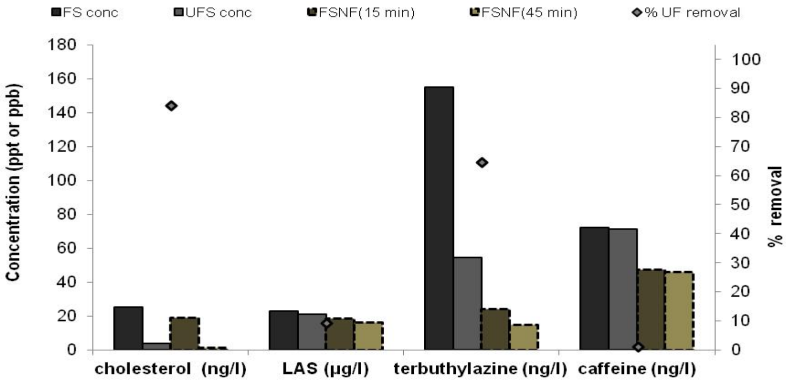

Figure 6.2: Concentration for the four compounds spiked in the pretreated water

First of all, after the four compounds were spiked and diluted with the dead volume of the NF installation, sample from NF feed water (FSNF) was taken at 15 min. On the other hand, in order to observe adsorption or volatilization phenomena, FSNF water was again collected and analyzed after 45 minutes (Figure 6.2).

As can be seen, caffeine and LAS are barely rejected by UF. However, cholesterol and tertbuthylazine showed 70% and 85% rejections, respectively.

For UF membranes, the removal of caffeine, terbuthylazine and LAS was expected to be negligible due to their small molecular weight. However, adsorption in organic particulate matter or into UF membrane could take place for terbuthylazine (Yoon et al., 2006). UF is highly effective rejecting large molecules and colloidal material, but cholesterol theoretically can pass through UF membrane pores because the MW is smaller than the MWCO of the membrane. Nevertheless, some adsorption phenomena or hindrance effects may occur to explain the observed rejection for this sterol at values higher than 80%. This rejection value indicates that UF would be able to remove this type of hydrophobic macromolecules from drinking water in case that secondary treatment as coagulation fails in cholesterol removal or a pollution episode takes place before UF.

In the present study, the suggested time to reach the steady state conditions for adsorption phenomenon, four days, was not considered (Verliefde, 2008). For this reason it is important to point that some pollutants experienced some losses during the sampling collection time because could be adsorbed into membrane or installation materials. Cholesterol and terbuthylazine had lower concentration in $FSNF_{45}$, possibly as a consequence of their hydrophobic interactions with the membrane. Figure 6.3 shows concentrations in permeates for all compounds analyzed in different points of the pilot plant.

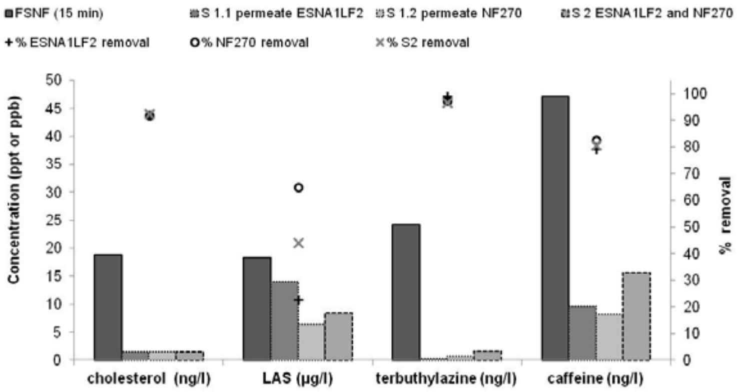

Figure 6.3: Rejection of the selected organic pollutants in the second scenario

Feed water concentration for LAS did not vary during 45 minutes, indicating low adsorption into the membrane or pilot plant materials and negligible volatilization (Figure 6.3). LAS compound became useful to elucidate some differences between both NF membranes. First of all, LAS has negative charge and its MW is slightly higher than membranes MWCO, which lead to think in high rejections because membrane are negatively charged and straining effects hamper pass through the membrane. However, this molecule has a linear hydrophobic part combined with an anionic and hydrophilic extreme, both properties are opposite and makes difficult to predict the rejection for this compound with intermediate hydrophobicity ($1 < \log K_{ow} < 3$).

Experimental rejections for LAS were 70% for NF270 in front of 40% for ESNA1LF2, indicating different separation mechanisms for each membrane. ESNA1LF2 presented higher desalting capacity together with lower water permeability than NF270, this fact could be explained considering lower MWCO for ESNA1LF2 because negative charge of membrane is higher for NF270 (Table 6.3). Sieving effects for both membranes could be neglected because solute present linear form. So, it is expected that membrane z-potential and hydrophobicity have the main influence in the separation capacity of this compound due to its intermediate hydrophobicity and its negative charge (Verliefde, 2008; Xu et al., 2006). NF270 presented higher rejections for LAS compound because negative charge of membrane is higher in addition to lower hydrophobicity (Table 6.3).

Related to materials and modifications in membranes manufacturing, NF270 membrane consists in a semiaromatic poly-piperazine membrane, much smoother ($R_{rms}$ on the order of 10 nm) than those fully aromatic ones ($R_{rms}$ on the order of 100 nm). In this sense, ESNA1LF2 could be a fully aromatic membrane, for example uncoated fully polyamide (PA), enriched with –COH groups to decrease: hydrophobicity, expressed as a contact angle near to 40° values and zeta potential values in the range between -10 to -30 mV at pH=7; as it can be contrasted in Table 6.3 (Tang et al., 2007). Lowering membrane hydrophobicity means decreasing fouling formation at the same time that affinity for hydrophobic organic solutes is lower. Consequently rejection may increase because adsorption-diffusion phenomena do not take place for hydrophobic compounds with similar (or higher) MW than membrane MWCO (Verliefde et al., 2009b).

Comparing both membranes, NF270 presented slightly higher rejection for caffeine, possibly indicating greater effectiveness than ESNA1LF2 for neutral and hydrophilic compounds separation. However, caffeine rejection using both membranes was around 70-90%, indicating the mid-high effectiveness of NF membrane technology for the removal of this kind of compounds, in spite of the MW of caffeine is lower than the reported MWCO of the membranes, and neutral charge did not experience negative charge repulsion. This is an interesting result because conventional treatments in DWTP have difficulties in order to remove hydrophilic compounds (Allpike et al., 2005).

These results using LAS and caffeine clearly showed that MW is not a good parameter to predict compounds rejection, in accordance to previous studies (Verliefde, 2008). In addition, desalting capacity of NF membranes could not explain higher rejections for LAS as semihydrophobic and anionc compound with linear shape. For molecules with similar or higher size to the MWCO of the membrane, hydrophobic affinity plays an important role if no electric charge exists, because these compounds pass across the membrane by means of adsorption-diffusion processes (Verliefde et al., 2009b).

Results from the rejection of cholesterol and terbuthylazine were very high for NF membranes, over 90%. As it has been said before, an overestimation of removal capacity can occur when no steady state is reached for the adsorption phenomenon (Verliefde et al., 2009b; 2009c). Then, these experimental results for terbuthylazine did not give any evidence of which separation mechanism acts in this membrane process. Cholesterol is logically rejected for NF membranes but the variation in its initial concentration (FSNF) is difficult to explain in this experiment because the reduction between samples $FSNF_{15}$ and $FSNF_{45}$ indicates adsorption phenomena in some part of the installation.

Literature review gives some key points that can be related to membrane properties when some organic compounds are considered. For example, in pesticides, structure and atom composition are highly variable, presenting different hydrophobic character depending on the specific compound. Aromatic pesticides present phenolic structures, usually conjugated with nitrogen and oxygen atoms, which increases membrane affinity by means of hydrogen bonds or van der Waals forces (Plakas et al., 2012). As a result, adsorption phenomenon is likely to take place in membrane surface or into membrane pores and steady state is required to experimentally study the separation for these hydrophobic compounds.

Desalination degree of membranes is a parameter commonly used to predict organic compounds rejection for NF membranes (Plakas et al., 2012; Kiso et al., 2001; Comerton et al., 2007), although in some cases membrane material and hydrophobic interactions play a major role in order to predict aromatic pesticides rejection (Kiso et al., 2001), or in case of intermediate hydrophobic compounds (LAS). For example, Kiso and co-workers, elucidated that sulfonated polyethersulfone membranes display lower rejection of aromatic pesticides compared to poly (vinyl alcohol)/polyamide ones, even though their desalination capabilities are similar, because membrane hydrophobicity is higher for the former.

## 6.4. CONCLUSIONS

The complexity of separation mechanisms in NF process was confirmed because different rejection values using four organic compounds with different characteristics were obtained from NF270 and ESNA1LF2 membranes. The pilot plant used in this study really allows simultaneous operation for both NF membranes, then direct comparison of organics rejection values can be carried out because operational conditions are the same for both NF membranes (pH of solution, feed water recovery, transmembrane flux, temperature and feed water quality). This can be used as a criteria to select the most suitable NF membrane for a full-scale drinking water treatment plant in case that conventional treatment do not face up to new challenges in drinking water quality with regards emergent organic pollutants.

UF performance was also evaluated as a pretreatment step before NF membranes. Generally, small organic compounds rejection was not observed using UF, for example in case of LAS and caffeine. Nevertheless, some unexpected low values in UF permeates could be explained as a result of organic compounds adsorption into NOM.

A pollution scenario in batch mode of operation was required for this study because, logically, real concentrations of organic compounds are very low for this freshwater feeding the drinking water treatment plant, and in NF permeates pollutants levels would be much lower being very difficult their quantification. Differences between membranes were evident: NF270 has higher water productivity and lower inorganic salt rejection than ESNA1LF2, but desalting capacity of NF membranes cannot always be related positively to organic compounds rejection. This is the case for LAS (anionic compound with moderate hydrophobicity) rejection, which is lower for ESNA1LF2 than for NF270 membrane. Caffeine, as a neutral, small and hydrophilic compound, is more rejected than LAS although presenting similar values for both membranes. These results lead to conclude that MW of solutes and desalting capacity of membranes are not useful parameters to predict some organic compounds rejection.

It is important to note that hydrophobic interaction can lead to false rejections and a period for adsorption process stabilization into membrane is required to predict accurately neutral organic compounds rejection with certain hydrophobic character (log $K_{ow} > 1$), as for examlpe aromatic pesticides as terbuthylazine. Cholesterol is logically well rejected for both membranes, and its absence in NF permeates is consequence of no biological activity.

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# Chapter 7: NF performance in flat sheet and spiral wound modules: prediction of full-scale performance and initial flux decline evaluation

Parts of this chapter were based on:

Ribera, G., Llenas, L., Martínez-Lladó, X., Rovira, M., de Pablo, J.; Comparison of nanofiltration membranes performance in flat sheet and spiral wound configuration: a scale-up study (2013). Desalination and Water Treatment 51 (1-3), 458-468.

## 7.1. INTRODUCTION

The simplest way to test an NF membrane is to use a flat sheet membrane with a plate and frame module in a laboratory scale plant. Out of laboratory experimentation, plate and frame configuration (flat-sheet) have been developed for small-scale applications because these units are expensive compared to its alternatives. This type of module appeared in the earliest stage of industrial membrane applications, presenting a simple structure and enabling an easy replacement of the membrane. Presently, this kind of modules is employed in electrodialysis and prevaporation systems, more than in pressure driven processes where a change of phase no take place (Mulder, 1996).

Spiral wound and plate and frame configurations work in cross-flow mode: where the feed mixture is forced across the surface of the membrane, and then a portion passes through the membrane obtaining permeate and concentrate streams. Both configurations also include a feed spacer to guarantee a good mass transfer at membrane surfaces and to minimise the concentration polarisation. Spacer design can be improved in order to optimize operational flux (related to capital costs) and pressure losses (related to operational costs) (Schäfer et al., 2005).

Therefore, the first step before developing a new NF treatment plant is to know which will be the most suitable membrane for each specific process. Although in industrial applications spiral wound membranes are used, flat-sheet modules provide a cheaper way to test between a wide range of commercial NF spiral membranes. Unfortunately, the hydraulics of spiral wound modules is quite more complex than in flat sheet modules (Schwinge et al., 2004), so it is not obvious that the performance of the membranes using both configurations is going to be the same (Amar et al., 2009).

In addition, when the studies are focused to specific compounds separation, usually traces or small substances, results from laboratory set-ups usually differ from those obtained in real plants (Verliefde, 2008). Especially for large membrane installations, operating at high feed water recovery, solutes rejection may be significantly lower than rejection obtained from single elements because, internally, solutes concentration increases.

Another limitation in order to predict performance in NF real plants is the tendency of membrane permeability to decrease in the first hours of operation, after the start-up of the plant. Numerous studies have been focused in membrane fouling tendencies (Chang et al., 2011; Hong and Elimelech, 1997; Shirazi et al., 2010; Wang and Tang, 2011) but less is known about compaction or other phenomena related to initial flux decline in case of NF and RO membranes (Malaisamy et al., 2002; Pendergast et al., 2010; Persson et al., 1995; Rahimpour et al., 2012).

Although technical manuals offer procedures for the correct start-up of the plant, few scientific references are found about preconditioning techniques before membrane operation (Visvanathan et al., 1998). During operation, membranes can experience compaction phenomena, which involves structural changes and consequently some negatives effects in permeability of rejection capacities. The degree of membrane compaction depends on the material and the manufacturing process for the membrane. For this reason, some studies are focused to check mechanical resistance of new membranes manufactured (Abuhabib et al., 2012; Bhanushali and Bhattacharyya, 2003; Gibbins et al., 2002).

The type of feed water has a major effect in flux decline, usually related to fouling phenomena: ionic strength, gel layer or cake formation, organic fouling or biofouling (Al-Amoudi, 2010). All this kind of fouling mechanisms are mainly influenced for water composition but also for operational conditions (hydraulic turbulence) or cleaning procedures, which implies correct frequencies and selection of the chemical products employed to recover initial permeate flux (Al-Amoudi and Lovitt, 2007b; Li and Elimelech, 2004). Nevertheless, the recovery of initial membrane flux results very complex in real applications as a result of irreversible fouling formation.

In the first section of this study, flat-sheet and spiral wound membranes have been evaluated to validate laboratory test as a useful technique of prediction for a real or pilot plants using NF membranes. The experimental results obtained were compared with those predicted by commercial design softwares for real NF and RO plants (ROSA from DOW Chemical and IMS design from hydranautics). In a second part of the study, comparison of both configurations have been performed in the Watercycle Research Institute, KWR (Nieuwegein, Netherlands), where compaction and other phenomena related to initial flux decline have been investigated. The final aim of the work is to know if the results obtained in a cross-flow module using flat sheet membranes and design softwares can be a good option to predict the spiral wound modules performance.

## 7.2. MATERIALS AND METHODS

### 7.2.1. Flat-*sheend* spiral wound performance comparison

The aim of the first experimental part is compare the rejection capabilities of two different nanofiltration membranes in flat sheet and spiral wound configurations, using the same feed water and similar operational conditions (cross-flow velocity, feed pressure, feed water recovery).

#### 7.2.1.1. Rejection experiments at pilot plant scale

The pilot plant used in this study is the same employed in previous 0 and Chapter 6, it is located in the drinking water treatment plant of Manresa. In this point, it is important to mention that the configuration of this two-staged pilot plant includes pressure vessels (PV) containing two elements each one, and three PV disposed in 2:1 disposition constitute one row of six nanofiltration elements (4-inch spiral wound modules). Two rows form part of the first stage (S1) in the pilot plant, with ESNA1LF2 (S1.1) and NF270 (S1.2) membranes that can operate separately in parallel to be compared with laboratory scale. Figure 7.1 shows the arrangement for a row containing the same model of membrane.

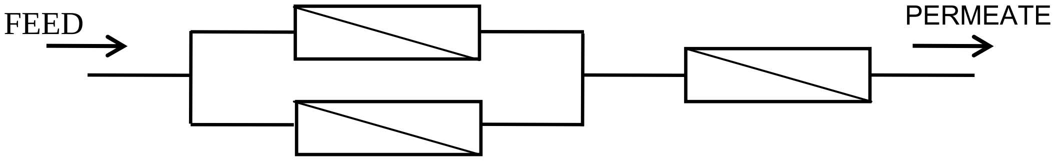


Figure 7.1: Arrangement of nanofiltration spiral wound modules in a row

Permeate and concentrate flows were measured using two flow-meters, and the sum of both streams corresponds to the feed flow. Pressure was measured using two pressure sensors on-line, one situated in the feed, and the other one in the concentrate. Finally, the conductivity was also monitored on-line using two sensors, one situated in the feed and two others in each permeate stream.

Flux and recovery of the modules are major parameters that govern concentration polarisation and thus also the risk of fouling of the membranes. Therefore, pilot plant operates between upper and lower operating constraints of the module as it must be designed for a real large scale NF plant (DOW Water & Process Solutions technical manual).

The total recovery of the pilot plant was fixed at 50% (PV with 6 spiral-wound modules), and the working pressure was adjusted in order to have the desired permeate flux, which was around 27 LMH. This value of the permeate flux is the one recommended when working with a municipal surface water with an SDI < 3 (Dow technical manual). About the feed flow rate, it was fixed at 2.4 $m^3 \cdot h^{-1}$.

### 7.2.1.2. Rejection experiments at laboratory scale

The laboratory scale experiments were performed using flat sheet membranes in a cross-flow module (SEPA CFII, GE Osmonics) as described in Chapter 4. However, in the test performed in this part some differences in the set-up were considered in the experimental design, the flow diagram in Figure 7.2 shows that the permeate was collected in another tank instead of typical recirculation mode. This modification pretends to simulate the pilot plant process that occurs in one row, so concentrate stream is continuously collected in feed tank, in total recirculation mode.

The final of each test takes place when the recovery used in the pilot plant was achieved, as stated in section 7.2.1.1 at a 50% recovery in each train, so in the laboratory scale setup a half of the feed solution was recovered as permeate. For that purpose, the feed solution was weighted before starting the experiment, and the permeate weight was monitored until reaching the desired value.

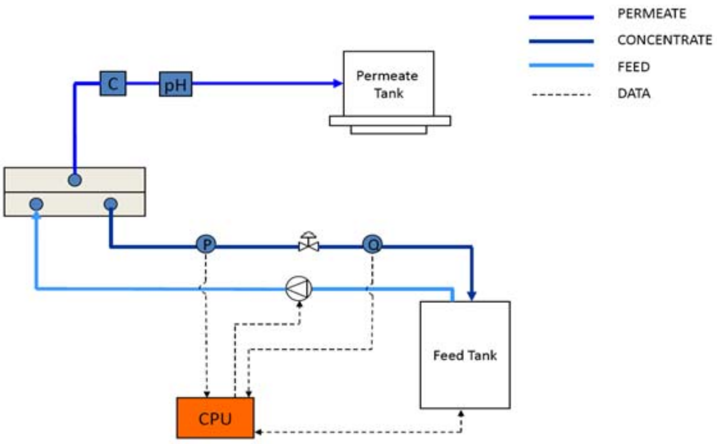


Figure 7.2: Experimental system flow sheet

The cross-flow velocity and the trans-membrane pressure were measured by two pressure sensors and a flow meter, connected directly to a data acquisition card. The permeate flux was chosen as the design parameter for setting the experimental conditions in the laboratory setup, so the pressure was adjusted in order to obtain the same permeate flux than in the pilot plant. Permeate flux in both scales was obtained dividing permeate flow per the total surface area of the membranes, expressed in LMH (liters/ square meter/ hour). Table 7.1 shows the operational parameters established for two sets of experiments carried out for each membrane (NF270 and ESNA1LF2), one in the pilot plant and the other in the laboratory configurations.

Table 7.1: Experimental conditions used in each set of experiments

| Membrane | Experimental system | Transmembrane flux (LMH) | Pressure (bar) | Cross-flow ($m·s^{-1}$) | Recovery (%) | T (ºC) |
|---|---|---|---|---|---|---|
| NF270 | Pilot Plant | 26.1 | 2.35 | 0.05 | 50 | 22 |
| NF270 | Laboratory | 25.8 | 2 | 0.09 | 50 | 22 |
| ESNA1LF2 | Pilot Plant | 27.8 | 4.05 | 0.1 | 50 | 22 |
| ESNA1LF2 | Laboratory | 30.5 | 2 | 0.08 | 50 | 22 |

Comparable values for all operational parameters are important in order to interpretate results from both experimental systems. However, it is important to notice that the pressure required in the pilot plant was twice the one used in the laboratory scale unit, indicating apparent hydraulic differences between flat-sheet and spiral-wound configurations for ESNA1LF2.

Regarding the cross-flow velocity, it was adjusted to be as similar as possible in the laboratory than in the pilot plant. It is important to state that the feed spacers used in the laboratory scale cross-flow cell were the same than in the pilot plant. Properties for these membranes have been shown in previous chapters.

### 7.2.1.3. Feed solution and membranes studied

The feed solution used for running the experiments in both membrane configurations was collected in the drinking water treatment plant of Manresa (Chapter 4 and 0). To perform the present comparative study between spiral-wound membranes (pilot plant) and flat-sheet (laboratory set-up), feed water used in laboratory was collected in the pilot plant during its operation (5L), exactly after the chemical addition of metabisulphite and scale inhibitor (Genesys LF).

Water analysis regarding major ions and organic carbon, non-purgable (NPOC), were performed as usual in the pilot plant and to assume the same concentrations to calculate rejection of components, water sample collected for laboratory experiments was also characterized. Results of feed water analysis are shown in Table 7.2.

Table 7.2: Feed water composition for pilot plant and laboratory set-up comparative study

| **Parameter** | **NF270 (22/06/2011)** | | **ESNA1LF2 (22/07/2011)** | |
|---|---|---|---|---|
| | **Pilot plant** | **Laboratory** | **Pilot plant** | **Laboratory** |
| Conductivity (µS·cm$^{-1}$) | 536 | 577 | 565 | 568 |
| $Ca^{2+}$ (mg·L$^{-1}$) | 76 | 75 | 79 | 78 |
| $Mg^{2+}$ (mg·L$^{-1}$) | 12 | 12 | 9.2 | 11 |
| $Na^{+}$ (mg·L$^{-1}$) | 18 | 18 | 19 | 19 |
| Cl (mg·L$^{-1}$) | 30 | 30 | 31 | 32 |
| $SO_4^{2-}$ (mg·L$^{-1}$) | 97 | 94 | 91 | 97 |
| IC (mg·L$^{-1}$) | 33 | 32 | 48 | 48 |
| TOC (µg·L$^{-1}$) | 2531 | 2897 | 2323 | 2333 |

### 7.2.2. Software employed for the prediction of NF performance

Most of membrane suppliers offer to user software to design real RO (NF) installations. Additionally, software predicts the productivity and the rejection for different membranes, so the user can know if a specific membrane could satisfy his needs. In this study, the software offered for DOW Chemical, ROSA, and Hydranautics, IMS design, were used to predict respectively NF270 and ESNA1LF2 membrane performance.

The installation design introduced in software was considered with the same configuration than one row in the first stage of the NF pilot plant (6 elements disposed in three PV (2:1), containing two spiral-wound membranes each PV).

Parameters employed in NF design imitating pilot plant conditions are indicated in Table 7.3. Operational parameters fixed at the same values than pilot plant for each type of membrane were feed water recovery and permeate flow, except in case of use software to predict 8-inch elements performance where feed flow was increased until reach similar values for permeate flux than in experimental cases. These considerations permitted to obtain from software calculation similar values of feed pressure and permeate flux to those governing pilot plant processes:

Table 7.3: Input data to ROSA and IMS design software

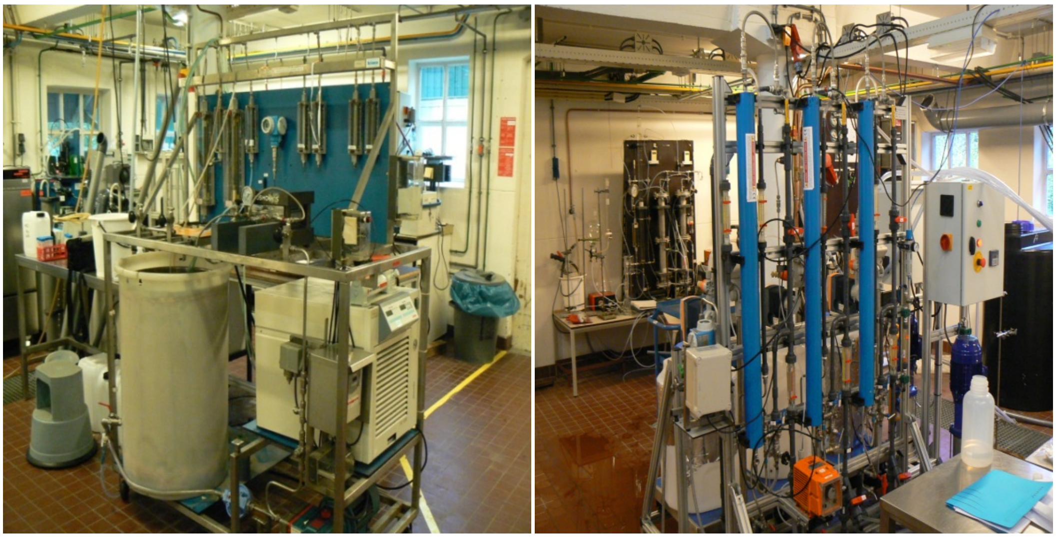
| | **ROSA** | | **IMS design** |
|---|---|---|---|
| Feed Flow (m$^3$·h$^{-1}$) | 2.4 | 11 | 13 |
| Recovery (%) | 50 | 50 | 50 |
| Permeate flux (LMH) | 26.25 | 24.67 | 29.2 |
| Feed pressure | 2.4 | 2.25 | 3.6 |
| Flow Factor | 0.9 | 0.9 | 0.6[a] |
| Feed water T (ºC) | 22 | 22 | 22 |
| Membrane module | NF270-4040 (4 inch) | NF270-400 (8 inch) | ESNA1LF2-8 inch |
| Feed water composition | See Table 2 | See Table 2 | See Table 2 |

[a]membrane age (years)

Similar values for operational parameters were predicted from software compared to those operating during the experimental part in both configurations, spiral wound (pilot plant) and flat-sheet (laboratory) (see Table 7.1). This is the first step in order to compare results predicted by software in front of experimental results using different NF configurations for major ions rejection.

### 7.2.3. Experimentation regarding initial flux decline in spiral wound membranes

This experimental part was carried out in KWR (Netherlands) using NF270 membrane (DOW Chemical) in a flat sheet (SEPA CFII module) and spiral wound (2.5 inch) configuration in (pilot plant) in order to evaluate initial flux decline that may occur in NF or RO membrane processes. The bench-scale systems used are shown in Figure 7.3.



a) b)

Figure 7.3: Images for the experimental set-up used in KWR a) flat-sheet using SEPA CFII (GE-Osmonics) cell; b) bench-scale for spiral wound membranes

Four hypotheses were evaluated in order to explain initial flux decline phenomenon: membrane compaction, the release of preservative liquid, the effects of ionic strength (IS) in the feed solution, humic acid (HA) fouling. NF270 from DOW Chemical was the only commercial NF membrane investigated in both configurations, and no preconditioning of the membrane was performed. Pieces for flat-sheet study were obtained cutting a spiral NF270 wound module. Deionised water and synthetic solution were used as feed water for these experiments. Table 7.4 summarises the experimental conditions performed in KWR indicating membrane configuration for each case.

Table 7.4: Experiments carried out in KWR to study initial flux declining in NF operation

| Experiment | Feed solution | Studied phenomenon | Pressure |
|---|---|---|---|
| F1: flat sheet | Deionised water | Compaction | Variable |
| F2: flat sheet | Deionised water | Preservative liquid | Constant |
| F3: flat sheet | NaCl 10 mM | Ionic strength (IS) | Constant |
| F4: flat sheet | NaCl 10 mM+$CaCl_2$ 5mM | Ionic strength (IS) | Constant |
| F5: flat sheet 24h | NaCl 10 mM+$CaCl_2$ 5mM | Ionic strength (IS) | Constant |
| F6: flat sheet 24h | NaCl 10 mM+$CaCl_2$ 5mM+HA | IS with low HA content | Constant |
| S1: spiral wound | Deionised | Compaction | Variable |
| S2: spiral wound | Deionised | Preservative liquid | Constant |

Experiments in order to observe membrane compaction for both configurations were performed using variable feed pressure in a range between 1 to 15 bars for flat sheet, and 3 to 10 bars for spiral wound module. This difference in operational pressure between membrane configurations is due to technical limitations for each set-up. Constant feed pressure for the rest of experiments was fixed at 10 and 3 bars for flat sheet and spiral wound modules, respectively.

Regarding other operational parameters, cross-flow velocity was maintained for all experiments and all configurations at 0.2 $m \cdot s^{-1}$. This value was obtained fixing feed flow at 60 $L \cdot h^{-1}$ and 350 $L \cdot h^{-1}$ for flat sheet and spiral wound modules, respectively. Temperature of the feed solution was maintained constant near to 20.0 ± 0.2 ºC.

Synthetic salt solutions were prepared from sodium chloride (NaCl from J.T. Baker) and calcium chloride ($CaCl_2$ from J.T. Baker) at respective concentrations of 10 mM and 5 mM. The last experiment in flat sheet configuration was carried out mixing humic acid (from Sigma Aldrich) solution into the solution containing the inorganic salts mentioned before. Unfortunately, concentration of total organic carbon (TOC) from dissolved humic acid (HA) was lower than it was expected theoretically. This can be explained because HA solution is similar to a colloidal suspension, although its transparency, and colloid or suspended HA are retained in security cartridge filter (1 µm meltblown, Van Borselen).

### 7.2.4. Analytical methods

Analysis of feed water and permeate samples were carried out by Ion Chromatography (Dionex ICS-2000) to determine anions ($Cl^-$, $SO_4^{2-}$) and cations ($Na^+$, $Ca^{2+}$, $Mg^{2+}$), and a total carbon analyzer (AnalytikJena Multi NC 3100) was used to analyse total inorganic carbon (IC) and organic carbon as NPOC.

In laboratory scale, permeate flow was measured dividing the weight of specific volume of permeate per the time required to collect this volume. Permeability considers permeate flow per unit of membrane area and the transmembrane pressure (TMP) in which filtration occurs during each sample collection. In pilot plant, flow-meters disposed on-line give directly the value of permeate flow, to calculate permeability of membrane is applied the same procedure than in laboratory scale.

## 7.3. RESULTS AND DISCUSSION

### 7.3.1. Flat-sheet and spiral wound rejection capacities comparison

In this part, results obtained in laboratory and pilot plant of CTM (technologycal center of Manresa) are compared in order to evaluate laboratory and design softwares as useful tools to predict real NF plants performance.

### 7.3.1.1. Anion and cation rejection results obtained with the NF270 membrane

Figure 7.4 shows the rejection of cations for each set of experiments using the NF270 membrane.

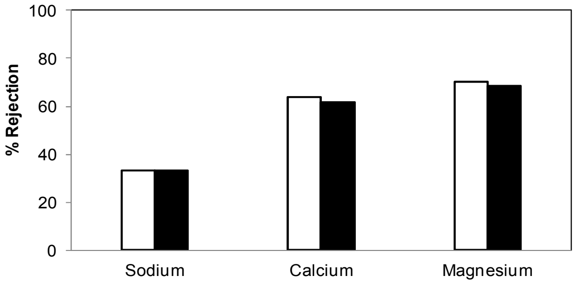


Figure 7.4: Cation rejections obtained with the NF270 membrane (white: laboratory scale, black: pilot plant)

Three different cations have been studied: sodium, which is a monovalent ion, and two divalent ions, calcium and magnesium. As it can be observed from the obtained results, sodium is less rejected than the divalent ions studied due to the electrostatic and steric effects between the ions and the membrane surface. Sodium presents rejections around 35%, whereas calcium and magnesium are more rejected with values higher than 60%. The obtained rejections have been compared with some other studies in the literature. De la Rubia and co-workers (De la Rubia et al., 2008) used the NF270 membrane for the nanofiltration of surface water, and the rejections obtained were very similar than the ones observed in this study (sodium: 35%, and calcium or magnesium: 57% of rejection).

Comparing the two sets of experiments performed, no noticeable differences can be observed between them. Therefore, with the obtained results corresponding to the cation rejection, it can be concluded that the results obtained in the laboratory setup and the ones obtained in the pilot plant are completely comparable between them.

The results obtained for the anions are shown in Figure 7.5.

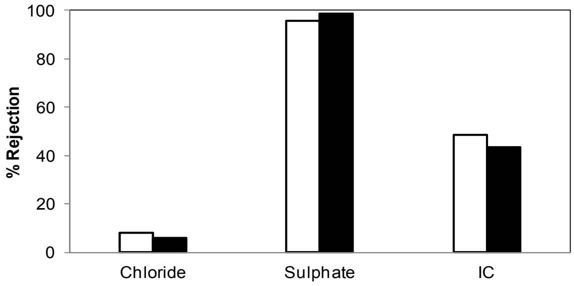


Figure 7.5: Anion rejections obtained with the NF270 membrane (white: laboratory scale, black: pilot plant)

The results obtained in the pilot plant and in the laboratory scale are very similar for the three anions studied. The rejection order in this case is $Cl^- < IC < SO_4^{-2}$. For the specific case of sulphate, it is practically totally rejected in both sets of experiments performed. In the study of De la Rubia et al. a rejection around 10% for chloride, 40% for TIC and rejection higher than 90% for sulphate were obtained (De la Rubia et al., 2008). Again, the results obtained in this study are very similar.

### 7.3.1.2. Anion and cation rejection results obtained with the ESNA1LF2 membrane.

The same set of experiments was also performed using ESNA1LF2 from Hydranautics was tested. The rejection results for the cations and anions are shown in Figure 7.6 and Figure 7.7.

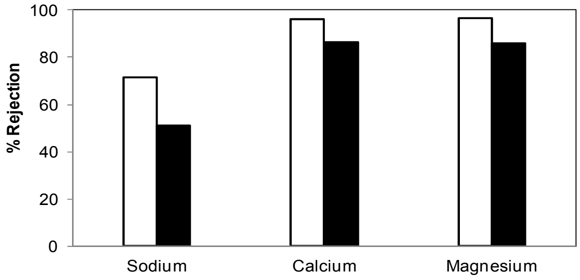


Figure 7.6: Cation rejections obtained with the ESNA1LF2 membrane (white: laboratory scale, black: pilot plant)

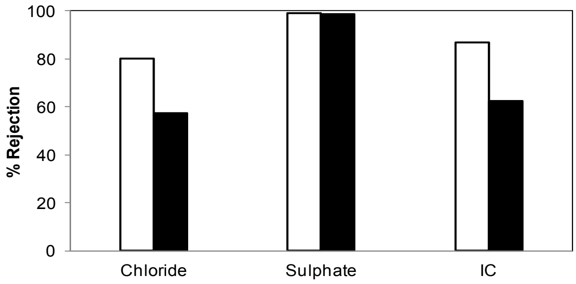


Figure 7.7: Anion rejections obtained with the ESNA1LF2 membrane (white: laboratory scale, black: pilot plant)

In comparison to the results obtained with the NF270 membrane, the rejections obtained when testing ESNA1LF2 are lower in the pilot plant than in the cross-flow filtration cell. The behaviour is the same for the anions and the cations, being the difference very similar in all cases, except for the sulphate, which is practically totally rejected in both configurations. Divalent cations (calcium and magnesium) rejection decrease approximately 10% at pilot plant in comparison to laboratory test, instead of nearly 30% in case of monovalent ions (sodium and chloride) and IC.

One possible explanation for the obtained results is that the spiral wound membranes were used for more than 6 months, so the membranes could be fouled. In order to check this hypothesis, one of the modules sacrified for membrane authopsy at the end of pilot plant experimentation was used to obtain flat-sheet membranes and to repeat laboratory test using a piece of the used membrane. Furthermore, the permeability of this membrane obtained was compared with that obtained in previous laboratory test for ESNA1LF2 (piece from a new membrane) (Table 7.1), observing a decrease of 14% approximately. This flux decline is similar to 12%, observed at the end of pilot plant experimentation, in Chapter 5 (Figure 7.3).

The new operation conditions used in the laboratory cross-flow cell for this new experiment performed with the fouled membrane are shown in Table 7.5.

Table 7.5: Experimental conditions for the fouled ESNA1LF2 membrane.

| Membrane | Experimental system | Transmembrane flux (LMH) | Pressure (bar) | Cross-flow ($m\cdot s^{-1}$) | Recovery (%) |
|---|---|---|---|---|---|
| ESNA1LF2 | Laboratory | 26.1 | 2 | 0.18 | 50 |

The results obtained in the flat-sheet cell with the used membrane are shown in Figure 8 and 9.

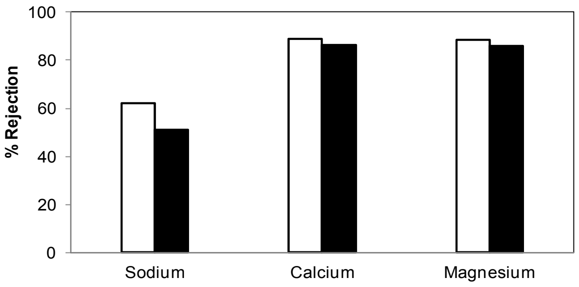


Figure 7.8: Cation rejections obtained with the ESNA1LF2 membrane (white: laboratory scale with used membrane, black: pilot plant)

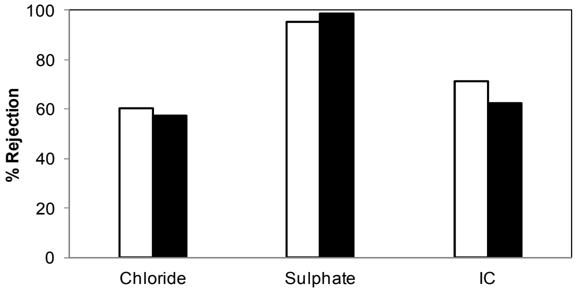


Figure 7.9: Anion rejections obtained with the ESNA1LF2 membrane (white: laboratory scale with used membrane, black: pilot plant)

The results obtained using samples from the pilot plant in the laboratory setup are more similar to those of the pilot plant than the ones obtained with the new membrane (Figure 7.6 and Figure 7.7). In this case, the rejections in both configurations are comparable, like they were for the NF270 membrane. In this last test, divalent cations (calcium and magnesium) rejection decrease only 3% at pilot plant in comparison to laboratory test, and sodium, chloride and IC, 18, 20 and 13% respectively.

The reason of this difference observed in permeate flux for both ESNA1LF2 membrane configurations may be because in the laboratory cross-flow cell a different feed spacer (related to height of feed channel) than in the pilot plant was used, so the mass transfer in the membrane surface was different. Specifically, the feed spacer used in all the laboratory experiments was the one corresponding to the NF270 membrane.

### 7.3.1.3. Organic Carbon rejection results

Due to the high importance of NOM removal in drinking water production, the rejection of Total Organic Carbon (TOC) was also studied. Figure 7.10 shows the rejection of TOC with both membranes in the two different configurations used in this work. In case of ESNA1LF2 membrane, the results showed in Figure 7.10 correspond to the measurements using the fouled membrane.

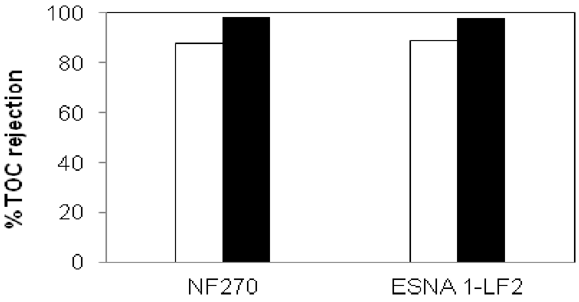


Figure 7.10: TOC rejections obtained with the two membranes studied (white: laboratory scale, black: pilot plant)

The results obtained for both membranes are very similar. In the pilot plant configuration, the TOC is practically totally rejected, whereas in the laboratory set up, the rejections are around 90%. These high rejection rates observed are greatly important for the removal of NOM, demonstrating that nanofiltration is a promising technology for that purpose.

On the other hand, regarding to the resemblance between the results obtained in both configurations, there is a difference around 10% between the rejection observed in the pilot plant and the values obtained in the laboratory cross-flow cell. This difference observed between both configurations may be attributed to analytical uncertainties due to the low TOC values observed in permeates. However, the results are good enough to conclude that the performance in both configurations is comparable.

### 7.3.2. Simulation using ROSA and IMS Design software

The predicted rejections when working with an 8-inch modules are very similar than the ones obtained when 4-inch modules are used, for this reason Figure 7.11 and Figure 7.12 show the comparison between the cations and anions rejection from experimental test using both configurations and the prediction calculated by ROSA software.

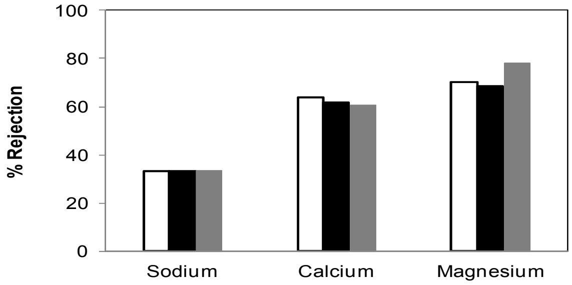


Figure 7.11: Cation rejections obtained with the NF270 membrane (white: laboratory scale, black: pilot plant, grey: ROSA software prediction)

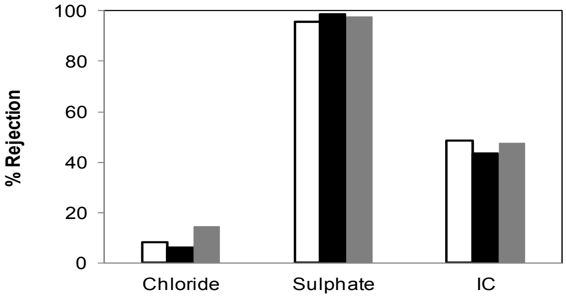


Figure 7.12: Anion rejections obtained with the NF270 membrane (white: laboratory scale, black: pilot plant, grey: ROSA software prediction)

With the obtained results, it can be stated that ROSA software is reliable to design and predict DOW membranes performance. The only rejections that deviate slightly from the behaviour observed experimentally are the magnesium and chloride rejections, which are overestimated by the software.

The main problem when using ROSA is that the user can only choose between DOW Filmtec membranes, so the range is very small compared with the high number of commercially available membranes. Another problem is that the user can just predict the inorganic ions rejection, so if the membrane process has to be applied to separate organic compounds the user will not be able to predict the membrane performance.

Finally, the software provided by Hydranautics, IMS Design, was also used to predict the ESNA1LF2 performance. In this case, only the prediction using the 8-inch module was available by the software. Figure 7.13 and Figure 7.14 show the results from software prediction in front of the previous obtained from experimental part.

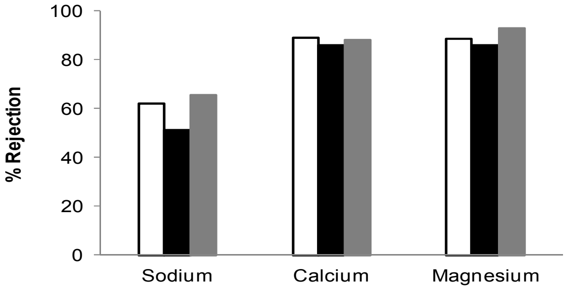


Figure 7.13: Cation rejections obtained with the ESNA1LF2 membrane (white: laboratory scale using the fouled membrane, black: pilot plant, grey: IMS-Design software prediction using 8-inch modules).

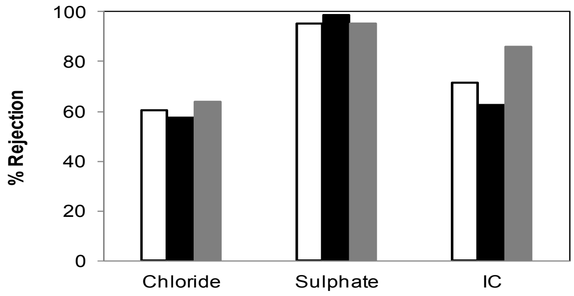


Figure 7.14: Anion rejections obtained with the ESNA1LF2 membrane (white: laboratory scale using the fouled membrane, black: pilot plant, grey: IMS-Design software prediction using 8-inch modules).

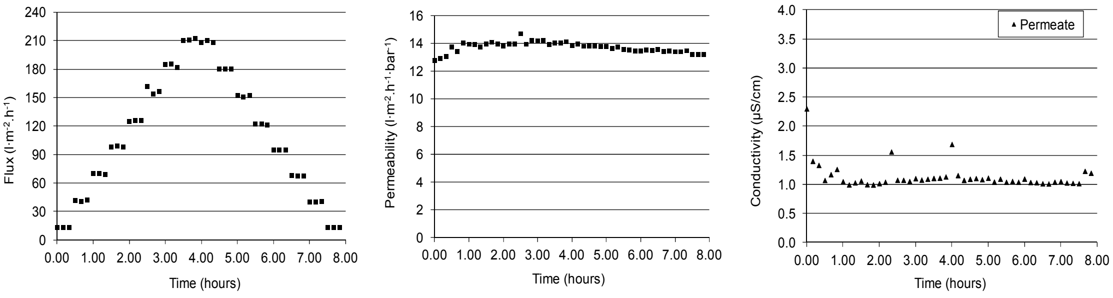
As it can be observed in Figure 7.13 and Figure 7.14, the rejections predicted by the software from Hydranautics are similar than the ones observed in the laboratory scale plant, and a little higher compared with the results obtained in the pilot plant experiments. So it can be concluded that the IMS-Design software can give to the user a correct approximation of the membrane performance to the membrane users (especially in flat sheet configuration), but it is less accurate than the software from Dow Chemical.

### 7.3.3. Results evaluating initial flux decline in the pilot plant using NF270

Evaluation of initial flux decline was carried out in both membrane configurations during the experimentation in KWR installations (Netherlands). Results are presented here with the intention to evaluate some hypothesis influencing flux decline phenomenon at the beginning of the NF process.

#### 7.3.3.1. Membrane compaction tests (F1 and S1)

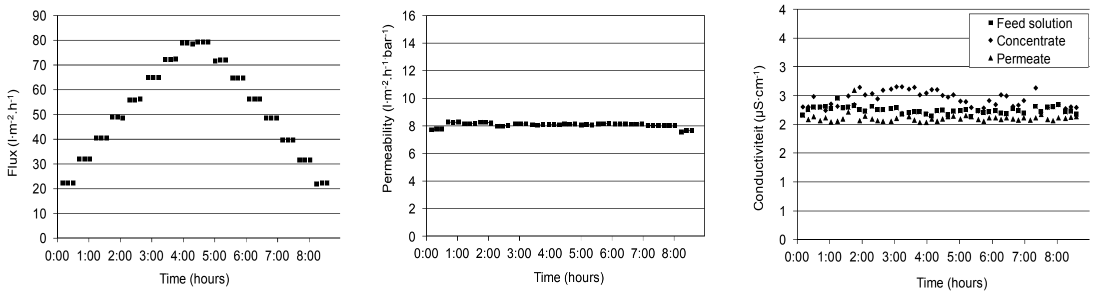
From the experimental part carried out in KWR, flat sheet and spiral wound modules for NF270 also showed similar performance regarding initial flux decline. Figure 7.15 shows higher permeate flux when feed pressure is increased from 1 to 15 bars for experiment F1 (flat sheet module), with variations of 2 bars for each sampling point. The same operation decreasing feed pressure at the same intervals was also evaluated. In addition, graphic b) in Figure 7.15 indicates how permeability remains constant although the applied feed pressures variations. From graphic c) conductivity measurements in permeate samples has been represented in front of the time for the test F1.



a) b) c)

Figure 7.15: Results from flat sheet in F1 experiment with NF of deionised water between a range of feed pressure regarding a) flux permeate, b) permeability and c) permeate conductivity

Results in terms of flux permeate indicate no compaction during the 8 hours of operation although feed pressure has been increased until 15 bars. This fact is easy to observe in graphic b) from Figure 7.16, where permeability is nearly constant. Slight decrease of permeability, lower than 4%, is observed in comparison to initial flux at 5 bars. These results from flat sheet membrane were contrasted with results from spiral wound membrane S1 in order to be sure that important compaction no takes place during the first hours of operation (Figure 7.16).



a) b) c)

Figure 7.16: Results from spiral-wound in S1 experiment with NF of deionised water between a range of feed pressure regarding a) flux permeate, b) permeability and c) conductivity for feed, concentrate and permeate flows.

Permeability in case of spiral module remains constant, less variation was observed in this case and this fact leads to confirm no compaction phenomenon for NF270 membrane. Variation in conductivity can not be really appreciated because deionised water conductivity showed no clear increase from its initial value (2.5 µS·cm$^{-1}$).

### 7.3.3.2. Influence of preservative liquid (F2 and S2)

The release of preservative liquid during initial NF tests was evaluated operating a constant pressure. Conductivity variations from the starting and ending times using deionised water indicated the decrease of salts in permeate samples by time. This behaviour is illustrated in Figure 7.17 for flat sheet and Figure 7.18. b) for spiral modules.

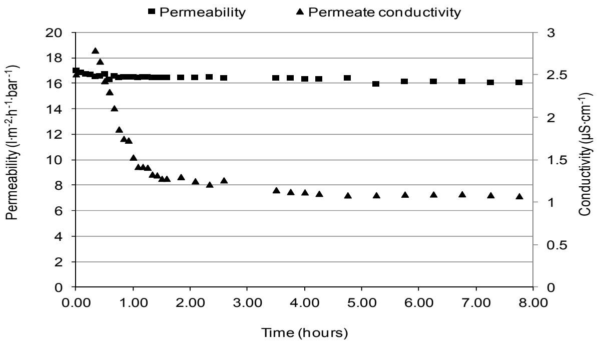
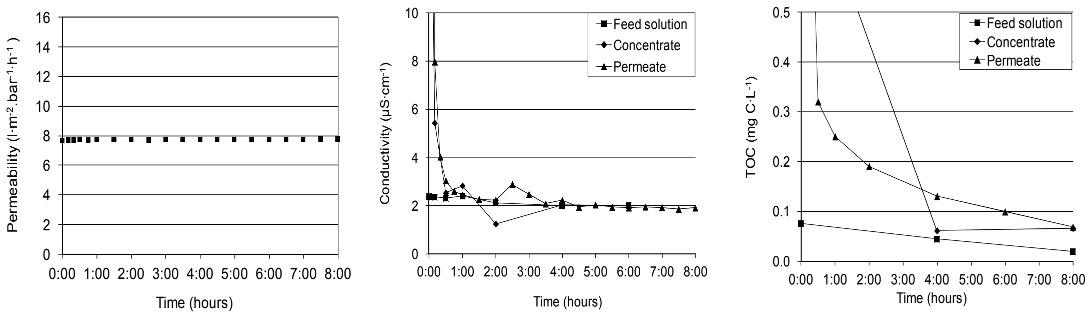


Figure 7.17: Results from experiment F2 regarding permeability and conductivity for permeate flow



a) b) c)

Figure 7.18: Results from spiral-wound in S2 experiment with NF of deionised water between a range of feed pressure regarding a) permeability, b) conductivity and c) TOC for feed, concentrate and permeate flows

Conductivity measurements in permeate samples during the 8 hours of experimentation show a reduction, approximately 70% for flat sheet and 80% for spiral tests, as a consequence of preservative liquid removal from the interior of the membrane. Another way to detect preservative liquid removal was by means of total organic carbon (TOC) analysis during the test. Figure 7.18.c) shows the decrease of TOC content in permeate samples as a result of its release from the interior of the membrane confirming the stated hypotheses.

On the other hand, permeability observed in the flat sheet experiment F2 (Figure 7.17) showed again the slight decrease between initial and final points (Figure 7.16.b). In this case, another explanation to this phenomenon could be the release of preservative liquid from membrane, because mass from permeable solutes also affects permeate flux measurements (performed in units of weight per time of permeate recollection). By contrast, in spiral wound measurements, permeate flow was automatically determined without the limitations of gravimetric method.

#### 7.3.3.3. Effects of inorganic salts content in feed solution (F3, F4, F5 and F6)

Two synthetic solutions were prepared as feed water, one with NaCl 10 mM and the other with NaCl 10 mM and $CaCl_2$ 5 mM (experiments F3 and F4). Respective permeability measurements and conductivities detected during the test in flat sheet are shown in Figure 7.19 and Figure 7.20.

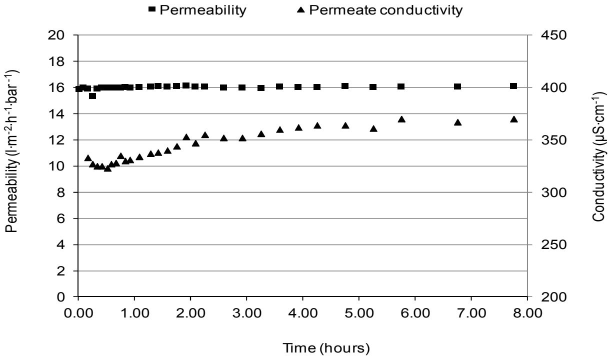


Figure 7.19: Results from experiment F3 regarding permeability and conductivity for permeate flow (Feed solution: NaCl 10 mM)

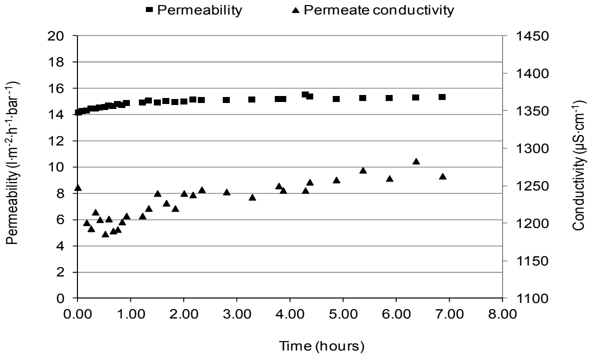


Figure 7.20: Results from experiment F4 regarding permeability and conductivity for permeate flow (Feed solution: NaCl 10 mM and $CaCl_2$ 5mM)

The ionic strength in feed solution and permeate samples is different in both experiments, for F3 was 0.01 mM and for F4 was 0.025 mM. These values correspond to initial conductivity of 1150 µS·cm$^{-1}$ and 2350 µS·cm$^{-1}$ and the average rejection for NF in respective experiments F3 and F4 were near to 70% and 50%. These differences in behaviour are related to charge effects between solutes and membrane surface (Childress and Elimelech, 2000; Freger et al., 2000). On the other hand, water permeability in case of F4 experiment is slightly lower than in F3 possibly due to the increase of concentration of polarization when calcium ions are added.

On the other hand, small increase in initial permeability is observed in Figure 7.20, which can be due to the effects of calcium (bivalent cation) interaction with negative charge of membrane surface (Freger et al., 2000). Although this small difference between permeability results from F3 and F4, no significative variation in permeate flux was detected.

The duration of experiments for the test F4 was increased to 24 hours in order to assure no initial flux decline as a result of the presence of sodium ($Na^+$), chloride ($Cl^-$) and calcium ($Ca^{2+}$). In Figure 7.21 is shown the represented permeability and conductivity in permeate samples during one day experimentation for the flat sheet module.

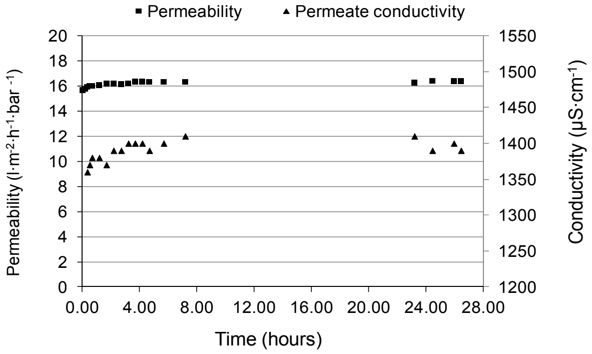
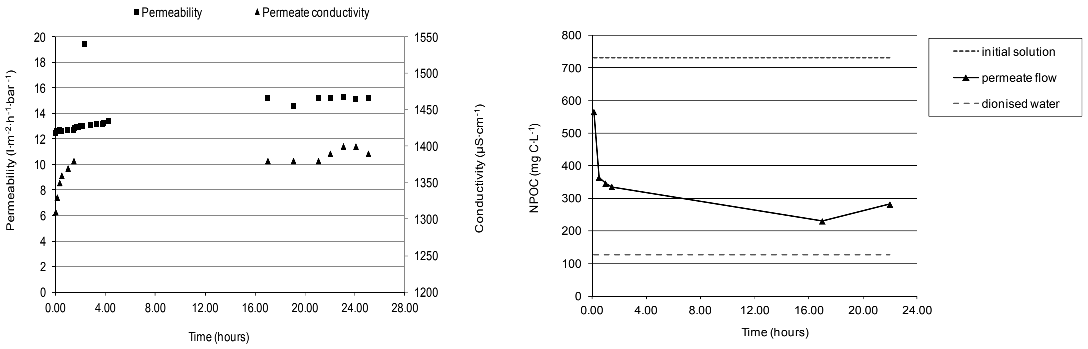


Figure 7.21: Results from experiment F5 regarding permeability and conductivity for permeate flow

Obviously the initial behaviour in Figure 17 is the same that in results presented in Figure 7.20 because the synthetic solution was prepared approximately at the same NaCl and $CaCl_2$ concentrations in feed solution. In accordance with these results, ionic strength as a result of $Na^+$, $Cl^-$ and $Ca^{2+}$ ions presence did not promote an initial flux decline, oppositely an slightly increase of initial permeability is observed during the first hour when calcium is added in the feed solution.

Last experiment carried out for flat sheet module (F6) to represent real processes phenomena has the aim to evaluate NOM effects in permeate flux, together with inorganic ions evaluated previously. Although the concentrations in feed solution was lower than the theoretical concentration calculated from a total dissolution of humic acid (HA) in F5 feed solution, results from test F6 are shown in Figure 7.22.



a) b)

Figure 7.22: Results from experiment F6 regarding a) permeability and conductivity for permeate flow with low content of HA, and b) NPOC reduction in permeate

In this case, the slight increase of initial permeability for flat sheet test F6 is again observed because calcium ions may interact with functional groups in membrane surface, as it was observed for the other test F4 and F5.

Organic carbon measurements measured in F6 are similar to those obtained in S2, which is explained as preservative liquid removal from the interior of the membrane. The only difference is the higher concentration of organic carbon in initial solution because HA solution was mixed in F6 test. Unfortunately, organic contents in feed solution (0.7 mg·L$^{-1}$) seems to be very small in F6 test to have noticeable influence in permeability results.

## 7.4. CONCLUSIONS

Two different nanofiltration membranes have been tested in two configurations, flat sheet and spiral wound, in order to compare the membrane performance in both. A cross-flow module was used to test the flat-sheet membranes, whereas a pilot plant was used to test 4 inch spiral wound modules of the two studied membranes.

With the obtained results, it can be concluded that the experimentation at the laboratory scale plant can be useful to design a full scale plant. However, it is important to perform the laboratory experiments working at the same recovery and the same permeate flux than the ones in the full scale plant because influence transport through the membrane, hence water permeability increase at higher feed pressures because feed flow is higher and water molecules are permeable to the membrane. On the other hand, solutes permeability depends on the type of separation mechanism in front of the membrane barrier (concentration polarization, adsorption interactions, fouling effects).

Results obtained testing the ESNA1LF2 membrane showed differences between laboratory tests using new or used membrane, obtaining better approximation when flat-sheet membrane was cut from the spiral-wound module sacrified from the pilot plant. It is important to consider that old membranes in large-scale plants can be fouled, so the performance of the membranes can decrease and the rejections obtained can be lower than the ones obtained using a clean membrane.

Simulations of the membrane performance have been done using the software provided for the membrane suppliers. The ROSA software, from Dow Chemical, could predict in an accurate way the experimentally obtained results, being the 4-inch or the 8-inch modules the one used for doing the simulation. About the IMS-Design software, from Hydranautics, it provided less accurate results compared with ROSA, predicting slightly higher rejections than the ones observed in the pilot plant. It can be considered that the software provided for the membrane suppliers is a good designing tool although laboratory or pilot experimentation is required when analytes of concern are not included in software (organic and inorganic traces, total organic carbon). Prediciton of flux decline and fouling formation is not possible with software design tool.

During the experiments performed in KWR, initial flux decline as a result of membrane compaction was not detected. Preservative liquid was observed to be removed in the first hour of filtration for both configurations. Some reduction in flux and total conductivity rejection were observed when feed solution was prepared at higher ionic strength, but permeability is almost constant during one day of experimentation. Unfortunately, the effects of organic matter were not observed because very low concentrations of NPOC were obtained in synthetic feed solutions. Consequently, at laboratory and pilot plant scales any of the hypotheses lead to reduce permeate flux at the beginning of NF process, deducing that initial fouling formation would explain the initial flux decline in industrial full-scale drinking water treatment plants.

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# Chapter 8: Environmental impact and human health risk study of nanofiltration in drinking water treatment

Parts of this chapter were based on:

G. Ribera, F. Clarens, X. Martínez-Lladó, I. Jubany, V.Martí, M. Rovira; LCA and HHR study for conventional and NF systems in a DWTP. *Submitted to Science of Total Environment journal*

## 8.1. INTRODUCTION

Implementation of new technologies, like membrane technology process, in drinking water treatments plants (DWTP) can improve quality of potable water and hence reduce human health risk (HHR) associated to its consumption. Financial, technical and public heatlh aspects are the main factors affecting the selection of one or another technology, although in last years life cycle assessment (LCA) regarding environmental impact can play an important role for decision makers.

LCA methodology is able to relate input and output data from construction, operation and demolition stages of a product or process (data inventory) to different environmental concerns, known as impact categories (such as climate change, ozone depletion, eutrophication). Consequently, evaluation of each stage is carried out and results are usually interpreted to improve or optimize processes, reducing their environmental impact, and in the best cases also reducing economic costs. For example, some LCA studies in water management have been developed in order to evaluate different systems and processes involved in water treatments from an environmental perspective (Table 8.1).

Global urban water management have been also evaluated in LCA studies, an energy consumption became the main contributor to environmental impact, where a great number of water processes are involved: from the water source, usually as a drinking water supply (Comandaru et al., 2012; Godskesen et al., 2011; Raluy et al., 2005; Stokes and Horvath, 2006) to the wastewater treatment and related discharges (Lassaux et al., 2007; Lundie et al., 2004; Lundin and Morrison, 2002; Vince et al., 2008). Another difficulty to compare LCA studies is due to differences in both feed and final quality, that lead to different treatments, which in turn will lead to variations in environmental impact and financial costs. Consequently, studies regarding technology comparison from these points of view have been increasing in last years due to its interest as a decision criteria (Barrios et al., 2008; Tapia et al., 2008).

In drinking water treatments, microbiological risk is reduced by including disinfection stages in both pretreatment and at the end of the process in DWTP. Nevertheless, disinfectant agents react with NOM present in most raw waters generating disinfection by-products (DBP). Trihalomethanes (THM) is the main group of DBP in chlorinated waters and has been extensively studied as a result of their toxicity (98/83/EC; RD140/2003; USEPA, 2001; WHO, 2004).

Table 8.1: Literature review regarding LCA of drinking water processes

| **Reference/ year/ Country** | **Water** | **Main treatments** |
|---|---|---|
| Canada (Bonton et al., 2012) | Lake | real NF in front of virtual GAC |
| Denmark<br>(Godskesen et al., 2011) | GW abstraction/ Desalination<br>RW harvesting/water recycling for toilet flush (Central and local treatment) | |
| Malaysia (Sharaai, 2010) | River | Conventional |
| USA<br>(Stokes and Horvath, 2009) | IW<br>SW<br>BGW<br>REC | Importing Water<br>Desalation+UF<br>MDesal BGW<br>WW reuse for industries/irrigation |
| France (Vince et al., 2008) | GW<br>FW | Different water resources and processes (UF, NF, SW by RO or Thermal Distillation) |
| Netherlands<br>(Barrios et al., 2008; Tapia et al., 2008) | Rhine River- Dune Lake | Evaluation of other important factors<br>(economics, water quality) |
| Netherlands<br>(Mohapatra et al., 2002) | | a) Soft+$O_3$+GAC+HCl+ RO<br>b) GAC+RO |
| South-Africa<br>(Friedrich, 2002) | Umgeni River | a) $Cl_2$+PAC+HCl+SF+NaClO<br>b) PreF+UF+Chlorination |
| Netherlands<br>(Sombekke et al., 1997) | GW | a) Pellet softening+GAC<br>b) RSF+NF |

IW: imported water; GW: ground water; SW: seawater; BGW: brackish groundwater; REC: reclaimed water; RW: rain water; WW: wastewater; GAC (PAC): granular (powdered) activated carbon; UF: ultrafiltration; NF: nanofiltration; RO: reverse osmosis; rapid sand filtration; Soft: softening; PreF: prefiltration; RSF: rapid sand filtration

Toxicological studies have suggested the development of cancer in digestive system (urinary bladder and rectal intestine), and animal studies have demonstrated the development of liver, kidney and intestinal tumors associated with chronic ingestion of THM (Dunnick and Melnick, 1993; Pilotto, 1995; Yang et al., 1998). Other studies have also demonstrated that exposure to chlorination by-products in water is related to spontaneous abortion, and other adverse reproductive outcomes (Gallagher et al., 1998; Waller et al., 1998). In case of HHR assessment regarding cancer effects, most studies only consider ingestion exposure, but since 1990, inhalation and dermal absorption are also taken into account in these works (Lee et al., 2004; Pardakhti et al.; Tokmak et al., 2004).

For these reasons, the present study aim to evaluate and relate results from both LCA and HHR studies, applied in a real drinking water plant equipped with NF as the technical option to improve drinking water quality. Initially, LCA methodology has been applied for NF process implementation in a real DWTP, including the analysis of different NF production capacities scenarios (25, 50, 75 and 100%). These results will be related to results from HHR considering the different qualities, estimated from THMFP determinations for final drinking water produced (Ribera et al., 2013).

## 8.2. MATERIALS AND METHODS

### 8.2.1. Description of the drinking water treatment process

Processes evaluated in this work correspond to actual treatments in the DWTP of Manresa (North East of Spain) with or without the inclusion of additional NF stage. The production capacity for the current DWTP is 23000 $m^3$ of drinking water per day. Conventional process has been described in Chapter 4.

The implementation of the NF step in the mentioned DWTP would treat part of the sand-filtered water with UF tubular membranes and NF spiral wound membranes. UF membranes reduce colloidal and particulate matter (measured as silt density index, SDI) to feed NF and cartridge filters prevent the accidental intrusion of particles. These steps are required to prolong NF membranes lifetime. Finally, NF permeate water would be mixed with conventional pretreated water from sand filters in order to supply the water with the desired quality.

The base case estudied in the first part of this LCA study is for a NF production capacity of 10000 $m^3 \cdot day^{-1}$, to be mixed in a final step with conventional pretreated water, representing a percentage of 43% of NF permeate water in the final drinking water at the output of the DWTP. This percentage was selected as a possible scale-up for a real NF installation according to water quality (Ribera et al., 2013) and economical assumptions. During this previous pilot plant experimentation described in Chapter 5, two commercial NF membranes (NF270 and ESNA1LF2) were simultaneously operated and their capacity to improve drinking water quality was evaluated considering different production capacities for NF: 0, 25, 50, 75 and 100%.

### 8.2.2. Environmental impact

The methodology used to evaluate the environmental impact is the LCA following the standardized guidelines under International Organization for Standardization (ISO, 2006a; b). LCA procedure involves four stages: goal and scope definition, life cycle inventory, impact assessment and finally, the interpretation of the LCA results. LCA study has been performed with the help of software Simapro v7.3.3.

#### 8.2.2.1. Goal and scope

The main goal in this LCA study is to evaluate the environmental impact of a real DWTP when an additional process of NF producing 43% of the final drinking water is implemented in order to improve its quality. This base case also compares differences during the operation stage when the two NF commercial membranes used in the pilot plant (NF270 and ESNA1LF2) were considered separately for its real implementation.

System boundaries in this work include construction and operational stages for the process considered in the DWTP (Figure 8.1). In the present study demolition stage was considered negligible in front of operational and construction stages, according to literature review (Bonton et al., 2012; Friedrich, 2002).

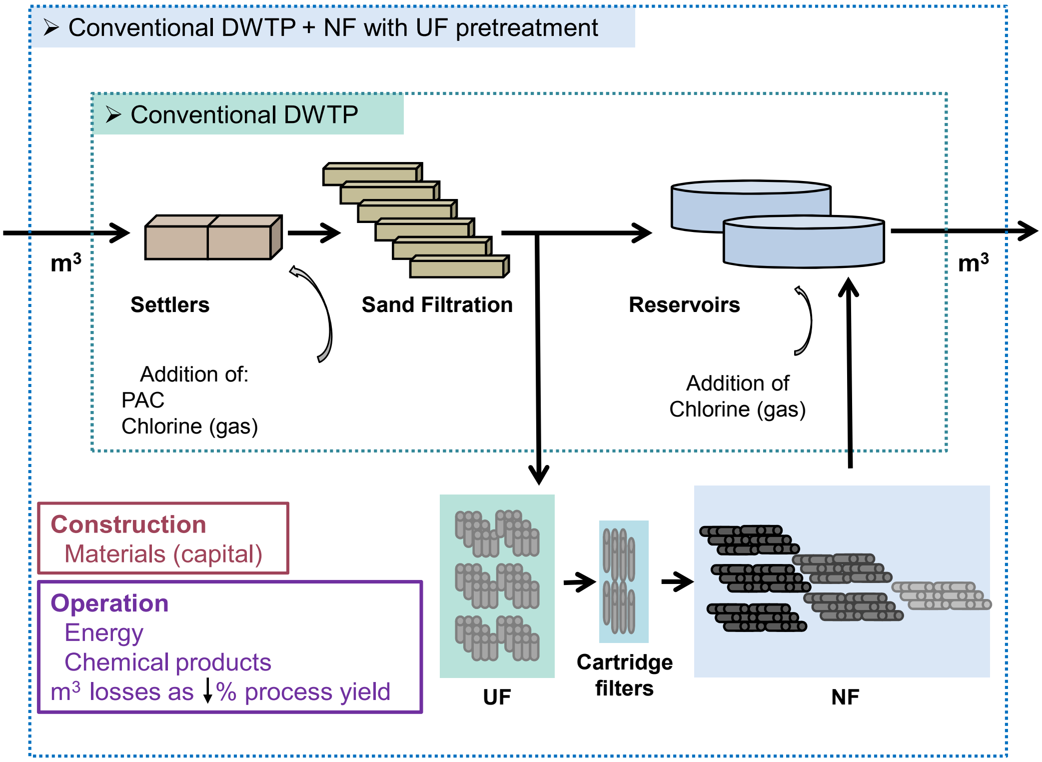


Figure 8.1: Basic scheme of the considered global system indicating the system boundaries

On the other side, primary data about transport of materials or emissions as brine discharge were out of the scope for this LCA study for the operation stage.

The functional unit (FU) was defined as one cubic meter of water produced considering a DWTP with a lifetime of 60 years.

### 8.2.2.2. Life cycle inventory

Primary data was collected from the real DWTP, such as the main material in capital investment (concrete), energy consumption and chemical products (chlorine, PAC). Table 8.2 summarises the data considered in the inventory for the current process in drinking water treatment. Secondary data were collected mainly from a recent study performed in the province of Quebec (Bonton et al., 2012), including capital materials like copper and other metals for electric and building installation. Additionally, Ecoinvent database was employed as default database to cover secondary data, including Spanish energetic mix production and processes related to chemical product manufacture (Ecoinvent, 2010).

Table 8.2: Specific data inventory for conventional real DWTP

| **Unit process** | **Input** | **Quantity/FU** |
|---|---|---|
| Construction stage (capital materials) | | |
| Decanters, reservoirs, bed filters | Concrete | $3.2 \cdot 10^{-4}$ $m^3 \cdot m^{-3}$ |
| Pumps, motors, tanks, building [a] | Steel | $2.8 \cdot 10^{-3}$ $kg \cdot m^{-3}$ |
| Building, tanks [a] | Glass wool | $2.2 \cdot 10^{-4}$ $kg \cdot m^{-3}$ |
| Pipes[a] | PVC | $1.6 \cdot 10^{-4}$ $kg \cdot m^{-3}$ |
| Motors[a] | Copper | $2.8 \cdot 10^{-5}$ $kg \cdot m^{-3}$ |
| Building (doors) [a] | Polyurethane | $1.8 \cdot 10^{-5}$ $kg \cdot m^{-3}$ |
| Building (ladders) [a] | Aluminum | $0.9 \cdot 10^{-5}$ $kg \cdot m^{-3}$ |
| Operational stage | | |
| Coagulation step | Aluminum polychloride | 0.021 $kg \cdot m^{-3}$ |
| Disinfection steps | Chlorine gas | $4.3 \cdot 10^{-3}$ $kg \cdot m^{-3}$ |
| Pretreatment step | Hydrochloric acid | $8.1 \cdot 10^{-3}$ $kg \cdot m^{-3}$ |
| Disinfection | Sodium Hypochloride | $5.3 \cdot 10^{-4}$ $kg \cdot m^{-3}$ |
| Sand filtration | Sand (silica) Hypochloride | $3.1 \cdot 10^{-4}$ $kg \cdot m^{-3}$ |
| Global process | Energy consumption | 0.095 $kWh \cdot m^{-3}$ |

[a] Based on capital materials from drinking water plant treating 2 $m^3 \cdot day^{-1}$ in the province of Quebec (Bonton et al., 2012)

The number of cartridge filters and UF modules were calculated following a similar procedure than in NF modules case, once the capacity of NF were defined at 10000 $m^3 \cdot day^{-1}$ of permeate. In these cases capital materials were calculated with geometrical approximations and supplier´s specifications about materials employed.

Operational data for NF was based on the pilot plant process carried out during 6 months using both NF270-4040 and ESNA1LF2-4040 modules simultaneously (Ribera et al., 2013). Additional chemical products added during the operation of the NF process are sodium metabisulphite and a scale inhibitor. These and other extra input data for the DWTP including NF are shown in Table 8.3.

The design for the NF plant in this study was based on typical tree-configuration, which implies the disposition of pressure vessels (PV) in three stages (AWWA, 2007), containing 460 spiral-wound modules in PV of 6-modules each one (Van der Meer, 2003). Chemical cleaning requirements were calculated by means of this scale up design and from pilot plant results, such as the required cleaning frequencies. Quantities of sodium hydroxide (NaOH) and ethylenediaminetetraacetic acid (EDTA), as the main cleaning products, were also deduced from concentrations recommended in manual guidelines (DOW, 1995- 2012).

Table 8.3: Inventory input data for membranes system

| **Unit process** | **Input** | **Quantity/FU** |
|---|---|---|
| Construction stage (capital materials) | | |
| Pumps, motors, tanks, building[a] | Steel | 0.9·10-3 kg·m-3 |
| Building, tanks[a] | Glass fibre | 1.5·10-4 kg·m-3 |
| Pipes[a] | PVC | 1.2·10-4 kg·m-3 |
| Motors[a] | Copper | 5.0·10-5 kg·m-3 |
| Building (doors)[a] | Polyurethane | 1.0·10-5 kg·m-3 |
| Building (ladders)[a] | Aluminum | 5.0·10-5 kg·m-3 |
| Operational stage | | |
| UF membranes material | PVC polymer | 2.4·10-5 kg·m-3 |
| UF membranes material | PDVF polymer | 6.6·10-5 kg·m-3 |
| NF membranes material[b] | Bis(chlorodiphenyl)sulfone | 3.1·10-5 kg·m-3 |
| NF pretreatment | Scale inhibitor, phosphonates | 7.2·10-3 kg·m-3 |
| NF pretreatment | Metabisulphite | 1.1·10-3 kg·m-3 |
| NF cleaning | EDTA | 9.0·10-5 kg·m-3 |
| NF cleaning | NaOH | 8.5·10-6 kg·m-3 |
| UF process[c] | Energy consumption | 0.02 kWh·m3 |
| NF270 process( ROSA)[d] | Energy consumption | 0.21 kWh·m3 |
| ESNA1LF2 process (IMS design)[e] | Energy consumption | 0.24 kWh·m3 |

[a] From NF drinking water plant treating 2 $m^3$·$day^{-1}$ in the province of Quebec (Bonton et al., 2012)

[b] United States patent 4277344 (USpatent, 1981)

[c] (Plappally and Lienhard, 2012)

[d] ROSA: design software for reverse osmosis membranes from DOW chemical

[e] IMS design: integrated membrane system design software from Hydranautics

Energy consumption in NF indicated in Table 8.3 was extracted from the respective simulation programs (ROSA from DOW Chemical and Integrated Membrane System (IMS) design, from Hydranautics) considering the scale-up design for the NF plant. Higher values of energy costs for ESNA1LF2 are in accordance to the lower permeability of this membrane.

A weak point of comparative LCA study between membranes is due to assumptions in membrane materials for both membranes. In fact, no information is available as a result of confidentiality in membrane production by manufacturers. For this reason, no differences in capital material data between membranes are considered. Membrane materials evaluated in this study were mainly based in Bonton approximations taking into account an autopsy for NF270 and some patents (Bonton et al., 2012), and their values were used for both NF membranes. By contrast, UF membrane material based on PVDF and PVC polymers were calculated considering geometrical approximations to membranes fibers and housing modules, respectively.

### 8.2.2.3. Life cycle impact assessment methodology

The methodology followed in this work implies the construction of the process structure with the help of Simapro v7.3.3. Results of LCA impacts were obtained using the Recipe Midpoint (H) method (v.1.06) as characterization method (PRéConsultants, 2011). In overall, results are discussed for 12 selected categories according to relevant environmental issues in water processes (Table 8.4) (Hospido et al., 2008; Lundie et al., 2004).

Table 8.4: Impact categories evaluated

| | **Abbreviation** | **Units/(FU)** |
|---|---|---|
| Climate change | CC | kg CO2 eq |
| Ozone depletion | OD | kg CFC-11 eq |
| Human toxicity | HT | kg 1.4-DB eq |
| Photochemical oxidant formation | POF | kg NMVOC |
| Particulate matter formation | PMF | kg PM10 eq |
| Terrestrial acidification | TA | kg SO2 eq |
| Freshwater eutrophication | FEU | kg P eq |
| Terrestrial ecotoxicity | TE | kg 1,4-DB eq |
| Freshwater ecotoxicity | FE | kg 1,4-DB eq |
| Water depletion | WD | $m^3$ |
| Metal depletion | MD | kg Fe eq |
| Fossil Depletion | FD | kg oil eq |

One of the limitations in LCA studies is that represent a punctual evaluation of the systems involved in product manufacturing or services. LCA is not useful to study the evolution in time or modifications in space for the considered system, for this reason the analysis of different scenarios permit to introduce modifications in the initial system and evaluate their impacts. Using the same scheme implemented in Simapro initially, NF process was modified in function of its capacity to produce percentages of 25, 50, 75 and 100% of NF permeate for final drinking water production. Table 8.5 indicates the different cases for the global LCA study presented here.

Table 8.5: Main characteristics for the cases evaluated in this LCA study of scenarios

| Case | Feed flow to | | Percentage of NF permeate water (%) | Final Flow for DW |
|---|---|---|---|---|
| | conventional DWTP | UF+NF plant | | |
| Conventional | 23590 | 0 | 0 | 23000 |
| Base case | 25065 | 11329 | 43 | 23000 |
| Scenario 1 | 24448 | 6586 | 25 | 23000 |
| Scenario 2 | 25306 | 13173 | 50 | 23000 |
| Scenario 3 | 26164 | 19760 | 75 | 23000 |
| Scenario 4 | 27021 | 26346 | 100 | 23000 |

It is assumed that the conventional plant have the enough production capacity to supply the requested feed flow for the different cases of NF process indicated, overcompensating the losses in membrane stages. For this reason, operational costs (enery and chemical products) have to be increased in comparison to conventional treatment because NF installation requires additional feed flow to maintain the same production at the output of the DWTP.

Finally results from the scenarios analysis regarding some environmental impacts (climate change, ozone depletion, human toxicity, freshwater eutrophication, human toxicity and metal depletion categories) were correlated with HHR results regarding carcinogenic effects of THM for the same scenarios previously defined (Ribera et al., 2013).

### 8.2.3. HHR assessment regarding THM in tap water

HHR assessment is used to evaluate the effects of toxic substances to human population taking into account factors as their presence in the environment, contact exposure and inherent toxicity of the chemical.

In this work, cancer risk related to different exposure pathways for THM was estimated for the associated drinking water uses. The approach to HHR assessment is based on the United States Environmental Protection Agency (USEPA, 2012) guidelines, for the determination of lifetime cancer risk.

Epidemiological studies indicate that exposure to THM increase the risk of cancer in digestive system, being the ingestion the main route to entry in the human body (Wang et al., 2007). However, inhalation and dermal absorption play an important role in THM exposition and thus, they are considered in this study. Toxicity data expressed as cancer slope factors were calculated from data published in RAIS (Risk Assessment Information System) database (USEPA, 2009a; b). Dermal slope factors were calculated dividing oral slope factors per a gastrointestinal absorption factor of 1. Inhalation slope factors were calculated from inhalation unit risk considering a body weight of 70 kg and an inhalation rate of 20 $m^3 \cdot day^{-1}$. Slope factors are indicated in Table 8.6.

Table 8.6: Cancer slope factors (SF) for four THM in different routes of exposition

| **Chemical** | **Cancer Group** | **Carcinogenic slope factors $(mg \cdot (kg \cdot day)^{-1})^{-1}$** | |
|---|---|---|---|
| | | Oral/dermal | Inhalation |
| Chloroform | B1 | $3.1 \cdot 10^{-2}$ | $8.05 \cdot 10^{-2}$ |
| Bromodichloroform | B2 | $6.2 \cdot 10^{-2}$ | $1.30 \cdot 10^{-1}$ |
| Dibromochloroform | C | $8.4 \cdot 10^{-2}$ | $9.50 \cdot 10^{-2}$ |
| Bromoform | B2 | $7.9 \cdot 10^{-3}$ | $3.85 \cdot 10^{-3}$ |

B1: probable human carcinogen with limited human data; B2: probable human carcinogen with sufficient animal data; C: possible human carcinogen

Exposure assessment has to consider concentrations of the toxic chemical substance in the environment of concern; for this case in water and air. THMFP determined experimentally during the pilot plant operation from April to October of 2011 (Ribera et al., 2013) represent THM concentrations in the present study for HHR calculations. Table 8.7 shows an average of the results for THMFP determined monthly taking into account the same water mixes than those considered in the LCA scenario study for different NF production capacities (25, 50, 75 and 100% of final drinking water).

Table 8.7: Concentration of THM estimated as THMFP for different NF scenarios

| **NF % in the final drinking water** | **THMFP** | **Average concentration ($\mu g \cdot L^{-1}$)** | |
|---|---|---|---|
| | | **NF270** | **ESNA1LF2** |
| Conventional | Chloroform | 147 | |
| | Bromodichloroform | 10.7 | |
| 25% NF | Chloroform | 120 | 119 |
| | Bromodichloroform | 10.2 | 9.30 |
| 50% NF | Chloroform | 87.7 | 94.0 |
| | Bromodichloroform | 9.10 | 8.30 |
| 75% NF | Chloroform | 59.8 | 57.0 |
| | Bromodichloroform | 8.20 | 6.20 |
| 100% NF | Chloroform | 30.5 | 23.5 |
| | Bromodichloroform | 4.90 | 3.70 |

Only TCM and BDCM were quantified as the main THM detected to consider carcinogenic effects during potable water uses. Exposure doses were calculated from lifestyle parameters for consumers (Table 8.8) and for each pathway of exposure in the Equations (1) to (4) for oral, dermal and inhalation pathways (Lee et al., 2004; Pardakhti et al., 2012; Tokmak et al., 2004). Cancer risk index was calculated from the exposure values and slope factors (SF) for each pathway indicated in Table 8.6.

**Oral pathway:** Cancer risk for THMs = $CDI_{oral} \times SF_{oral}$ (1a)

$CDI_{Oral}$ (Chronic Daily Intake) = $(C_{water} \times IR \times EF \times ED) / (BW \times AT)$ (1b)

**Dermal absorption pathway:** Cancer risk for THMs = CDI x $SF_{ingestion}$ (2a)

$AD = (C_{water}\ x\ SA\ x\ PC\ x\ ET\ x\ EF\ x\ ED) / (BW\ x\ AT)$ (2b)

**Inhalation exposure pathway:** Cancer risk for THMs = $CDI_{inhalation}$ x $SF_{inhalation}$ (3a)

$CDI_{inhalation} = (C_{air}\ x\ VR\ x\ AE\ x\ ET\ x\ EF\ x\ ED) / (BW\ x\ AT)$ (3b)

**Total risk** = $(CDI_{oral}\ x\ SF_{oral}) + (CDI\ x\ SF_{ingestion}) + (CDI_{inhalation}\ x\ SF_{inhalation})$ (4)

Table 8.8: Input parameters and abbreviations for exposure assessment

| **Cancer risk calculation parameters** | | **Units** | **Value** | **Reference** |
|---|---|---|---|---|
| THM conc. water | $C_w$ | $\mu g \cdot L^{-1}$ | Table 8.6 | (Ribera et al, 2013) |
| THM concentration air | $C_{air}$ | $\mu g \cdot L^{-1}$ | Table 8.9 | (Little, 1992) |
| Ingestion rate | IR | $L \cdot dia^{-1}$ | 2 | (Pardakhti et al. 2011) |
| Exposition Frequency | EF | $days \cdot year^{-1}$ | 365 | (Lee et al., 2004) |
| Exposition duration | ED | years | 30 | (Lee et al., 2004) |
| Ventilation Rate | VR | $m^3 \cdot h^{-1}$ | 0.83 | (Pardakhti et al. 2011) |
| Absorption efficiency | AE | % | 50 | (Lee et al., 2004) |
| Body weight | BW | Kg | 70 | (Lee et al., 2004) |
| Average Lifetime | AT | days | 25550 | (Lee et al., 2004) |
| Skin surface area | SA | $m^2$ | 1.8 | (Pardakhti et al. 2011) |
| Fraction of skin in contact with water | F | % | 90 | (Lee et al., 2004) |
| Permeability coefficient | PC | $cm \cdot h^{-1}$ | $6.83 \cdot 10^{-5}$<br>$4.02 \cdot 10^{-5}$ | (USEPA 2009b) |
| Exposure Time | ET or *t* | $min \cdot dia^{-1}$ | 35 | (USEPA 2009b) |
| **Additional parameters to calculate $C_{air}$** | | **Units** | **Value** | **Reference** |
| Bathroom volume | Vs | $m^3$ | 10 | (Chen et al., 2003) |
| Water flow rate | $Q_L$ | $L \cdot min^{-1}$ | 5 | (Little, 1992) |
| Air flow rate | $Q_G$ | $L \cdot min^{-1}$ | 50 | (Little, 1992) |
| Conversion Factor | CF | $L \cdot m^{-3}$ | 1000 | (Lee et al., 2004) |
| Water Temperature | T | ºC | 40 | (Lee et al., 2004) |
| Henry's constant at 40ºC | H TCM<br>H BDCM | | 0.25<br>0.124 | (Lee et al., 2004) |
| Mass transfer coefficient | $K_{olA}$ TCM<br>$K_{olA}$ BDCM | $L \cdot min^{-1}$ | 7.4<br>5.9 | (Little, 1992) |

Concentrations of THM in water ($C_{water}$) are directly the values of THMFP in Table 8.7, however, THM concentrations in air ($C_{air}$) were estimated using the two-resistance theory proposed by Little in Equation (5) to (9) (Little, 1992) and considering the shower room as the scenario where takes place the dermal and the inhalation exposition (parameters indicated in Table 8.8).

$C_{air} = (Y_{s(t)} + Y_{s(i)}) / 2$ (5)

Where $Y_{s(i)}$ is the initial THM concentration in the shower room, assumed as 0 $\mu g \cdot L^{-1}$ $Y_{s(t)}$ is the THM concentration in the shower room at time *t*

$$Y_{s(t)} = [1\text{-exp}(\text{-}bt/CF)] \cdot (a/b) \qquad (6)$$

$$b = \{ (Q_L/H) \cdot [1\text{-exp}(\text{-}N)] + Q_G \} / V_S \qquad (7)$$

$$a = \{ Q_L \cdot C_w \cdot [1\text{-exp}(\text{-}N)] \} / V_S \qquad (8)$$

$$N = K_{OL} / Q_L \qquad (9)$$

In Table 8.9 results from Equation (5) for $C_{air}$ are shown for TCM and BDCM, considering different percentages of NF permeate water in potable water.

Table 8.9: Results for air concentrations results from previous equations

| NF % in the final drinking water | THMFP | Average concentration ($\mu g \cdot L^{-1}$) | |
|---|---|---|---|
| | | NF270 | ESNA1LF2 |
| Conventional | Chloroform | $8.9 \cdot 10^{-4}$ | |
| | Bromodichloroform | $5.7 \cdot 10^{-5}$ | |
| 25% NF | Chloroform | $7.2 \cdot 10^{-4}$ | $7.2 \cdot 10^{-4}$ |
| | Bromodichloroform | $5.4 \cdot 10^{-5}$ | $4.9 \cdot 10^{-5}$ |
| 50% NF | Chloroform | $5.3 \cdot 10^{-4}$ | $5.6 \cdot 10^{-4}$ |
| | Bromodichloroform | $4.8 \cdot 10^{-5}$ | $4.4 \cdot 10^{-5}$ |
| 75% NF | Chloroform | $3.6 \cdot 10^{-4}$ | $3.4 \cdot 10^{-4}$ |
| | Bromodichloroform | $4.3 \cdot 10^{-5}$ | $3.3 \cdot 10^{-5}$ |
| 100% NF | Chloroform | $1.8 \cdot 10^{-4}$ | $1.4 \cdot 10^{-4}$ |
| | Bromodichloroform | $2.6 \cdot 10^{-5}$ | $1.9 \cdot 10^{-5}$ |

## 8.3. RESULTS AND DISCUSSION

### 8.3.1. LCA of the DWTP including NF membranes technology

NF process implementation in conventional DWTP increases environmental impact mainly as direct consequence of additional energy and resources consumption during operation stage. Table 8.10 indicates LCA results for the conventional case in front of the base case. The latter was studied in two systems using different NF membranes: NF270 and ESNA1LF2 membranes.

Table 8.10: Results from environmental LCA impacts

| Environmental category | Units/(FU) | Conv. | Base case | |
|---|---|---|---|---|
| | | | NF270 | ESNA1LF2 |
| Climate change | kg CO2 eq | 0.096 | 0.147 | 0.154 |
| Ozone depletion | kg CFC-11 eq | $1.31 \cdot 10^{-8}$ | $2.07 \cdot 10^{-8}$ | $2.11 \cdot 10^{-8}$ |
| Human toxicity | kg 1,4-DB eq | 0.045 | 0.079 | 0.082 |
| Photochemical oxidant formation | kg NMVOC | $3.4 \cdot 10^{-4}$ | $5.4 \cdot 10^{-4}$ | $5.7 \cdot 10^{-4}$ |
| Particulate matter formation | kg PM10 eq | $2.6 \cdot 10^{-4}$ | $4.1 \cdot 10^{-4}$ | $4.3 \cdot 10^{-4}$ |
| Terrestrial acidification | kg $SO_2$ eq | $6.1 \cdot 10^{-4}$ | $1.1 \cdot 10^{-3}$ | $1.2 \cdot 10^{-3}$ |
| Freshwater eutrophication | kg P eq | $4.4 \cdot 10^{-5}$ | $7.3 \cdot 10^{-5}$ | $7.5 \cdot 10^{-5}$ |
| Terrestrial ecotoxicity | kg 1,4-DB eq | $1.3 \cdot 10^{-5}$ | $2.3 \cdot 10^{-5}$ | $2.4 \cdot 10^{-5}$ |

| | | | | |
|---|---|---|---|---|
| Freshwater ecotoxicity | kg 1,4-DB eq | $1.9\cdot10^{-3}$ | $2.6\cdot10^{-3}$ | $2.6\cdot10^{-3}$ |
| Water depletion | $m^3$ | $8.3\cdot10^{-4}$ | 0.0012 | 0.0013 |
| Metal depletion | kg Fe eq | 0.044 | 0.062 | 0.062 |
| Fossil depletion | kg oil eq | 0.027 | 0.043 | 0.045 |

Conv.: current process in the DWTP; NF270: DWTP with NF270 membranes; ESNA1LF2: DWTP with ESNA1LF2 membranes

Climate change (CC) category expressed as equivalent emissions of carbon dioxide, have increased 53% and 60% for NF270 and ESNA1LF2 systems, respectively. The main difference between both membrane systems is due to different energy consumption during the operational stage. Observing other categories, the tendency is quite similar to that obtained in CC. Nevertheless, this negative impact on the environment could be compensated with the improvement of drinking water quality when NF is implemented in a DWTP.

Consumption of some chemicals products can also vary for both types of membranes, resulting as a possible criterion for membrane selection as a result of different environmental and economic costs effects. Even though, in this study no differences in chemical addition were considered because this data was taken as primary data from the pilot plant, where both membranes were fed with the same chemical doses.

The variations observed in different impact categories for this comparative study have different origins in function of the input data. The assemblage of unit processes modeled in Simapro is used to know the contribution of the inventory data associated to the process. Figure 8.2 shows a network diagram for CC impact in case of DWTP including NF270 membranes. The scheme for conventional system and ESNA1LF2 membrane can be found in Annex 5.

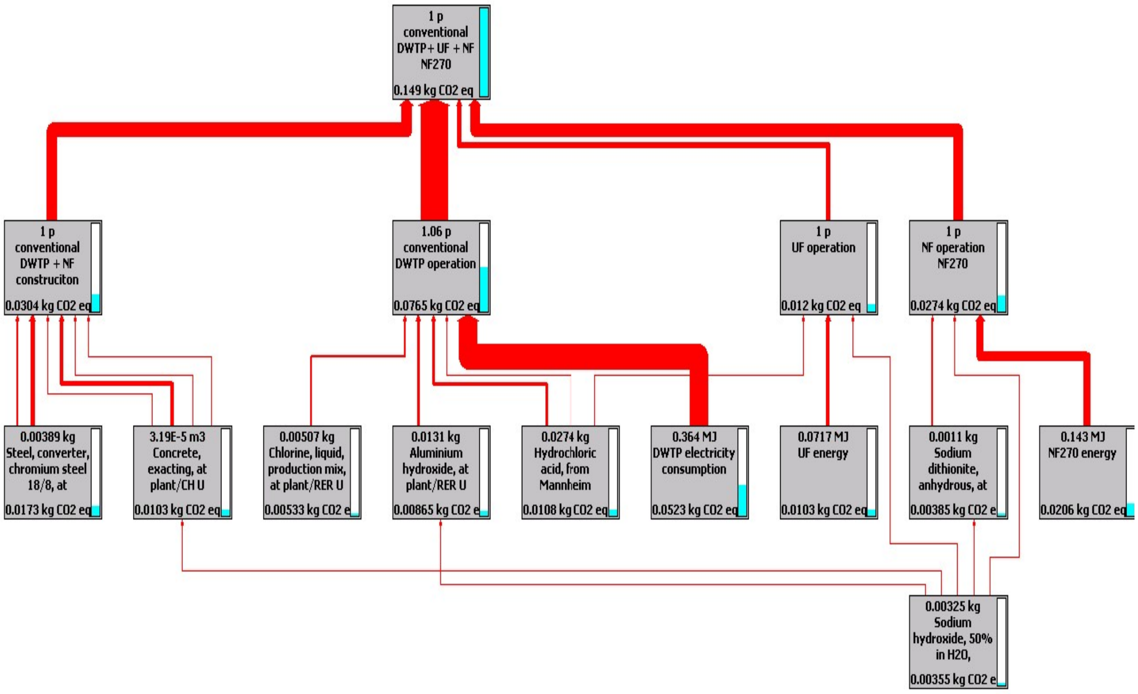
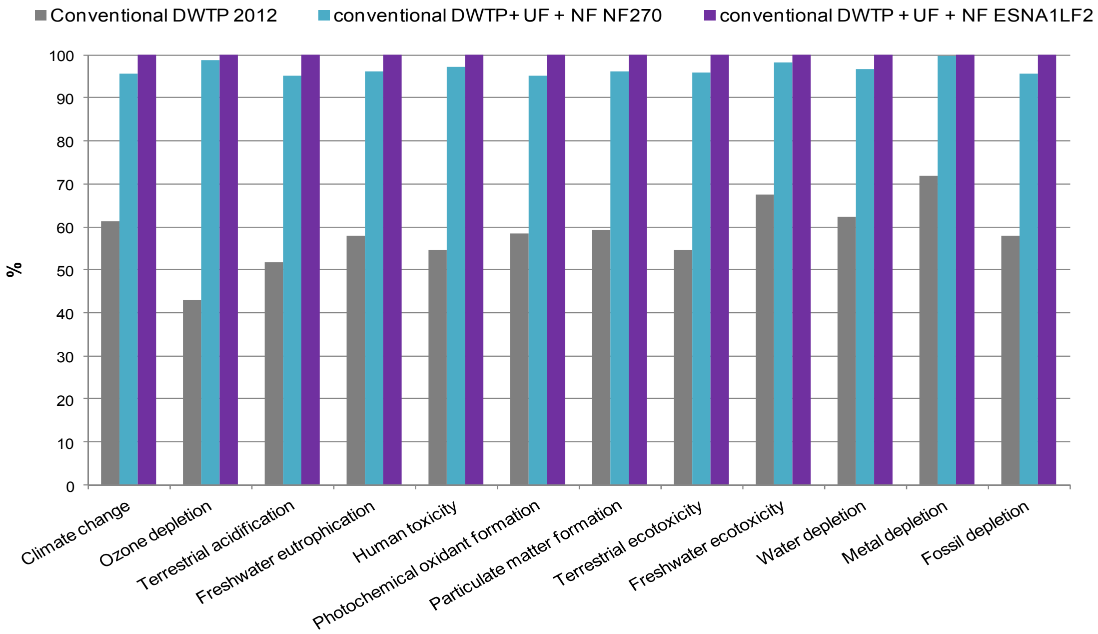


Figure 8.2: Network diagram for climate change category for the system including UF and NF270 process. Cut-off treshhold at 2% (limit to stablish major process units contributing over the global results for each impact category).

In climate change, energy consumption is the main contribution to environmental impact, approximately 60% and 70% for conventional and NF systems respectively. Other contributions arises from the addition of chemical products (PAC, chlorine, hydrochloric acid) or construction materials (concrete, steel), 7% and 12%, respectively, in accordance to the base case. Additional chemical products are added in NF process, but in this case, the major contribution is for sodium metabisulfite (sodium dithionite) at only 2.5% over CC impact.

The tendencies for terrestrial acidification (TA), freshwater eutrophication (FEU), formation of photochemical compounds (POF) or particulate matter (PMF) and fossil depletion (FD) are very similar to climate change category, as it can be observed in the environmental profile of Figure 8.3. This fact is expected as a consequence of the current electricity production mix in Spain, related to fossil combustion.



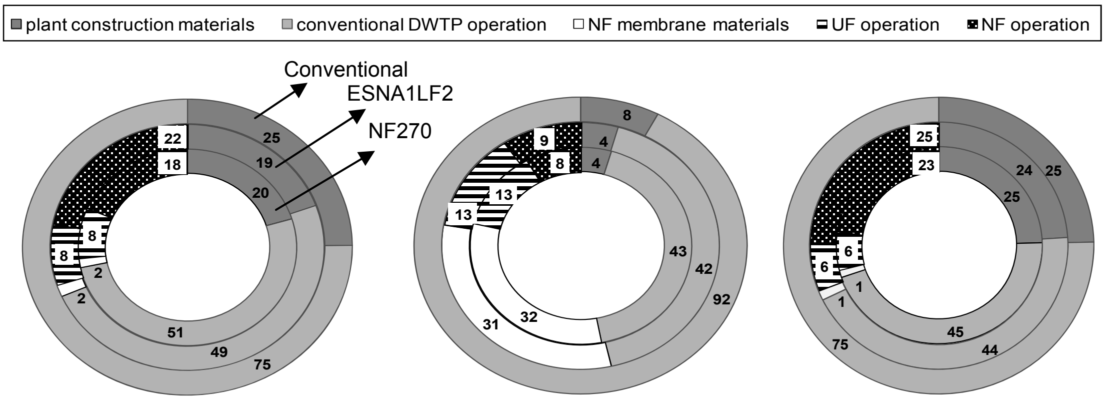
**Comparing 1 p 'conventional DWTP+ UF + NF NF270', 1 p 'Conventional DWTP 2012' and 1 p 'conventional DWTP + UF + NF ESNA1LF2';**
**Method: Recipe Midpoint (H) V1.07 / Europe ReCiPe H / Characterisation**

Figure 8.3: Comparison of overall environmental scores for 12 selected impact categories

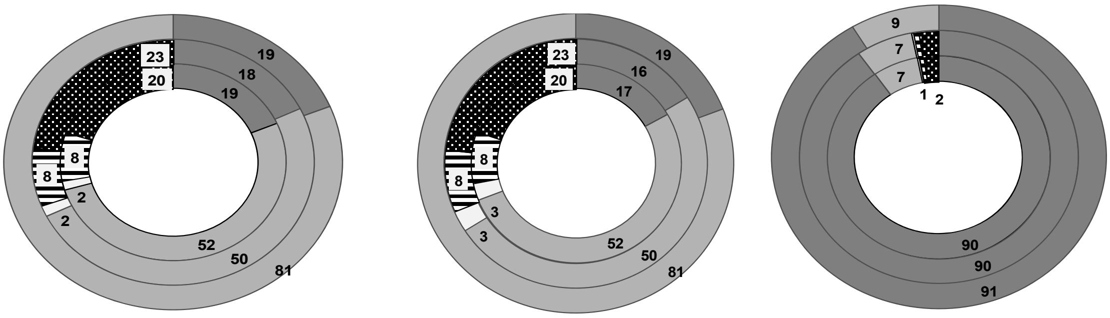
In order to elucidate some differences between impact categories, more exhaustive analysis for the three systems is presented in Figure 8.4. Graphics in this figure show the environmental impact split in five process units for six categories selected for its importance in this work.

Graphically it can be observed how conventional operation in the three DWTP systems has a similar contribution tendency for climate change, human toxicity, freshwater eutrophication and fossil depletion. But in case of DWTP with NF membranes, NF operation play an important role with contributions around 20% in the same categories cited before increasing their total value. Slightly differences are contemplated between NF270 and ESNA1LF2.

In contrast, ozone depletion category presents higher contribution for NF membrane materials, around 30%, as a result of polymers employed in the fabrication of UF and NF modules. In this category, also UF operation has supposed an increase due to the chemical cleaning using sodium hypochlorite.



a) Climate change b) Ozone depletion c) Human toxicity



d) Freshwater eutrophication e) Fossil depletion f) Metal depletion

Figure 8.4: Main results from LCA impacts considering NF membrane technology with a UF pretreatment in a DWTP

Metal depletion in Figure 8.4.f) show the most different profile regarding the contribution of construction stage for the three plants considered. This is logically explained for the high amounts of metal resources (steel, copper, aluminum) involved in the plant construction.

In a general point of view, NF implementation supposes an increase over the total environmental impact of a DWTP, distributed in approximately 50% for its operation and near to 2% for membrane materials, in most of the impact categories analyzed. The benefits in human health will be evaluated for drinking water consumption in the following part 8.3.3 where HHR is assessed for estimated THM concentrations (THMFP) in simulated final drinking water.

More information can be extracted regarding environmental impact for operation or construction stages in this study. For example in case of chemical products used in all cases studied, such as chlorine (for main disinfection steps in drinking water process) presenting a contribution of 42% over ozone depletion, or hydrochloric acid impact contribution near to 10% in human toxicity and nearly 20% in water depletion. Reductions in the use of these products can imply cost savings and less impact on environment, although in this work these savings were out of the study.

### 8.3.2. Scenarios analysis as a function of the NF production capacity improving final drinking water quality

As it is expected, higher content of NF permeate in final drinking water reduce THM concentrations in final water samples (Table 8.7) at expenses of increase in environmental impact. Table 8.11 indicates the results regarding the same environmental categories than the studied base case at 43% of production capacity for NF installation.

Table 8.11: Results from LCA in each scenario for the alternative NF systems with NF270 and ESNA1LF2

| | **25% NF** | | **50% NF** | | **75% NF** | | **100% NF** | |
|---|---|---|---|---|---|---|---|---|
| | **NF270** | **ESNA1LF2** | **NF270** | **ESNA1LF2** | **NF270** | **ESNA1LF2** | **NF270** | **ESNA1LF2** |
| CC | 0.129 | 0.133 | 0.154 | 0.162 | 0.180 | 0.192 | 0.206 | 0.222 |
| OD | $1.8\cdot10^{-8}$ | $1.8\cdot10^{-8}$ | $2.2\cdot10^{-8}$ | $2.2\cdot10^{-8}$ | $2.6\cdot10^{-8}$ | $2.7\cdot10^{-8}$ | $3.0\cdot10^{-8}$ | $3.0\cdot10^{-8}$ |
| HT | 0.069 | 0.070 | 0.083 | 0.086 | 0.098 | 0.102 | 0.113 | 0.118 |
| PCOF | $4.7\cdot10^{-4}$ | $4.8\cdot10^{-4}$ | $5.7\cdot10^{-4}$ | $6.0\cdot10^{-4}$ | $6.7\cdot10^{-4}$ | $7.2\cdot10^{-4}$ | $7.8\cdot10^{-4}$ | $8.4\cdot10^{-4}$ |
| PMF | $3.6\cdot10^{-4}$ | $3.7\cdot10^{-4}$ | $4.3\cdot10^{-4}$ | $4.5\cdot10^{-4}$ | $5.1\cdot10^{-4}$ | $5.4\cdot10^{-4}$ | $5.8\cdot10^{-4}$ | $6.2\cdot10^{-4}$ |
| TA | $9.1\cdot10^{-4}$ | $9.4\cdot10^{-4}$ | $1.2\cdot10^{-3}$ | $1.2\cdot10^{-3}$ | $1.4\cdot10^{-3}$ | $1.5\cdot10^{-3}$ | $1.7\cdot10^{-3}$ | $1.8\cdot10^{-3}$ |
| FEU | $6.3\cdot10^{-5}$ | $6.5\cdot10^{-5}$ | $7.6\cdot10^{-5}$ | $8.0\cdot10^{-5}$ | $9.0\cdot10^{-5}$ | $9.5\cdot10^{-5}$ | $1.0\cdot10^{-4}$ | $1.1\cdot10^{-4}$ |
| TE | $1.9\cdot10^{-5}$ | $2.0\cdot10^{-5}$ | $2.4\cdot10^{-5}$ | $2.6\cdot10^{-5}$ | $2.9\cdot10^{-5}$ | $3.1\cdot10^{-5}$ | $3.4\cdot10^{-5}$ | $3.7\cdot10^{-5}$ |
| FE | $2.4\cdot10^{-3}$ | $2.4\cdot10^{-3}$ | $2.6\cdot10^{-3}$ | $2.6\cdot10^{-3}$ | $2.6\cdot10^{-3}$ | $2.7\cdot10^{-3}$ | $2.7\cdot10^{-3}$ | $2.7\cdot10^{-3}$ |
| WD | $1.1\cdot10^{-3}$ | $1.1\cdot10^{-3}$ | $1.3\cdot10^{-3}$ | $1.3\cdot10^{-3}$ | $1.3\cdot10^{-3}$ | $1.4\cdot10^{-3}$ | $1.3\cdot10^{-3}$ | $1.4\cdot10^{-3}$ |
| MD | 0.061 | 0.061 | 0.062 | 0.062 | 0.063 | 0.063 | 0.064 | 0.064 |
| FD | 0.037 | 0.039 | 0.045 | 0.048 | 0.054 | 0.057 | 0.062 | 0.066 |

A lineal increase in the environmental impact is observed as a result of higher volumes of pretreated water to be treated by NF when its production capacity is incremented. In case of ESNA1LF2 membranes, higher impacts were obtained for most of environmental categories because during operation higher feed pressure is required to obtain the same permeate flow.

In categories related to construction costs as is the case of metal depetion (MD), the same values were obtained when both membranes are compared because no distinction was made in inventory data.

### 8.3.3. HHR results regarding THMFP in final drinking water and relation with LCA study

The lifetime cancer risk calculated from the average concentration of all THMFP determinations in conventional treated water resulted in an index value of $1.8\cdot10^{-4}$, as the sum of the three pathways: inhalation, digestion and dermal contact; with an average contribution to the total index of 63%, 35% and 1.1%, respectively. However, this elevated value is due to an overestimation of the real THM concentration of the trihalomethane formation potential (THMFP), which determines precursor material in raw water that may form THM (AWWA, 1998). Increasing the percentage of NF permeate, lower concentration of THM expressed as THMFP were determined, and thus, reducing the cancer risk index as shown in Figure 8.5 for each NF membrane tested.

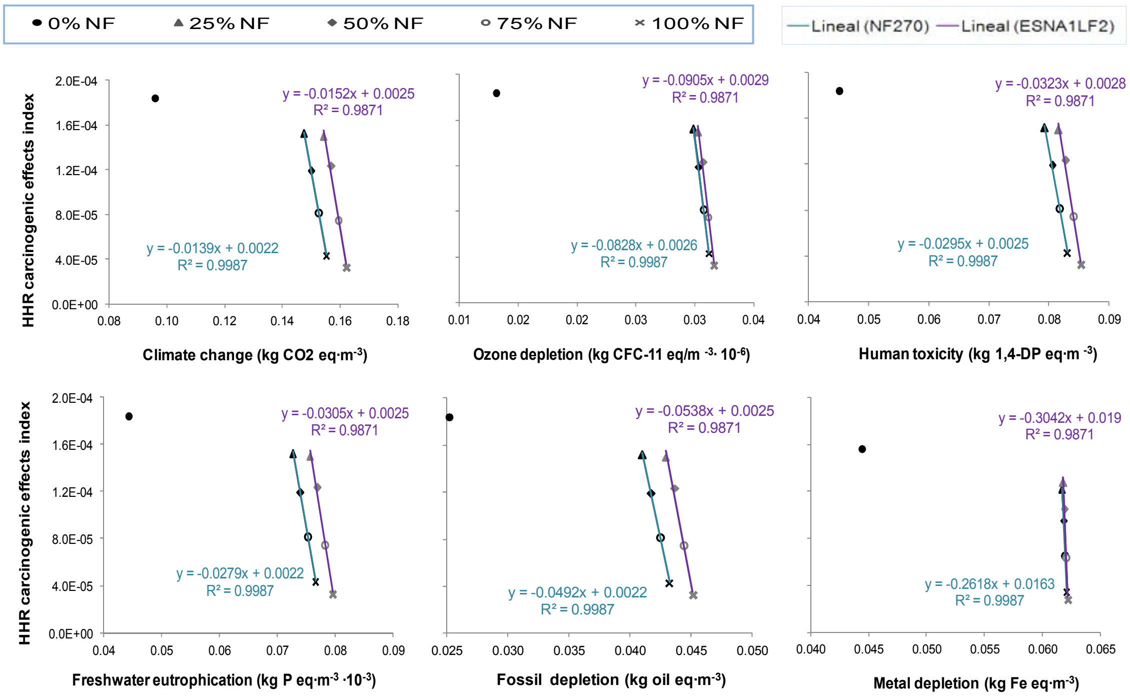


Figure 8.5: Correlation of different environmental categories with the HHR calculated regarding the THM cancer risk as sum of three routes of exposition of humans to tap water

A multicriteria tool in order to evaluate NF technology in DWT processes shows a negative linear tendency between HHR and environmental impact for each impact category, indicating the decrease in HHR when higher NF production capacity is considered. Conventional DWTP treatment supposes the minimum environmental impact in all categories and the maximum HHR, as a result the improvement in drinking water process increment the need of energy and some materials resources to obtain high quality of potable water, increasing the environmental impact.

Differences between both NF membranes are mostly due to lower energy consumption for NF270. This effect can be observed in climate change, ozone depletion, freshwater eutrophication and fossil depletion, all related to electricity production mix. On the other hand, ESNA1LF2 provided a slightly lower HHR, more noticeable when 100% of drinking water was produced by NF, because its higher ability to remove THM precursor material in the water (Table 8.7).

These results lead to important conclusions to select the percentage of water to be nanofiltered in a full-scale DWTP, relating the overall environmental impact to the benefits for the human health. For example, supposing an acceptable cancer risk index of $10^{-5}$, 50% of final drinking water in the studied case should be treated by NF. On the other hand, if emissions of equivalent carbon dioxide were fixed as a maximum level of 0.15 kg $CO_2 \cdot m^{-3}$ of drinking water produced, final water could be produced by NF until 75% using NF270, being excluded the use of ESNA1LF2.

## 8.4. CONCLUSIONS

The environmental impact and the benefits for the human health resulting from the implementation of nanofiltration in DWTP have been studied. Membrane technology supposes an increment of the environmental impact around 50% over the real conventional system in the majority of the categories evaluated by LCA methodology (climate change, human toxicity, freshwater eutrophication, fossil depletion). These results have been related to the final drinking water quality in terms of HHR due to the presence of THM. If all water is treated by NF, results indicate a reduction in lifetime cancer index of 75%.

The major difference between membranes considered in this work is the different energy consumption during operational stage, because THMFP in permeates produced by both membranes gave similar results in carcinogenic risk index.

The study using different scenarios (25, 50, 75 and 100 of NF water) provide useful information regarding the influence of the percentage of water nanofiltered into the environmental impact and the benefits for the human health of the overall drinking water treatment. The tendency indicated that major NF capacity in the DWTP lead to decrease cancer risk of drinking water consumption at the same time that proportionally increases the environmental impact. In this sense, the presented work offers a multicriteria tool to select the desired quality for final drinking water taking into account environmental effects and human health risk, considering other decision criteria apart from the economical one.

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# Chapter 9: Winery wastewater treatment for water reuse purpose: Conventional activated sludge versus membrane bioreactor (MBR)

Parts of this chapter were based on:

Valderrama, C., Ribera, G., Bahí, N., Rovira, M., Giménez, T., Nomen, R., Lluch, S., Yuste, M., Martinez-Lladó, X.; Winery wastewater treatment for water reuse purpose: Conventional activated sludge versus membrane bioreactor (MBR): A comparative case study (2012). Desalination 306, 1–7.

## 9.1. INTRODUCTION

Wine production processes generate organic and inorganic pollution mostly associated with solid wastes and liquid effluents. The liquid effluents usually referred as “winery wastewater” are mainly originated in washing operations during grape harvesting, pressing and first fermentation phases of wine processing (Lucas et al., 2010; Mosteo et al., 2007; Mulidzi, 2010). As a consequence of the working period and the winemaking technologies, volumes and pollution loads greatly vary over the year (Petruccioli et al., 2002; Agustina et al., 2008). Consequently, the treatment system must be versatile to face both the loading regimen and stream fluctuation; typical specific production is reported in the range 1–4 $m^3$ per $m^3$ of wine produced, 60–70% during the vintage period (Andreottola et al., 2009). Winery wastewaters contain large amounts of biodegradable organics in addition to relatively small concentrations of recalcitrant compounds: polyphenols, organic acids and sugars and high chemical oxygen demand (COD) concentrations, up to 10 kg per $m^3$ and relatively low presence of solids and nutrients (Serrano et al., 2011; Braz et al. 2010). The disposal of winery effluents in streams, creeks, rivers and on soils involves unacceptable environmental risks (Lucas et al. 2010). Therefore, the disposal of winery wastewater is one of the main environmental problems related to wine industries (Agustina et al., 2008).

Several winery wastewater treatments are available, among them biological treatment methods have been recognized as a reasonable alternative way for a significant degradation of wastewater with high organic content, however, the presence of recalcitrant compounds for the microorganisms frequently makes impossible the complete treatment of a winery wastewater (Lucas et al. 2010). In Europe, where 50% of the wine is produced worldwide, wastewaters are pre-treated by small wastewater treatment plants adopting the activated sludge process and then are released in the sewerage system, which represents more than 70% of the produced wastewaters are treated by means of the activated sludge process in large wineries (Bolzonella et al. 2010). However, the intrinsic variability in flow and characteristics, and the necessity to face high organic loading for relatively short periods during harvesting and vintage generally determine problems for the operation of the activated sludge process.

Recently, the use of membrane bioreactors (MBR) has been considered as a suitable option for winery wastewater treatment as they combine efficiently the biochemical oxygen demand (BOD), suspended solids, nitrogen and phosphorus removal and microbial decontamination (Artiga et al., 2005; Artiga et al. 2007; Guglielmi et al. 2009). The advantages of the MBR system over conventional biological treatment processes include maximum flexibility of the biology according to the influent loadings, small footprint, the reduced sludge production and a compact system with better solids removal, and disinfection (Jeison et al., 2007; Judd, 2006; Tewari et al., 2010).

The increasing shortage of water resources in arid zones, zones where grapes are usually grown, and the need to preserve the primary source for drinking purposes has increased interest in the reuse of treated wastewater for irrigational, urban or industrial purposes (Zanetti et al. 2010). Further, reuse of treated effluents provides a regular supply to users and aids to assure the quality from a sanitary point of view as well as environmentally (Iglesias et al., 2010). In Spain, reclaimed water quality is regulated by the Royal Decree (RD 1620/2007) which is based on International guidelines (Iglesias et al., 2010; Queensland government, 2005; USEPA, 2004; WHO, 2006) and aim to minimize the potentially negative impact on public health. MBR systems are one of the best available techniques for wastewater reclamation because treated water quality easily meets the regulations requirements.

The objective of this work is to compare the performance of a full scale conventional activated sludge (CAS) process for winery and distillery wastewater treatment with a pilot scale MBR system in order to evaluate the feasibility to, in the future, reclaim and reuse winery wastewater, which is not being done at the moment. For this purpose, a pilot scale MBR system was installed parallel to the existing CAS winery wastewater treatment into the Miguel Torres S.A. facilities. The treated effluents were evaluated in order to achieve the quality criteria defined by the Spanish RD 1620/2007 for wastewater reuse.

## 9.2. MATERIALS AND METHODS

### 9.2.1. Existing productive process and wastewater treatment

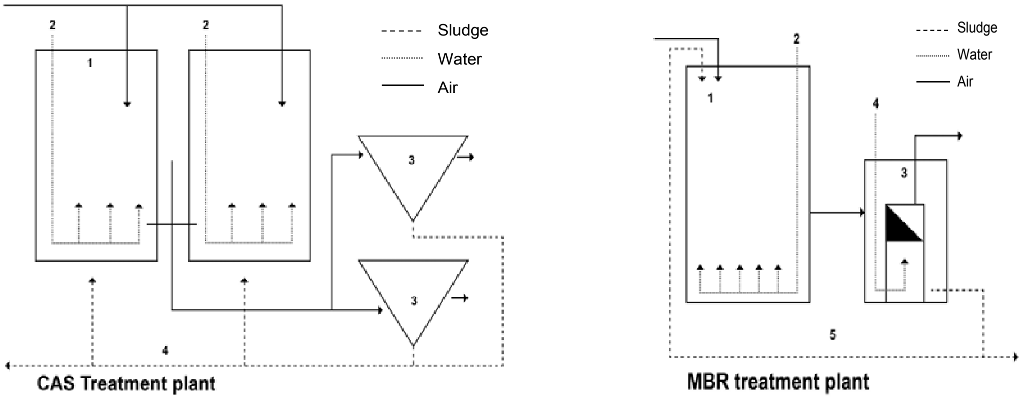
The productive process comprises several stages, including grape reception, destemming, crushing, pressing, fermentation, aging, clarification, stabilization, filtration, bottling, storage and expedition. Bottling is carried throughout the year. Both tap and groundwater are used and they are decalcified by ion exchange previously to entering the productive process. Brine from ion exchange resins regeneration is sent to the wastewater treatment plant.

The conventional wastewater treatment plant located at Miguel Torres S.A. facilities receives, throughout the year, sanitary and industrial wastewaters from the winemaking process. Both wastewaters get mixed at the plant header.

Distillery vinasses from the brandy making process enter the treatment plant from October until May. They are neutralized with NaOH and stored in open ponds before being mixed with wastewater.

The CAS system comprises aerobic biological degradation and secondary clarification (Figure 1a). The system consist of a pre-treatment unit (screening and grit removal units), a homogenizer tank (500 m$^3$) and then two biological reactors of 1050 m$^3$ each one. Prior to enter the homogenizer tank, influent to the wastewater treatment plant is neutralized with NaOH, $(NH_4)_2HPO_4$ and $NH_4Cl$ are also added as nitrogen and phosphorous source for the activated sludge process.

The schematic diagram of both full scale CAS and pilot scale MBR wastewater treatment plants is shown in Figure 9.1. The CAS system comprises aerobic biological degradation and secondary clarification (Figure 9.1a). The system consist of a pre-treatment unit (screening and grit removal units), a homogenizer tank (500 m$^3$) and then two biological reactors of 1050 m$^3$ each one. Prior to enter the homogenizer tank, influent to the wastewater treatment plant is neutralized with NaOH, $(NH_4)_2HPO_4$ and $NH_4Cl$ are also added as nitrogen and phosphorous source for the activated sludge process.



a) 1. Aerobic reactors; 2. Fine bubble aeratioin; 3. Clarifiers; 4. Recirculation and purge

b) 1. Aerobic reactor; 2. Fine bubble aeration; 3. MBR; 4. Coarse bubble aeration; 5. Recirculation and purge

Figure 9.1: Flow diagram for a) CAS and b) MBR treatment plants

It is important to point out, that is possible to work with only one reactor if is required, which represents a critical factor due to the wide fluctuation of winery wastewater. The two biological reactors operate at high mass loading and in the activated sludge both at total oxidation conditions. This continuous process is characterized by an aeration phase by liquid oxygen (300 kg/h), automatically controlled on the dissolved oxygen, oxidation reduction potential and pH. After the aerobic step, two secondary clarifiers (180 $m^3$) separate the sludge and permeate by conventional settling.

### 9.2.2. MBR pilot plant description

The MBR treatment plant (Figure 9.1b) was designed, constructed and installed by Hera-Amasa. It was designed to perform the treatment in two stages. In the first zone, the bioreactor (aerobic conditions) in which the organic matter is oxidized by means of an aeration system, the reactor volume is variable, which suit to the temporality of the winery wastewater loading. This continuous process is characterized by an aeration phase which is guaranteed by a blower able to supply air through a grid of fine bubble diffusers. This step is automatically controlled on the dissolved oxygen, oxidation reduction potential and pH.

The second zone is the filtration stage; here the effluent is filtered by means of flat sheet (Kubota) membranes modules. The solid concentration was equilibrated between the bioreactor and the filtration zone throughout a recirculation system. The membrane module was physically cleaned by 1 minute membrane relaxation every 9 minutes of operation. During membrane cleaning, water filtration is stopped and membrane fouling is removed through air scouring. Although air flows lower than 0.5 $Nm^3 \cdot m^{-2} \cdot h^{-1}$ are usually used at full scale plants, 0.9 $Nm^3 \cdot m^{-2} \cdot h^{-1}$ was used in this study due to pilot scale considerations.

In Table 9.1 are summarized the most important design parameters for MBR pilot plant. Finally the data collection and control process were performed by means of programmable logic controller (PLC). It should be noticed that, due to the inherent configuration of both systems, it would be difficult that a malfunction would limit the production in the CAS system while in the MBR, in case of inactivity, there would not be permeation of water through the membrane.

Table 9.1: Design parameters of MBR pilot treatment plant

| Parameter | | MBR (Flat sheet) |
|---|---|---|
| Volume ($m^3$) | Bioreactor | 11-17 |
| | Membranes | 3.5 |
| Membrane surface area ($m^2$) | | 20 |
| Inflow rate ($m^3$/day) | | 6 |
| Outflow rate ($m^3$/day) | | 6 |
| Permeated flux ($L/m^2/h$) | | 12.5 |
| Air scouring ($Nm^3/m^2/h$) | | 0.9 |
| Recirculation flow rate (%) | | 100 to 400 |
| Operating conditions | | Permeation: 9 (min)<br>Relaxation: 1 (min) |

### 9.2.3. Experimental procedure

Winery wastewater treatment experiments started on October of 2009 for the MBR pilot plant. Both CAS and MBR plants were continuously fed with winery wastewater from the wine production process. This water was pre-treated by a screening unit (1 mm) and then pumped into the buffer tank of 500 $m^3$ from which both CAS and MBR plants were fed. Both treatment plants were simultaneously operated for a period of five months controlling physico-chemical and biological parameters in influent (buffer tank) and the effluents from both plants.

### 9.2.4. Sampling, analysis and control

During the initial wastewater characterization, samples were collected hourly using a fraction collector system (ISCO 6712) equipped with 24 bottles (1 L). COD, pH, and conductivity were analysed in hourly samples. Turbidity, TSS, P-total and N-total were analysed in daily samples obtained by composition of hourly samples.

In order to monitor MBR and CAS performance, inlet wastewater samples were collected from the homogeniser tank that fed both systems. Outlet samples from the MBR system were collected after the membrane separation, effluent samples from the CAS system were collected after the secondary clarifiers. All samples were preserved according to (Clesceri et al., 1998) and stored in a refrigerator (4 °C) until analysis.

COD, turbidity, $BOD_5$, total and volatile suspended solids (TSS and VSS) were analysed following methods 5220D, 2130D 5210B, 2540G defined in the Standard Methods for the Examination of Water and Wastewater (Clesceri et al., 1998), respectively.

Total nitrogen was analysed by a total nitrogen analyser (Analytik-Jena 3100 N/C). Total phosphorous was analysed following method UNE-EN ISO 6878. Microbiological characterisation was also performed following standard methods 9222B, 9222D and UNE EN ISO 9308-1 for total coliform, faecal coliform, Escherichia Coli. Extracellular polymeric substances (EPS) and soluble microbial products (SMP) were analysed following the method proposed by Judd (Judd, 2006). COD fractionation was determined combining COD and respirometric analysis to quantify biodegradable fractions (Respirometer SURCIS BMT). Briefly, soluble fractions were determined by filtering through 0.45 μm acetate filters, colloidal fractions were determined flocculation with zinc sulphate 1M according to Mamais et al. (Mamais et al., 1993). Total anions and cations were analysed by ion chromatography (Dionex ICS-2100).

## 9.3. RESULTS AND DISCUSSION

### 9.3.1. Wastewater characterization

In order to evaluate the variability of the wastewater generated in the wine making process, a characterization of the wastewater generated was performed from October 2008 to June 2009. Sampling periods were divided in four different annual stages according to the wine production process: harvesting (September to October), harvesting and vinasse generation (November to January), vinasse generation (January to May) and process (May to August).

Harvesting is the time of the year with the highest production and when the highest amount of wastewater is generated. Grape processing and bottling is carried through this period but also sanitary wastewaters are entering the wastewater treatment plant. During the harvesting and vinasse generation period take place the final harvesting processes, no more grapefruits are entering the process but sanitary wastwaters are still generated. Vinasses start to arrive at the wastewater treatment plant.

Vinasse period is characterised by high vinasse generation, sanitary wastewater and other process wastewaters including bottling. Finally, during the process period, cleaning, bottling and sanitary wastewaters comprise the highest part of generated wastewater.

Hourly samples of the influent wastewater were collected during each period by means of an automatic sampler and mixed to generate daily average wastewater. Results from wastewater characterisation are summarized in Table 9.2. A significant COD variability was observed for each production stage with exception of the process wastewater which reported typical values of urban wastewater, as can be seen in Figure 9.2.

Table 9.2: Physico-chemical characterization of the influent winery wastewater during the different annual stages of the wine production process (standard deviation)

| Parameter | Harvesting | Harvesting and vinasse | Vinasse | Process |
|---|---|---|---|---|
| pH | 6.7 (2.5) | 6.6 (2.1) | 8.7 (1.4) | N.D. |
| Conductivity (mS/cm) | 5.6 (4.4) | 3.6 (3.5) | 4.1 (2.6) | 4.5 (0.5) |
| Turbidity (NTU) | 692 (407) | 313 (100) | 155 (20.5) | 121 (21) |
| MES (mg/L) | 1230 (985) | 662 (759) | 271 (391) | 178 (38) |
| COD (mg/L) | 13448 (5055) | 3887 (2106) | 3400 (1682) | 2323 (194) |
| P-total (mg/L) | 39.5 (14.8) | 6.5 (0.6) | 7.5 (0.4) | 5.0 (0.8) |
| N-total (mg/L) | 34.0 | N.D. | 41.0 | 40.0 |

ND: Not determined

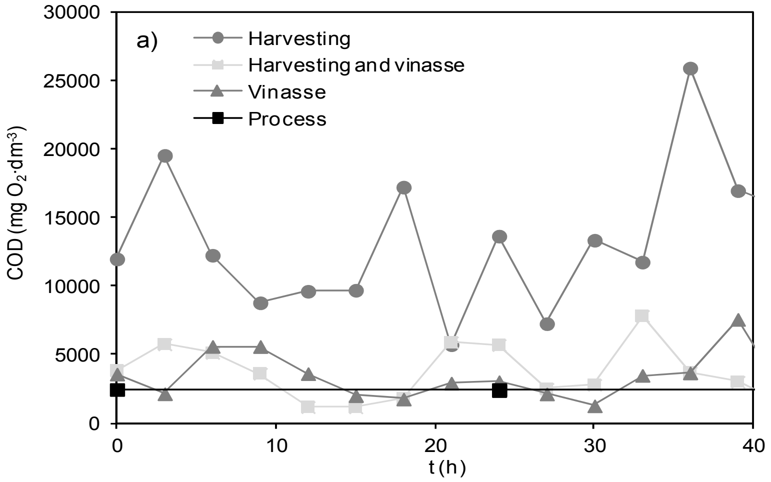


Figure 9.2: Winery wastewater characterization COD variability in hourly samples during the different annual stages of the wine production process

Previous studies also report the concentrations observed and the elevated variability during the harvesting and the process seasons (Andreottola et al., 2005, Bustamante et al., 2005). These variations in COD content of the wastewater produced in wineries should be taken into account when designing their treatment (Artiga et al., 2007). Similar values of COD concentration were observed in the influent wastewater during the pilot plant operation (data not shown).

The COD fraction characterization was performed to two consecutive daily samples for the vinasse and process stage (Figure 9.3).

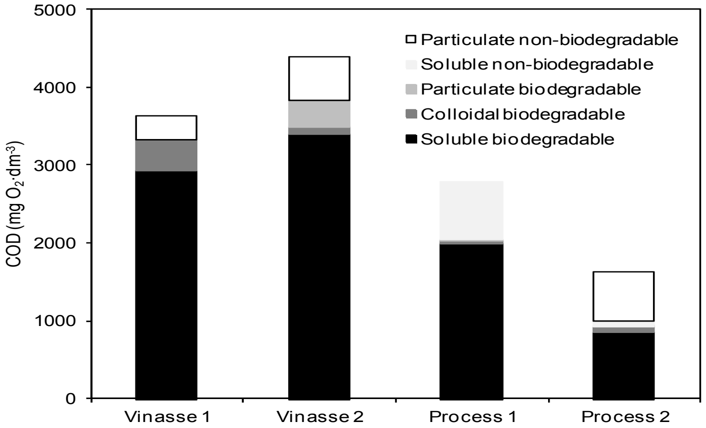


Figure 9.3: COD fraction characterization in daily average samles from winery wastewater vinasse and process stage

The results indicate that the readily biodegradable soluble complex fraction is the higher for both stages, however an increase in non biodegradable fraction is observed in process water. In fact, the ratio between the readily biodegradable COD and the total COD varies from 0.2 to 0.6 during the sanitary period to 0.9 during the vinasse period. These results are in agreement with results shown in previous studies and reveal that, despite the high organic pollution generated, most of the winery wastewater is readily biodegradable (Braz et al., 2010, Beck et al., 2005).

The conductivity values observed are higher than those previously reported in the literature (Beck et al., 2005). This is probably due to the discharge of brine from the ion exchange process and the neutralization and addition of nutrients in the wastewater treatment process. As can be seen in Table 9.2, taking into account the total amount of COD in the effluent, there is a lack of nutrients, especially nitrogen, for the correct operation of the aerobic biological oxidation process (Tchobanoglous et al., 2003).

The microbiological parameters of the wastewater treatment plant effluent were also monitored by the annually stages of the wine production process. The results obtained for total and faecal coliform and E. coli are shown in Figure 9.4. The presence of this kind of contamination in the wastewater is related to the sanitary part of the treated wastewater. Results obtained indicate that microbiological parameters observed a significant variability along the whole year and additionally confirm that CAS treatment requires a post-treatment process in order to reduce the microbial concentrations to the levels defined in RD 1620/2007.

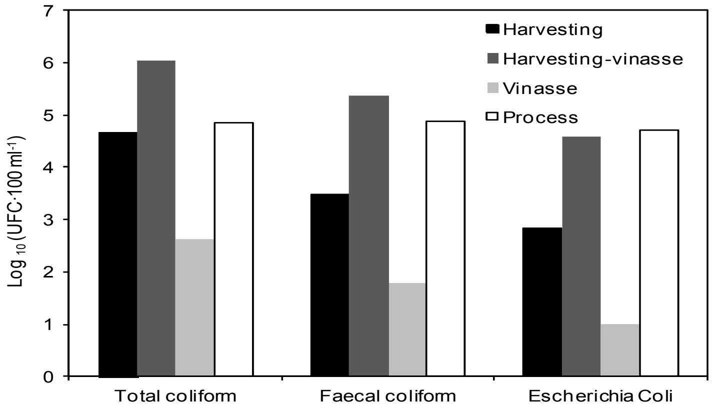


Figure 9.4: Microbial characterization of winery CAS effluent by different stages of wine production process

### 9.3.2. MBR and CAS performance

The MBR pilot plant started to operate at the end of the harvesting period in 2009. Influent COD during fluctuated from 100 mg/L to more than 8000 mg/L. The influent and removal of COD during the experimental period are presented in Figure 9.5. No significant variability was observed for the MBR treatment, obtaining removals over 90%. Despite the high pollution loads of the influent wastewater the average CODs removal was 97 and 95% for MBR and CAS respectively. Food-to-microorganism (F/M) ratios observed were slightly lower than the typical values for a complete mix activated-sludge reactor (Tchobanoglous et al., 2003). This is due to the high biomass content in the reactors of both processes.

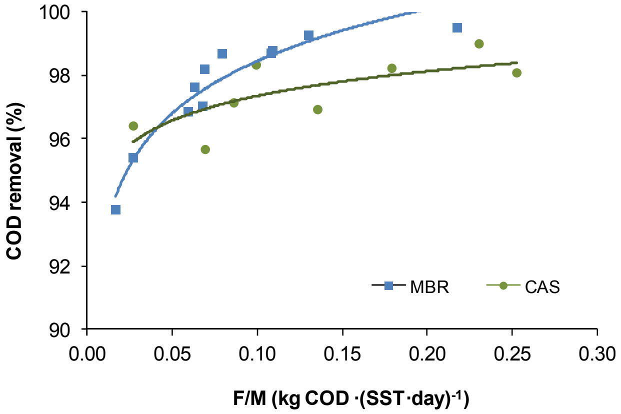


Figure 9.5: COD removal efficiency as a function of food-to-microorganism (F/M) ratio for winery treatment by MBR and CAS process

The biomass content (in terms of mixed liquor suspended solids or MLSS) is plotted in Figure 9.6. The volatile suspended solids (VSS) content was also monitored. Although the MLSS of the CAS system are high compared with values found in urban wastewater (Tchobanoglous et al., 2003) and other winery wastewater treatment plants (Fumi et al., 1995), the MBR system allows working with even higher MLSS concentrations than CAS, which represents higher organic matter removal (Figure 9.6) as function of the reactor volumetric unit and under the same hydraulic retention time (HRT).

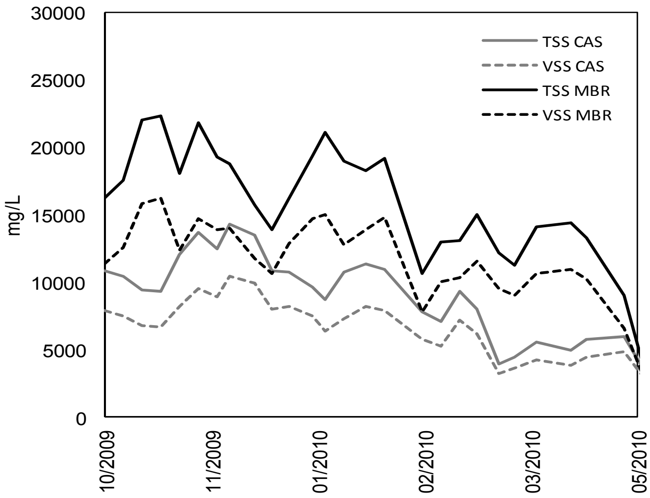


Figure 9.6: MLSS and VSS evolution in CAS and MBR treatment process for winery wastewater

VSS was observed to be fairly stabilized, accounting for around 75% of the total MLSS, which is within the reported limits of 70–90% in biological treatment (Tewari et al. 2010). Despite the high concentration of MLSS in the reactors of both systems, no problems of bulking in the CAS neither membrane fouling in the MBR, were reported.

### 9.3.3. Membrane performance

The variation of permeate flux and the trans-membrane pressure (TMP) is shown in Figure 9.7. As can be seen, the maximum flux (15 $L\cdot m^{-2}\cdot h^{-1}$) was reached after 51 days and resulted in a clearly increase of the TMP (> 160 mbar). The TMP was reduced by reducing the permeate flux, however after 56 days and accidental purge of the solids in reactor affected the TMP (Figure 9.7) and the permeability. In this case, the flow rate was reduced and the recirculation rate was modified in order to achieve higher solid concentration into the membrane reactor. It is important to point out that this kind of incidents can be easily solved due to the flexibility of the MBR configuration. Additionally, the MLSS concentration inside the MBR reactor was rather stable during the experimental period, with a respective average and maximum concentration of 16 and 22 $g\cdot L^{-1}$.

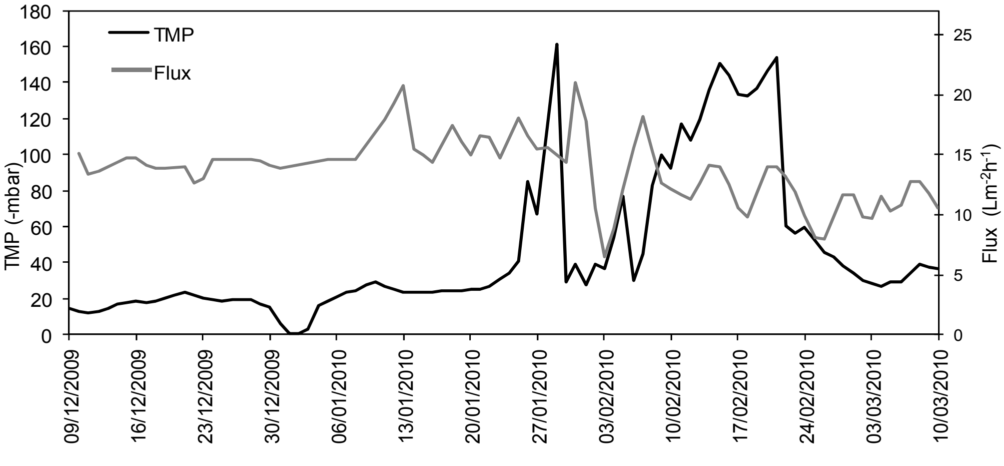


Figure 9.7: Transmembrane pressure (TMP) and temperature corrected flux (20ºC) variations during the experiment for MBR pilot plant in winery wastewater treatment

In order to determine the fouling potential of membranes, the extracellular polymeric substances (EPS) and soluble microbial products (SMP) were monitored during the experiment. Deposition/accumulation of SMP or EPS has been reported to have large fouling ability due to their interaction with membrane material (Pendashteh et al., 2011). Typically, the EPS and the SMP solution are characterised according to its relative content of protein (p) and carbohydrate (c). The EPS and SMP were correlated to different process parameters, such as: TMP, permeate flux and permeability calculated according to Judd

(Judd, 2006). A fairly good correlation was obtained between EPS and permeability as can be seen in Figure 9.8.

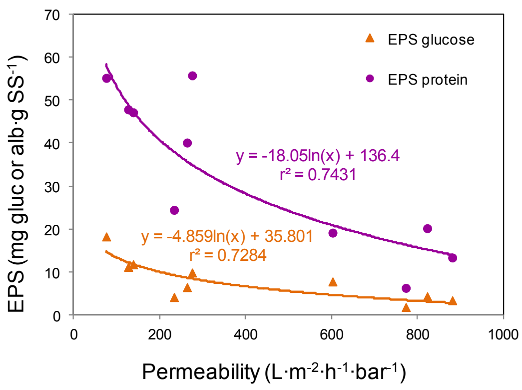


Figure 9.8: EPS and permeability correlation for MBR pilot plant in winery wastewater treatment

This correlation indicates that permeability decreases when the EPS content increases and vice versa. In this case the EPSp reported higher correlation coefficient than EPSc. It can be explained since EPSp generally has hydrophobic tendencies while EPSc is more hydrophilic (Liu and Fang, 2003) and may therefore interact more strongly with the membrane (Judd, 2006). On the other hand the SMP showed poor correlation to the process parameters (data not shown). Finally the EPS and SMP contents were also monitored in the CAS system and compared to the MBR configuration. The significant differences observed were the variability and the higher values obtained in the MBR plant due to the higher SS and SSv concentrations.

From the point of view of economomical analysis, an operational cost estimation of both CAS and MBR plants was perfomed based on energy and chemicals consumption, considering these as the main components on the total operational cost (Cotè et al., 2004). The results showed that total operational cost were 0.38 and 0.40 €·$m^{-3}$ for CAS and MBR plants, respectively. The influence of other operations imputs were not considered, for instance, the membrane replacement, or the cost of labor, which was assumed equal for both plants; however, a fully automate MBR plant requires less labor than a CAS plant. In this sense, a more detailed economical analysis is required, for instance, a life cicle costing study which considers the capital investment, actual rates for financial parameters of credits and energy prices.

### 9.3.4. Quality criteria for wastewater reuse

During winery wastewater treatment with both CAS and MBR plants, the quality of effluents for both systems was monitored and evaluated according to the limits determined by the Spanish R.D 1620/2007 for wastewater reuse. The evolutions of effluent TSS for both processes are shown in Figure 9.9. Furthermore, the values of 10 and 20 mg·L$^{-1}$ (for wastewater effluents) determined by the Spanish royal decree for residential and urban use, respectively are also showed in Figure 9.9. It can be observed that MBR effluent was lower than the limits defined for urban, agricultural and recreational use. Furthermore, the average effluent TSS concentration reported was 2 mg·L$^{-1}$, with an average removal of 99% was achieved confirming a higher TSS efficiency removal for the MBR process. The quality criteria defined for the international guidelines varied from 5 to 30 mg·L$^{-1}$ for some states in the USA (USEPA, 2004) to 20 mg·L$^{-1}$ in certain government regulations (Queensland Government, 2005). Thus, the values obtained in this study are under the Spanish Royal decree and other international guidelines and regulations for water reuse.

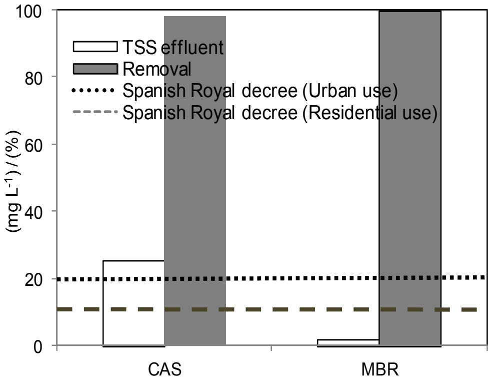


Figure 9.9: Average removal in MBR and CAS effluents

On the other side, the most commonly used indicators of sewage treatment effectiveness are thermotolerant (or faecal) coliforms. *Escherichia coli*, which is the thermotolerant coliform species most commonly found in human waste, is generally accepted as being a suitable indicator of reduction of bacterial pathogens in recycled water before storage (Queensland Government, 2005). For this purpose the microbial parameters were also monitored in order to define if the effluent from MBR pilot plant was under de limits defined for wastewater reuse. The evolution of the influent and effluent concentration of *Escherichia Coli*, total and faecal coliform ($\log_{10}$ CFU/100 mL) as well as the limit defined by the Spanish Royal decree for this parameter for wastewater reuse are shown in Figure 9.10. It can be observed that MBR effluent was more than 10 times lower than limit defined for agricultural, which is, apart from the residential, the most restrictive use.  Most of the days *E. Coli* was not detected in the effluent, which is the limit of wastewater treated for residential use. Considering the results of *E. Coli* removal, which is the indicator used in all regulations, MBR treatment for winery wastewater will provide water suitable for urban, agricultural and recreational uses, according to present regulations and guidelines (RD1620/2007; Queensland Government, 2005; USEPA, 2004; WHO, 2006). However, it should be point out that most of these guidelines and regulations define other microbial parameters which are necessary required to determine the quality classification for water reuse.

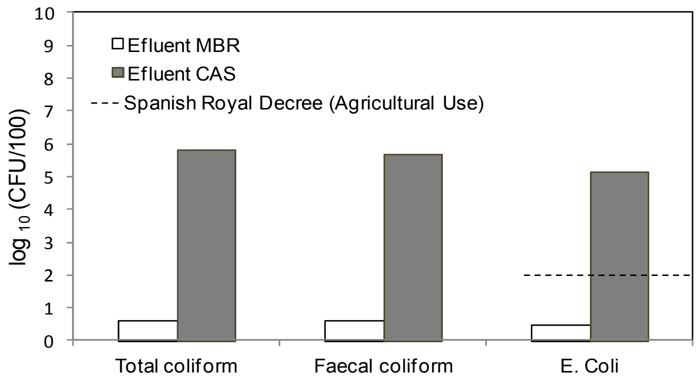
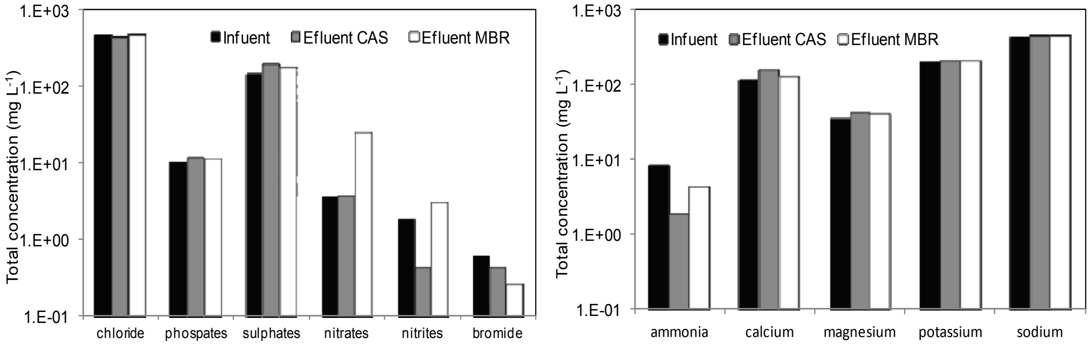


Figure 9.10: Microbial evaluation for the MBR and CAS effluents and quality criteria for reuse purpose

The total and faecal coliform, which are generally used as indicators to determine the degree of disinfection (USEPA, 2004) were also monitored during the experiment (also showed in Figure 9.10), it can be observed that influent concentration was around 6log$_{10}$ CFU/100 mL, while MBR effluent was lower than 10 CFU/100 mL. Other microbial parameter measured was the helminth eggs, which must be in a concentration lower than 1 egg/10L in the water to be reclaimed. In this case, the average concentrations were <1 and 386 eggs/10 L for MBR and CAS effluents, respectively. Thus, confirming that CAS process requires an additional treatment to achieve the microbial requirements for water reuse purpose.

Finally, major cations and anions were also monitored in effluents as can be seen in Figure 9.11. No significant differences were observed between the influents and both effluents with the exception of ammonium, nitrates and nitrites (related to the biological activity). The high values of chloride and sodium concentration observed could be related to the nutrient addition and influent neutralization with NaOH and $NH_4Cl$. Also the discharge of decalcification brine could be responsible to the values observed. Microfiltration membranes used in the MBR system only rejected suspended solids larger than 0.2 µm. In both systems, CAS and MBR, in case that dissolved salts should be removed prior to water reuse, an additional desalination stage (reverse osmosis, nanofiltration, electrodialysis reversal, ion exchange) must be considered. A physico-chemical characterization of MBR effluent is summarized in Table 9.3.



a) b)

Figure 9.11: a) Anions and b) cations evaluation in the influent and MBR and CAS effluents, determined by ion chromatography

Table 9.3: Physico-chemical characterization of CAS and MBR effluents during experimental period (standard deviation)

| **Parameter** | **CAS** | **MBR** |
|---|---|---|
| pH | 7.3 (0.4) | 7.3 (0.3) |
| Conductivity (mS·cm$^{-1}$) | 3.3. (0.9) | 3.4 (0.9) |
| Turbidity (NTU) | 38.2 (40.4) | 4.0 (3.4) |
| BDO$_5$ (mg·L$^{-1}$) | 7 (9) | 9 (22) |
| TSS (mg·L$^{-1}$) | 26 (8.1) | 2.0 (9.0) |
| COD (mg·L$^{-1}$) | 222.8 (321.2) | 113.7 (150.4) |
| P-total (mg·L$^{-1}$) | 5.3 (3.3) | 4.9 (2.3) |
| N-total (mg·L$^{-1}$) | 1.7 (5.1) | 5.7 (7.1) |
| Cl$^-$ (mg·L$^{-1}$) | 423.4 (92.4) | 459.2 (97.9) |
| PO$_4^{3-}$ (mg·L$^{-1}$) | 11.4 (5.9) | 11.0 (6.6) |
| SO$_4^{2-}$ (mg·L$^{-1}$) | 194.5 (68.4) | 171.1 (69.3) |
| NO$_3^-$ (mg·L$^{-1}$) | 3.7 (10.8) | 24.6 (8.1) |
| Ca$^{2+}$ (mg·L$^{-1}$) | 152.8 (56.1) | 125.9 (46.5) |
| Mg$^{2+}$ (mg·L$^{-1}$) | 40.3 (35.9) | 39.6 (37.4) |
| K$^+$ (mg·L$^{-1}$) | 199.8 (95.1) | 198.0 (85.9) |
| Na$^+$ (mg·L$^{-1}$) | 438.4 (115.5) | 444.6 (140.0) |
| NH$_4^+$ (mg·L$^{-1}$) | 1.8 (2.2) | 4.3 (6.1) |
| Hardness (mg·L$^{-1}$) | 547 (288) | 477 (269) |
| Intestinal nematode (eggs·10 L$^{-1}$) | 386 (103.6) | 1 (0) |
| Escherichia coli Log$_{10}$ (CFU·100 mL$^{-1}$) | 5.14 (5.46) | 0.47 (0.34) |
| Total coliform Log$_{10}$ (CFU·100 mL$^{-1}$) | 5.81 (6.12) | 0.60 (0.30) |
| Faecal coliform Log$_{10}$ (CFU·100 mL$^{-1}$) | 5.66 (6.00) | 0.61 (0.26) |

The results obtained in this study can be compared to other winery wastewater strategies, in this sense, literatura review indicate that different tecnologies are considered for this pourpose; however few of them are focused on the water resuse. In most of the studies, the COD removal efficiency is the key parameter to assess the technical feasibility of the winery wastewater treatment. In this sense the COD removal rates obtained by MBR plant are higher than those reported when using a jet-loop activated sludge reactor (Petruccioli et al., 2002), long term aerated storage and chemical coagulation/flocculation (Braz et al., 2010), a hybrid constructed wetland (Serrano et al., 2011), and a photocatalytic/photolytic reactor (Agustina et al., 2008). Furtheremore, the MBR effluent achieved the quality criteria defined for for urban, agricultural and recreational reuse. Finally, the operational cost of MBR is higher than CAS plant, however can be considered competetitve when compared with other technologies (Lucas et al., 2010; Kirzhner et al., 2008).

## 9.4. CONCLUSIONS

This study evaluates the treatment of winery wastewater by a CAS system and MBR pilot plant installed in the Miguel Torres facilities. The winery wastewater characterization showed a wide variability in terms of COD due to the different annual stages in the wine making process. The MBR pilot plant build and operated by Hera-Amasa showed significant flexibility to reduce the COD concentration with removal efficiency over close 100% biodegradable fraction of the COD. Furthermore, the MBR performance showed a fairly stable operation in terms of TMP and permeability despite the high variability of the wastewater treated.

From the point of view of the fouling potential a direct correlation within EPSp and permeability was obtained, it can be explained by the hydrophobic character of this fraction and its potential interaction with the membrane. The results indicate that MBR pilot plant can achieve high removal efficiencies in winery wastewater treatment and that MBR permeate is suitable for urban, agricultural and recreational reuse according to the quality criteria defined by the Spanish Royal decree for water reuse. Furthermore, the effluent reached most of the quality specifications defined by international guidelines and regulations for water reuse and reclamation.

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# Chapter 10: Environmental evaluation of membrane bioreactor technology in front of conventional activated sludge for winery wastewater treatment

Parts of this chapter were based on:

Ribera, G., Bahí, N., Rovira, M., Giménez, T., Nomen, R., Martinez-Lladó, X., Rovira, M.; Environmental evaluation of membrane bioreactor system in front of conventional activated sludge for winery wastewater treatment. *To submit*

## 10.1. INTRODUCTION

In order to emit the effluent according to legislation in water bodies, as rivers, lakes or directly to the sea, wastewater treatments plants (WWTP) must improve quality of different influents, generally from urban or industrial origins, to reduce pollutant charges in receiving water bodies (91/271/EEC; 2006/11/EC). Furthermore, advanced technologies have been developed to increase effluents quality in order to face up to more restrictive future legislations or for water reuse proposals, especially in regions with periodic problems of water scarcity (Comandaru et al., 2012).

In this sense, water reclamation and reuse may have some advantages involved in reduction of freshwater resources intakes and the preservation of water bodies. However, the effects of water reuse in some applications are still unknown, including social acceptance or because health risks are difficult to predict (Toze, 2006). In case of Spain, as others regions with water scarcity problems, physico-chemical and microbial parameters have been legislated to guarantee a safe management for urban services, agricultural and recreational uses of reclaimed water as non conventional resource (RD1620/2007).

Advanced technology processes can provide high effluent qualities from wastewater, but unfortunately, environmental impacts can be increased because normally, increasing the sophistication in water treatments implies higher resource consumption (energy, chemicals and/or infrastructure). Benefit in water bodies preservation and options in water reuse are advantages of upgrading wastewater effluent quality but other negative effects may result, as chemicals emissions to atmosphere and soil (Foley et al., 2010). Methodologies such as life cycle assessment (LCA) have been applied to evaluate and compare the environmental cost of water treatments.

Generally, sewage plants in Spain are based on conventional system of activated sludge (CAS) providing the quality of secondary treatment in their discharges. The addition of membrane technologies, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO), provide an increase in final quality of the wastewater effluent for interesting chances in water reclamation and reuse. The number of MF and UF membranes applications in immersed membrane bioreactors (MBR) has been increased for urban and industrial wastewaters providing the option for alternative water resource for some applications (Lesjean and Huisjes, 2008). In this point, water reuse can suppose savings in freshwater resources preferred for drinking water proposals.

Most of the LCA studies regarding wastewater treatment are focused in urban sewage plants, being less known the environmental impact of industrial wastewater sector (Foley et al., 2010; Ortiz et al., 2007; Weiss et al., 2008). Industry usually makes use of LCA tool to estimate the environmental impact of their products (Aranda, 2005; Petti, 2010; Point, 2008; Vazquez-Rowe et al., 2012), such is the case of agro-food industry where consumers and governments are paying a growing attention in all processes and wastes involved to its global process (Gabzdylova et al., 2009). However, in industry sector few studies have been focused in wastewater treatment and less is known about water reuse applications for each case (Comandaru et al., 2012; Toze, 2006).

The degree of treatment in case of industrial effluents basically depends on wastewater discharges requirements and industrial activity. In case of winery wastewater, the effluent is characterized to present large loading regimen fluctuations during the year, as a consequence of harvesting and vintage periods, becoming the disposal of winery wastewater one of the major environmental problems related to wine industries. For example, chemical oxygen demand (COD) should not exceed 75 $mg{\cdot}L^{-1}$ but usually winery wastewater has COD of 800-12000 $mg{\cdot}L^{-1}$ (Agustina et al., 2008; Rosso and Bolzonella, 2009).

The main objective of this LCA study is to evaluate and compare the environmental impact associated to the construction and operation of a MBR, assisted during high load periods by the current CAS process, in front of the current CAS process for a real winery wastewater treatment plant. Additional aims for this work have been 1) study the environmental impact of the current CAS in a winery industry; 2) calculate differences in energetic costs and equivalent carbon dioxide ($CO_2$) emissions when MBR is implemented; 3) evaluate the influence of the higher energy consumption due to higher cleaning requirements of the membranes and lower oxygen transfer rates over different environmental categories evaluated in the base case.

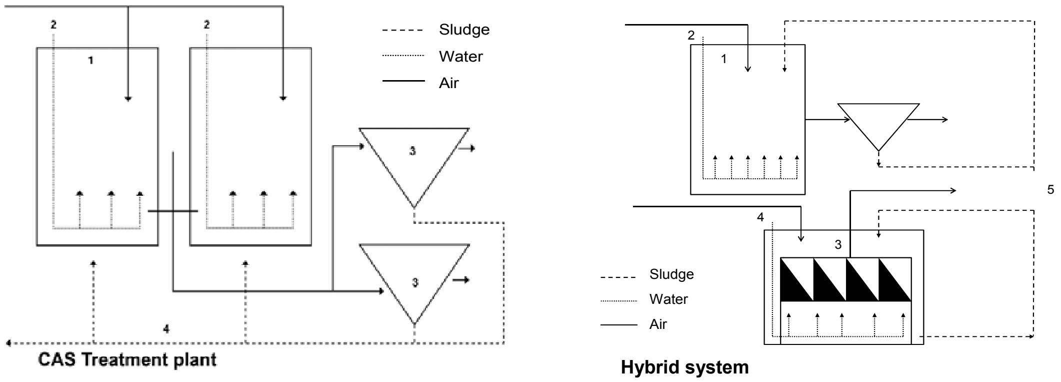
## 10.2. MATERIALS AND METHODS

### 10.2.1. Description of the system studied

A MBR was considered to be implemented in addition to the actual CAS process to treat the wastewater from Bodegas Torres (NE Spain). The proposed hybrid system considered here as a base case consists in a scale-up from the previous pilot study based in submerged flat-sheet membranes bioreactor, presented in Chapter 9 (Valderrama et al., 2012). Hybrid system has been defined as the process to treat the annual flow by both MBR and CAS bioreactors at different percentages of capacity, 92% and 8%, respectively. These percentages are based on the MBR capacity, and the overflow that should be treated by CAS process. The base case will be compared with the labeled CAS system, in which 100% of winery wastewater is treated by CAS bioreactor. Both wastewater treatment systems can be divided in three main parts:

1) Subsystem 1: Pretreatment and homogenizer
2) Subsystem 2: Biological reactor (MBR or CAS+decanters) and tertiary treatment
3) Subsystem 3: Sludge thickener line

Schematic representations for subsystem 2 in both cases are illustrated in Figure 10.1. First and third subsystems are the same for both systems studied, although a reduction of sludge volume has been calculated in case of a hybrid system. This lower sludge formation is a technical consideration because MBR usually operates at higher levels of suspended solids in the bioreactor than in the CAS system (Ortiz et al., 2007).



a) 1. Aerobic reactors; 2. Fine bubble aeratioin; 3. Clarifiers; 4. Recirculation and purge

b) 1. Aerobic reactor; 2. Fine bubble aeration; 3. MBR; 4. Coarse bubble aeration; 5. Recirculation and purge

Figure 10.1: Schematic flow diagrams for bioreactor in a) base case, b) hybrid system

First of all, winery wastewater is pre-treated by preliminary screening before passing to the homogenizer, where diammonium phosphate and sodium hydroxide are added to equilibrate nutrient contents and neutralize the influent water, respectively. The next step or process unit is the bioreactor, where microorganisms degrade organic loads. Effluents from bioreactors have been considered to be discharged to the tertiary treatment, which consists in stabilization pond.

### 10.2.2. Environmental impact

The LCA in this work was carried out following the standardized guidelines under International Organization for Standardization (ISO, 2006a; b). LCA methodology involves four stages: goal and scope definition, life cycle inventory (LCI), impact assessment) and finally the interpretation of the LCA results. The last two steps are presented in section 10.3.

#### 10.2.2.1. Goal and scope

The goal of this research was evaluate the environmental impact to treat winery wastewater using MBR technology assisted by CAS reactor when peaks of organic loads occur in this industrial activity (hybrid system).

A conceptual outline of the hybrid system boundaries is presented in Figure 10.2, where those aspects that differ significantly with CAS system can be contemplated.

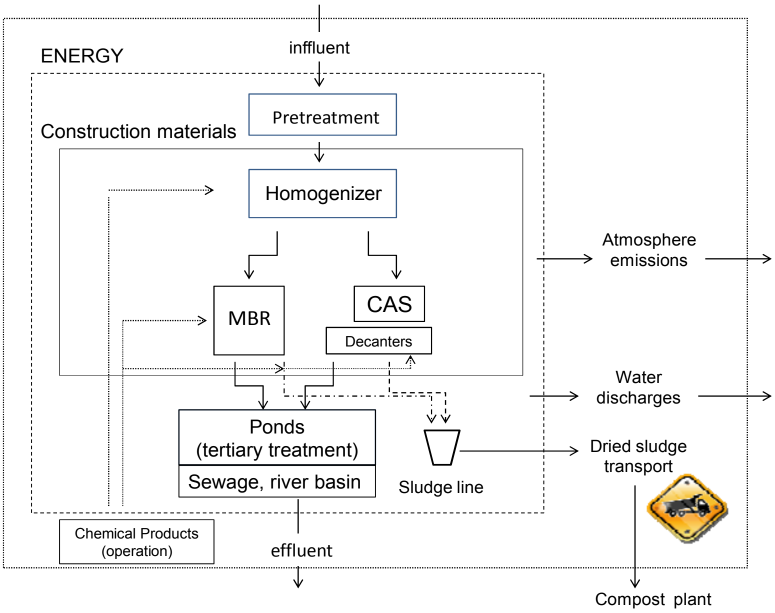


Figure 10.2: Boundaries for the hybrid system

Construction and operational data were taken into account for each unit processes indicated in Figure 10.2. Dismantling stage has been dismissed in accordance to other studies in the area of LCA applied to water treatments (Friedrich, 2002; Gaterell et al., 2005; Lundin et al., 2000). Sludge line as a process unit involves sludge thickener in the plant and dried sludge transport to a compost plant. Final treatment and disposal for the sludge are out of this LCA study, neither taking into account positive (reduction of fertilizers) or negative effects (undesired emissions to the soil) of sludge use in agricultural practices (Foley et al., 2010).

Water reuse is out of the scope for this study because final applications for this non-conventional water resource are still unknown, and hence benefits and risks associated to water reuse cannot be evaluated (Mosse et al., 2011; Toze, 2006). However, effluent quality was considered in LCA comparing hybrid and CAS systems to observe differences in freshwater eutrophication like in other works (Comandaru et al., 2012).

The functional unit (FU) of the study was defined as one cubic meter of treated wastewater in the WWTP in function of the annual flow and considering a plant lifetime of 25 years. The installation capacity in the winery wastewater treatment plant was considered able to treat 0.164 $Mm^3 \cdot year^{-1}$ of winery wastewater. In case of hybrid system, this annual wastewater flow is divided in 0.150 $Mm^3$ to be treated by MBR bioreactor and 0.014 $Mm^3$ by current CAS bioreactor. On the other hand, CAS system is referred to treat the total annual effluent of the winery industry by CAS bioreactor.

#### 10.2.2.2. Life cycle inventory

Data considering materials, energy, emissions and transport were collected for infrastructure construction (capital) and operational stages for both MBR and the real CAS processes. Capital data were carried out during fieldworks in the WWTP and from some supplier's specifications. In addition, primary data were provided by Bodegas Torres regarding energy and chemical products consumption during the process in 2010 for the CAS system. On the other hand, Hera-Amasa provided operational data for MBR installation. Table 10.1 summarizes the main inventory data considered for construction and operational stages during the wastewater treatment using CAS and MBR technologies.

Biological reactor supposes 52% of all electricity consumed at the WWTP during 2010 in Bodegas Torres. The rest is divided mostly between pretreatment (23%), tertiary treatment (12%) and sludge thickeners line (9%). These figures are in well agreement with reported values between 30-60% for energy consumption during aerobic digestion in a WWTP based in CAS system, (CEE, 2010; Fenu et al., 2010). In addition, MBR increases energy consumption to prevent fouling deposition on membrane surface during bioreactor operation, this extra electricity demand corresponds to 0.40 $kWh \cdot m^{-3}$.

Additionally, Ecoinvent database has been employed as default database to cover secondary data, including Spanish energetic mix production (Ecoinvent, 2010). On the other hand, a reduction of 9.2% in the sludge line for hybrid system was applied due to higher sludge age, according to the literature (Ortiz et al., 2007) (Table 10.1).

Table 10.1: Inventory data used in the present LCA study

| Unit process | Inputs | Quantity/ FU |
|---|---|---|
| **Construction stage** | | |
| Homogenizer | Chromium steel 18.8 | 0.011 $kg{\cdot}m^{-3}$ |
| Biological reactor CAS | Chromium steel 18.8 | 0.017 $kg{\cdot}m^{-3}$ |
| Decanters CAS | Concrete | $1.2{\cdot}10^{-4}$ $kg{\cdot}m^{-3}$ |
| Biological reactor MBR | Concrete | $2{\cdot}10^{-5}$ $kg{\cdot}m^{-3}$ |
| Biological reactor | Reinforced steel | $1.5{\cdot}10^{-3}$ $kg{\cdot}m^{-3}$ |
| Sludge treatment line | Chromium steel 18.8 | 0.003 $kg{\cdot}m^{-3}$ |
| Membrane material | Polyethylene (PE) | $1.2{\cdot}10^{-3}$ $kg{\cdot}m^{-3}$ |
| Membrane modules | Polyvinyl chloride PVC | $1.8{\cdot}10^{-3}$ $kg{\cdot}m^{-3}$ |
| Membrane modules | Stainless steel | $7.1{\cdot}10^{-4}$ $kg{\cdot}m^{-3}$ |
| Membrane modules | Polyethylene terephtalate PET | $7.1{\cdot}10^{-6}$ $kg{\cdot}m^{-3}$ |
| **Operational stage** | | |
| Ammonnium chloride | Homogenizer | 0.030 $kg{\cdot}m^{-3}$ |
| Diammonium phosphate | Homogenizer | 0.030 $kg{\cdot}m^{-3}$ |
| Sodium hydroxide (15%) | Homogenizer | 0.486 $kg{\cdot}m^{-3}$ |
| Ethanolamine phosphate | Decanters (CAS) | 0.002 $kg{\cdot}m^{-3}$ |
| Acrylonitrile (polyelectrolit) | Sludge thickener | 0.027 to 0.030 $kg{\cdot}m^{-3}$ |
| Sodium hypochlorite | MBR (cleaning) | 0.003 $kg{\cdot}m^{-3}$ |
| **Energy consumption** | | |
| Energy consumption | Pretreatment | 1.8 kWh $m^{-3}$ |
| | Homogenizer | 0.3 kWh $m^{-3}$ |
| | CAS bioreactor | 4.1 kWh $m^{-3}$ |
| | MBR bioreactor | 4.5 kWh $m^{-3}$ |
| | Decanters (CAS system) | 0.02 kWh $m^{-3}$ |
| | Sludge line (CAS system) | 0.7 kWh $m^{-3}$ |
| | Sludge line (MBR system) | 0.6 kWh $m^{-3}$ |
| | Tertiary treatment | 0.9 kWh· $m^{-3}$ |

Table 10.2 shows the average results during pilot plant experimentation, which were introduced as primary data for water discharges to the environment.

Table 10.2: Emissions to water, atmosphere and soil

| Outputs (primary data) | CAS process | MBR process | Influent |
|---|---|---|---|
| **Emissions to water** | | | |
| COD (kg glucose$\cdot m^{-3}$) | $16{\cdot}10^{-2}$ | $8.4{\cdot}10^{-2}$ | 3.7 |
| BOD (kg glucose$\cdot m^{-3}$) | $7.0{\cdot}10^{-3}$ | $8.7{\cdot}10^{-3}$ | 1.4 |
| TOC (kg glucose$\cdot m^{-3}$) | $4.9{\cdot}10^{-2}$ | $3.2{\cdot}10^{-2}$ | 1.3 |
| Nitrates (kg $NO_3^-{\cdot}$ $m^{-3}$) | $2.0{\cdot}10^{-4}$ | $1.7{\cdot}10^{-4}$ | $11{\cdot}10^{-4}$ |
| Nitrites (kg $NO_2^-{\cdot}$ $m^{-3}$) | $1.3{\cdot}10^{-4}$ | $1.7{\cdot}10^{-4}$ | $6.7{\cdot}10^{-4}$ |
| Ammonia (kg $NH_4^+{\cdot}$ $m^{-3}$) | $3.5{\cdot}10^{-3}$ | $6.3{\cdot}10^{-3}$ | $8.8{\cdot}10^{-3}$ |
| N organic (kg N· $m^{-3}$) | $6.2{\cdot}10^{-4}$ | $4.9{\cdot}10^{-4}$ | $2.6{\cdot}10^{-3}$ |
| Phosphate (kg $PO_4^{-3}{\cdot}$ $m^{-3}$) | $9.8{\cdot}10^{-3}$ | $8.3{\cdot}10^{-3}$ | $1.0{\cdot}10^{-2}$ |
| **Emissions to air** | | | |
| Carbon dioxide (kg $CO_2{\cdot}$ $m^{-3}$) | 1.58 | 1.71 | *biogenic* |

Primary data about direct emissions to water bodies of nutrients, such as phosphates and nitrogen, were considered because have direct effects in the eutrophication of water. Organic nitrogen was calculated as the difference between total N and the rest of N forms indicated in the table above.

Carbon dioxide emissions from aerobic processes are considered to be neutral as emissions to air due to its biogenic origin (Wang et al., 2012).

#### 10.2.2.3. Life cycle impact assessment methodology

Hybrid system described in section 10.2.1 has been evaluated in front of CAS system based on annual flow. LCA was developed with the help of SimaPro software (versión 7.3.3). Results for environmental impact have been calculated using Recipe Midpoint (H) European calculation methodology (version 1.07) for the impact categories shown in Table 10.3 (where abbreviations used and equivalent units are indicated for each category).

Calculation method sort input and output data into one or more impact category. In accordance with international guidelines for LCA studies, normalization and weighting are out of this study because they involve subjective criteria, as reference values and regional considerations (ISO, 2006b).

Table 10.3: Impact categories evaluated

| | **Abbreviation** | **Units** |
|---|---|---|
| Climate change | CC | kg CO2 eq |
| Ozone depletion | OD | kg CFC-11 eq |
| Human toxicity | HT | kg 1.4-DB eq |
| Photochemical oxidant formation | POF | kg NMVOC |
| Particulate matter formation | PMF | kg PM10 eq |
| Terrestrial acidification | TA | kg SO2 eq |
| Freshwater eutrophication | FEU | kg P eq |
| Freshwater ecotoxicity | FET | kg 1,4-DB eq |
| Water depletion | WD | $m^3$ |
| Metal depletion | MD | kg Fe eq |
| Fossil depletion | FD | kg oil eq |

In particular, climate change (CC) and ozone depletion (OD) are the main impact categories with global effects. FEU, FET and WD resources are categories directly related to quality and quantity of the natural water resource. Freshwater eutrophication (FEU) category is directly affected for direct emissions of nutrients to the water, instead of freshwater ecotoxicity (FE) and human toxicity (HT), categories which are usually quantified in function of persistent toxic compounds emissions to water, atmosphere or soils. The origin for toxic compounds in this work is related to secondary processes involved in construction or operation stages for the process (i.e. chemical products manufacture).

In water processes, impact categories such as TA, POF and PMF are usually related to energy production from fossil resources (FD), as a result of solar photosensitive compounds (ozone, hydrocarbons, carbon or nitrogen oxides) and small particles release to the atmosphere.

### 10.2.3. Scenario study

MBR technology has been improving in last years with different configurations and as a result providing more efficient membranes. In the scenario analysis of labelled hybrid system 2, alternatives membranes, requiring less energy for its maintenance than those employed in hybrid system had been evaluated. The use of these membranes implies lower energy-demand by means of air scouring to prevent membrane fouling. In addition some differences exist in capital materials for the module construction in comparison with the base case. Table 10.4 shows these input data calculated from supplier's specifications.

Table 10.4: Different input values introduced in inventory data for hybrid system 2

| Unit process | **Inputs** | **Quantity** |
|---|---|---|
| **Construction stage** | | |
| Membrane material | Polyethylene (PE) | $1.1\cdot10^{-3}$ kg·m$^{-3}$ |
| Membrane modules | Polyvinyl chloride PVC | $1.3\cdot10^{-3}$ kg·m$^{-3}$ |
| Membrane modules | Stainless steel | $1.1\cdot10^{-3}$ kg·m$^{-3}$ |
| Membrane modules | Polyethylene terephtalate PET | $5.1\cdot10^{-6}$ kg·m$^{-3}$ |
| **Energy consumption** | | |
| Energy consumption | MBR bioreactor | 4.3 kWh· m$^{-3}$ |

Energy consumption during operational stage are 0.24 kWh·m$^{-3}$, lower than the reported value for previous case (0.4 kWh·m$^{-3}$).

### 10.2.4. Sensitivity analysis

Sensitivity studies are useful to evaluate how critical parameter may affect LCA results. In this case, the most critical parameter is energy consumption during operational stage of the bioreactor because MBR, additionally to the extra supply for membrane maintenance, operates at higher MLSS (usually up to 13 g·L$^{-1}$). This fact directly influences oxygen transfer rates to the biomass and consequently, energetic demands, because blowers power must be increased (Gander et al., 2000). In the base case, according to similar approach than previous LCA studies, the energy to degrade organic loads for MBR was based on energetic consumption from CAS bioreactor (Krzeminski et al., 2012).

In this sensitivity study, higher energetic requirements were considered for the organic degradation in the MBR bioreactor contained in both hybrid systems. For this reason, the named α-coefficient (defined as a rate between oxygen transfer efficiency in mixed liquor and water) was used to determine energy consumption for the MBR bioreactor in a sensitivity analysis.

Based on previous studies, two values of α-coefficient were considered for energy consumption calculations in this sensitivity analysis, 0.6 and 0.2, respectively for the aeration efficiency in membrane bioreactors when MLSS was supposed to be 13 $g \cdot L^{-1}$ (efficiency of 60 and 20% with regards CAS bioreactor) (Henkel et al., 2009).

### 10.2.5. Economical estimation for $CO_2$ emissions

Some calculations about energetic costs during operation and the associated ones to equivalent dioxide carbon emissions were determined as important point to compare the three cases in the scenario study: hybrid system, hybrid system 2 and CAS system. Energetic costs are expressed as $€ \cdot m^{-3}$ of treated wastewater when an average price for industrial kWh is fixed at 0.113€. On the other hand, costs associated to equivalent carbon dioxide emissions are calculated considering prices in 2009 and 2012, fixed at 12.31 and 4.49 $€ \cdot Tn^{-1}$ $CO_2$ emitted (http://www.sendeco2.com).

## 10.3. RESULTS AND DISCUSSION

### 10.3.1. Life cycle impact assessment results and interpretation

Results for the hybrid system are presented in Table 10.5 regarding contributions for the different process units. Values are expressed in equivalent units per cubic meter of treated wastewater in each environmental category (indicated in Table 10.3).

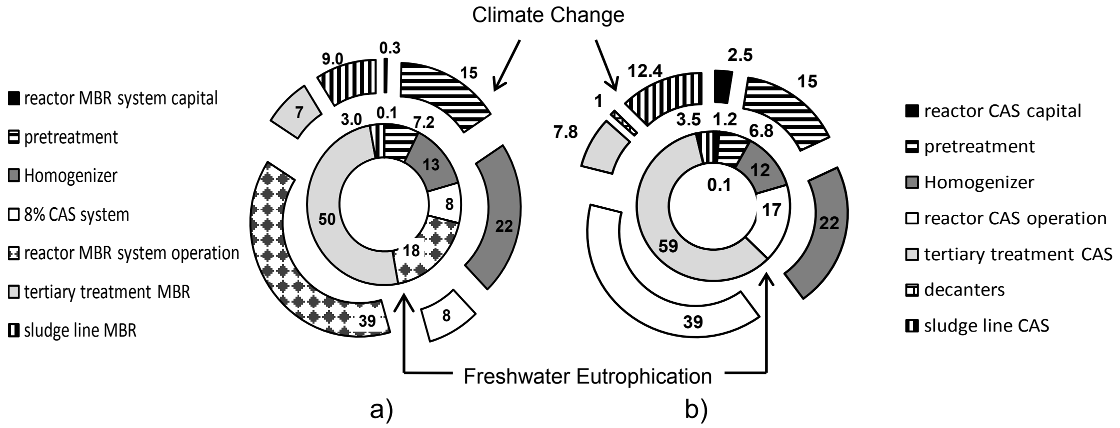
CAS bioreactor operation in hybrid system only represents 8% of the total wastewater treatment process, resulting in a lower contribution than MBR bioreactor operation (which consists in 92%). However, tabulated values not maintain this proportion in total bioreactor unit process of the hybrid system, showing relative contribution between 10-17% for CAS bioreactor in most of impact categories. This fact is explained because capital materials and decanters operation are processes included in CAS bioreactor operating at 8%.

Furthermore, the proposed hybrid system which considers MBR technology is oversized regarding CAS bioreactor plant.

Table 10.5: Environmental impact for different process units and categories in hybrid system

| | Total | Pre-treatment | Homoge-nizer | bioreactor | | Tertiary treatment | Sludge line | |
|---|---|---|---|---|---|---|---|---|
| | | | | MBR | CAS 8% | | MBR | CAS 8% |
| **CC** | 6.1 | 0.92 | 1.3 | 2.36 | 0.41 | 0.43 | 0.54 | 0.059 |
| **OD** | $3.9{\cdot}10^{-7}$ | $5.4{\cdot}10^{-08}$ | $9.0{\cdot}10^{-08}$ | $1.4{\cdot}10^{-07}$ | $2.0{\cdot}10^{-08}$ | $2.8{\cdot}10^{-08}$ | $5.2{\cdot}10^{-08}$ | $5.4{\cdot}10^{-09}$ |
| **HT** | 2.3 | 0.31 | 0.75 | 0.78 | 0.16 | 0.15 | 0.14 | 0.014 |
| **POF** | 0.024 | $3.7{\cdot}10^{-03}$ | $4.6{\cdot}10^{-03}$ | $9.4{\cdot}10^{-03}$ | $1.3{\cdot}10^{-03}$ | $1.9{\cdot}10^{-03}$ | $2.6{\cdot}10^{-03}$ | $2.7{\cdot}10^{-04}$ |
| **PMF** | 0.015 | $2.3{\cdot}10^{-03}$ | $3.1{\cdot}10^{-03}$ | $5.8{\cdot}10^{-03}$ | $1.2{\cdot}10^{-03}$ | $1.2{\cdot}10^{-03}$ | $1.2{\cdot}10^{-03}$ | $1.2{\cdot}10^{-04}$ |
| **TA** | 0.047 | $7.7{\cdot}10^{-03}$ | $9.7{\cdot}10^{-03}$ | 0.019 | $2.3{\cdot}10^{-03}$ | $3.9{\cdot}10^{-03}$ | $3.7{\cdot}10^{-03}$ | $3.9{\cdot}10^{-04}$ |
| **FEU** | $6{\cdot}10^{-03}$ | $3.9{\cdot}10^{-04}$ | $1.2{\cdot}10^{-03}$ | $1.0{\cdot}10^{-03}$ | $1.5{\cdot}10^{-04}$ | $3.0{\cdot}10^{-03}$ | $1.6{\cdot}10^{-04}$ | $1.6{\cdot}10^{-05}$ |
| **FE** | 0.056 | $6.2{\cdot}10^{-03}$ | 0.015 | 0.016 | 0.013 | $3.1{\cdot}10^{-03}$ | $2.8{\cdot}10^{-03}$ | $2.8{\cdot}10^{-04}$ |
| **WD** | 0.043 | $5.8{\cdot}10^{-03}$ | 0.014 | 0.015 | $2.6{\cdot}10^{-03}$ | $2.9{\cdot}10^{-03}$ | $2.9{\cdot}10^{-03}$ | $3.1{\cdot}10^{-04}$ |
| **MD** | 0.73 | 0.012 | 0.20 | 0.042 | 0.46 | $6.0{\cdot}10^{-03}$ | 0.014 | $1.6{\cdot}10^{-03}$ |
| **FD** | 1.7 | 0.26 | 0.38 | 0.66 | 0.097 | 0.13 | 0.17 | 0.020 |

Results in Table 10.5 have been graphically represented in Figure 10.3.a) in order to evaluate the relative contribution of process units over total impact for climate change (outer circle) and freshwater eutrophication (inner circle) categories. LCA results for CAS system are also represented in Figure 10.3.b) for comparison proposals with the base case.



a) b)

Figure 10.3: Results from LCA for a) hybrid system or b) current CAS system regarding climate change and freshwater eutrophication as impact categories

Major energy consumption in hybrid system has been reflected in a higher impact over CC, which in this study takes into account an increase near to 10% in MBR operation (4.5 kWh·m$^{-3}$) in comparison to CAS bioreactor operation (from 4.1 kWh·m$^{-3}$). For the CAS system, total impact in this category was 6.0 kg $CO_2$ equivalent·m$^{-3}$, resulting 1.6% of reduction with regards hybrid system (Table 10.5). Major contribution in both systems are from bioreactor operation, but higher energy consumption in hybrid system has also been translated to major relative contribution for this process unit than in CAS system: 47% in front of 39% for CC and 26% in front of 17% for FEU categories.

In general, reactor MBR system operation in hybrid system has the highest contribution for all categories, except in case of freshwater eutrophication (FEU). For this category, tertiary treatment played the major role for both systems, in congruence with nutrients emissions to water body from tertiary treatment (Table 10.2). Comparing the base case with CAS system, an increase of 7.4% for the total impact for FEU category was observed for the latter ($5.8 \cdot 10^{-3}$ kg P eq$\cdot$m$^{-3}$ in front of $5.4 \cdot 10^{-3}$ kg P eq$\cdot$m$^{-3}$ in the hybrid system).

On the other hand, sludge process unit has different impact on both systems, for example in CC category CAS system supposes emissions of 0.74 kg $CO_2$ equivalent$\cdot$m$^{-3}$, resulting an increase of 23% with regards the sludge line in the hybrid system (0.60 kg $CO_2$ equivalent $\cdot$m$^{-3}$ in Table 10.5). This result is due to less sludge volumes formation when MBR is used, which implies a reduction in transport to the compost plant and in energetic demands for this process unit (see additional information). In addition, this saving in the sludge line compensates in some degree the increase of total impact as a result of higher energy demand during MBR operation in hybrid system.

Freshwater ecotoxicity (FE) and human toxicity (HT) categories are usually quantified in function of persistent toxic compounds emissions to water, atmosphere or soils. The origin for toxic compounds in this study was related to secondary processes involved in construction or operation stages for the process (i.e. chemical products manufacture). Stainless steel manufacture highly contributes to increase impact in FE and metal depletion (MD) categories. Environmental impact with regards materials employed in the construction of the reactor MBR showed low contribution in most of the categories analysed (< 0.3%), indicating suitable amortization for materials employed in MBR construction stage from an environmental point of view.

In this wastewater treatment process, other impact categories such as terrestrial acidification (TA), photochemical organics formation (POF) and particulate matter formation (PMF) have been related to energy consumption, derived from Spanish energetic mix. As a consequence, sulfur oxides, solar photosensitive compounds (ozone, hydrocarbons, and carbon or nitrogen oxides) and small particles are released to the atmosphere.

### 10.3.2. Scenario study results

In Figure 10.4 LCA impacts for hybrid system 2 (with more efficient membrane) are compared in front of those previously calculated for base case and CAS system for each impact category.

In case of hybrid system 2 operational costs imply savings of 1.8% in energy consumption during MBR operation in base case. This supposes a reduction of equivalent carbon dioxide emissions around 1.6% for climate change category.

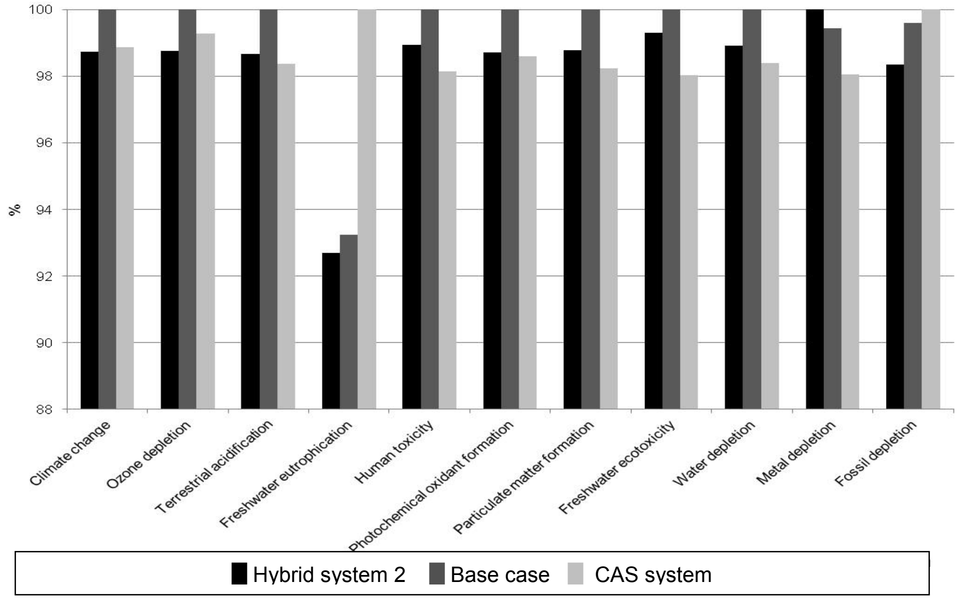


Figure 10.4: Environmental profile for scenario study in this LCA study

Energy savings in membrane aeration to prevent fouling were translated to similar reduction in all energy-related categories for this study (OD, TA, HT, POF, PMF, FD). In case of freshwater eutrophication, impact for hybrid system 2 was maintained similar to that for the base case because direct emissions to water were considered the same.

By the contrary, the impact in metal depletion increases in the hybrid system 2 because extra quantities of steel were used to build membrane modules (see Table 10.1 and Table 10.4).

Comparing hybrid system 2 and CAS system, it is important to note that impacts on energy-related categories were similar because energy in bioreactor operation has been considered nearly the same using the more efficient membranes. However, transport of sludge to the compost plant influences directly over fossil depletion and climate change categories, consequently a reduction in sludge formation leads to decrease in some degree the impact on both categories for hybrid system 2, as indicated in columns of Figure 10.4. Energy consumption and some chemicals (polyelectrolyte manufacturing) employed in the sludge line process unit were also reduced, but no noticeable effects have been observed in the rest of impact categories.

### 10.3.3. Sensitivity analysis results

Table 10.6 shows the increase of energy consumption at 60% and 20% (α-coefficient as aeration efficiencies) in the bioreactor for both hybrids systems considered. Energy consumption for CAS system is indicated in this table for comparison proposals.

Table 10.6: Energy consumption corrected considering α-coefficient

| Process unit | Energy consumption (kWh·m$^{-3}$) | | | |
|---|---|---|---|---|
| | **CAS** | **α coefficient** | **Base case** | **Hybrid system 2** |
| Pretreatment | 1.8 | | 1.8 | 1.8 |
| Homogenizer | 0.3 | | 0.3 | 0.3 |
| Bioreactor | 4.1 | worse case (α=0.2) | 20.5 | 20.3 |
| | | better case (α=0.6) | 6.8 | 6.6 |
| Decanters | 0.02 | | 0 | 0 |
| Sludge line | 0.7 | | 0.6 | 0.6 |
| Tertiary treatment | 0.9 | | 0.9 | 0.9 |

Environmental impacts for each impact category dramatically increased with the reduction of α-coefficient, as it can be observed in Table 10.7.

Table 10.7: LCA sensitivity analysis results varying α-coefficient for the bioreactor aeration

| **Impact category** | **Base case** | | **Hybrid system 2** | | **CAS system** |
|---|---|---|---|---|---|
| | **Better** | **Worse** | **Better** | **Worse** | |
| CC (kg CO2 eq·m$^{-3}$) | 7.1 | 13.4 | 7.0 | 13.3 | 6.0 |
| OD (kg CFC-11 eq·m$^{-3}$) | $4.5\cdot10^{-7}$ | $8.2\cdot10^{-7}$ | $4.4\cdot10^{-7}$ | $8.2\cdot10^{-7}$ | $3.9\cdot10^{-7}$ |
| HT (kg 1,4-DB eq·m$^{-3}$) | 2.6 | 4.7 | 2.6 | 4.7 | 2.3 |
| POF (kg NMVOC·m$^{-3}$) | 0.028 | 0.053 | 0.028 | 0.053 | 0.023 |
| PF (kg PM10 eq·m$^{-3}$) | 0.017 | 0.033 | 0.017 | 0.033 | 0.015 |
| TA (kg SO2 eq·m$^{-3}$) | 0.056 | 0.11 | 0.055 | 0.11 | 0.046 |
| FEU (kg P eq·m$^{-3}$) | $5.8\cdot10^{-3}$ | $8.5\cdot10^{-3}$ | $5.8\cdot10^{-3}$ | $8.5\cdot10^{-3}$ | $5.8\cdot10^{-3}$ |
| FE (kg 1,4-DB eq·m$^{-3}$) | 0.063 | 0.11 | 0.062 | 0.10 | 0.055 |
| WRD (m$^{3}$·m$^{-3}$) | 0.049 | 0.089 | 0.049 | 0.089 | 0.043 |
| MRD (kg Fe eq·m$^{-3}$) | 0.74 | 0.82 | 0.75 | 0.83 | 0.72 |
| FD (kg oil eq·m$^{-3}$) | 2.0 | 3.7 | 2.0 | 3.7 | 1.7 |

Results show that for a 66% of reduction in aeration efficiency, between worse and better α-coefficient, implies nearly the double of equivalent carbon dioxide emissions. Then, for the overall plant, taking into account the contribution of bioreactor unit process operation, the impact score in climate change category increases between 20% (α=0.6) and 120% (α=0.2) in comparison to CAS system. This variation is similar in fossil depletion category (FD) as a result of energetic mix. The same happens for other categories, such as photochemical oxidant formation (POF) and terrestrial acidification (TA), presenting increases between 22% and 140%, respectively for each α-coefficient. In contrast, lower variation for freshwater eutrophication (FEU) or metal depletion (MD) is observed because the correlation with energy, and then with α-coefficient is lower.

From this results can be concluded than changes in aeration efficiency are more important than the aeration requirements for membrane scouring recommended by suppliers to prevent fouling in membrane surface.

Operating with MBR technology may suppose higher energy requirements to maintain the same oxygen transfer than in CAS bioreactor, because usually the design parameters take into account higher MLSS in order to save space and be able to treat major organic loads. Good balancing among design parameters and energy demand of the bioreactor are key factors when this technology is evaluated from an environmental point of view.

### 10.3.4. Economical estimation for $CO_2$ emissions

In this part, costs about energetic demand and equivalent carbon dioxide emissions were calculated and results are indicated in Table 10.8.

Table 10.8: Supplementary information regarding energetic cost and $CO_2$ emissions

| **Systems:** | **CAS** | **MBR** | **MBR 2** |
|---|---|---|---|
| Bioreactor energy consumption (kWh·m$^{-3}$) | 4.1 | 4.5 | 4.3 |
| Operational energetic costs (€·m$^{-3}$) | 0.91 | 0.95 | 0.93 |
| Climatic change (kg $CO_2$ eq·m$^{-3}$) | 6.0 | 6.1 | 6.0 |
| $CO_2$ emissions costs 2012 (€·year$^{-1}$) | 4430 | 4500 | 4430 |
| $CO_2$ emissions costs 2009 (€·year$^{-1}$) | 12150 | 12350 | 12150 |

Operational costs associated to energy consumption were estimated in the process unit with more impact in climate change category, obviously cost is higher in the MBR system because membrane operation was not optimized. On the other hand, economic costs related to equivalent $CO_2$ emissions are more influenced by the price evolution in emission rights than changing WWTP technology, from CAS system to MBR system.

## 10.4. CONCLUSIONS

This LCA study provides the evaluation of the MBR technology implementation in a wastewater treatment plant of a winery industry. Slightly impact scores increases have been determined in climate change, and other energy production related categories, in the base case comparing MBR and CAS systems. By the contrary, impact on freshwater eutrophication is lower in MBR system because nutrients emissions to water bodies have been slightly diminished as a result of effluent quality improvement.

Moreover, MBR technology has a positive environmental impact regarding lower sludge production volumes than in CAS system, which reduce the needs of transport to the compost plants in addition to energetic saving in the sludge process unit line.

Although evolution in membrane technology conducts to more efficient membrane modules, requiring less energy to its maintenance, the sensitivity analysis showed that aeration efficiency during the organic matter degradation is the most critical parameter over CC and other categories related to energy source. Aeration efficiency corresponding to a wide range of α-coefficient values, from 0.6 to 0.2, increases energy consumption for MBR systems that has been translated in increases from 20% to 120% over CC and TA impact categories.

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# Chapter 11: General conclusions

The main objective of this thesis was to assess if two types of pressure driven membrane technologies, NF and MBR, are technically and environmentally feasible in drinking water supply and wastewater treatment to upgrade water quality in comparison to conventional techniques.

## NANOFILTRATION IN DRINKING WATER TREATMENT

Laboratory set-up provided useful results to differenciate commercial NF membrane available in the market. The most important variations among flat-sheet membranes tested were membrane water permeability and inorganic salt rejection. However, parameters regarding organic composition, such as organic carbon contents (NPOC), ultraviolet light absorbance and trihalomethane formation potential (THMFP), were reduced near to 95% in permeate samples for the great majority of NF membranes tested. Results from the different campaigns performed using flat-sheet membranes demonstrated NF capacity to reduce THM concentrations in drinking water, although feed water is collected in different seasons or different points of the selected hydric system.

Two membranes selected from this preliminary study showed technical feasibility in a NF pilot plant, whose design allows comparing simultaneously both membranes (NF270 and ESNA1LF2). Analysis of different parameters carried out during the six-monts operation for the pilot plant indicated differences between both membranes for inorganic salt rejections and similar organic parameters reductions in the permeate. Nevertheless, high inorganic ions separation in case of the most impermeable membrane, ESNA1LF2, have negative impacts on operational costs (energy demand) which requires higher transmembrane pressure (TMP) to obtain the same permeate flow than NF270.

Decline in permeability measured at the final of pilot plant operation was approximately 12% of the initial value. Cleaning practices on-site, using a basic solution and detergent were useful to recover partially the initial permeability of both membranes. UF module as a pretreatment was able to reduce silt density index (SDI) to values < 3 in order to prevent fouling formation. The addition of sodium metabisulfit and scale inhibitor was confirmed as necessary to remove free chlorine and to prevent inorganic salts precipitation, respectively.

However, four membranes were sacrified in order to evaluate possible fouling formation by means of visual observation and cleaning experiments carried out at the laboratory scale. Images from electronic microscope and infrared spectroscopy showed changes on membrane surface composition before and after cleanings, but neither with permeability measurements no clear evidences of the type of fouling were elucidated.

In both membrane cases, high rejections of THM precursor material were obtained, which resulted in very low THMFP in the permeate water. A blending ratio of 0.5 between filtered and feed water ensured a THMFP lower than 100 μg $THM\cdot l^{-1}$ in all cases regardless the seasonal and operational conditions variation (transmembrane flux and total water recovery). Specific ultraviolet light absorbance (SUVA) values were closely related to the THMFP of the feed water, which demonstrated the ability of this parameter to indicate the THMFP of raw water in DWTP, especially in warm periods (from June to September). Furthermore, residual THMFP in the filtered samples could be related to the presence of permeable low molecular weight THM precursor material.

Differences in trace elements and organic compounds rejection can be observed for both membranes. Similar results were obtained in accordance to separation capacities for inorganic ions, such as barium, silica and strontium. Uranium and aluminum rejections are high for both membranes indicating interesting abilities for NF in their removal. However, trace element speciation play an important role, in case of molibdeum, NF270 showed higher rejection than ESNA1LF2 (80% in front of 40%, respectively). Organic pollutants rejection by NF was evaluated considering real water and simulating a pollution episode with caffeine, cholesterol, LAS and terbuthylazine. The most important conclusion was that not always higher desalting membranes lead to better organic removals, although this organics are negatively charged (LAS). Results from pilot plant comparing both membranes can be useful to select the most appropriate membrane for further design in an industrial full-scale NF drinking water treatment plant in case of feed water pollution.

Laboratory experiments (flat-sheet membranes) and design software results showed good predictions for NF performance in pilot plant, where spiral-wound membranes are employed as in industrial full-scale drinking water plants. Comparison between both configurations was also used to elucidate initial flux variations concerning NF processes. The suggested hypotheses (membrane compaction, effects of preservative liquid and ionic strength) demonstrated no influence in initial flux variations and these results lead to think that flux decline is likely to happen as a result of initial flux formation.

Scale-up for a real drinking water process was performed using data from the studies inpilot plant with the intention to evaluate environmental impacts of NF technology in real applications. NF implementation treating 43% of final drinking water has supposed an increment around 50% over the real conventional system in the majority of environmental impacts studied in the life cycle assessment (LCA) study performed. Energy consumption for membranes operation is the major factor for this increase in environmental impact, although some benefits were obtained with regards human health risk related to THM ingestion, inhalation and dermal contact for drinking water consumers. Cancer risk index was reduced nearly to one order of magnitude when final drinking water contemplated 100% NF permeate. The relation stablished between LCA and HHR results provide a useful tool to design NF installations according to the desired final water quality, or conversely to less environmental impact.

## MEMBRANE BIOREACTOR TECHNOLOGY TO TREAT WASTEWATER FOR FURTHER REUSE APPLICATIONS

MBR pilot plant was technically evaluated during the six-month operation (including vintage period) in a real wastewater plant, demonstrating the reliability to produce reclaimed wastewater source for urban, agricultural and recreational reuse applications. Furthermore, the MBR performance showed a fairly stable operation in terms of TMP and permeability despite the high variability of the wastewater treated. However, fouling potential was directly correlated within EPSp contents and permeability because the hydrophobic character of this fraction makes possible the interaction of these substances with the membrane material.

LCA evaluation considering CAS and MBR technologies for wastewater treatment in a winery industry indicated higher impact in MBR because high energy consumption takes places during its operation. Although evolution in membrane technology lead to more efficient membrane modules, requiring less energy to its maintenance, the sensitivity analysis has shown that aeration efficiency during the organic matter degradation is a more critic parameter increasing impact in CC and other categories related to energetic mix source.

Impact in other categories, for example freshwater eutrophication for MBR system presents lower impact than CAS system because nutrients emissions to water bodies were slightly diminished. Another advantage for MBR technology is the positive environmental impact regarding lower sludge production volumes than in CAS system. However, the limits established in this LCA study only contemplate energetic and transport emissions for the produced sludge.

## ANNEX 1: Membrane classification in function of process driving force

Membrane processes are classified in Table A1 according to the driving force that makes the separation possible and the phase state of the two main streams.

Table A1: Membrane processes and driving forces

| Membrane process | phase 1 | phase 2 | Driving force as a gradient of: |
|---|---|---|---|
| Microfiltration | L | L | Pressure |
| Ultrafiltration | L | L | Pressure |
| Nanofiltration | L | L | Pressure |
| Reverse osmosis | L | L | Pressure |
| Piezodialysis | L | L | Pressure |
| Gas separation | G | G | Pressure |
| Vapour permeation | G | G | Pressure |
| Pervaporation | L | G | Pressure |
| Electrodialysis | L | L | Electrical potential |
| Membrane electrodialysis | L | L | Electrical potential |
| Dialysis | L | L | Concentration |
| Diffusion dialysis | L | L | Concentration |
| Membrane contactors | L<br>G<br>L | L<br>L<br>G | Concentration<br>Concentration/pressure<br>Concentration/pressure |
| Thermo-osmosis | L | L | Temperature/pressure |
| Membrane distillation | L | L | Temperature/pressure |

L: liquid; G: gas

## ANNEX 2: Membrane characterization

Characterization tests for membranes are usually carried out before, during and after real applications in order to evaluate membrane modifications during the process. Table A2 shows the main membrane properties characterized in order to understand separation capacities and membrane behavior for specific cases.

Table A2: Characterization methods for commercial membranes

| Property | Method | Impact of membrane performance |
|---|---|---|
| Retention rating (pore size or MWCO) | Bubble point, permeability test with PEG | The size of material retained by the membrane. Also affects pressure loss |
| Hydrophobicity | Contact angle | Hydrophobic materials will be more susceptible to fouling than hydrophilic |
| Surface or pore charge | Streaming potential | Repulsion against negatively charged substances because usually membrane surface is negatively charged |
| Surface roughness | Atomic force microscopy | Rough material will be more susceptible to fouling than smooth materials |
| Porosity (surface and bulk) | Thickness/ weight measurements | Higher porosity results in lower pressure losses |
| Thickness | Thickness gauge, electron microscopy | Thinner membranes have lower pressure losses |
| Surface chemistry | ATR-FTIR, SIMS, XPS, SEM-EDX | Fouling tendencies |
| Chemical and thermal stability | Exposure to chemicals and temperatures | Affects longevity of membranes |
| Biologycal stability | Exposure to organisms | Affects longevity of membranes |
| Chlorine/oxidant tolerance | Exposure to chlorine/oxidants | Affects the ability to disinfect the membrane equipment o requires disinfectant removal |
| Internal physical structure, tortuosity | Electron microscopy | Affects the hydrodinamics of flow |

ATR-FTIR: attenuated total reflectance-Fourier transform infrared spectrometry; SIMS: secondary ion mass spectrometry; X-ray: photoelectron spectrometry; SEM-EDX: scanning electronic microscopy-energy dispersion X-ray.

### Hydrophobic characteristics of some materials

Hydrophobicity of membranes is estimated by contact angle measurements, high contact angles mean more hydrophobic surfaces (the water droplets spread out). Higher contact angles, higher hydrophobicity of the membrane

PVDF, PTFE and PP have some similar properties as hydrophobicity, with higher fouling susceptibility and stronger resistance to water pass than hydrophilic materials. Hydrophobicity is one of the most important properties in membrane material because influence permeability and separation capacities in addition to having effects over the fouling phenomena. On the other hand, the best known class in hydrophilic polymers is the group cellulose esters, cellulose nitrates and acetates, however they present poor resistance in front of thermal, chemical and biological degradation

Intermediate hydrophobic character are for polysulfones (PS) and poly(ether sulfones) (PES), which are widely employed in UF and as support material in TFC, or the group of polyamides (-CO-NH-), polyacrilonitriles, (-$CH_2$-CHCN-), polyether ether ketones (-O-R-CO-R-O-R-) and polyimides (-R-CO-NH-CO-R-), with high thermal and chemical resistances.

## ANNEX 3: Membrane process operation in water treatment

Hydraulics phenomena are different depending on factors such as membrane type, module configuration and operation mode. At the same time, these parameters are selected in function of the type of feed solution and the desired product.

In large scale water treatments, the design parameters are feed water recovery and the desired permeate flow. Once these parameters are selected, the number of membranes is calculated as function of their area and specific trans-membrane flux. Table A3 shows the main equation related in membrane processes, especially in case of NF and RO membranes operating at cross-flow mode.

Table A3: main equations related to membrane plant design and operation

| **Process parameter** | **equation** | **Definitions** |
|---|---|---|
| Global feed water recovery ($\% R_{fw}$) | $\% R_{fw} = \frac{Q_p}{Q_{fw}} \cdot 100$ | $Q_P$: permeate flow; $Q_{fw}$: feed flow |
| Transmembrane flux | $F_w = \frac{Q_p}{A}$ | $Q_P$: permeate flow ($l \cdot h^{-1}$)<br>$F_w$: water flux ($l \cdot m^{-2} \cdot h^{-1}$);<br>$A$: effective membrane area ($m^2$) |
| Number of membrane elements | $N_E = \frac{Q_P}{F_w \cdot A}$ | $N_E$: number of elements<br>$Q_P$: total permeate flow for the plant design |
| Number of pressure vessels (PV) | $N_V = \frac{N_E}{N_{E_{pV}}}$ | $N_V$: number of PV<br>$N_{E_{pV}}$: number of elements in each PV |
| Cross-flow velocity ($m \cdot s^{-1}$) | $V_{cf} = \frac{Q_F}{H_c W_c}$ | $Q_F$: feed flow ($m^3 \cdot h^{-1}$)<br>$H_c$: channel high (feed-spacer high) ($m^3$);<br>$W_c$: width channel ($m^3$) |
| Solvent flux (J) | $J = \frac{\Delta P}{\eta R_M}$ | $\Delta P$: difference in transmembrane pressure<br>$\eta$: dynamic solvent viscosity<br>$R_M$: membrane resistance |
| Constituents rejection ($R_i(\%)$) | $R_i (\%) = (1 - \frac{C_{pi}}{C_{fi}}) \cdot 100$ | $C_{pi}$= permeate concentration for solute i;<br>$C_{fi}$= feed water concentration for solute i; |

## ANNEX 4: Different classes of biodegradation processes

Process configuration in MBR derives into different classes of biodegradation processes, also depending on the feeding regime and reduction-oxidation (redox) conditions. Table A4 shows characteristics of different biological processes.

Table A4: Examples of biological processes and their characteristics

| | **Process configuration** | | **Feeding regime** | | **Redox conditions** | | |
|---|---|---|---|---|---|---|---|
| | **Fixed film** | **Suspended growth** | **Continuous** | **Fed-batch** | **Aerobic** | **Anoxic** | **Anaerobic** |
| AD | | X | (X) | (X) | | | X |
| AF | X | | X | | | | X |
| CAS | | X | X | | X | (X) | (X) |
| BAF | X | | X | | X | | |
| RBC | X | | X | | X | | |
| SBR | | X | | X | X | (X) | |
| TF | X | | | | X | | |
| UASB | | X | X | | | | X |
| MBR | | X | X | | X | (X) | |

AD: anaerobic digestion; AF: anaerobic filter; CAS: conventional activated sludge; BAF: biological aerated filters; RBC: rotating biological contactor; SBR: sequencing batch reactor; TF: trickling filter; UASB: upflow anaerobic sludge blanket; MBR: membrane bioreactor

## ANNEX 5: Network diagram from Simapro in LCA study about NF technology implementation in DWTP to improve final drinking water

Next three Figures A1, A2 and A3 indicate graphically the contribution of inventory data (grouped in process units) over the climate change impact category for the LCA study carried out in a real DWTP with a possible implementation of NF technology.

Figure A1: Network diagram for conventional treatment in the real DWTP of Manresa

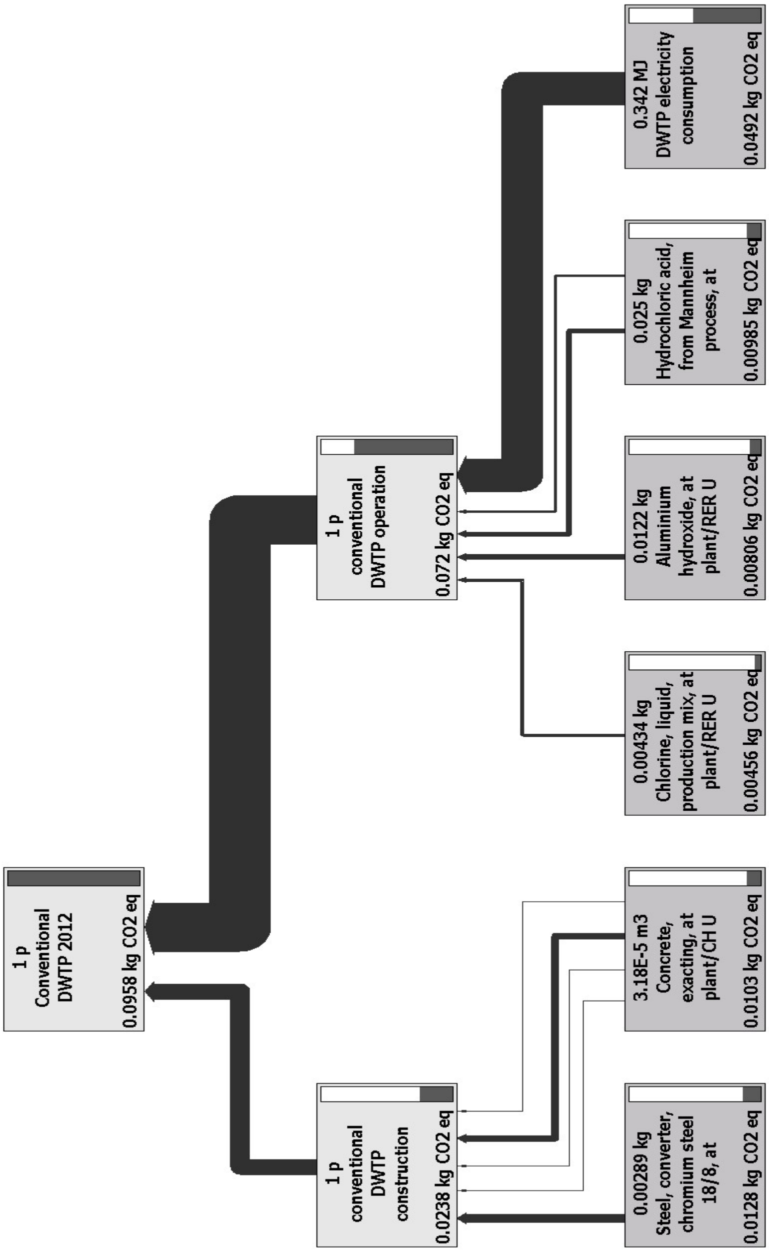


Figure A2: Network diagram for NF system with NF270 membranes in the real DWTP of Manresa

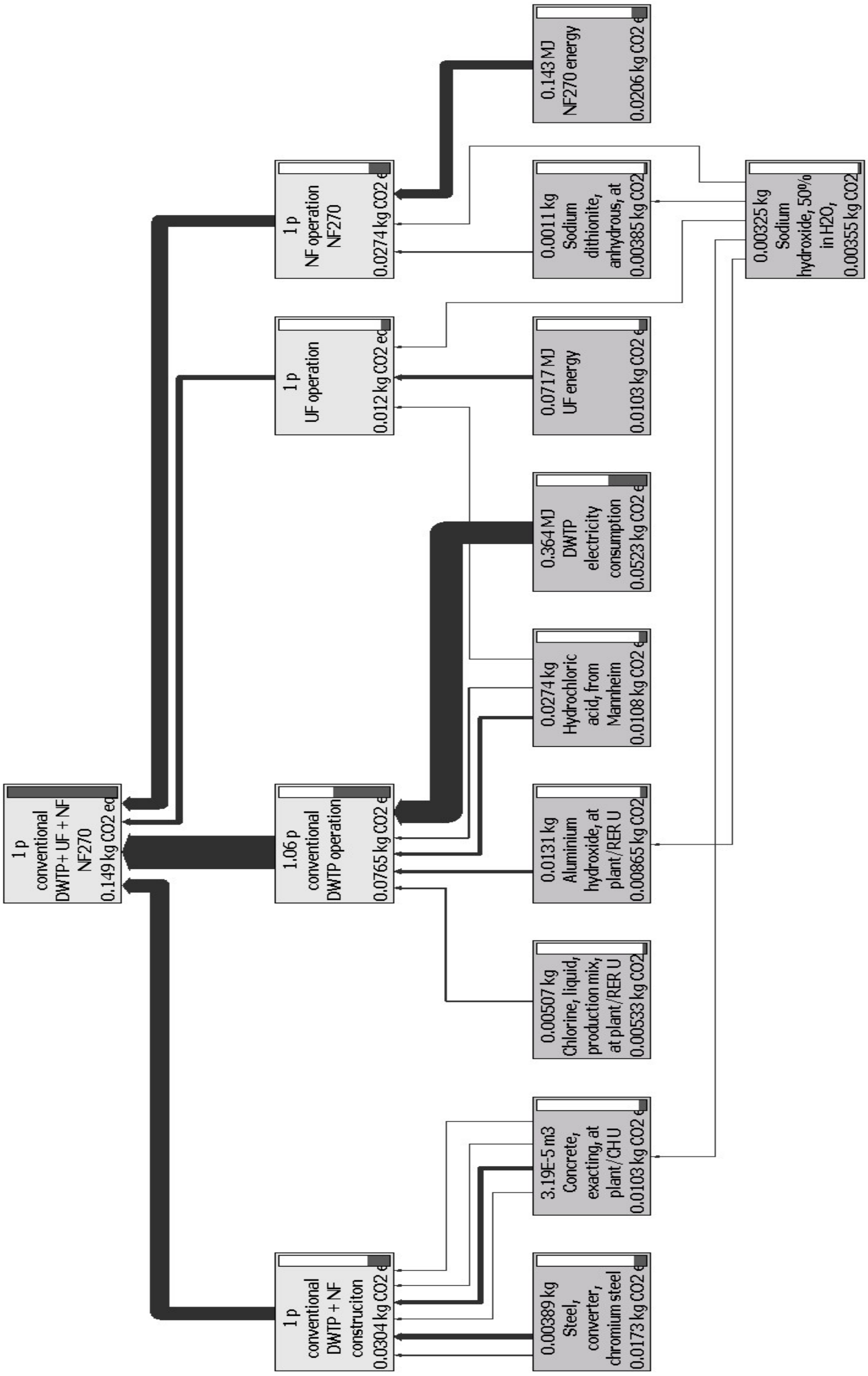
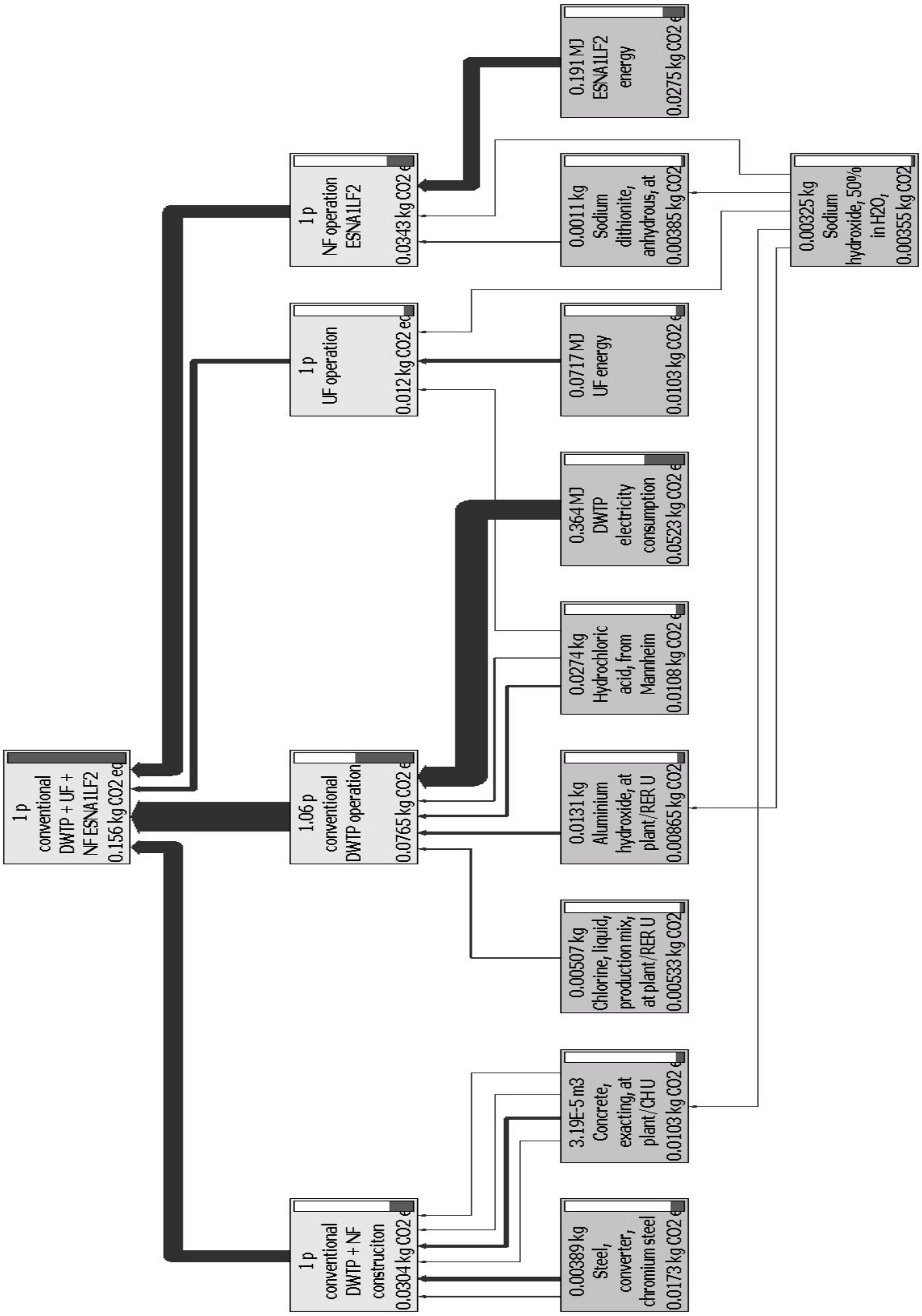


Figure A3: Network diagram for NF system with ESNA1LF2 membranes in the real DWTP of Manresa



## ANNEX 6: Network diagram from Simapro in LCA study about MBR technology implementation in a real WWTP to obtain an effluent for reuse proposals

Next Figures A4, A5, A6 and A7 indicate graphically the contribution of inventory data (grouped in process units) over the climate change (CC) and freshwater eutrophication (FEU) impact categories for the LCA study carried out in a winery WWTP with a possible implementation of MBR technology.

Figure A4: Network diagram for MBR system 1 for CC category

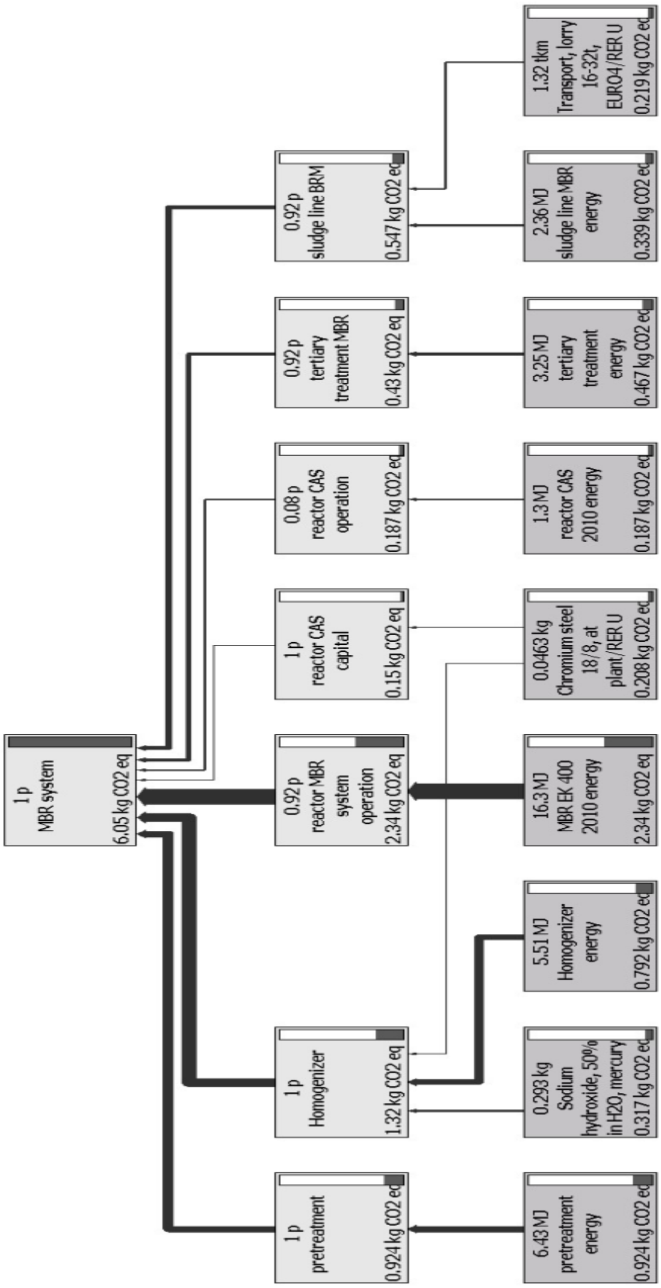


Figure A5: Network diagram for MBR system 1 for FEU category

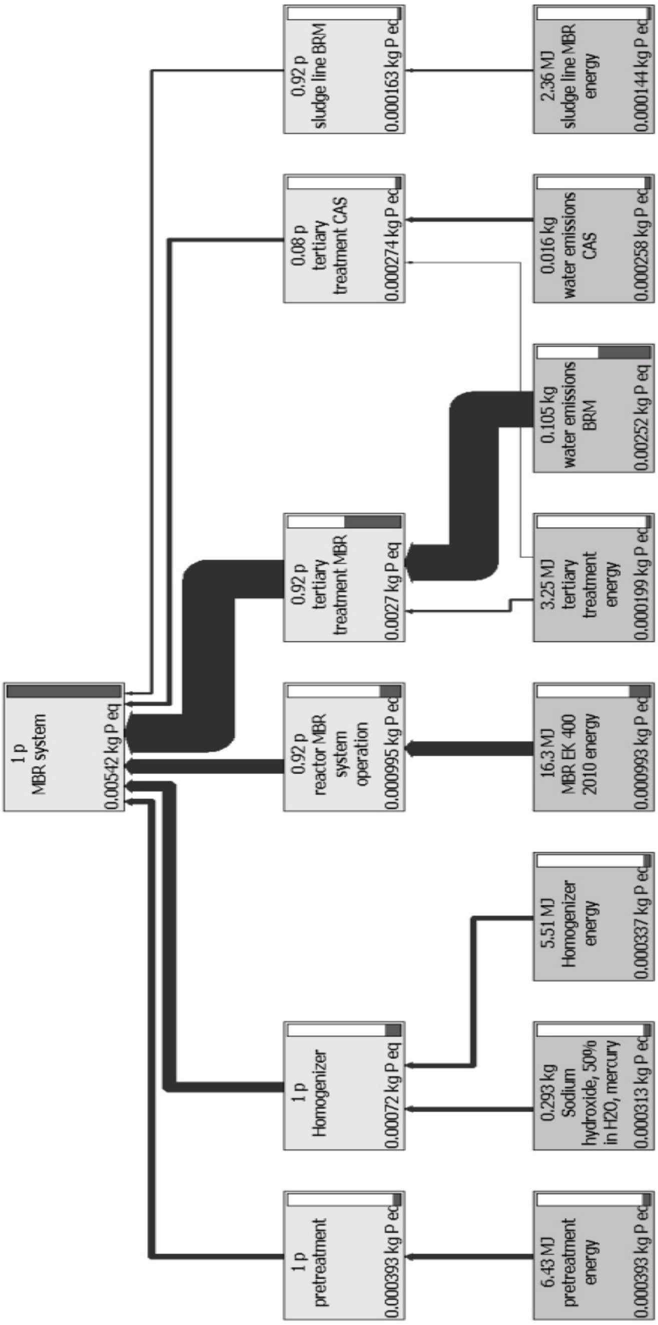


Figure A6: Network diagram of CAS system for CC category

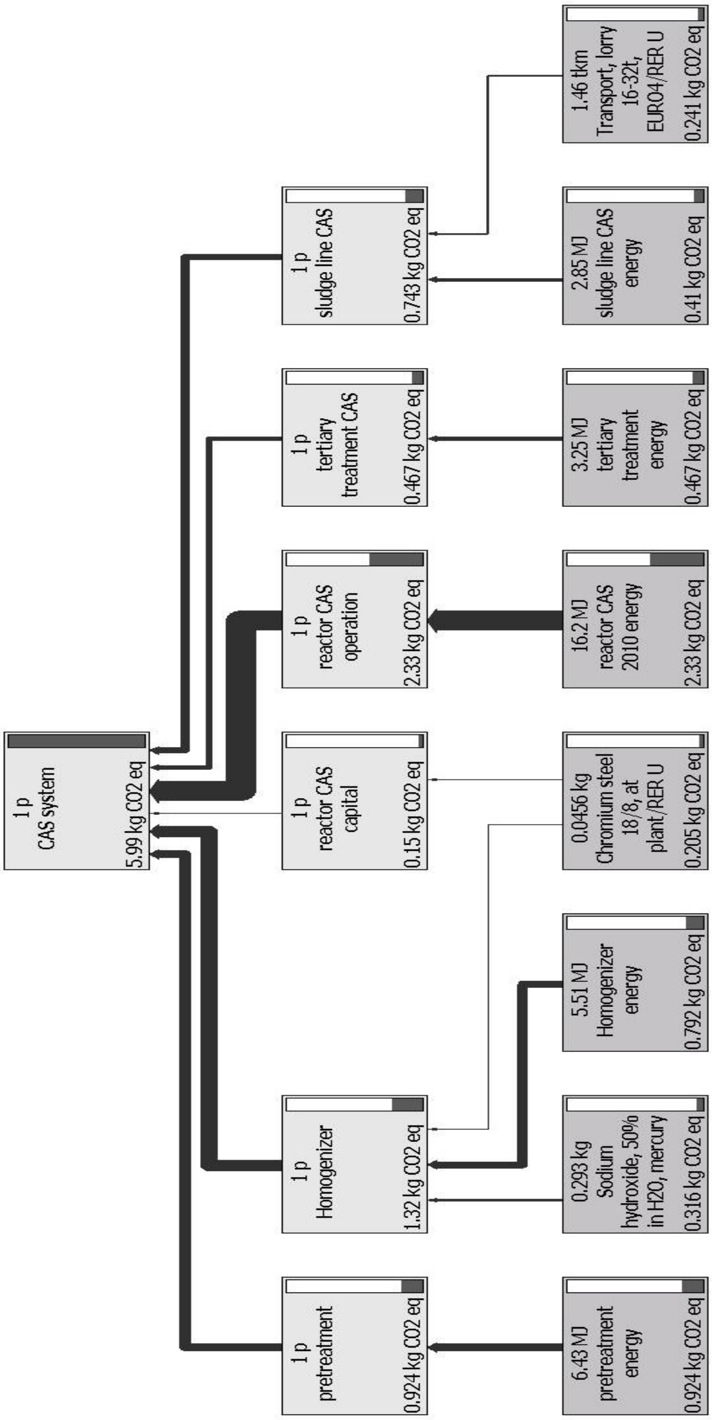
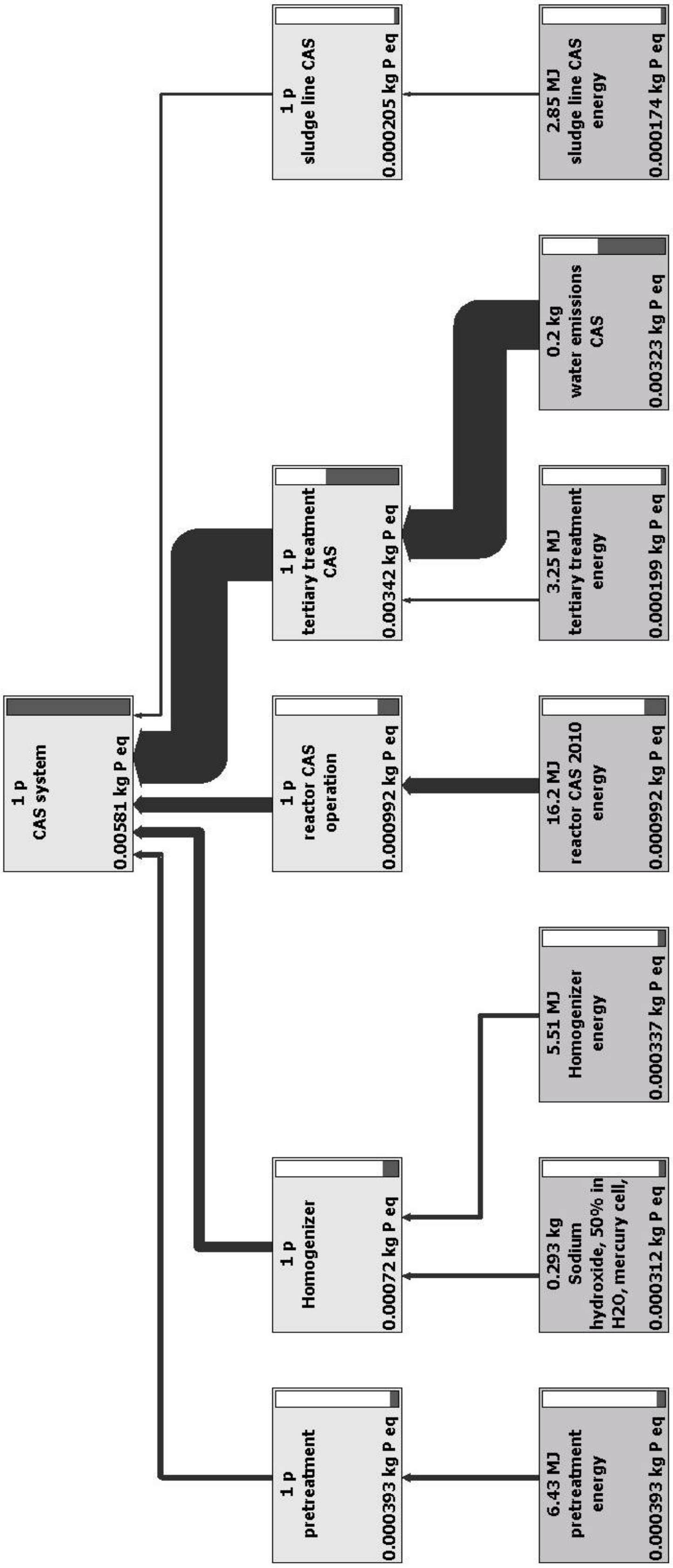


Figure A7: Network diagram of CAS system for FEU category



*"Thousands have lived without love; not one without water."*

*W. B. Auden*