



Application of nanofiltration for pool water treatment: Assessing reduction potential of disinfection by-products

Bachelor Thesis

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Aufgabenstellung für die Studienarbeit von Herrn Guillermo Cuesta

Thema: Minimierung von Desinfektionsnebenprodukte (DNP) durch Nanofiltrationsmembranen bei der Schwimmbeckenwasseraufbereitung

Problemstellung:

Öffentliche Schwimmbäder haben in der Freizeitgestaltung vieler Bürger einen hohen Stellenwert. Jedoch bedeuten die besonderen Anforderungen an die Wasserqualität und an die Temperatur des Wassers in den Schwimm- und Badebecken häufig eine große finanzielle Belastung für die Kommunen. Für die hygienische Sicherheit ist die Desinfektion ein erforderlicher Schritt der Schwimmbeckenwasseraufbereitung, die aber zu sogenannten Desinfektionsnebenprodukte (DNP) führen kann.

Nanofiltration (NF) ist unter Berücksichtigung der Kosten und dem Anwendungsbereich eine interessante Alternative für Schwimmbeckenwasseraufbereitung, da sie eine gute Rückhaltfähigkeit von TOC hat (Frimmel et al. 2004, de la Rubia et al. 2008) und für die Elimination von Desinfektionsnebenprodukten (DNP) in Trinkwasseraufbereitung bereits untersucht wurde (Chellam et al. 2008, Sentana et al. 2010).

In Schwimmbeckenwasserbereich wurde die Anwendung von NF noch wenig untersucht. Die Besonderheit von Schwimmbeckenwasser z.B. die kontinuierlich neu eingebrachten natürliche und anthropologische organischen Stoffe und die hohen Oxidationsfähigkeit von Chlor im Beckenwasser können Auswirkungen auf die Performance der Membran haben.

Aufgabestellung:

Im Rahmen dieser Bachelorarbeit soll die Elimination von DNP mit der Hilfe von Nanofiltrationsmembranen untersucht werden. Hierzu sind Versuche mit einer großtechnischen Nanofiltrationsanlage in einem öffentlichen Schwimmbad und mit einer am Engler-Bunte-Institut bereits vorhandenen Flachkanalzellenanlage in einem weiteren Schwimmbad vorgesehen. Die

Flachkanalzellenanlage erlaubt es, mehrere Membranmodule gleichzeitig zu betreiben und somit Aussagen über den zeitlichen Verlauf der Verblockung der Membranen zu treffen.

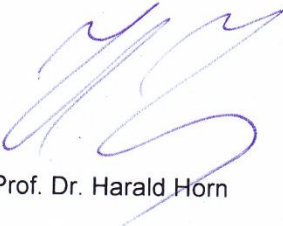
Der Schwerpunkt der Untersuchungen liegt neben Messungen der Permeabilität und Rückhalt von DNP (z.B. THM, AOX und gebundenes Chlor) auch im Vergleich der Membranleistung bei zwei verschiedenen Rohwassern. Während des Versuchs mit der großtechnischen Anlage soll der Verlauf von DNP-Konzentrationen im Schwimmbecken und der Zusammenhang mit weiteren Parametern (z.B. Besucherzahl, DOC und Zeit) berücksichtigt werden. Während des Versuchs mit der Flachkanalzellenanlage ist besonderes Augenmerk auf die Bildung von Fouling und auf die Auswirkung von Fouling auf die Durchlässigkeit der Membranen zu legen. Dafür werden neben Messungen der Permeatflüsse, auch die Konzentration von DOC, AOX, Ionen, freies- und gesamtes Chlor sowie die el. Leitfähigkeit und der pH-Wert im Feed und Permeat bestimmt. Nach den Versuchen sind ergänzende Untersuchungen (Rasterelektronenmikroskopie (REM), ATR-Infrarot-Fourier-Spektroskopie (ATR-FTIR), Kontaktwinkel (Hydrophobie) der Oberfläche von originalen und gefaulten Membranen vorgesehen.

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Karlsruhe, den 2 Februar 2015

Unterschrift

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Abstract

Disinfection of water is mandatory for swimming pools. Most of them use Chlorine or its derivatives for that purpose. When entering the pool bathers bring substances such as sweat, hairs and cosmetics that react with disinfectants and form disinfection by-products (DBPs) which are known to be harmful for human health.

In order to avoid the formation of these undesirable products new technologies for pool water treatment must be developed or alternatively a control system of the DBPs in the pool. The most important DBPs and their precursors are organic. Nanofiltration (NF) comes up as a possible solution for the problem as it is capable of rejecting organic matter.

A nanofiltration filtration plant was installed in an indoor pool in Germany. The existed pool water treatment included flocculation, powdered activated carbon adsorption and ultrafiltration. During this study a branch current was treated by the new NF plant. The nanofiltration plant treated 0.3% of the global recycle flow, meaning approximately 9.7m³/day.

During 110 days the of dissolved organic carbon (DOC), trihalomethanes (THM), adsorbable organic halogens (AOX), Ions, UV-absorbance, electrical conductivity and pH were measured every day from different key positions of the water treatment process. This intensive analysis of the effects and behaviour of the nanofiltration plant in a real scale application and its subsequent interpretation were carried out and the obtained information can be relevant for future applications in swimming pool water treatment.

The rejection of DOC by the membrane has been shown to be 84% ± 4% while THM and AOX were 70% ± 11% and 95% ± 2% respectively. Ion rejection ranged from 57% to 99% depending on charge and size. THM and AOX formation potentials before and after nanofiltration were also evaluated, showing a significant decrease in 78% and 93% respectively. Umu-tests were also carried out in order to assess possible genotoxicity effects of the pool water. All results obtained were negative in genotoxicity.

Despite of the high rejections shown by nanofiltration no significant decrease of THM concentration in pool water was achieved. THM showed a positive correlation with DOC with time delay and high variability in its concentrations. AOX showed an increase after the activated carbon shutdown. But compared to previous research AOX was also reduced in a 49% by NF.

During the study the membrane presented an increasing flow decline. By the end of the investigation losses of 17.5% from the initial permeate flow were observed.

Nanofiltration has shown its potential as a suitable pool water treatment process. Later studies should further investigate the operational settings needed in order to provide further improvement of water quality, the development of more fouling and chemical resistant membranes and more suitable cleaning strategies.

Zusammenfassung

Desinfektion vom Schwimmbeckenwasser ist eine Pflicht in vielen Ländern. Die meisten verwenden Chlor oder die Derivate für diesen Zweck. Badegäste bringen Substanzen wie z.B. Schweiß, Urine, Haare und Kosmetika, die mit Desinfektionsmitteln reagieren und die für den Menschen schädliche Desinfektionsnebenprodukte (DBPs) bilden können.

Um diese unerwünschten DBPs zu vermeiden, müssen neue Technologien für die Schwimmbeckenwasseraufbereitung entwickelt werden. Nanofiltration (NF) bietet einen hohen Rückhalt von organischen Stoffen. Unter diesem Zusammenhang kommt die Nanofiltration als eine mögliche Lösung für das Problem.

Für diese Arbeit wurde eine Nanofiltrationsanlage in einem Hallenbad in Deutschland installiert. Die existierende Aufbereitung umfasste Flockung, Dosierung der Pulveraktivkohle und Ultrafiltration. Ein Teilstrom wird mit NF-Anlage. Die Anlage hat fünf Druckrohre, jeweils mit zwei NF90-4040 Wickelmodule (DOW FILMTEC™) ausgestattet. Die Nanofiltrationsanlage behandelt zur Zeit 0,3% des gesamten Umwälzvolumenstroms, d.h. 7,6 m³/Tag.

Für 110 Tage wurden täglich gelöster organische Kohlenstoffe (DOC), (Trihalogenmethane) THM, an Aktivkohle adsorbierbare organisch gebundene Halogene (AOX) und auch weitere Parameter (z.B. Chlor, Ionen, UV-Absorption, pH-Wert und el. Leitfähigkeit) im Schwimmbeckenwasser von verschiedenen Positionen des Wasseraufbereitungsprozessen untersucht.

Diese umfassende Analyse der Wasserqualität und des Verhaltens einer Nanofiltrationsanlage in einem großtechnischen Maßstab und die anschließende Interpretation hat Informationen, die zuverlässig für zukünftige Anwendungen bei der Schwimmbeckenwasseraufbereitung sein kann, ausgewiesen.

Der Rückhalt von DOC durch NF war 84 % ± 4 %, während der Rückhalt von THM und AOX waren 70 % ± 11 % und 95 % ± 2 % bzw. Ionen abweisende reichten von 57 % bis 99 %. THM und AOX-Bildung Potentiale wurden auch bewertet, die eine signifikante Abnahme (jeweils 78 % und 93 %) zeigten. Der Umu-Test wurde auch durchgeführt, um mögliche Genotoxizität des Beckenwassers zu prüfen. Alle Proben waren negativ im Genotoxizität.

Trotz der hohen Rückhalt von Nanofiltration hatte keine signifikante Abnahme von der THM-Konzentration gezeigt. THM zeigte eine positive Korrelation mit DOC und eine hohe Abweichung der Konzentrationen. Eine Zunahme von AOX wurde beobachtet nach der Ausschaltung der Pulveraktivkohle. Während der Untersuchung die Membran zeigte einen Flussniedergang, der bis Ende einen Verlust von 17,5% gegenüber dem ersten Permeatfluss hat.

Nanofiltration hat sein Potenzial als geeignete Beckenwasseraufbereitung Prozess gezeigt, spätere Studien sollten den Betrieb weiter untersuchen und optimieren, um eine bessere Wasserqualität des Schwimmbeckens zu haben.

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List of abbreviations

DOC	Dissolved Organic Carbon
THM	Trihalomethanes
AOX	Adsorbable Organic Halogens
DBP	Disinfection By Products
HAA	Halo-Acetic Acids
HAN	Halo-Aceto Nitriles
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
GC	Gas Chromatography
PAC	Powered Activated Carbon
FP	Formation Potential
MF	Microfiltration
UF	Ultrafiltration
NF	Nanofiltration
RO	Reverse Osmosis
SB	Swimming Pool "Schwimmbad"
NSB	Non-Swimmer pool "Nichtschwimmerbad"
ZN	Feed of nanofiltration "Zulauf von Nanofiltrationsanlage"
PN	Permeate of nanofiltration
MW	Molecular Weight

1 Introduction and motivation

During the 1700s, filtration was established as an effective method of removing particles from water, although the degree of clarity achieved was not measurable at that time. By the early 1800s, slow sand filtration was beginning to be used regularly in Europe.

During the mid to late 1800s, scientists achieved a greater understanding of the sources and effects of drinking water contaminants, especially those that were not visible to the naked eye. In 1855, Dr. John Snow proved that cholera was a waterborne disease by linking an outbreak of illness in London to a public water source that was contaminated by sewage water (Pasteur, 2000).

The disinfecting properties of chlorine were first realized in the mid 1800's where it was used to wipe down contaminated surfaces. The use of chlorine as a disinfectant in municipal water systems started in Europe around the end of the century and became the standard form of water disinfection in the United States by 1920. Legislation governing water quality standards encouraged an ever increasing demand for chlorine throughout the twentieth century (Olsen, 2007).

Chlorine is now one of the most widely used disinfectants and has played an important role in lengthening the life-expectancy of humans. It is fast and very effective for the deactivation of pathogenic microorganisms. Chlorine can be easily applied, measured and controlled. It is fairly persistent and relatively cheap.

Currently, to achieve a sufficient disinfection capacity, in Germany the concentration of free chlorine must be kept in the range of 0.3 - 0.6 mg/L in pool water (DIN 2012).

However at this time it has been shown that the addition of chlorine and other disinfectants lead to some undesirable reactions and to the formation of a variety of compounds called disinfection by products (DBP) (Kim et al., 2002; Richardson et al., 2007).

The DBPs found in pool water have been proven to be potentially irritating and toxic for swimmers and for the people near the pool (Florentin et al., 2011).

The aim of this work is to investigate the performance and potential of an alternative pool water treatment, combining Ultrafiltration (UF) and Nanofiltration (NF). It is flexible depending on the load of the pool, which would allow us to increase swimmers safety and reduce energy, water and chemical consumption.

2 State of the art

2.1 Water disinfection

“The greatest risk of bacterial, protozoa, and viral gastroenteritis during the swimming season is likely not from exposure through food consumption, drinking water, or at day care, but rather from exposure to recreational water” (Sanborn and Takaro, 2013).

Swimming pool water needs to be disinfected. As mentioned, the most common method used to control the hygiene and safety of the pool water is by adding chemical substances such as chlorine gas or Sodium hypochlorite (the most common in Germany). These substances allow to prevent the spread of waterborne diseases like Cholera, Dysentery, Jaundice, Typhoid etc. and eliminate possible hazardous substances that we may find in stagnate and recreational waters (Sanborn and Takaro, 2013).

To understand the potential of using chlorine to disinfect the recreational water it is first mandatory to understand its properties and reaction mechanisms.

2.1.1 Chlorine

When chlorine is added to water, it is involved in three types of reaction. These affect the availability of chlorine in the water and its efficiency as a disinfectant.

First, substances such as manganese, iron or other metals dissolved in the water will react irreversibly with chlorine. These reactions remove these substances, thereby improving water quality and taste. Chlorine, which reacts in this way is, however, lost and does not contribute to disinfection.

Secondly, chlorine may react with organic matter, ammonia or other nitrogen based substances in water, the compounds formed are mostly weak disinfectants. The products are referred to as combined chlorine and form the so-called DBP group.

Thirdly, chlorine may react with and dissociate in water. The products are efficient disinfectants and are referred to as free chlorine. When dissolved in water, chlorine converts into an equilibrium mixture of chlorine, hypochlorous acid (HOCl) and hydrochloric acid (HCl).



There is also equilibrium between hypochlorous acid and hypochlorite ions present in the dissolution. The amount of each substance in water solution depends on the pH. The higher pH the more hypochlorite ion found.

Both substances have very different behaviour. Hypochlorous acid is more reactive and is a stronger disinfectant than hypochlorite. It is converted into hydrochloric acid (HCl) and atom oxygen (O). The oxygen atom is a powerful disinfectant. The disinfecting properties of chlorine in water are based on the oxidative capacity of the free oxygen atoms and on chlorine substitution reactions. The way chlorine kills pathogens such as bacteria and viruses is by breaking the chemical bonds in their molecules. When pathogens or viruses first contact chlorine, one or more hydrogen atoms in the molecule are replaced by chlorine. This makes the entire molecule change its shape, properties and become harmless.

Despite of the powerful disinfecting capacity of chlorine at this time it has been shown that the addition disinfection substances may bring on some undesirable reactions and the formation of a variety of compounds called disinfection by products (DBP) (Kim et al., 2002; Richardson et al., 2007).

2.1.2 Disinfection by products

Swimming pools are environments with high levels of DBPs in the water and in the surrounding atmosphere due to continuous disinfection, elevated water temperature and continuous organic matter load from bathers (Kim et al., 2002).

These DBPs compounds appear when the disinfectant is used to process the water (chlorine, sodium hypochlorite) and reacts with DBP precursors. The DBPs present in pool water are composed of a wide range of compounds. In fact more than 600 different DBPs have been currently reported (Richardson et al., 2007). However, not all disinfection by products has been thoroughly researched and there are many still to be characterized.

DBP precursors include any kind of organic matter that may be found in our pool water, such as human sweating, hair, saliva, sun screen, cosmetics, urine and many other things that can fall into a swimming pool.

The DBPs formation and concentration in a pool correlates with the organic matter dissolved into the water, therefore it should also correlate with the number of visitors and the quantities of organic matter they introduce to the water (Glauner and Frimmel, 2007). Because of that a swimming pool is a complex and dynamic system that changes depending on the season, day and hour.

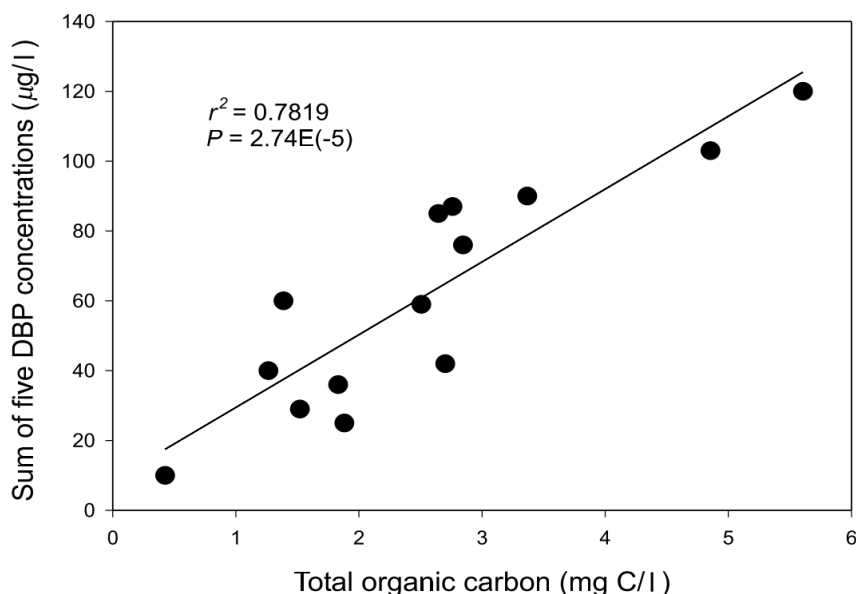


Figure 1 The correlation between TOC and the summed concentration of five DBP. The two variables were significantly correlated with a coefficient of determination (r^2) of 0.7819.

Adapted from (Kim et al., 2002).

2.1.2.1 THM

The most well-known DBPs are the trihalomethanes (THM). Trihalomethanes (CHX_3) were among the first disinfection by-products discovered in chlorinated water. The most common form in which we can find trihalomethane is chloroform (CHCl_3), dichlorobromomethane (CHCl_2Br), dibromochloromethane (CHClBr_2), bromoform (CHBr_3) (Renhun, 1993; Kim and Yu, 2005). There is a high variability of THM concentration values found in pool water in the literature. This may be due to the different analysis methods and the dependence of THM on the disinfection method used and water characteristics (pH, bromide concentration etc.) (Chowdhury et al., 2014; Lee et al., 2010).

The control of the total DBP levels in pool water is based primarily on the regulation of the THM concentration (max. 20 $\mu\text{g/L}$ in Germany) (DIN 2012) as it is the most well-known and studied DBP group.

2.1.2.2 HAAs

Halogenated acetic acids (HAAs) are a much more recently discovered DBP group than THM but recent studies have been shown that HAAs may also play an important role on the global DBP group. The most common studied HAAs are dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA). There is currently no legal restriction for the HAAs concentration in pool water in Germany.

Some studies suggested that controlling the DBP level of a pool by taking only THMs as indicator may not be enough, and proposed larger analyses that include HAAs.

These studies have obtained results which indicate that HAAs are a bigger part of the DBPs than THM when it comes to pool water, and therefore a more relevant group (Lee et al., 2010).

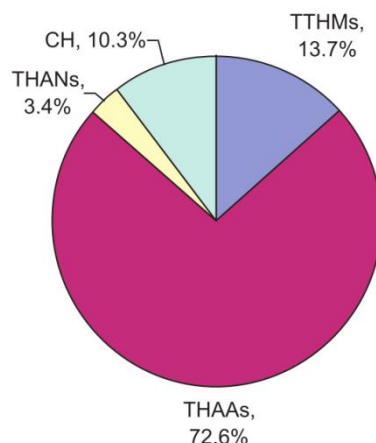


Figure 2 Percentage of the DBP species present in swimming pool water treated with chlorine in Korea. (TTHMs) Total Trihalomethanes, (THAAs) Total Haloaceticacids, (THANs) Total Haloacetonitriles. Adapted from (Lee et al., 2010).

2.1.2.3 HANs

Haloacetonitriles (HANs) group of DBP has not been widely studied. But as shown before it is not supposed to be a big part of the total DBPs. The formation of HANs in the water needs nitrogen, unlike THM and HAAs that are carbon based molecules. Therefore the main precursors for HANs are introduced by humans. Sweat and urea are thought to be the main precursor agents for the HANs formation (WHO, 2006).

Due to the law-regulation of the THM levels some water utilities have changed from chlorine to alternative disinfectants, such as chloramines and ozone, to lower the concentration of carbonaceous DBPs (THM, HAAs) (mainly in the US) (Gan et al., 2013).

Those alternative disinfectants reduce the regulated THMs and HAAs but increase the formation of nitrogenous DBPs (HANs), which have been shown to be more genotoxic than the carbonaceous DBPs (Gan et al., 2013; Richardson et al., 2007).

2.1.2.4 Others DBPs of interest

Many others groups of DBPs can be found in swimming pool water. Some of them have not been yet identified. These other DBPs are less known by the scientific community because they do not appear in tap water and so they have lower research priority. Among these we can cite the aldehydes, the haloketones, or the chloral hydrate (Lee et al., 2010).

2.1.2.5 Associated diseases

Some studies emphasized the relation between pool-workers or professional swimmers and eyes or skin irritation. Elite swimmers monitoring suggested that spending much time in a chlorinated atmosphere may increase the risk of asthma, bronchial hyperactivity and airways inflammation, as well as allergic reactions such as conjunctivitis, rhinitis or laryngitis (Goodman and Hays, 2008). Long-term THM exposure was associated with a two-times increase of bladder cancer risk, with a ratio of 2.10 for average THM concentrations between 49 µg/L and 8 µg/L (Villanueva et al., 2007).

Studies on babies and elderly people also suggested an increase of diarrhoea illnesses in babies who attend regularly to swimming pool. They were recommend to wait until a certain age before going to indoor swimming pools due to the high levels of chloroform in the atmosphere (Sanborn and Takaro, 2013; Schoefer et al., 2008).

It has been shown that some DBPs may have a genotoxic effect on humans. Genotoxicity describes the property of chemical agents to damage the genetic information within a cell, causing mutations which may lead to cancer. The genotoxicity of the DBP seems to be dependent on the molar weight. High molar weight DBPs do not have a relevant genotoxicity but as we get to the lower molecular weight fraction the genotoxicity raises (Glauner et al., 2005).

2.1.2.6 Exposure paths

The THM exposure paths are not only through water ingestion but also by inhalation and skin adsorption. Due to the high volatility, the atmosphere of a swimming is usually enriched in THM (usually in less ventilated spots such as indoor swimming pools or spas). Because of this many assistants to the pool, although not bathers, have also shown high levels of THM in blood and organs (like lifeguards or cleaning staff).

2.2 Membrane technology in water treatment

As the use of alternative disinfectant is not a suitable option for the reduction of all kinds of DBPs membrane technology comes up as a possible solution to the problem.

In particular, two stage membrane systems using low pressure membranes (ultrafiltration) followed by NF membranes have been improved enough to allow their use in pool water purification, and seem a good alternative. Due to their high treatment efficiency for the removal of salts, metals, pharmaceuticals, personal care products and other emerging contaminants (Kim and Yu, 2005).

To fully understand the characteristics and transport phenomena that occur in a membrane we will review the membrane technology evolution and the current transport theories focusing on nanofiltration.

2.2.1 Introduction to membrane technology

Membrane technology has seen an important development in the last century, in both industry applications and research lab-scale studies. We just have to take a look backwards. 50 years from now membranes were used only in a few laboratory and in small, specialized industrial applications. No significant membrane industry existed. Nowadays membrane technology is present in medicine, oil industry, separation and purification processes and water treatment and keeps growing quickly in many other industries as a potential future technology (Baker, 2012; Padaki et al., 2015).

The benefits of membrane technology can be summarised as follows:

- separation can be carried out continuously
- energy consumption is generally low
- membrane processes can easily be combined with other separation processes
- separation can be carried out under mild conditions
- membrane properties are variable and can be adjusted
- compact system

The following drawbacks should be mentioned:

- concentration polarisation/membrane fouling
- Flow with high load of undesirable substances
- limited membrane lifetime and chemical resistance
- Modelling and simulation are complex

A membrane is a semi-permeable barrier that allows passage of certain compounds, but not others, when a driven force is applied.

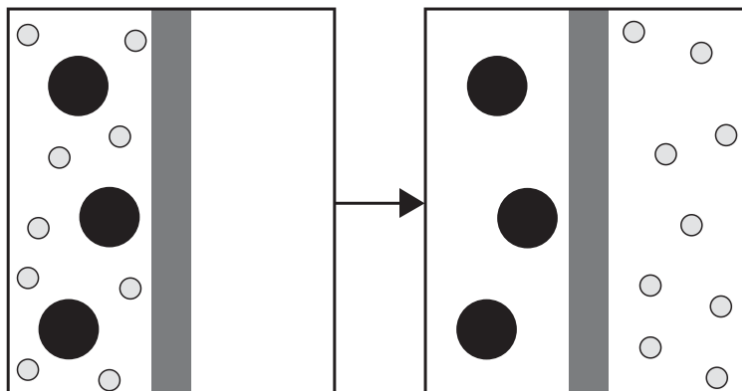


Figure 3 Description of the basic concept of membrane separation. Initially, all solutes are on one side in a mixed solution. During the separation process, some solutes pass through the membrane, while others are retained (Hoek et al., 2013).

When a feed flow, formed by a solvent and a solute, is applied to a membrane module two outlet flows are obtained, concentrate and permeate. The permeate flow contains the solvent and those solute or particles that have gone through the membrane. In other words in the concentrate we find those species that could not pass through the membrane.

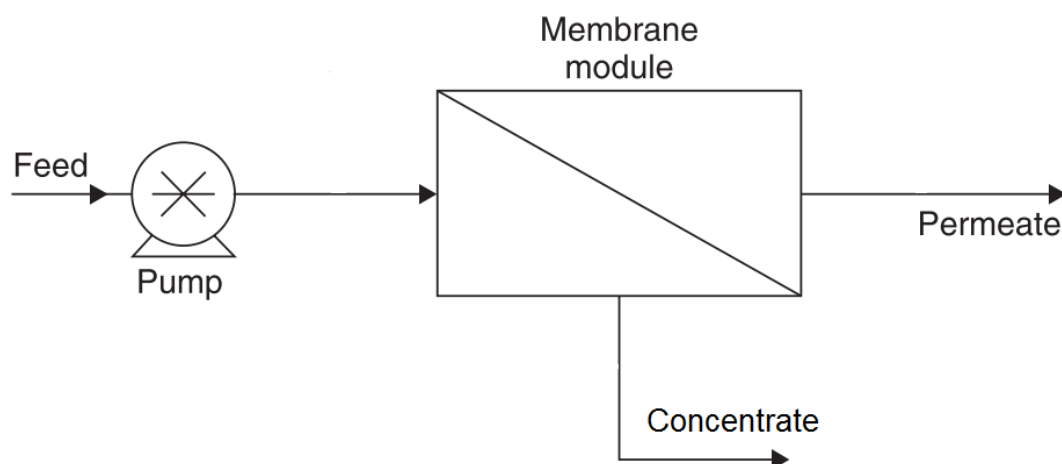


Figure 4 Basic sketch of a pressure-driven membrane module. Adapted from (Hoek et al., 2013).

Nowadays the market has a wide range of membranes available. In this study we will only overview the group of pressure driven and synthetic polymer-based membranes and then focus on those truly relevant and important for pool water treatment.

2.2.2 Membrane types

Synthetic membranes can be classified by how is their internal structure conformed, we may find 2 groups *Isotropic*, for those membranes that have always the same internal composition no matter the depth of the layer, and *Anisotropic* membranes where the internal composition of the membrane changes depending on the depth.

2.2.3 Isotropic

Micro-porous membranes

The micro-porous membrane is very similar to what we understand for a normal filter. It has a rigid structure with a surface full of randomly distributed pores. However, the pores we may find in a filter are much bigger than those we can find in a micro-filter, which have a diameter that goes from 0.01 to 10 μm .

- All particles larger than the largest pores are completely rejected by the membrane.
- Particles smaller than the largest pores, but larger than the smallest pores are partially rejected.
- Particles smaller than the smallest pores will pass entirely through the membrane.

Therefore the main mechanism of selectivity is based on molecular size and pore size (Padaki et al., 2015).

Non-porous membranes

Nonporous membranes are made of a dense film through which molecules are transported by diffusion under the driving force of a pressure, concentration, or electric potential gradient. In this case the separation of the components is related to their relative transport rate within the membrane, which is determined by their diffusivity and solubility with the membrane material. Because of that nonporous membranes are able to separate molecules of similar size if their solubility differs significantly.

Electrically charged membranes

Electrically charged membranes can be non-porous or micro-porous membranes with the walls carrying fixed positively or negatively charged ions.

- A membrane with fixed positively charged ions is called an anion membrane because it binds anions in the surroundings of the wall.
- A membrane containing fixed negatively charged ions is called a cation membrane because it binds cations in the surroundings of the wall.

Separation with charged membranes is produced mainly by the exclusion of the ions of the same charge as the fixed ions of the membrane. The separation is affected by the charge and concentration of the ions in solution. I.e. monovalent ions are excluded less effectively than divalent or trivalent ions (Baker, 2012).

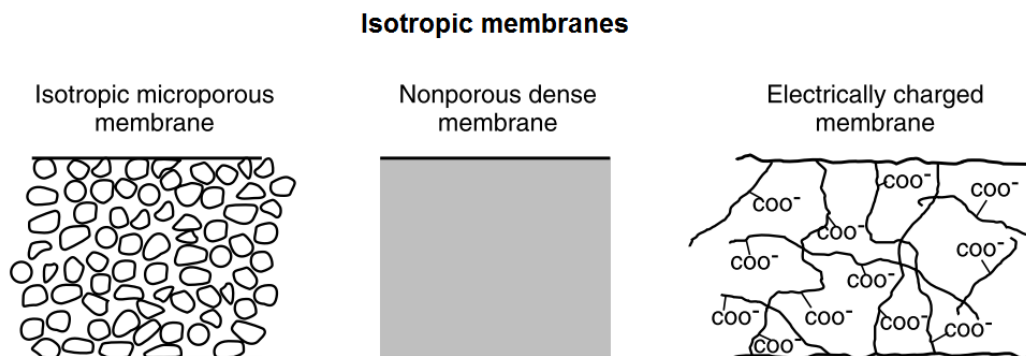


Figure 5 Types of isotropic membranes. Adapted from (Baker, 2012).

2.2.4 Anisotropic

When fabricating membranes the transport rates indicates the flow we will be able to take through the membrane. Therefore it indicates the flow treatment potential of a membrane which directly correlates with its economic viability, the higher flow the better. This transport rate is inversely proportional to membrane thickness, hence membranes must be as thin as possible and that is what anisotropic membranes achieve.

Anisotropic membranes consist of an extremely thin surface layer (which may be an isotropic membrane) supported on a much thicker, porous substructure. The separation properties and permeation rates of the membrane are determined exclusively by the surface layer. The substructure acts only as a mechanical support. The advantages of the higher flows provided by anisotropic membranes are so good that almost all commercial processes use this membranes (as it is our case) (Baker, 2012).

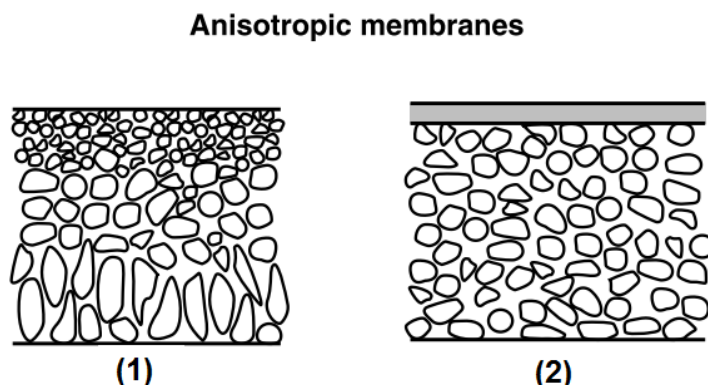


Figure 6 Types of anisotropic membranes (1): Loeb-Sourirajan anisotropic membrane (2): Thin-Film Anisotropic membrane. Adapted from (Baker, 2012).

2.2.5 Membranes of interest

The reliable group of membranes for pool water treatment are those synthetic, pressure-driven and liquid-liquid separation membranes.

With the characteristics stated above the possible membranes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). They are conceptually similar processes but have key differences in surface pore size and transport phenomena.

Table 1 Summary of membrane characteristics commonly used in water treatment (Baker, 2012; Padaki et al., 2015).

Membrane Technology (pore size, nm)	Microfiltration (50 - 1000)	Ultrafiltration (2 - 50)	Nanofiltration (<2)	Reverse osmosis (0.3 – 0.6)
Pore Diameter (nm)	100 - 10000	2 - 100	0.5 - 2	< 0.5
Pressure range (bar)	0,1 – 2	1 - 5	5 - 20	10 - 120
Transport Phenomena	Pore - Flow	Pore - Flow	Pore – Flow, Solution - diffusion	Solution - diffusion

2.2.6 Transport mechanisms

There are two mechanisms that describe the phenomena happening in a membrane when a solution is going through it, *pore-flow* and *solution-diffusion*.

2.2.6.1 Pore- Flow:

The pore-flow mechanism appears when the solution is forced to pass through the membrane due to a pressure gap between each side. The separation of the feed species is done by pore size, where the size and the geometry of the molecules decide whether the molecule passes or not. It is a fully physic mechanism. The Pore-Flow mechanism can be expressed with the Darcy's law:

$$J_i = K' c_i \frac{dp}{dx}$$

Where J_i is the flow of the component going through the membrane ($\text{g}/\text{cm}^2\cdot\text{s}$), K' is a constant that depends on the environment, c_i is the concentration of the component and dp/dx is the pressure gradient between the membrane's sides.

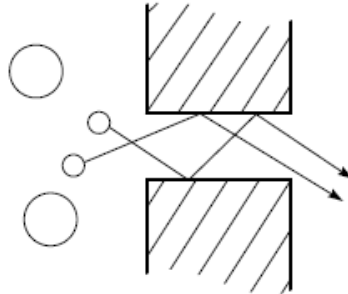


Figure 7 Sketch of the pore-flow mechanism (Baker, 2012).

We may find two different kinds of membrane pore-flow rejection mechanisms, depth filtration and screen filtration.

Screen filters have small pores in their top surface that collect particles smaller than the pore diameter and let them pass through the membrane. Particles bigger than the pore size accumulate on the surface or are rejected and purged.

Depth filters have relatively larger pores on the top surface. Particles go by into the inside of the membrane. The particles are then captured at constrictions in the membrane.

Screen filter membranes rapidly become fouled by the accumulation of retained particles at the top surface. Depth filters have a much larger surface area available for collection of particles, providing a larger treatment capacity before fouling.

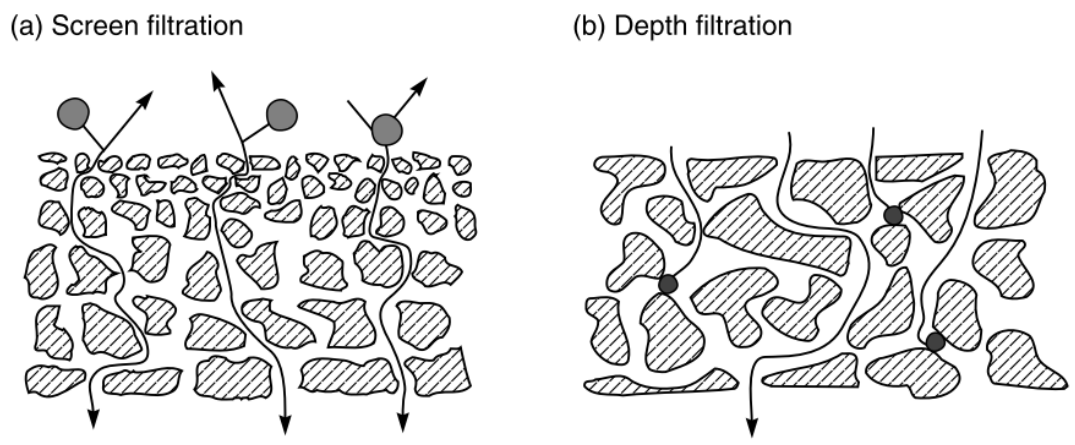


Figure 8 Separation of particulates happen at the membrane surface according to a screen filtration mechanism (left) or in the interior of the membrane by a capture mechanism in depth filtration (right) (Baker, 2012).

2.2.6.2 Solution-diffusion

The solution diffusion mechanism occurs when the species of the feed are dissolved into the membrane's material and diffuse through it due to a concentration gradient. This species are rejected depending on different solubility and their different diffusion coefficients through the membrane. The concept of diffusion is the movement from a point with high concentration to point with lower concentration which happens inside a system due to a difference of concentration in each side of the system, in our case the membrane. The diffusion through a membrane can be expressed with the equation of Fick's law:

$$J_i = -D_i \frac{dc_i}{dx}$$

Where J_i is the flow of the component ($\text{g}/\text{cm}^2 \cdot \text{s}$), D_i is the diffusion coefficient of the component ($\text{cm}^2 \cdot \text{s}$) the negative sign shows that the direction of the particle movement is opposite to the gradient concentration and dc_i/dx is the concentration gradient of the component i (Baker, 2012).

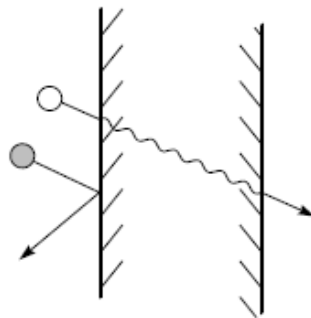


Figure 9 Sketch of the transport mechanism of solution-diffusion (Baker, 2012).

The diffusion is a slow phenomenon and depends on the membrane thickness. Because of that in the separation applications that use the solution-diffusion mechanism the membrane layer is extraordinarily thin and the concentration gradients between each side are really high.

2.2.7 Nanofiltration

2.2.7.1 Background of nanofiltration membranes

The nanofiltration membrane technology was born in the late 1950 as an intermediate between reverse osmosis and ultrafiltration. It was developed by Loeb-Sourirajan who employed asymmetric membranes made of cellulose acetate in the desalination of sea water. By that time it was called loose reverse osmosis or tight ultrafiltration.

In 1964, Loeb and Sourirajan patented and commercialized a new generation of membranes, half a way between RO and UF made of asymmetric cellulose acetate. Those will become the first generation of nanofiltration membranes. Cellulose acetate had bad chemical or biological stability, this weak point produced changes in rejection and loss of flow (Schäfer et al. 2005).

In later years (late 70's) new membranes were developed, increasing chemical and biological stability, mechanical performance and trans-membrane flow rates in order to enhance their application into the chemical industry. In 1975 the first polymer-compound membranes were developed as an improvement of the membranes made only of one polymer. This membranes where mainly UF membranes, and above them a new membrane was added in order to improve their selectivity.

It was not until 1980 when nanotechnology becomes an independent technology. New membranes were commercialized as nanofiltration membranes. Subsequently new types of NF membranes were developed such as the ceramic membranes.

Today nanofiltration technology is capable of solving some separation problems. But the applications are yet little in comparison to the potential applications it can have in the future as the investigation progresses (Schäfer et al. 2005).

2.2.7.2 Characteristics

The transport of the species through the membrane is produced by a mixture of pore-flow and solution-diffusion models. The trans-membrane pressure needed to operate the NF membrane is much lower than those required on the RO, and closer to UF pressures.

NF has higher trans-membrane flows than RO and therefore a major treated water production rate. The rejection of species by NF membranes depends on many factors. In *Table 2* some of the basic operating parameters and its effect are listed.

Table 2 Operating parameters with effect on membrane's separation process. Adapted from (Padaki et al., 2015).

Operating parameter	Effect
Cross Flow Velocity	Increasing Cross Flow velocity the concentration polarization effect decreases and the permeate flow increases.

Temperature	Increasing the temperature increases the mass transfer and the diffusion through the membrane.
Trans membrane pressure	Increasing the trans membrane pressure increases the driving force.
Molecular size of the solute	Larger molecular size increases rejection with concentration polarization.

Many studies have reported the rejection of THM and AOX by NF, the levels are greater than 90% for THM and about 75% for AOX. Depending on the NF membrane employed and the characteristics of the membrane (Ates et al., 2009; Doederer et al., 2014; Uyak et al., 2008).

When it comes to ion rejection it can be seen that the charge of the ion clearly influences the rejection level, the higher the charge the better the rejection. This is because of the own charge of the membrane (normally negative) and the Donnan effect (which will be further explained below).

2.2.7.3 Transport phenomena

By definition the pore size of nanofiltration (NF) membranes is approximately 1 nm. Clearly, with a pore size that small the interactions between solutes and membrane cannot be governed only by steric hindrance and size but also by solutes solubility and diffusion coefficients. Moreover, three transport phenomena are produced in the membrane when substances go through it. These phenomena must be known in order to understand the transport process. These phenomena are the concentration polarization effect, the Donnan exclusion, and the dielectric exclusion (Yaroshchuk, 2001).

Concentration polarization effect:

This phenomenon is produced when rejected solutes accumulate in the layer immediately adjacent to the membrane. Because of this the concentration of the solute increases as we approach to the surface of the membrane, always getting higher. A concentration gradient forms in the solutions on each side of the membrane.

This phenomenon creates a diffusion flow on the opposite direction to what we want, lowering our total trans-membrane flow (Baker, 2012; Bruggen, 2012).

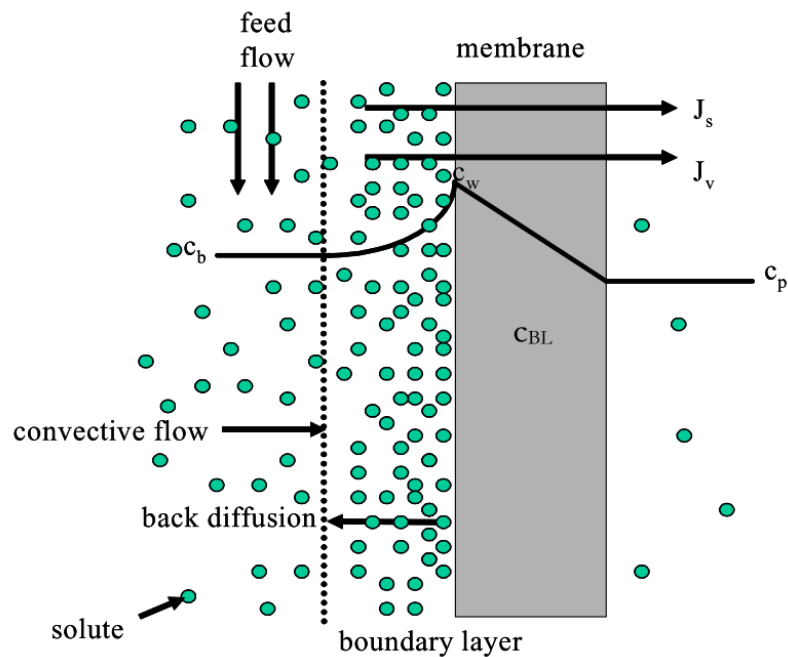


Figure 10 Schematic description of concentration-polarization effect (Schäfer et al., 2004).

This effect is inherent to any membrane separation process, but it is always reversible and disappears when the flow conditions are adjusted. Concentration gradients due to concentration polarization are assumed to be confined to the boundary layer. Because of that it is often minimized by increasing the cross-flow velocity.

Donnan exclusion:

The Donnan exclusion phenomenon occurs when the surface of a membrane has an electrical charge (positive or negative), then the solutes with an opposite charge are attracted to the membrane and form a superficial layer above it.

This way solutes with the opposite charge are repelled by that new layer. For example, a cationic nanofiltration membrane that has negative groups attached to the polymer external surface will repel negative anions, such as SO_4^{2-} , while attracting positive cations such as Ca^{2+} .

We should take into account that multivalent ions will be more rejected than monovalent ions due to that electrical rejection.

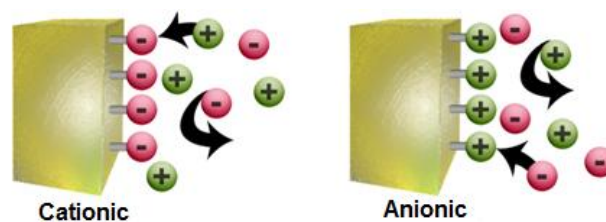


Figure 11 Schematic of the Donnan exclusion effect on membranes

Dielectric exclusion:

This phenomenon is also produced due to the membrane charge and its interaction with the dipolar moment of the water molecules. It arises when aqueous ionic solutions are in contact with different dielectric media (in our case a diluted aqueous solution is in contact with a polymeric membrane and it goes through it).

In NF can be observed that the polarization charges have the same sign as the ions of the aqueous solution. As a consequence the interactions always cause the repulsion of ions, independently of its sign. Therefore it is considered as an additional rejection mechanism.

The water going through the porous is influenced by an electrical field. Due to its dielectric constant, water, stops acting like a dissolvent and the porous acquires similar properties to a hydrophobic dissolvent (Bandini and Vezzani, 2003; Yaroshchuk, 2001).

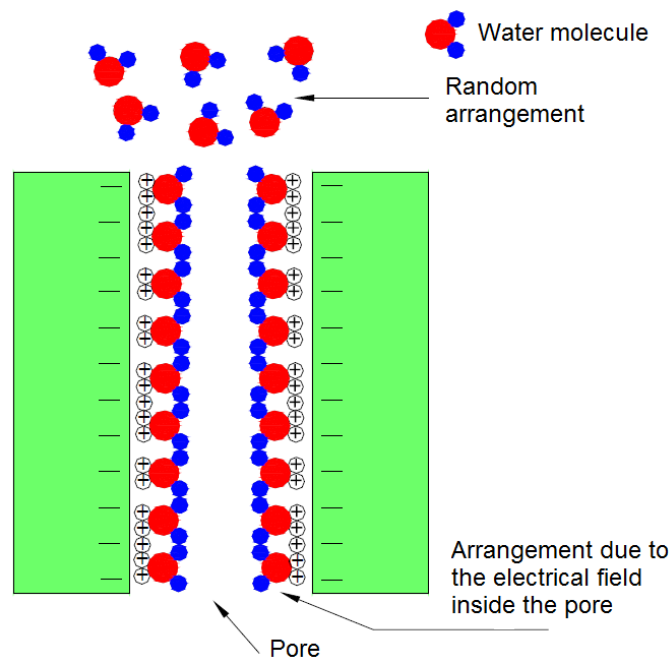


Figure 12 Sketch of the distribution inside a pore due to the Dielectric exclusion phenomenon. Adapted from (Uribe et al., 2005).

2.2.7.4 Limitations

The number of applications for nanofiltration technology increases constantly, nevertheless, several challenges must yet to be solved in order to allow the use of nanofiltration in more demanding applications. The biggest challenge is membrane fouling. It has huge adverse effects on membrane operation such as, increase in pressure drop, decrease in salt rejection and flow decline. Furthermore, there are some other drawbacks that should also be taken into account such as membrane cleaning, membrane lifetime, chemical resistance, concentrate flow treatment and modelling & simulation (Doederer et al., 2014).

Fouling:

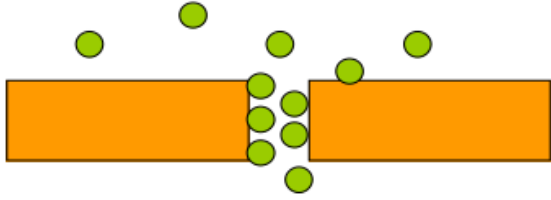
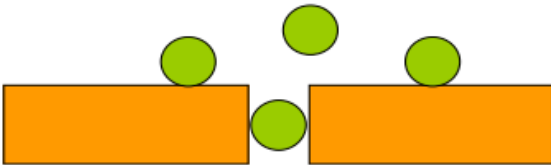
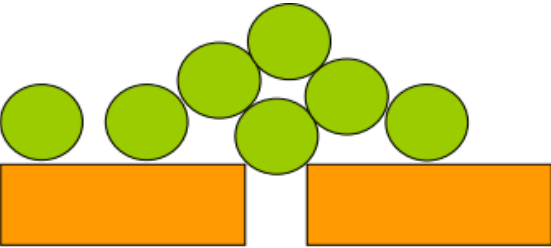
Fouling is one of the main problems in any membrane separation process. For nanofiltration it might be somewhat more complex because the interactions leading to fouling take place at nano-scale and therefore are more difficult to understand.

Fouling is the accumulation of elements rejected by the membrane but not expelled from the system. These elements can then stay on the membrane surface or inside the membrane. Its negative consequences are obvious and include: need for pre-treatment, membrane cleaning, limited recoveries, feed water loss, and short lifetimes of membranes.

A total control of fouling would reduce the need of cleaning and would enhance the permeate levels. Foulants playing a role for nanofiltration membranes can be organic solutes, inorganic solutes, colloids, or biological solids (Saha et al., 2007).

Depending on the relative size of colloidal particles and membrane pores, colloidal fouling may occur either due to accumulation of particles on the membrane surface and build-up of a cake or by penetration within the membrane pores.

Table 3 Summary of types and consequences of membrane fouling. Adapted from (Schäfer et al., 2004).

	<p>Pore adsorption ($d_{\text{solute}} \ll d_{\text{pore}}$): Solute adsorb on the membrane walls, effective pore size is restricted and flow declines.</p>
	<p>Pore Plugging ($d_{\text{solute}} \approx d_{\text{pore}}$): Solute of a similar size to pore diameter walls, block pores completely, reduction in membrane porosity and severe flow decline.</p>
	<p>Cake formation ($d_{\text{solute}} \ll d_{\text{pore}}$): Solute larger than the pores are retained due to sieving effects and form a cake on the membrane surface. Depending on pore to particle size ratio flow decline occurs.</p>

Classical solutions to fouling are the optimization of pre-treatment methods and cleaning of membranes. Suggested pre-treatment methods often make use of other pressure driven membrane separations such as ultrafiltration and microfiltration.

Other options include ozonation, UV/H₂O₂ oxidation or flocculation (Schäfer et al., 2004; Van der Bruggen et al., 2008).

As stated above the chosen membranes for water treatment are typically made of polymeric materials.

Although they share this common fact they are manufactured and operated in a diversity of configurations such as hollow fibre, spiral wound or tubular structure. Each type of configuration or operation possesses a different degree of separation and some different characteristics. We will overview the most important configurations and operation methods.

2.2.8 Classification by operation method

There are two principal operation methods for a membrane module depending on the feed direction in relation to the membrane surface. These two methods are in-line filtration and cross-flow filtration.

2.2.8.1 In-line:

In the in-line filtration the flow is driven perpendicularly to the membrane and through it. The rejected solute particles accumulate on the membrane surface and inside the membrane, lowering the permeability and therefore increasing the necessary pressure gap to maintain the permeate flow until the membrane must be replaced.

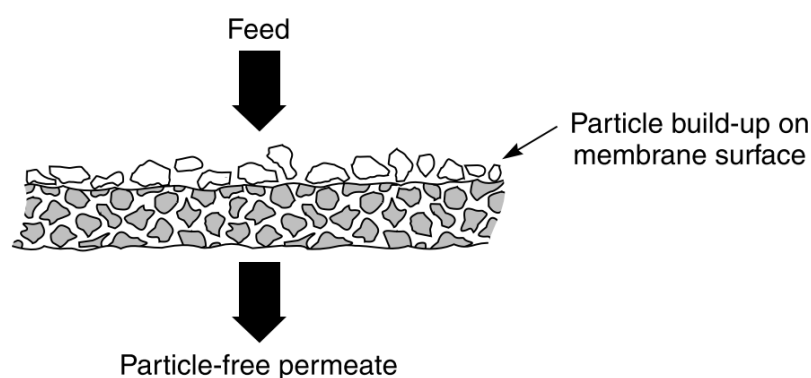


Figure 13 In-line filtration (Baker, 2012).

2.2.8.2 Cross-flow:

In the cross-flow the flow is driven tangentially to the membrane surface, this produces the formation of 2 different flows. One that goes through the membrane free of solute particles (so-called permeate) and one containing all the rejected particles (so-called concentrate).

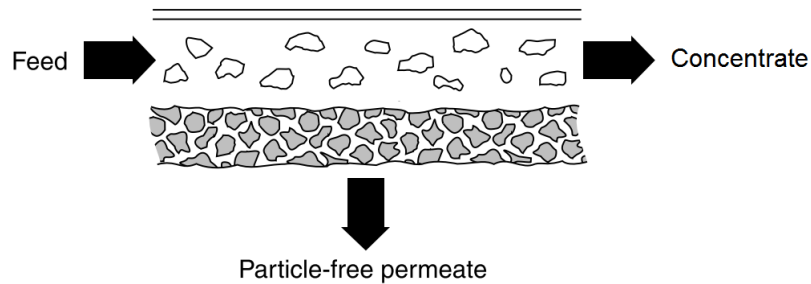


Figure 14 Cross-flow filtration operation (Baker, 2012).

This method takes an advantage in comparison to in-line filtration because in this tangential flow the rejected particles don't accumulate on the surface but are dragged by the flow and expelled from the membrane. Therefore the life time of a cross-flow operated membrane is much higher than an in-line operated membrane.

2.2.9 Classification by module configuration

The availability of many different module configurations arises because of the necessity to obtain better dimensional properties for the industry, which normally requires a large membrane surfaces but has a limited space. The module configuration must also look for a reduction of associated costs such as installation or maintenance of the equipment.

When constructing a module we should take care of possible membrane fouling or concentration polarization due to the module design (Baker, 2012).

At this moment in the market we might find flat modules, plate and frame modules, tubular modules, hollow fibre modules and spiral Wound modules. We will focus only on the last one as is the one reliable for this study.

2.2.9.1 Spiral wound Modules

The spiral wound modules consist in a thin layer composed by a membrane and two spacers rolled up around a central collector tube. All this system is placed inside a pressurized housing that gives the shape of the module. Usually one module contains more than 1 membrane inside.

The feed flows tangentially to the membrane in its external side and is forced to cross through the membrane. Permeate trespassing the membrane flows in a spiral gutter formed by the two spacers of adjacent membranes and finally reaches the central collector tube.

The flow that does not trespasses the membrane is expelled on the other side of the module as concentrate (Baker, 2012). This type of module is the most commonly used in water treatment industry and is the kind of module that will be used in this study.

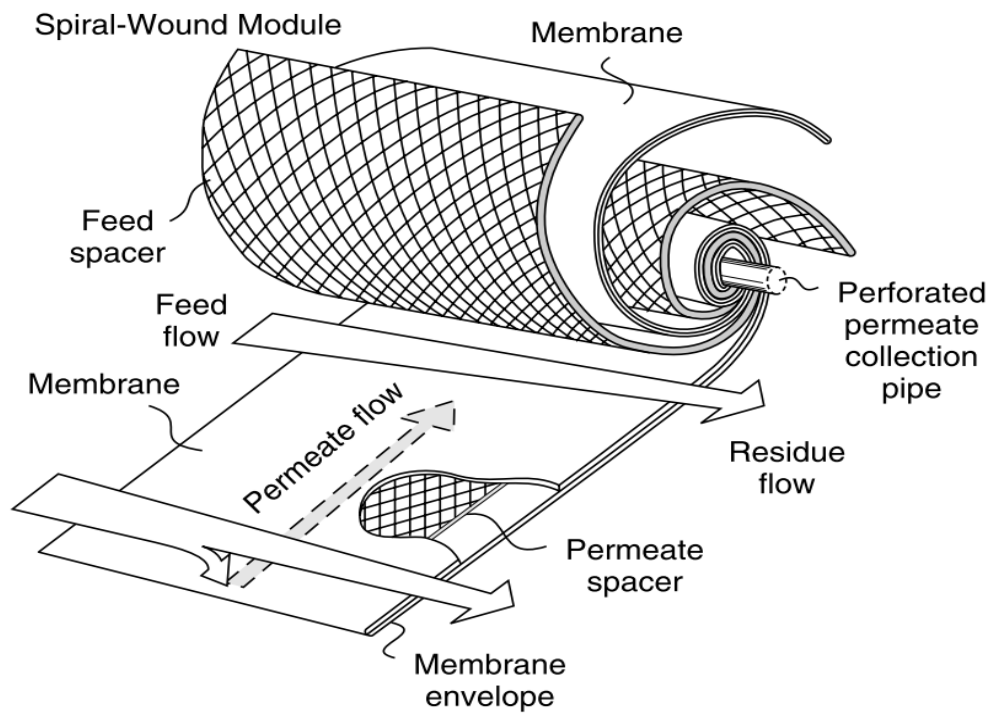


Figure 15 Sketch of a Spiral-Wound module (Baker, 2012).

3 Materials and methods

3.1 Investigated swimming pool

The aim of this work is to investigate and evaluate the performance of a real scale nanofiltration plant for swimming pool water treatment for a period of time of 3.5 months (110 days). To do so we have chosen an indoor public swimming pool in Germany with a recently installed nanofiltration plant.

The pool has 817 m³ of water inside the whole system and consist of 2 indoor pools, one big standard sized swimming pool (SB) and one small pool (NSB). The total treatment flow is 135 m³/h and the disinfection is carried out by chlorine gas. The water temperature of the pool ranges between 28 to 30°C, the visitors mean is 198 visitors per day and the main fraction is between 40 – 60 years old. The rush hours are from 08:00 to 12:00 and from 15:00 to 18:00. The pool also takes school groups at certain hours (mornings).

Fresh filling water is added to lower the levels of the control parameters (Free and bound chlorine, THM etc.) and balance the volume loss. The raw water has a DOC mean value of 3 mg/L and 22 m³ are added every day (it varies depending on the pool assistants and the parameter values).

Our treatment system is composed of an ultrafiltration pre-treatment and the nanofiltration plant. The ultrafiltration is placed after the flocculation allowing us to take out the high MW DOC and achieve the necessary conditions in order to enter into the nanofiltration without risking the membrane's integrity.

3.2 Nanofiltration plant

3.2.1 Capacity and plant parameters

In the NF plant enters approximately a 0.3% of the total recycle flow, the rest of the water goes through the normal stages of the pool's water treatment. The nanofiltration system treats approximately 2.5 m³/h. The plant works with a pressure of approx. 5.5 bar measured with manometers. The different flows of the plant (concentrate, feed and permeate) were measured with rota-meters.

3.2.2 Module

Our nanofiltration plant consists in 5 filtering vessels each of them equipped with 2 spiral-wound nanofilters inside. The vessels are positioned in parallel, with 2 initial modules and followed by the 3 left.

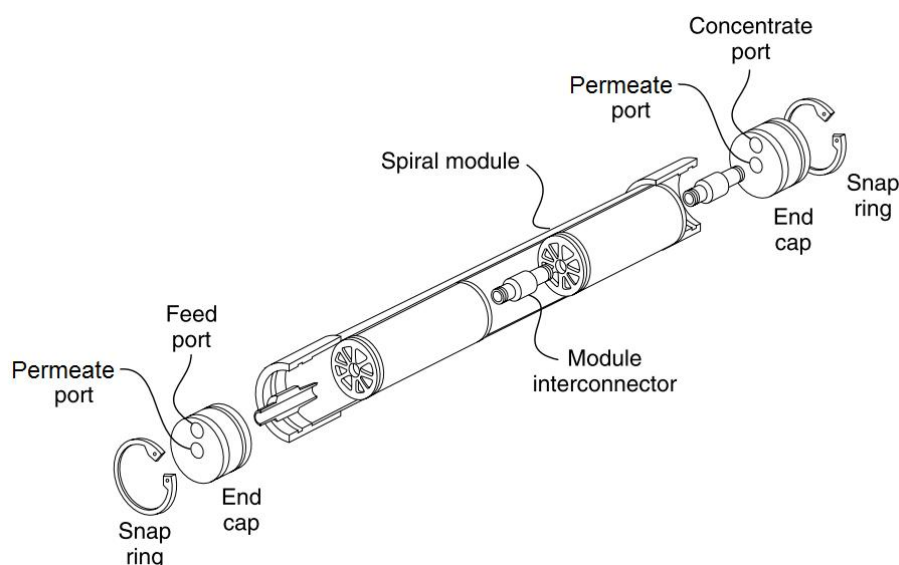


Figure 16 Sketch of the modules used. Adapted from (Baker, 2012).

3.2.3 Membrane NF90 - 4040

The membrane used is the NF90-4040 from DOW FILMTEC™ Membranes, this membrane is made of Polyamide Thin-Film Composite, operates in a pH range of 2 - 11 and the free Chlorine resistance is <0.1 ppm.

3.3 Water sample collection

3.3.1 Membrane evolution samples

In order to know the status, efficiency and yield of the plant, samples from different stages of the water treatment process were taken nearly every day for 110 days. The locations were selected in order to provide key information at each point. 5 positions were chosen and filling water was sampled to provide reference values:

- Swimming pool (SB) (every day)
- Non-swimmer pool (NSB) (every day)
- Filling tap water (LW) (once a week)
- Permeate from Ultrafiltration (P-UF) (once a week)
- Feed of Nanofiltration plant (Z-NF) (once a week)
- Permeate of Nanofiltration plant (P-NF) (every day)

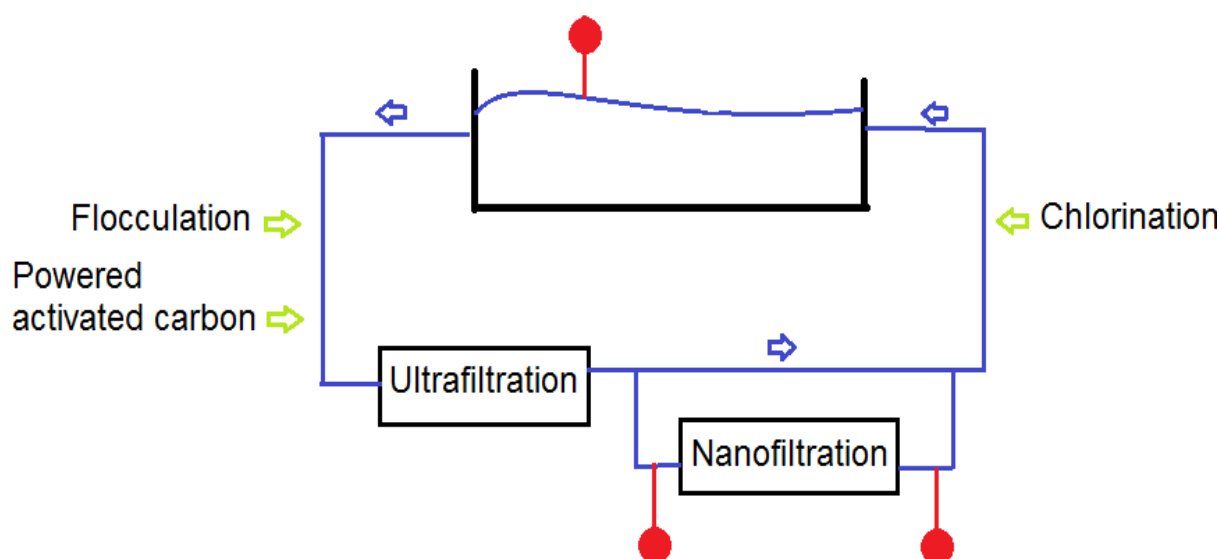


Figure 17 Scheme of the pool system and places selected for sample collection. The red points show the places chosen for sampling.

At each location 3 samples were picked up

- 1 borosilicate bottle of 200 mL was carefully filled for the DOC, IC, ICP-OES, UV-absorbance, electrical conductivity and pH measurement.
- 2 vials of 40 mL for the THM measurement were filled to the top and were tightly sealed with screw caps. A little amount of sodium sulphite was added to these samples in order to stop the reaction of THM formation. Both containers were also properly labelled and filled carefully avoiding any kind of air or bubble inside the container. The tap cap has Teflon layer in order to avoid gas transpiration on chemical interactions.
- 1 borosilicate bottle of 500 mL, for the measurement of absorbable organic halogens (AOX), was filled also with a little amount of sodium sulphite in it in order to stop the ongoing reactions.

3.3.2 Formation potential and Umu-test samples

Samples for the measurement of AOX and THM formation potential (FP) were taken 3 times during the entire study (AOXFP and THMFP respectively). The selected places to calculate the formation potential were SB (swimming pool), Z-NF (NF feed) and P-NF (NF permeate). 2 brown-crystal bottle of 1 L were used in each site, the bottles were previously washed, heated in the oven for 4 hours at 180 °C and then washed again with a chlorine solution of 20 mg/L according to the standard procedure. Once the experimental water was filled in the bottle, sodium hypochlorite (NaOCl 13%) was added until the chlorine concentration of the solution reaches 20 mg/L. After 48h we proceed to the measurement of THM and AOX.

Samples for the determination of the pool water genotoxicity were also taken 3 times during the study. 5 flows were selected; from each flow 2 containers of 40 mL and 1 brown-crystal bottle of 1 L were filled.

- 40 mL containers were filled approximately to the middle and then frozen.
- 1 L brown-bottle was previously filled with 200 g of NaCl and then filled with exactly 1 L of pool water and then 25 mL of Methyl tert-butyl ether (MTBE) were added to the mixture. At this point the mixture was shaken for 20 minutes in horizontal position at 130 rpm. Afterwards, by Liquid-Liquid extraction, the organic phase was concentrated in a GC-vial up to 100 μ L via a cold nitrogen stream, the concentration factor is 10.000. Procedure (Meike Kramer, Iris Hübner, Ocke Rürden, 2009).

3.4 Analytical methods

3.4.1 pH, electrical conductivity and temperature

All the samples from swimming pool and NF plant had the pH, electrical conductivity and temperature measured.

pH was measured using a multi-meter P4 and an electrode SenTix 41 of “Wissenschaftlich-Technischen Werkstätten” (WTW). The measurement of the electrical conductivity was performed using the same multi-meter P4 and the measuring sensor WTW TetraCon 325.

3.4.2 UV – Absorbance

In order to see changes in the DOC fractions UV-absorbance tests were carried out to all the samples. UV absorbance should contribute to the characterization of the organic matter present in our water. For the test a Cary 50 (Varian, Darmstadt) spectrophotometer was used.

3.4.3 Quantification of the dissolved organic carbon (DOC)

The concentration of the dissolved organic carbon in different sampling positions was measured with a TOC-analyser Sievers 820 PMT (Ionics instruments, Boulder, Colorado USA). In this study there was barely difference between DOC and TOC because almost all the organic carbon is dissolved. So is assumed in this study TOC = DOC.

Sievers TOC analyser works with the principle of wet-chemical oxidation. In this kind of measurement, the samples are acidified with phosphoric acid (pH <2) and treated with ammonium peroxy-disulphate as the oxidant. In one part of the sample, the CO₂ is formed and then dissolved in water where becomes HCO₃⁻ which is conductimetrically determined (as total inorganic carbon TIC).

In another part of the sample, oxidation of the organic carbon is produced at 40°C under UV irradiation. The CO₂ created in this stream (total carbon TC) is quantified in a second conductivity test and calculated from the difference between the TIC and the TOC content in the sample. The analyzer was calibrated in a concentration range <5 mg/L.

Every sample was measured 5 times in order to obtain a proper final value.

3.4.4 Determination of THM concentration

The determination of the concentration of THM in the water samples was carried out by gas chromatography and electron capture detection after the dynamic headspace method with an HP 6890, Agilent Technologies.

10 mL of the water sample were firstly put into a 20 mL vial and then heated to 60°C and shaken. Afterwards 1 mL of the gas phase was taken with a pump. Then the sample is frozen to -40°C. Now the samples were heated from -40°C to 250°C with an increase of 12°C/s and driven with the carrier gas (N₂, 1 mL/min) into the column (DB-5MS, Agilent technologies; 30m x 0,25mm; stationary phase: 5% Phenyl-methyl-siloxan, layer-thickness 0,25 µm). While the samples are passing through the column a temperature program supports the separation of the analytics (6min 40°C, 30°C/min until 175°C; 1min 175°C). Finally the halogen substances were quantified with the electron capture detection.

The concentration of the different samples of THM is then converted to its equivalent in chloroform which will be summed as THM.

3.4.5 Determination of AOX concentration

For the determination of AOX the samples were measured using a TOX analyzer euro glass ECS 1200 (Thermo Electron GmbH, Dreieich, Germany).

100 mL of sample were acidified with HNO₃ (pH <2) and mixed with 5 mL of sodium nitrate acid solution (0.2 mol/L NaNO₃ and 0.02 mol/L HNO₃). After the addition of 50 mg powdered activated carbon, the samples were shaken in a 250 mL Erlenmeyer at 140 rpm for at least 24h in horizontal.

Afterwards, the suspended active carbon was filtered off through a glass frit with 3 bar pressure, for the removal of halide ions the sample was washed several times with nitrate solution (0.01 mol/L sodium nitrate and 0.001 mol/L nitric acid) and then burnt in the TOX Analyzer at 1000°C. This formed the organically bound halogens, hydrogen halides (HX), which were then quantified by a micro-coulometric titration.

3.4.6 Determination of water genotoxicity by umu-test

Salmonella typhimurium bacteria in the phase of growth are exposed for 2 hours to decreasing concentrations of samples in triplicate, as well as blanks. After 2 hours, the exposure cultures are diluted into fresh growth media and allowed to grow for a further 2 hours. The induction of the umuC gene and fused lacZ reporter gene and subsequent expression of β -galactosidase. Colourless ONPG (o-nitrophenyl- β -D-galactopyranoside) is converted to the yellow product o-nitrophenyl in the presence of the induced β -galactosidase. The intensity of the colour correlates with the amount of the induced protein and thus genotoxic potential of the sample (Gutenberg-universiteit, 1991).

3.4.7 Ion chromatography (IC)

The concentration of the anions chloride, nitrate and sulphate in aqueous samples by ion chromatography was determined (IC) with an IC 881 (Methrom).

This works on the principle of the single-column with an anion exchange column as the stationary phase (Dionex AS9 – HC 250/4.0). The eluent used was a solution of sodium carbonate in 9 mmol/L phthalic acid. After separation, the anions were detected by conductimetry.

3.4.8 Inductively coupled plasma optical emission spectrometry (ICP-OES)

The quantification of various cations and elements in aqueous solution was performed by ICP -OES with a Vista-PRO CCD Simultaneous ICP–OES from Varian. In this technique, the sample is atomized in a carrier gas (argon) and introduced as an aerosol into an argon plasma ($T \approx 6800^\circ\text{C}$), where the atoms of the sample are atomised and become excited.

The excitation sends, depending on the element, magnetic waves with characteristic wavelength, which with the help of the CCD detector (charge-coupled device) can be quantified. Before measurement, the aqueous samples were acidified with concentrated nitric acid to ensure that all the metals remain in solution (1% HNO_3).

4 Results and discussion

4.1 Global pool values achieved

In this section will be reviewed the different measurements obtained from the whole system. It must be said that this values are not only affected by the performance of the studied nanofiltration plant but also by many other variables that should be considered such as visitors per day, type of visitors (children or grown people), fresh water added to the pool etc. These variability inlets are likely to change due to an enormous number of events, and are uncontrollable and unpredictable.

4.1.1 DOC evolution in pool water

During approximately 3.5 months (110 days) the DOC concentration of the pool water has been analysed once a day. The results obtained are shown in *Figure 18*, a weekly pattern can be observed.

A progressive increase of the DOC values during 5 - 6 days and afterwards a sudden decrease of it. This profile may be produced due to an accumulation of the dissolved organic carbon during some days (as a result of insufficient elimination of the incoming DOC) and a subsequent elimination in a day with lower activity.

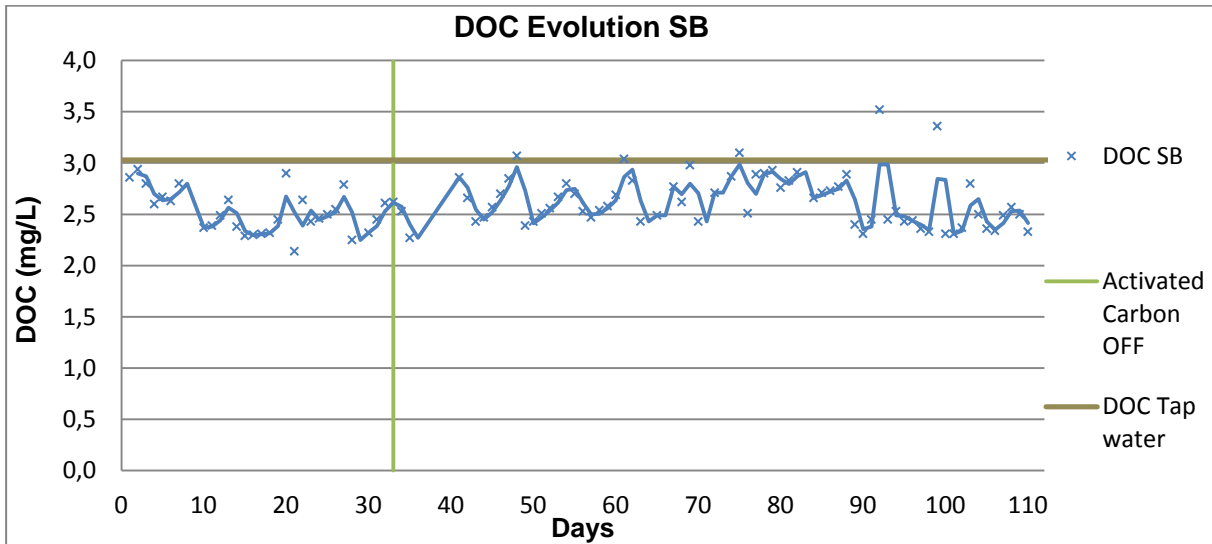


Figure 18 DOC results obtained from the pool water sample for a period of 110 day. The line is the mean value between 2 consecutive points.

The hypothesis of fresh water addition being the consequence of the DOC decrease is dismissed as the mean value of the fresh water DOC is higher (3 mg/L) than the mean value of the pool water (2.6 mg/L) thanks to the removal by the NF plant. Therefore the addition of fresh water would increase the DOC values of the pool instead of lowering them.

Although this is the most likely hypothesis a correlation between pool assistance and DOC could not be confirmed (Figure 19). To completely verify this hypothesis a widely statistical study of the behaviour of the swimmers should be done, because it is not only the number of visitors affecting the DOC but also their behaviour and routines inside the pool that can increase or decrease the DOC concentration of the pool water.

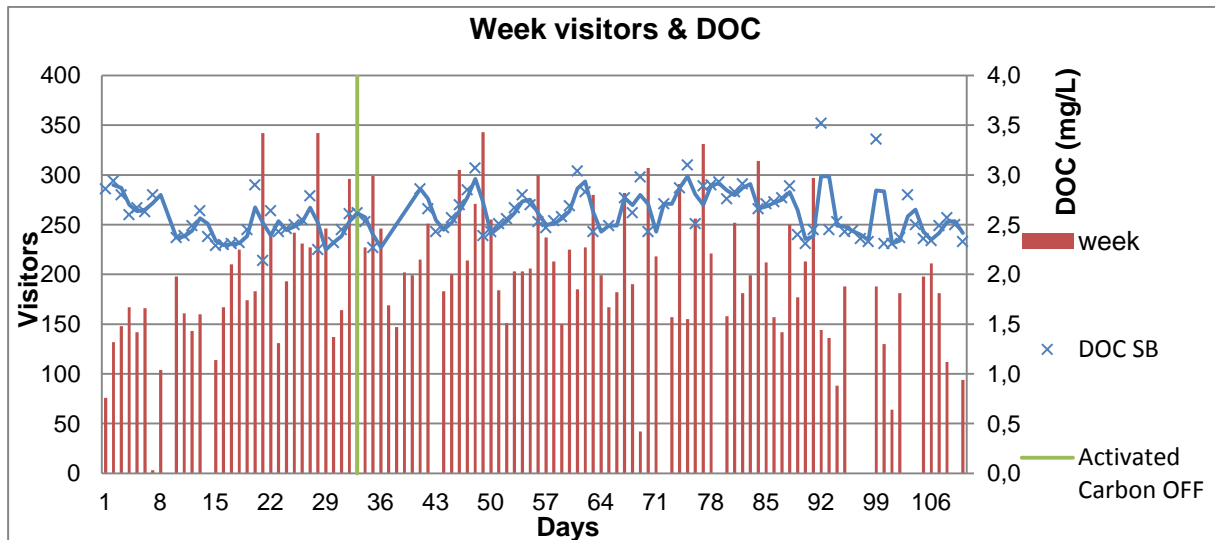


Figure 19 No correlation found between the pool visitors and the DOC evolution. The green line represents the day of the activated carbon shutdown. The visitor's data was obtained from the pool's office.

A relation between DOC and regular additions of fresh water was neither found (Figure 20). Therefore the origins of the pattern could not be determined.

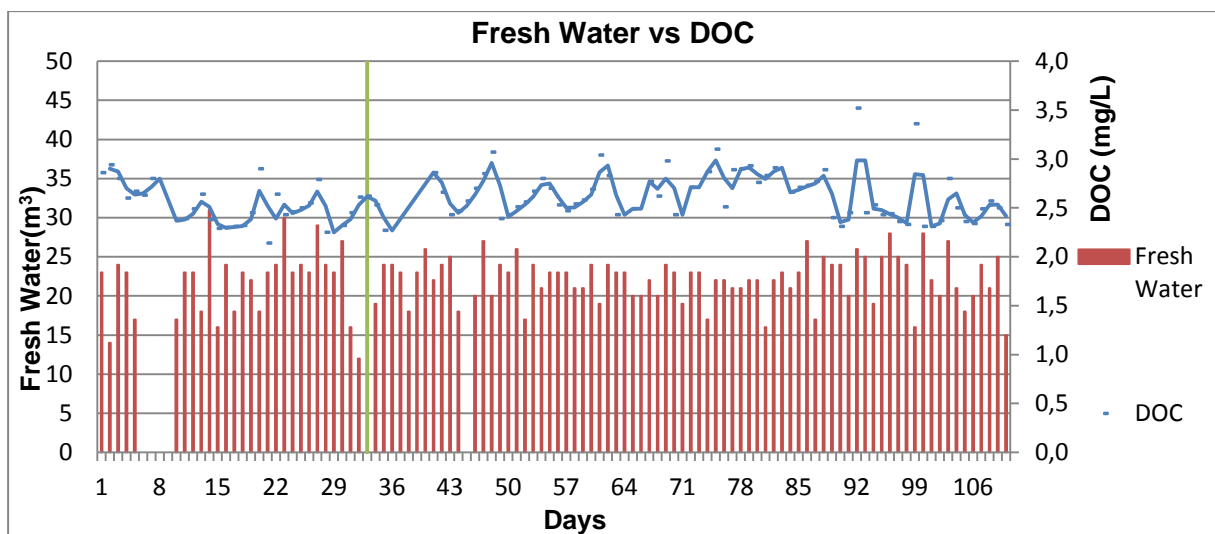


Figure 20 No correlation found between the pool visitors and the DOC evolution. The green line represents the day of the activated carbon shutdown.

Despite of the pattern shown by the DOC of the pool, the overall DOC values obtained compared to the DOC values from the raw water have been reduced even with the income of DOC produced by the bathers.

A comparison of the DOC concentration previous to the NF installation (with powered activated carbon) and the DOC concentration after the NF show the reduction obtained due to the NF plant (*Table 4*).

Table 4 Comparison of the DOC levels with the different stages of the pool water treatment activated or deactivated. Powered Activated Carbon (PAC), Ultrafiltration (UF), Nanofiltration (NF).

Parameter	DOC (mg/L)
UF+PAC (n = 82)	3.3
UF+PAC+NF (n = 25)	2.5
UF+NF (n = 37)	2.6

As can be observed NF produces a reduction of approximately 24.3% of the total DOC concentration of the pool. Considering that the plant is treating only a 0.3% of the total recycle flow the reduction is noteworthy.

In view of this reduction, the NF effects in the total pool system can be considered as positive. DOC is the precursor of DBP therefore this reduction will reduce as well the DBP concentration. No reliable influence in the DOC levels has been observed due to the activated carbon shutdown (*Figure 18, Table 4*).

4.1.2 AOX and THM evolution

AOX and THM have also been analysed during this study (AOX for 78 days).

The results for AOX, as seen in *Figure 21*, show a change of magnitude that coincides with the activated carbon shutdown.

Despite of that, this correlation cannot be appreciated on the THM results (shown in *Figure 22*). This could be due to the many different activated carbons available in the market. Some of them are able to reduce the AOX yet not reducing THM and vice versa. This activated-carbon selectivity applies to many other substances. The activated carbon retention characteristics may vary depending on its surface area, pore size or surface reactivity.

The contact time between the activated carbon and the substance plays also major role in the adsorption of the specie. In our pool the contact time between the water and the activated carbon has shown to be 22 seconds, which is really low. Increasing the contact time may lead to a better effect of activated carbon on the reduction of THM and AOX.

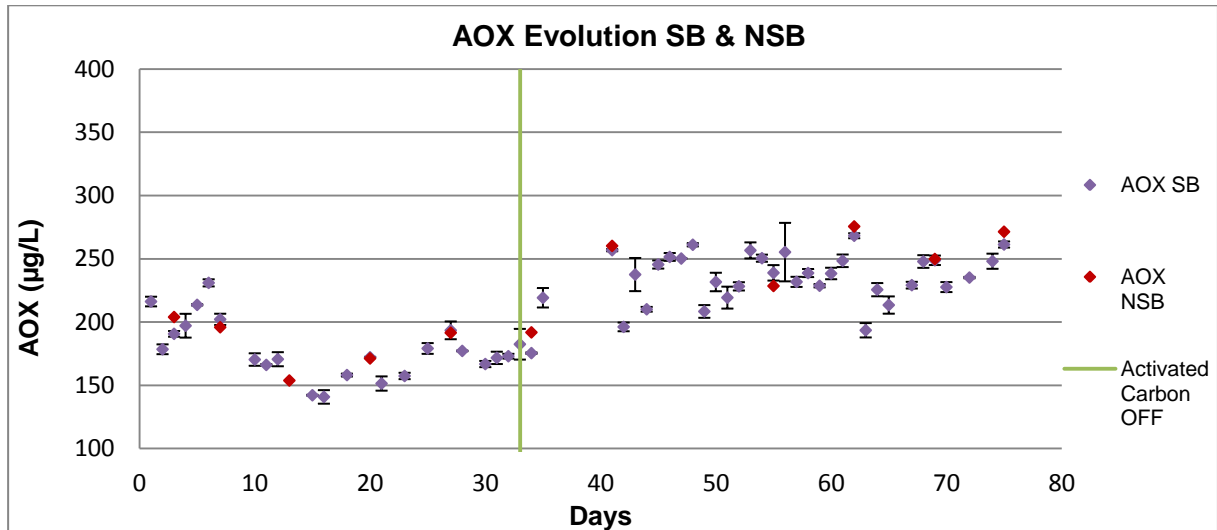


Figure 21 Values of AOX obtained from the pool (Blue) and Small pool (Red) with its error bars. The green line indicates the exact day when the activated carbon treatment of the water pool was shut down.

On the Graph shown above (*Figure 21*) the effect of the NF in the reduction of AOX could not be appreciated. As the study began when the NF plant was already working, the evolution from the previous state and to the state reached after the NF could not be observed.

In order to provide this comparison, data from previous studies that took place in the same pool and also evaluated the AOX concentration has been used. Allowing seeing the reduction produced by NF.

Table 5 Comparison of the AOX levels with the different stages of the pool water treatment activated or deactivated. Powered Activated Carbon (PAC), Ultrafiltration (UF), Nanofiltration (NF). n refers to the number of measurements (EBI, 2013).

Parameter	AOX (µg/L)
UF+PAC (n = 82)	328
UF+PAC+NF (n = 25)	166
UF+NF (n = 37)	232

As shown in *Table 5*, AOX values previous to the NF plant installation show a much higher value than those when the NF plant was working. In fact the installation of the plant leads to a decrease of the AOX concentration of approximately 49.4%.

A later shut down of the activated carbon will increase again the AOX values (this is what can be seen in *Figure 21*) of the pool water but not arriving to the initial values. This table clearly shows a better performance of the NF rather than the activated carbon.

As will be reviewed in later stages the NF has shown an enormous rejection of the AOX from the pool water. Giving a hint of the great potential that NF has in the reduction of harmful substances in pool water as most of them are included in the AOX group.

THM concentration levels (as seen in *Figure 22*) show high variability (15 µg/L – 68 µg/L) and do not seem to go down even with the nanofiltration plant working. Although, as will be reviewed in chapters 4.2.2.1 and 4.2.2.1 the NF plant actually rejects a high portion of DOC and THM. The levels of DOC in the water are still too high. Therefore the THM formed after the chlorine reaction with the DOC is also still high. The recommended value for THM in Germany for pool water is 20 µg/L and we clearly still exceed that limit with a mean THM value of 39 µg/L.

The high variability of the THM concentrations is a consequence of the DOC oscillation. Their close relation will be shown in point 4.1.4.

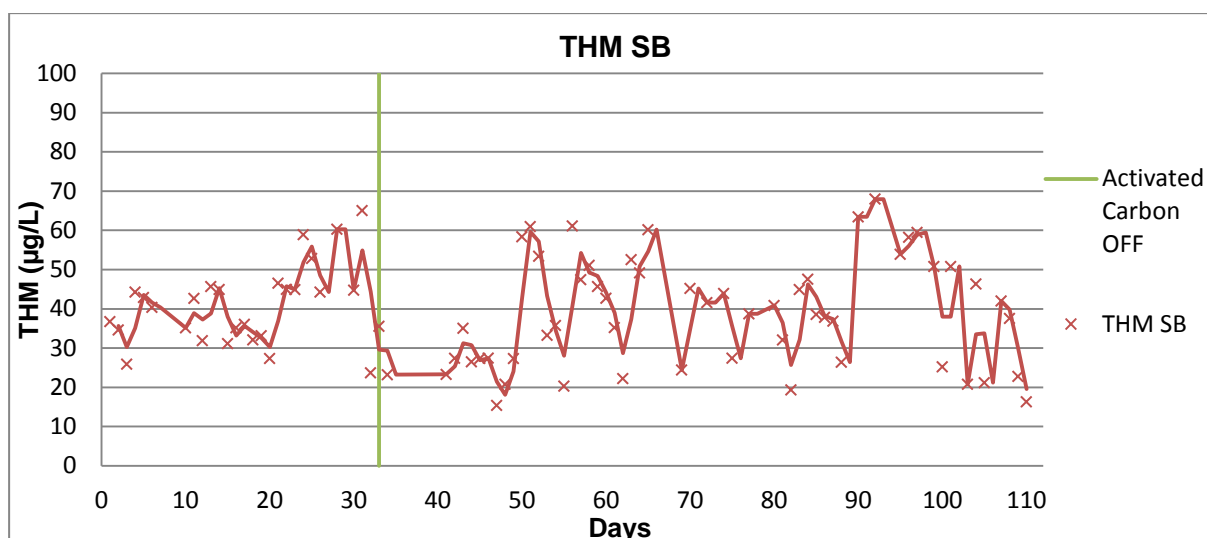


Figure 22 Values of THM obtained from the pool for 110 days. The red line is the mean value between 2 consecutive days, the green line responds to the activated carbon shut down.

As mentioned before, the mean value of the DOC in the raw water is 3 mg/L. With this concentration an input of raw water into the system increases the DOC levels rather than lowering them, making the nanofiltration DOC rejection ineffective for THM reduction.

Nowadays the pool adds approximately 22 m³ per day to the pool. Further studies must be carried out on this field in order to improve and minimize the inputs of raw water needed as this inputs bring about a deterioration of our water quality.

4.1.3 AOX and THM formation potentials and water genotoxicity

The performance of the AOX and THM formation potentials showed up the potential of nanofiltration for decreasing the DBP concentrations by reducing its precursors and the DBP groups.

Figure 23 shows the AOX and THM formation potential for water from the swimming pool (SB), water from the feed (ZN) and nanofiltration permeate (PN). The Formation Potential of the water is an important value that shows the maximum concentration of our species that can be reached with the worse conditions possible.

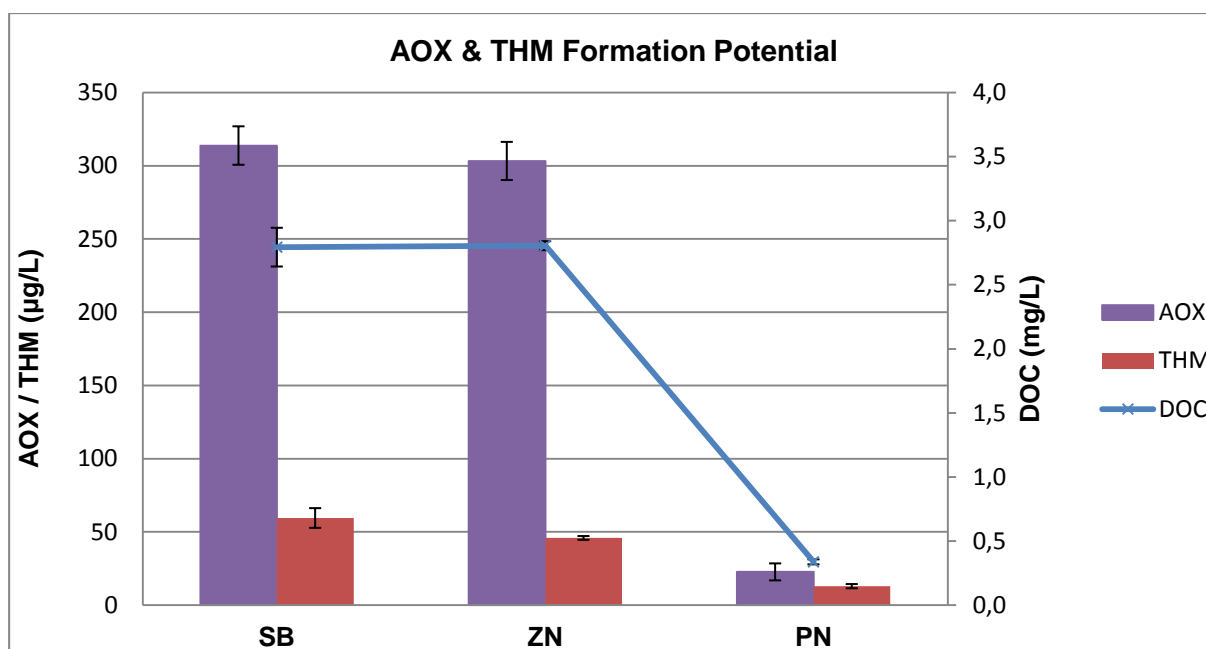


Figure 23 Representation of AOX and THM formation potential in the different samples. $n=3$ for SB, $n=2$ for ZN and PN samples.

As can be appreciated the reduction of DBPs formation potential is enormous by nanofiltration. With a reduction rate greater than 10 (reduction of 93%) when comparing the AOX concentration before and after the NF. The THM formation potential reduction is in the order of 4 times less after the NF than before (78% of reduction).

This high reduction of the formation potentials for AOX and THM reveal the effect of the NF's rejections for the different species and show its real effect in our pool water, even if we don't see it clearly reflected in the THM concentration values.

No genotoxicity was detected in any of the pool samples by the realisation of the Umu-test. Therefore the performance of the membrane concerning genotoxicity reduction could not be assessed.

4.1.4 Correlation between DOC and THM in pool water

The comparison between DOC and THM concentrations each day lead us to conclude that there is a clear relationship between each other. An increase of the DOC concentration (who acts as a precursor) leads after a time delay of 2- 3 days to a proportional increase of THM (Figure 24).

Some studies already pointed out this relation (Hansen et al., 2012; Kim et al., 2002; Klüpfel et al., 2011). In this case it can be seen in a real scale pool-water treatment. Especially on the period of time that goes from the day 45 to day 85 where the correlation is really precise.

During those days the plant had a period of time of good stability and the bather visits were also stable. It is even possible to notice how in day 68 the DOC did not reach the expected peak and the THM mirrors its profile with an incredible precision 3 days later, showing also an unexpected decrease.

Further studies of this plant will possibly corroborate this result and obtain even a better correlation between DOC and THM as this experiment was carried out right after the installation of the plant and some instability and adjustments had to be made at the very beginning.

With later studies a better stability of the plant will be achieved and longer periods of time could be compared. With those results a better determining correlation between DOC and THM could be established, determining down to the last detail the time delay relation between the two of them.

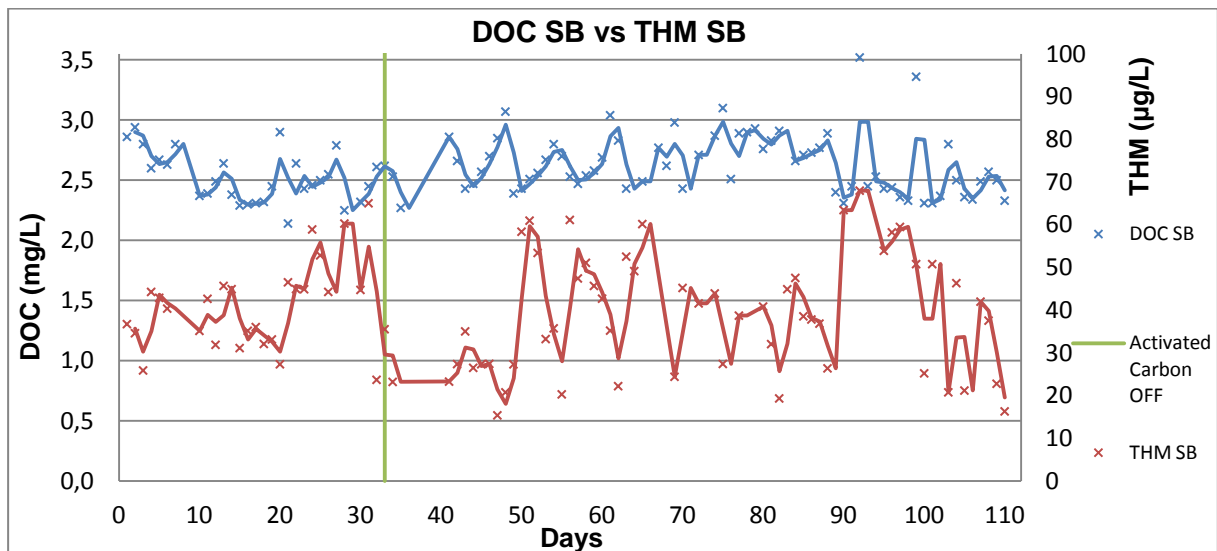


Figure 24 Correlation between DOC and THM in the pool. The line correspond to the mean value between each 2 consecutive days

As this relation has been shown the reduction of the THM precursors (DOC) should lead to an unavoidable decrease of THM. It can also be observed that an abrupt increase of the DOC followed by an immediate decrease is not mirrored by the THM as precisely as if the increase or decrease is made progressively where the relation is much clearer.

4.1.5 Discussion about Electrical conductivity and UV-absorbance evolution

The recurrent analysis of the electrical conductivity and the UV-absorbance of every sample have reported the following results. As can be seen in *Figure 25* the electrical conductivity has been lowered since the installation of the nanofiltration plant (approximately 14%).

This reduction is due to the high ion rejection of the NF90 membrane, which will be further developed in point 4.2.2.4. The rejection of ions by NF showed the already expected results. As previous studies reported NF90 has a good rejection for ions capable of having a certain selectivity depending on its charge (de la Rubia et al., 2008).

From day 71 to day 81 the plant had to be shut down due to some problems with the bisulphite sensor. An immediate increase of the electrical conductivity was produced revealing the irrefutable positive effect that NF has on the reduction of ions. Once the plant was turned back on the ion concentration levels were re-established and the electrical conductivity went down again.

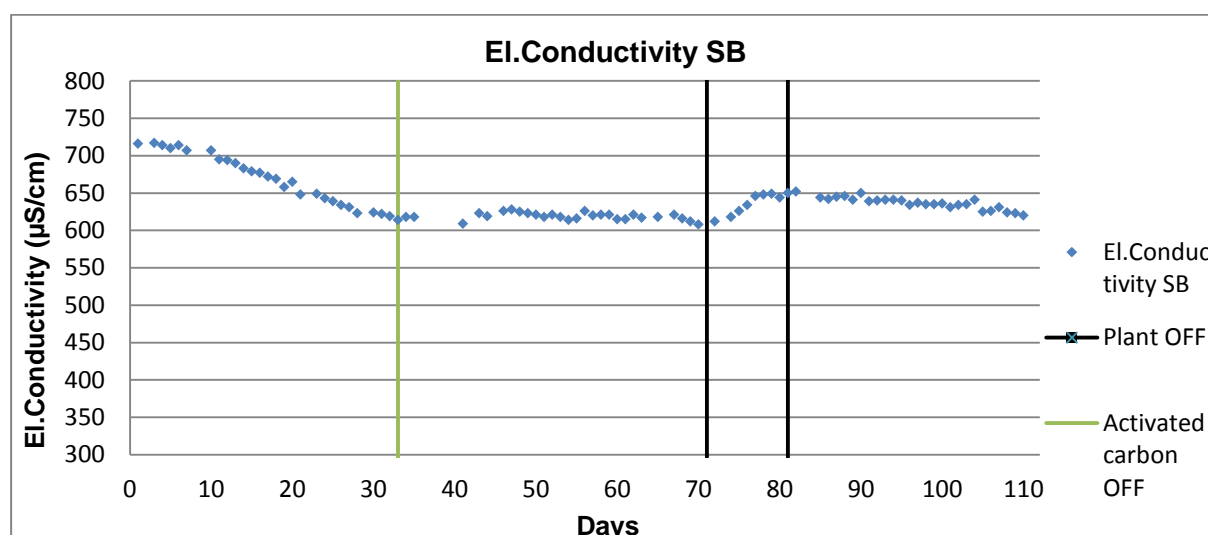


Figure 25 Values obtained from the systematic evaluation of the electrical conductivity from the pool samples. The period between black lines correspond to a failure of the bisulphite sensor of the plant and its subsequent shut down for 10 days.

The UV-absorbance results are not exactly the desirable but also show important information about the treatment plant performance. In *Figure 27* it can be appreciated an increase of UV-absorbance. The UV-absorbance of the local raw water has been calculated obtaining a mean value of 6 Abs/m. This value is clearly above of the values of the pool water.

This increase is speculated to be a consequence of an oscillation of the UV-Absorbance at the beginning of the study until the final equilibrium between the raw water inputs and the rejection from the nanofiltration plant is achieved.

The main contributors to the UV-absorbance are the aromatic compounds. Hence the local water must have a high concentration of these compounds producing an increase of the UV-absorbance of the pool water when it is added to the system.

It must be said that the water inputs were also produced before the installation of the NF treatment, therefore the increase of the UV-Absorbance during the study must be produced due to other sources.

As said before the main hypothesis is the need of reaching equilibrium between the rejection achieved by nanofiltration and the inputs coming from the raw water. As can be observed on the rejection values obtained, the membrane does eliminate a high fraction of the aromatics from the water (*Figure 26*) and in the later days of the study the UV-Absorbance was already decreasing back to the initial values. But further tracking of the plant must be carried out in order to determine the origin of the UV-absorbance increase.

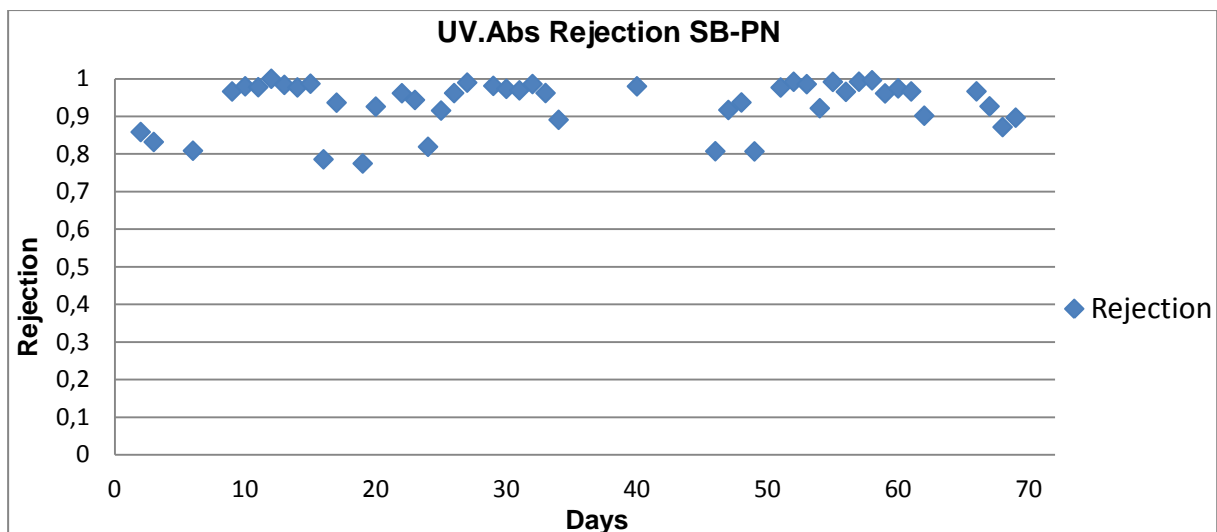


Figure 26 UV-Absorbance rejection values comparing pool water values and Permeate values. Mean value: 93%

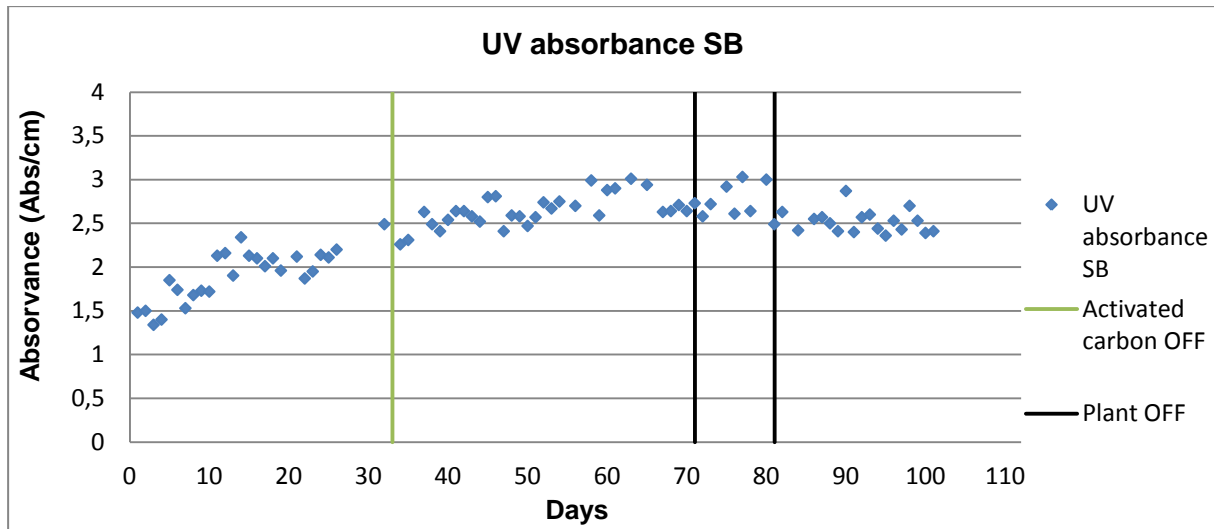


Figure 27 Representation of the values obtained of UV-absorbance of the pool water samples. The period between black lines correspond to a failure of the bisulphite sensor of the plant and its subsequent shut down for 10 days.

4.1.6 Free & Bound Chlorine

The levels of bound and free chlorine were measured daily from the pool. The results shown in *Figure 28* suggest a smooth decrease of the free chlorine concentration possibly due to the activated carbon shut down but it is not possible to clearly conclude that it has a direct relation.

As explained in previous chapters the substance in charge of disinfecting the water is the free chlorine. Therefore a decrease of its levels implies a worse disinfection potential of the water.

In the last days of the measurements it can be observed an increase of the bound chlorine. It is believed that this increase is produced due to the problems with the bisulphite sensor of the nanofiltration plant that compelled a complete shutdown of the plant for 10 days (from 71th to 81th day). No relation with this shutdown has been observed in the rest of the parameters of the pool, with the exception of electrical conductivity.

The free chlorine concentrations of the pool water are always between 0.3 and 0.6 mg/L as the German recommendations states. This chlorine concentration implies the need of reducing its levels prior to entering into the membrane as the free chlorine resistance of it is 0.1 mg/L. To do so we used a bisulphite solution.

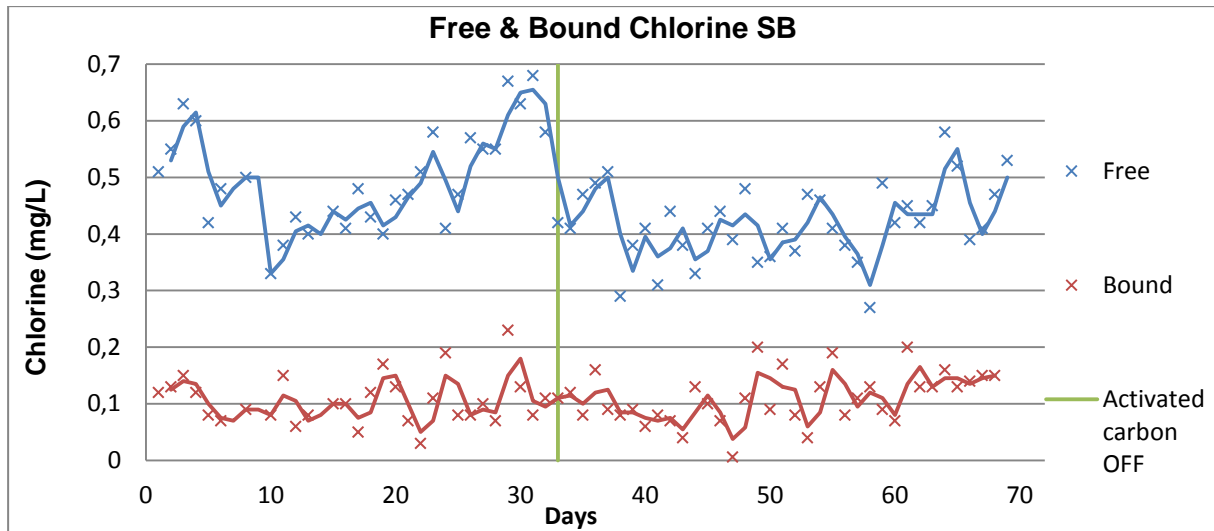


Figure 28 Evolution of the Free and Bound Chlorine of the pool water. The last days problems with the bisulphite sensor appeared that forced a shutdown from 71 to 81 but may have started affecting the plant on earlier stages.

4.2 Nanofiltration specific results

In this section will be reviewed only the parameters directly affected by the nanofiltration plant. The yield of the plant will be evaluated by taking into account the results before and after the nanofiltration plant without looking at its effects on the pool. The analysis of the membrane system lasted for 70 days.

4.2.1 Arrival at steady state for the membrane

The analysis of the membrane system lasted for 70 days. As the results in the permeate flow are really sensitive to any event happening on the membrane system the graphs listed below (Figure 29 & Figure 30) show all the issues, even those not directly caused by the plant but affecting it somehow. The explanation of all these events can be found below in point 0.

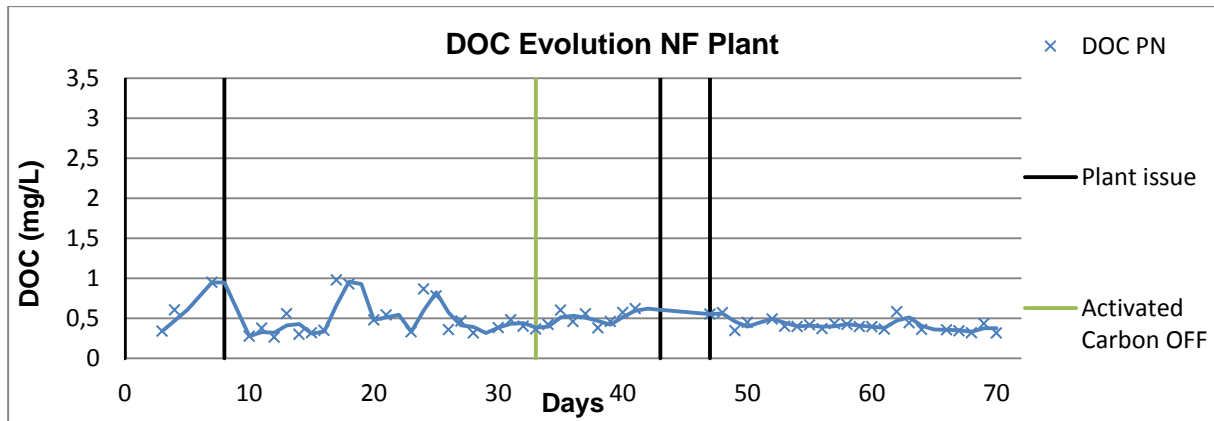


Figure 29 DOC steady state in permeate flow reached approximately 70 days after the beginning of the experiment.

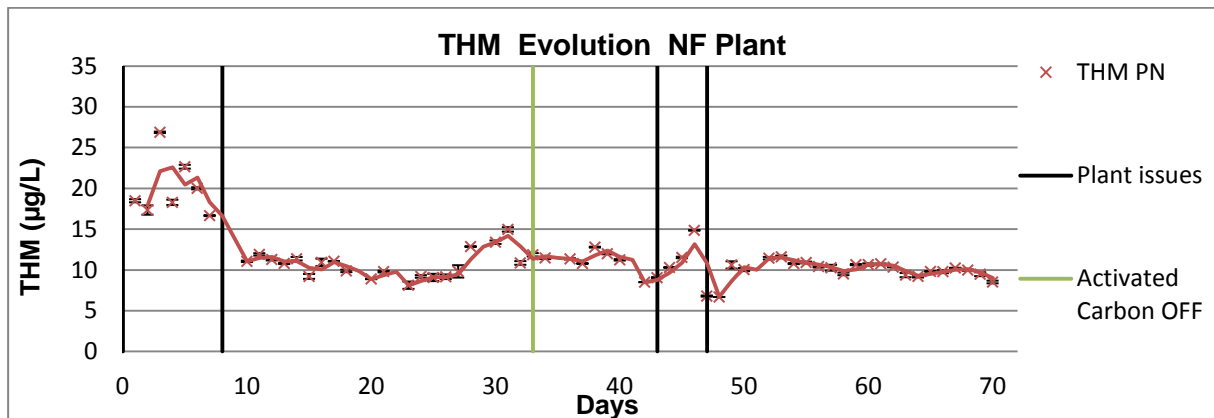


Figure 30 THM steady state in permeate flow reached approximately 70 days after the beginning of the experiment.

4.2.2 Rejection performance of nanofiltration plant (NF90 – 4040)

4.2.2.1 DOC

The rejection of DOC by the plant is $84\% \pm 4\%$, as can be seen in the results obtained (Figure 31), the NF90 membrane is one of the best nanofiltration membranes in DOC rejection performance, some studies also used this membrane because of its great properties and rejection rates (de la Rubia et al., 2008). In the study from de la Rubia cited before the reduction of DOC by the NF90 was assessed, for this purpose waters from different rivers of Spain was employed. The DOC from each river and its corresponding rejection by the NF90 membrane are listed below (Table 6).

Table 6 Table with the different DOC rejections by the NF90 membrane. Adapted from (de la Rubia et al., 2008).

Initial DOC (mg/L)	NF90 Rejection (%)
6.2	94.7
1.4	70
2.6	74.9
5.4	99.1
1.9	93.6
6,5	88.5
6.3	89
7.1	90.3
6.3	94.4
1.6	84.2

As can be observed in the results obtained from de la Rubia the rejection of DOC by the NF90 is always high, regardless of the DOC concentration found in water.

Despite of its benefits, this high rejection levels combined with the high levels of DOC present in water and the total amount of water treated implies a fast fouling of the membranes that may cause a more regular need of membrane cleaning than expected.

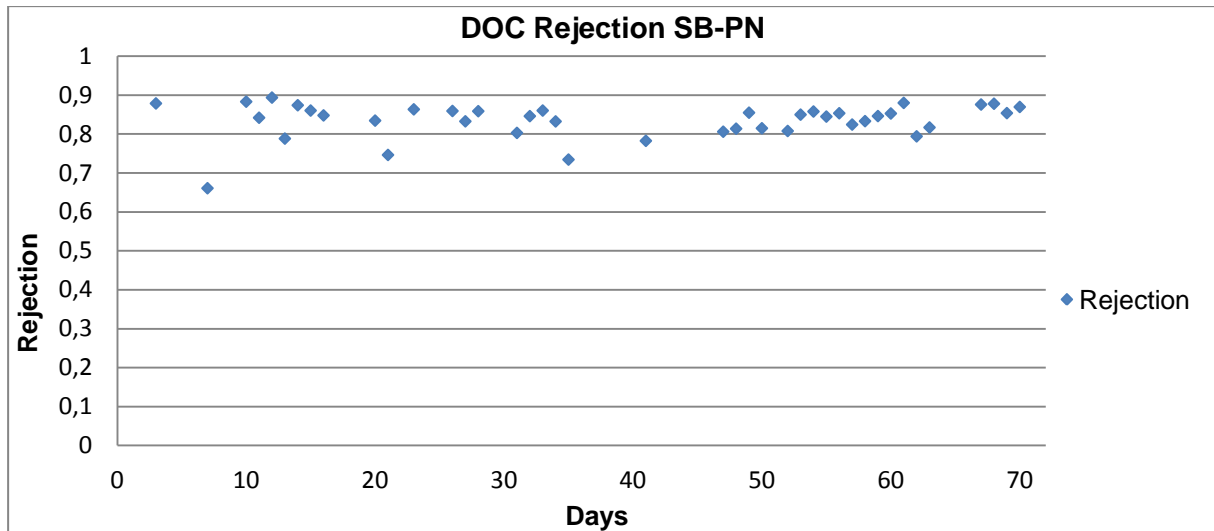


Figure 31 DOC rejection by the membrane, the variability is decreasing as it approaches to the steady state. Mean value 84%.

4.2.2.2 AOX

The AOX rejection levels are good and stable for 70 days ($95\% \pm 2\%$) (Figure 32). At the beginning of the experiment it is observed a progressive increase of the membrane rejection. This happening is originated by an initial membrane compression and the need of the membrane to reach a stable equilibrium in its surface since the plant was installed at the same moment the study began.

The high rejection of AOX is, as the huge reduction of its formation potential seen before, the proof of the suitability of NF for pool water treatment. With this rejection values NF is reducing the AOX concentration much more than what we achieved with activated carbon. The AOX group includes all adsorbable organic halogens (THM, HAAs, etc.) hence the reduction of AOX is our main target as we want to reduce the DBPs as much as possible.

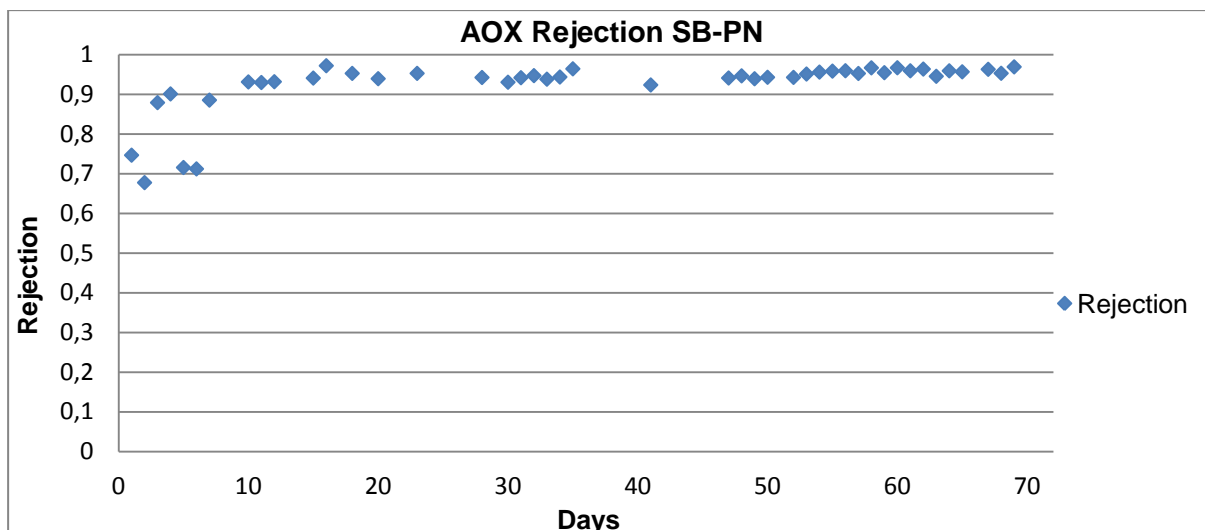


Figure 32 AOX rejection by the membrane, with a mean value of 93% the membrane showed a very constant and stable rejection for absorbable organic halides.

4.2.2.3 THM

The values obtained for the rejection of THM show a wide variability ($70\% \pm 11\%$) (Figure 33). The explanation for this phenomenon can be found in the variable THM concentration of the feed (explained in 4.1.2). The rejection of species by a membrane is close related to its concentration in the feed. A higher concentration in the feed leads to a higher rejection and a lower concentration on the feed leads to lower rejection. Therefore, when the concentration of THM in the feed changes the rejection of the THM by the membrane changes as well, producing high variability in the results.

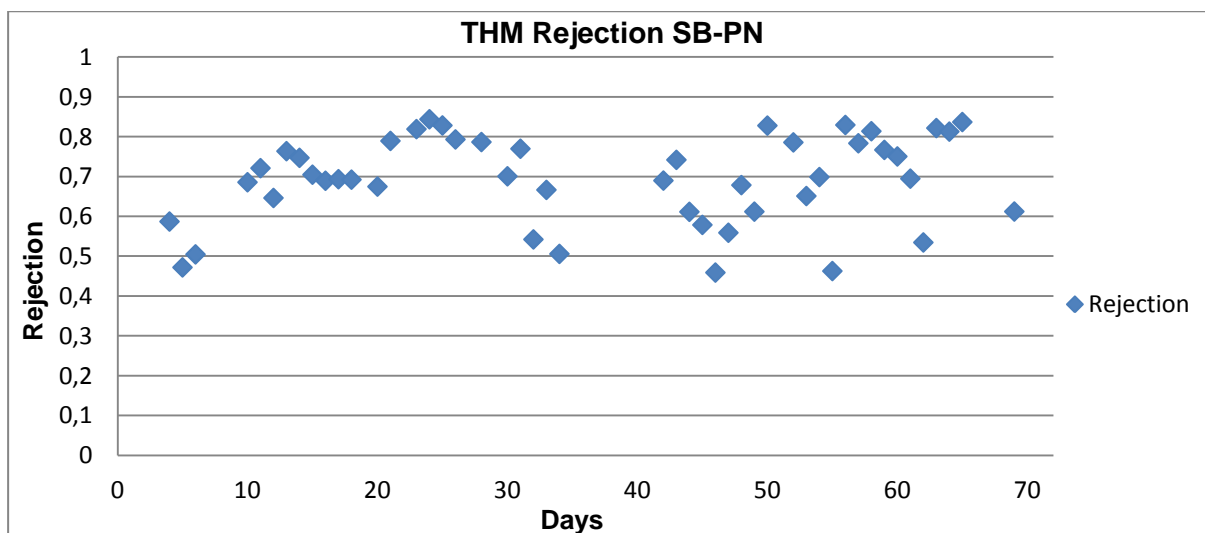


Figure 33 THM rejection values comparing pool water concentration and Permeate concentration. Mean value: 70%.

Despite of the variability in the THM rejection rates, the overall rejection is on the usual values of NF for the rejection of THM, which lead us to conclude that NF90 could be a suitable option for the reduction of THM concentrations in pool water. Bearing in mind, not only the THM must be lowered but also its precursors (DOC).

In *Table 7* can be observed that most of the membrane rejection values are similar to those we obtained. Some of them higher but it must be taken into account that the majority of this results were obtained in a lab scale experiment with controlled feed and parameters.

In our case the NF90 membrane is working in a real environment making its operation much more complex and difficult to control.

Table 7 Comparison between different membranes regarding the reduction of THM in water sources.

Water Characteristics	Membrane	Rejection	Observations	Source
Lab Prepared Water	NF200 (Dow FlimTec)	90 - 95%(15 bar) 74% (Low pressure)	Concentration 40µg/L	(Uyak et al., 2008)
Lab Prepared Water	DS5 (OSMONICS)	80 – 85% (10 bar)	Conc. 40µg/L	(Uyak et al., 2008)
Lab prepared Water	NF90, Dow Filmtec, Minneapolis, MN, USA	Rejection NF (%)= 40+37* MV-18*MW (2.2 ± 0.1 bar)	50 µg/L	(Doederer et al., 2014)
Real Drinking Water (Alibeykoy)	DK-NF (GE Osmonics)	THM 93% (AOX 75%) (6.9 bar)		(Ates et al., 2009)
Real Drinking Water (Alibeykoy)	DL-NF (GE Osmonics)	THM 96% (AOX 78%) (6.9 bar)		(Ates et al., 2009)

4.2.2.4 Ions

The performance of the NF90 for ion rejection can be qualified as excellent comparing to other nanofiltration membranes. NF90 presents one of the closest values to what we can achieve with a reverse osmosis process, but still maintaining the benefits from using nanofiltration.

In the table shown below (*Table 8*) there is a comparison between different nanofiltration membranes, assessing its ion rejection. This values were obtained by de la Rubia (de la Rubia et al., 2008). In this study water from different rivers of Spain was used, 3 membranes were compared and they used a dead-end-stirred cell.

As can be distinguished, NF90 has the better ion rejection of the 3 membranes compared. Having a rejection higher than 60% in almost all the species and increasing the rejection in more than a 30% compared to the other two membranes.

Table 8 Comparison between 3 diferent membranes NF90 (Dow Filmtec), NF270 (Dow Flimtec) and NFT50 (Alfa Laval). All the rejection are expressed as a percentage. Adapted from (de la Rubia et al., 2008).

Ion	NF90	NF270	NFT50
Ca ²⁺	97.4 ± 1	56.7 ± 9.8	50 ± 18.9
Mg ²⁺	93.6 ± 12	57.3 ± 26.6	52.8 ± 24.4
K ⁺	62.4 ± 15.8	31.2 ± 16.5	27.5 ± 9
Na ⁺	68.4 ± 15.2	35.1 ± 14	30 ± 8.4
CL ⁻	73.6 ± 18.1	12.2 ± 8.1	8.5 ± 6
NO ₃ ⁻	46.1 ± 28.1	27 ± 29.4	10.9 ± 12.4
SO ₄ ²⁻	98.5 ± 0.8	93 ± 1.8	81.6 ± 30.4

Ion sample evaluation was stopped after 36 days of running due to the constant values obtained since the steady state in the membrane was reached.

In the results obtained (Figure 34 & Figure 35) can be observed the relation between ion charge and the rejection by the membrane. This membrane presents a negatively charged surface, therefore the rejection of the membrane increases as the charge of the solute increases. For example a monovalent ion will be less rejected than a divalent ion, the higher charge of the calcium ion produces an addition of water molecules around it that make the rejection increase (e.g. Potassium is less rejected than Calcium). Steric hindrance and molecular size should also be taken into account in order to fully explain the rejection of the membrane.

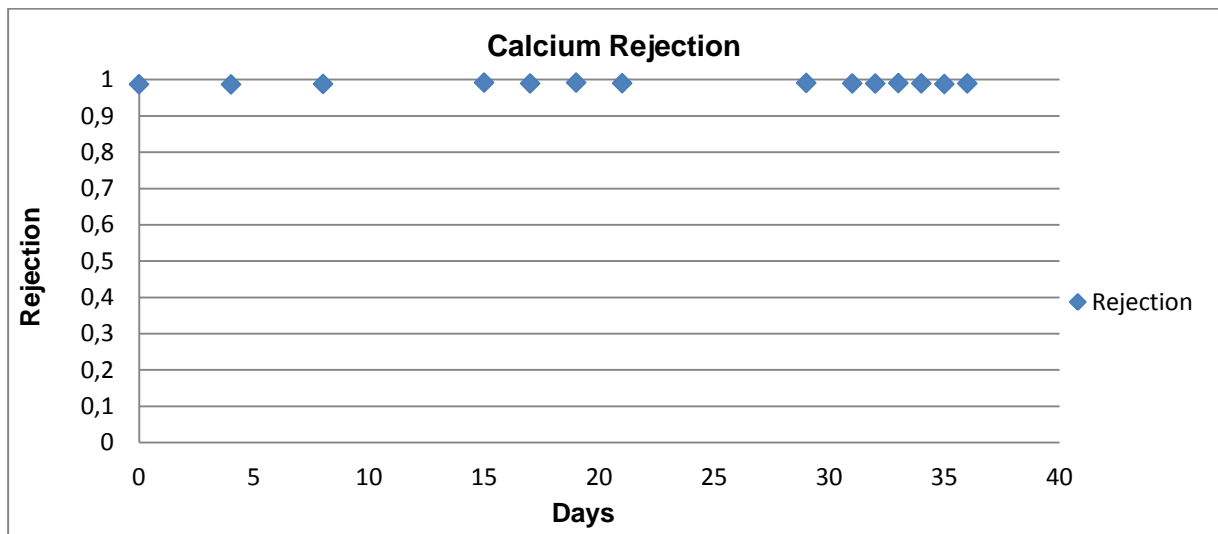


Figure 34 Rejection NF90 - 4040 of calcium ions.

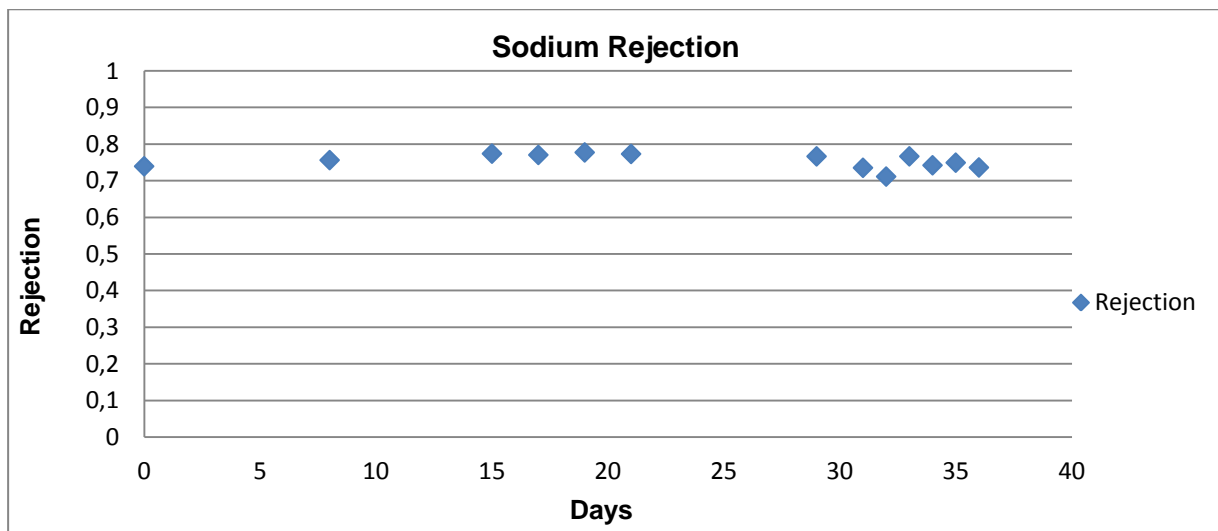


Figure 35 Rejection of NF90 - 4040 of sodium ions.

The ions evaluated in this study by IC and ICP-OES present the following rejections:

Sodium	75% ± 2%
Potassium	82% ± 3%
Calcium	99% ± 0%
Magnesium	99% ± 0%
Silicon	89% ± 2%
Chloride	87% ± 1%
Nitrate	57% ± 4%
Sulphate	99% ± 1%

For complete rejection graphics and tables for all the ions and substances refer to appendix.

4.2.3 Evolution of plant operational parameters

As shown by the data collected from the control panel (*Figure 36*) the permeate flow is decreasing quickly probably due to the fouling of the membrane. In 110 days of operation 17.5% of the flow capacity has been already lost, later data will give us information if this trend will keep like this or the flow loss will become smoother.

However the flow decline was not expected to be that underscored at this early time. Fouling is an important phenomenon for the plant as depending on these results the regular membrane cleaning will be planed affecting also membrane life time and productivity.

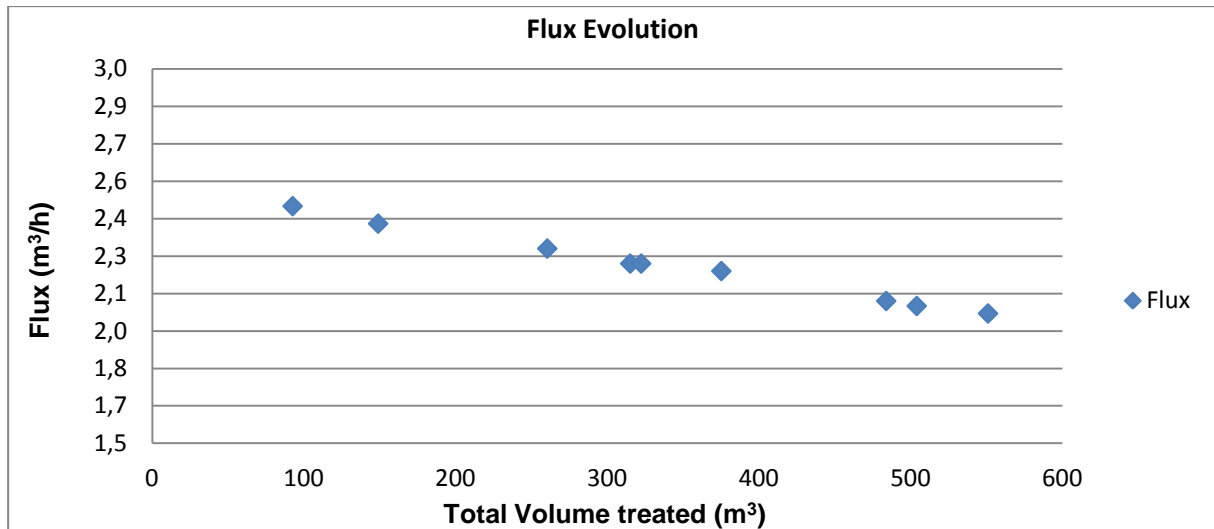


Figure 36 Permeate flow evolution in comparison with the total volume treated. The flow loss with 551 m³ of water treated is 17.5%.

Some studies suggest a relation between increased membrane fouling and the rejection of DOC combined with the rejection of Calcium. (Chang et al., 2012; de la Rubia et al., 2008) As seen before in this case we are rejecting both species. In this study no evaluation of the type of fouling occurring at the membrane was made.

Further studies must be carried out in order to clearly characterize this phenomenon and fully characterize the type of fouling occurring in the case of pool water samples, to know the reason for this exceptionally fast membrane flow decline.

As a consequence of fouling the pressures applied to the system in order to pass through the membrane, maintaining the treatment flow, are also increasing (Figure 37).

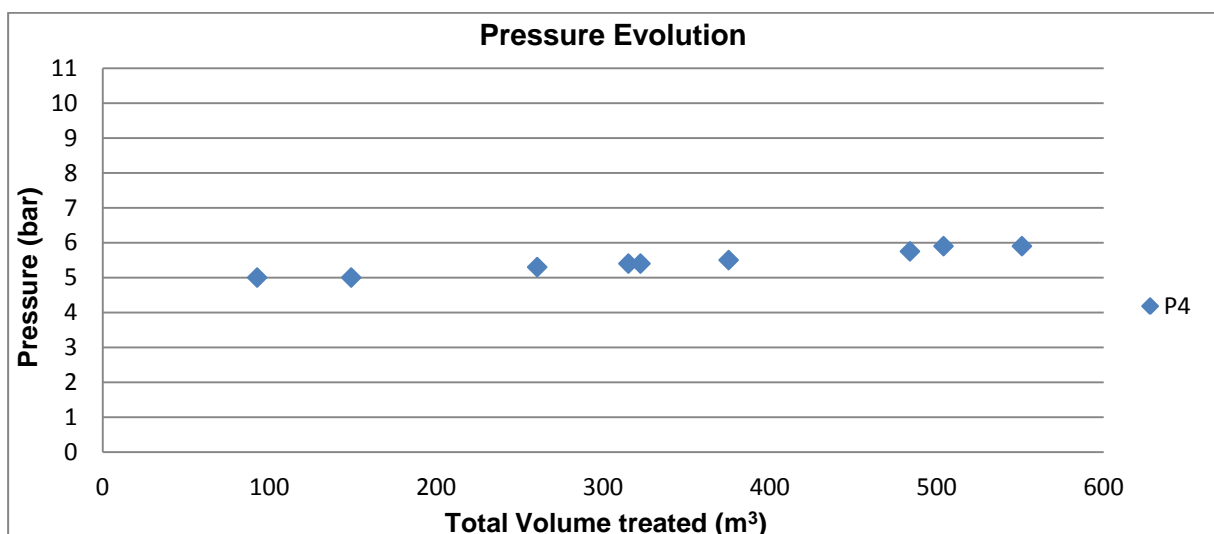


Figure 37 P4 refers to the pressure measured right before the entrance of the flow in the membrane.

4.2.4 Discussion of the effects of the NF plant in the swimming pool system

The comparison between the values of THM, AOX, DOC, formation potentials and ions obtained from the permeate of the nanofiltration and the final values found in the pool water show in some cases good correlations with the global pool values such as the decrease of the global DOC, the formation potential reduction or the ion concentrations.

However, THM and UV-absorbance values have shown no decrease or correlation with the implantation of the new nanofiltration treatment. A possible explanation for this event is the highly DOC-charged raw water of the local area.

Due to its value even a high rejection of DOC achieved by the nanofiltration produces no global change in the pool concentration levels. Every day the pool adds approximately 22 m³ of raw water to the system which far from being beneficial raises the DOC concentration and therefore THM and UV as well. The raw water has a mean of DOC concentration of 3 mg/L.

Our nanofiltration plant treats currently only a 0.3% of the total recycles flow of the pool, meaning approximately 9.7 m³ per day. A comparison (*Table 9*) between the levels of the nanofiltration permeate and the swimming pool water shows the big difference between each state and brings up the need of adjusting the flow rates with the data analysed.

Table 9 Comparison between the parameters of the water taken in the pool (SB) and taken in the permeate flow (P-NF).

Species	SB	P-NF
THM (µg/L)	39 ± 13	12 ± 4
AOX(µg/L)	213 ± 36	11 ± 2
DOC (mg/L)	2.6 ± 0.2	0.5 ± 0.2
EI. Conductivity (µS/cm)	637 ± 20	38 ± 6
UV absorbance ₂₅₄ (Abs/m)	2.4 ± 0.4	0.1 ± 0.1

4.2.5 Plant issues and other events

Since this study has been performed in a real pool some considerations must be made. The first days, (first 8 days) at beginning of the experiment, the plant was not working at full capacity as there were still plant adjustments on going. From the 42nd to the 46th day the plant had problems with completing all the programmed working hours as a consequence of variations on the previous water treatment stage (ultrafiltration).

From day 71 to 81 the nanofiltration plant had a problem with the bisulphite sensor and was shut down for a period of time of 10 days (this event is marked on previous graphs).

Apart from the issues affecting directly to the NF plant during the study, in that period of time, the pool also had events that may affect the results; the most reliable ones are the pool-closing days and the presence of the Christmas holidays during the last part of the study.

5 Conclusions and Future outlook

The nanofiltration plant did show a positive effect on the reduction of the DOC and AOX levels of the pool which are now lower than the levels on the raw water of the area, even with the extra DOC income received by the swimmers.

The DOC rejection rate of the membrane is confirmed to be $84\% \pm 4\%$ which is considered a really good value and show the potential of nanofiltration membrane technology in the removal of dissolved organic matter (so the precursors) from recreational water.

Despite of the DOC reduction, no significant reduction of THM has been found in the global pool water system. Regardless of the large rejection of THM shown by the membrane ($70\% \pm 11\%$) the global pool water did not seem to reduce its high THM levels ($39 \mu\text{g/L} \pm 13$), the most likely explanation is the still too high concentration of precursors (DOC) in the pool water that turns out to be $2.6 \text{ mg/L} \pm 0.2$. The AOX rejection values are also commending ($95\% \pm 2\%$).

These exceptional high levels of precursors are caused by the DOC levels found in the raw water of the local area, with a mean of 3 mg/L plus the DOC received from the swimmers of the pool cause that, even with the high reduction produced by the nanofiltration, the pool concentration levels are yet too high to accomplish the German limits for THM concentration in recreational waters ($20 \mu\text{g/L}$).

The nanofiltration system has shown a great reduction of both AOX and THM formation potentials (93% and 68% respectively). This reduction levels prove the viability of nanofiltration as a method for the reduction of hazardous substances from recreational waters. No genotoxicity was found in the pool water; therefore no characterisation of the membrane behaviour on this field could be done.

Concerning ion rejection the plant showed a good performance with a reduction of the global water electrical conductivity in a 14% (approximately from $710 \mu\text{S/cm}$ to $610 \mu\text{S/cm}$).

The unusual behaviour of the UV absorbance of the pool water must be further analysed to see if an equilibrium point is finally reached and check if the activated carbon shut down had some relation with the initial UV increase.

NF90 – 4040 has shown a fast flow decline during the 110 days of the plant monitoring, having a flow loss of approximately 17.5% (from $2.45 \text{ m}^3/\text{h}$ to $2 \text{ m}^3/\text{h}$) and its corresponding increase in working pressure.

Further studies should be carried out to determine the origin of DOC in pools as in this work no relation between pool assistants/bathers and pool DOC concentration was found. As seen DOC is clearly the precursor of THM. Therefore being able to know the main DOC source will allow to reduce it and to reduce THM concentration.

Future studies should determine the fouling evolution of a membrane like NF90 - 4040 and its characteristics, specifically for pool water treatment. As seen in this work the membrane has experienced a high level of fouling in only 110 days. As this phenomenon is the main drawback of using nanofiltration the development of membranes more fouling-resistant might be a huge evolution in membrane technology.

In the other hand, the fouling phenomenon is inherent to any filtration process and it cannot be completely eliminated. Therefore it is also important to improve the cleaning processes. An improvement of the cleaning processes would also produce an enormous positive impact on the NF industry, as it usually reduces the membrane life time and have limited cycles. An improved membrane cleaning can extend the life of the membrane and enhance its industrial viability.

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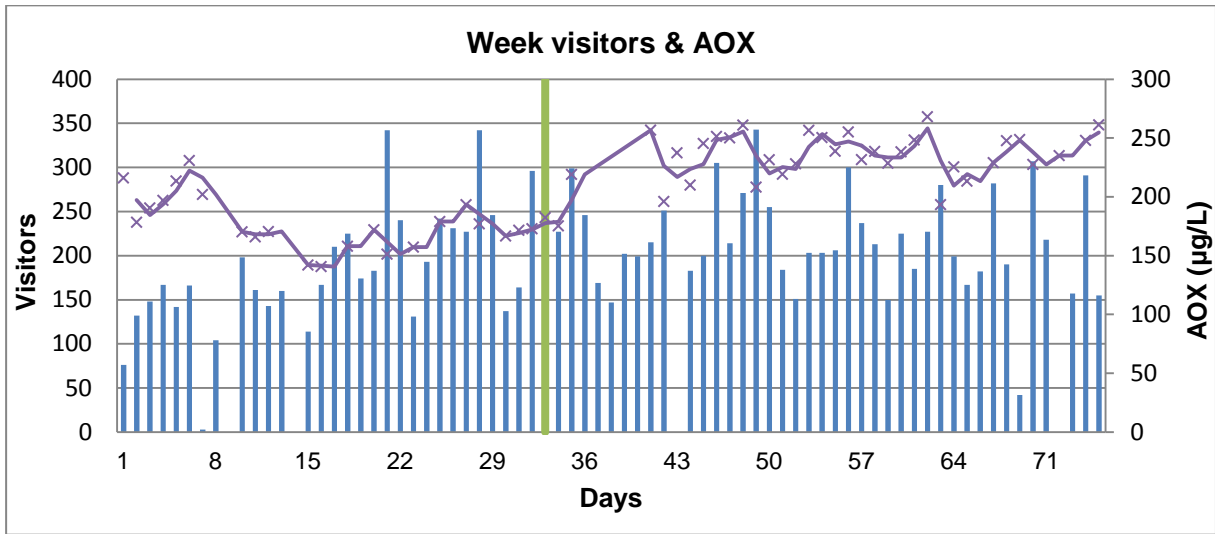


Figure 38 Relation between Week visitors and AOX

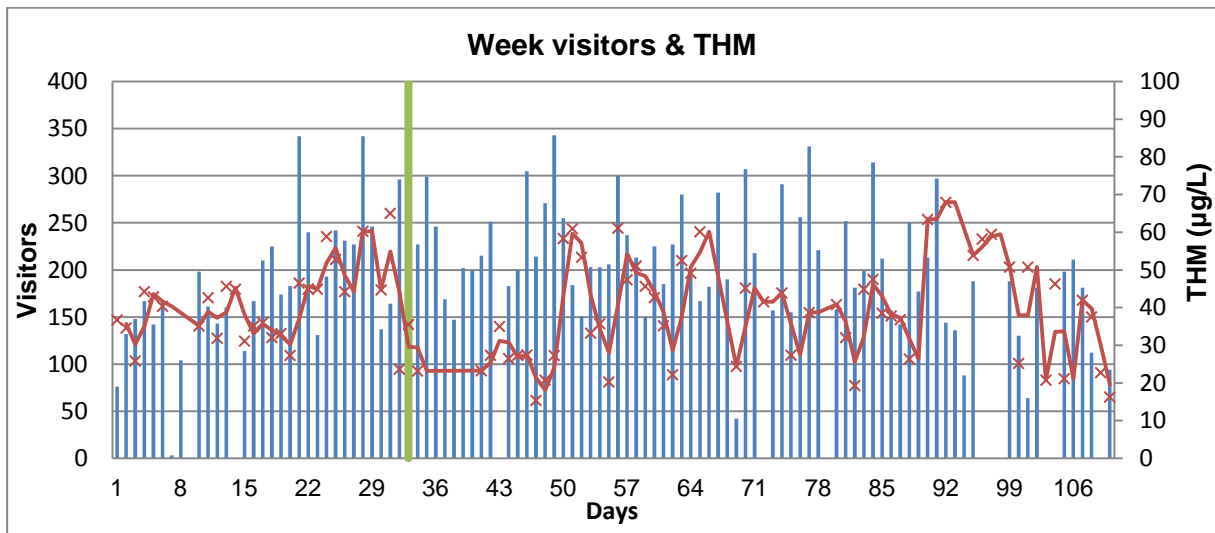


Figure 39 Relation between week visitors and THM

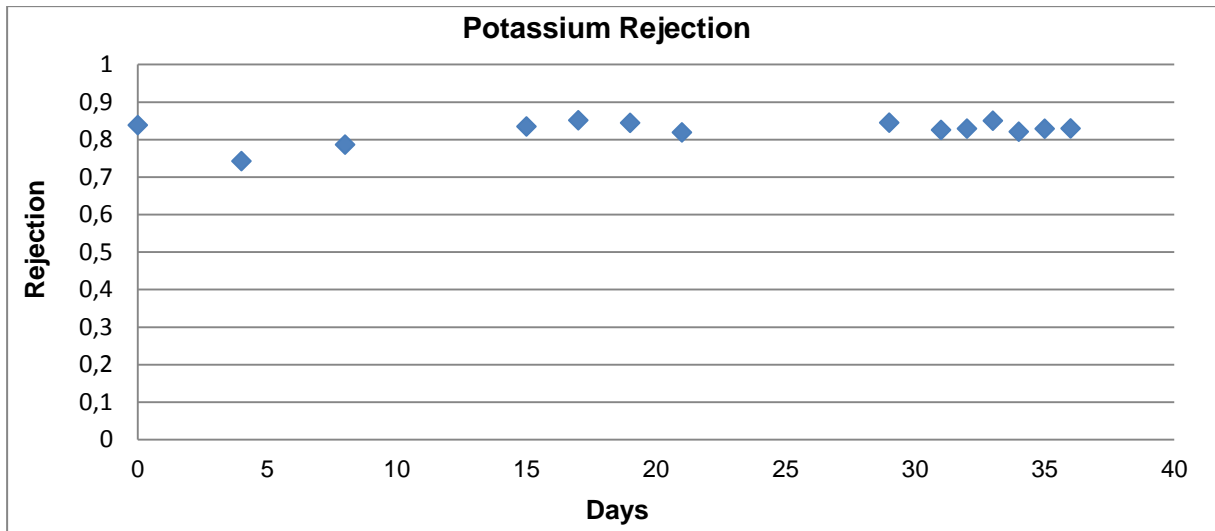


Figure 40 Potassium rejection by the membrane.

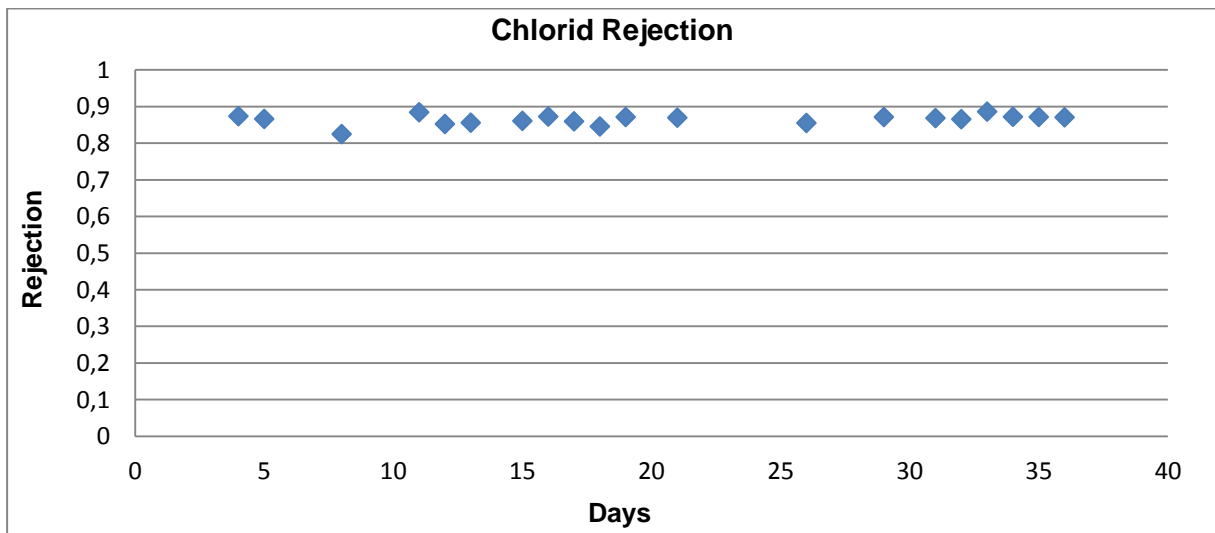


Figure 41 Chlorid rejection by the membrane.

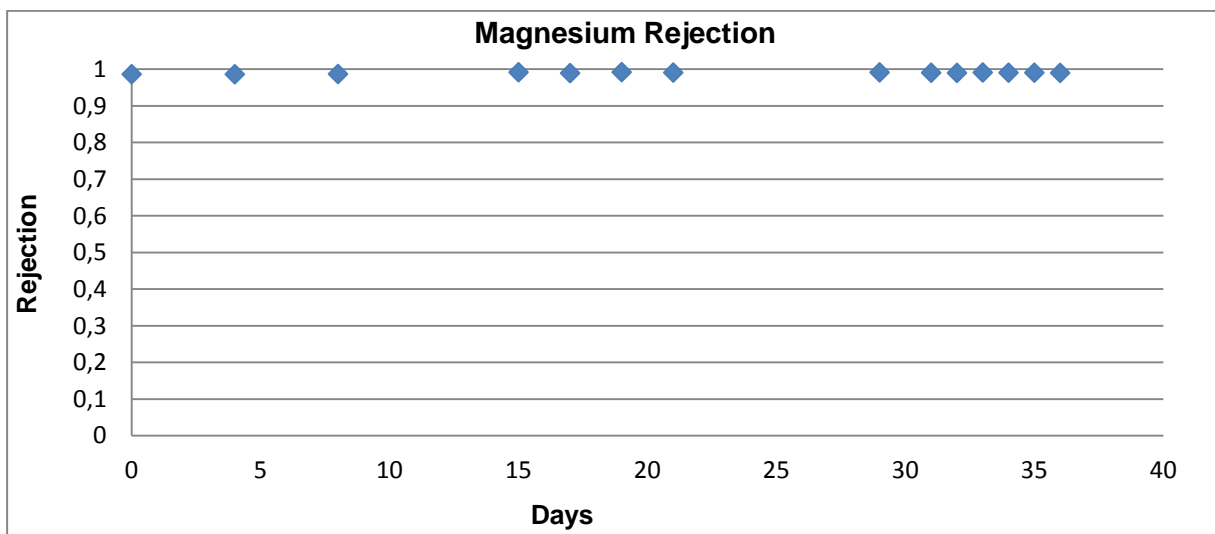


Figure 42 Magnesium rejection by the membrane.

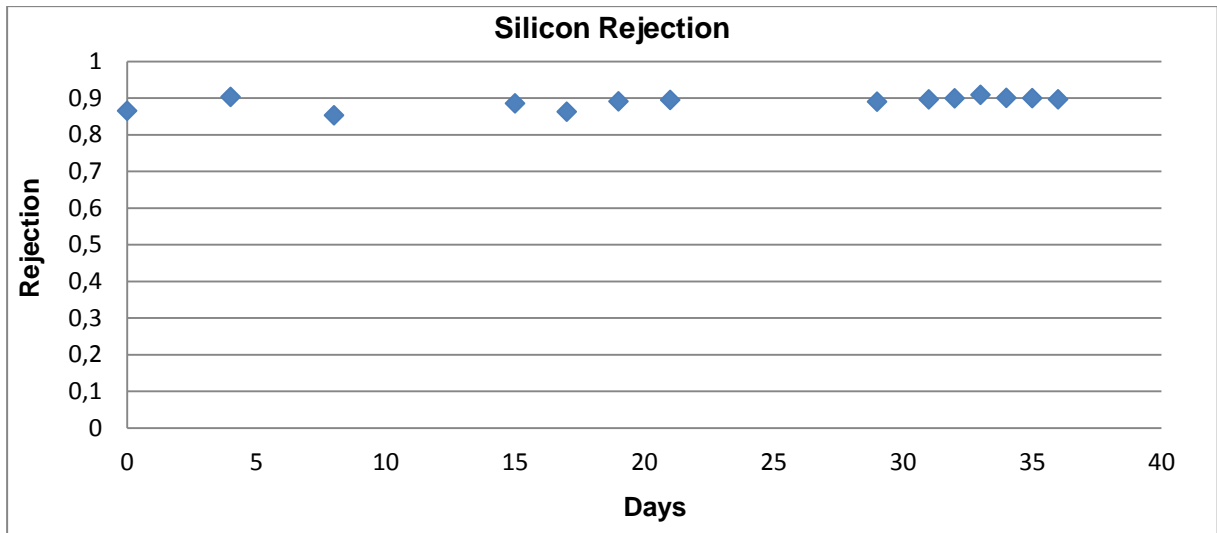


Figure 43 Silicon rejection by the membrane.

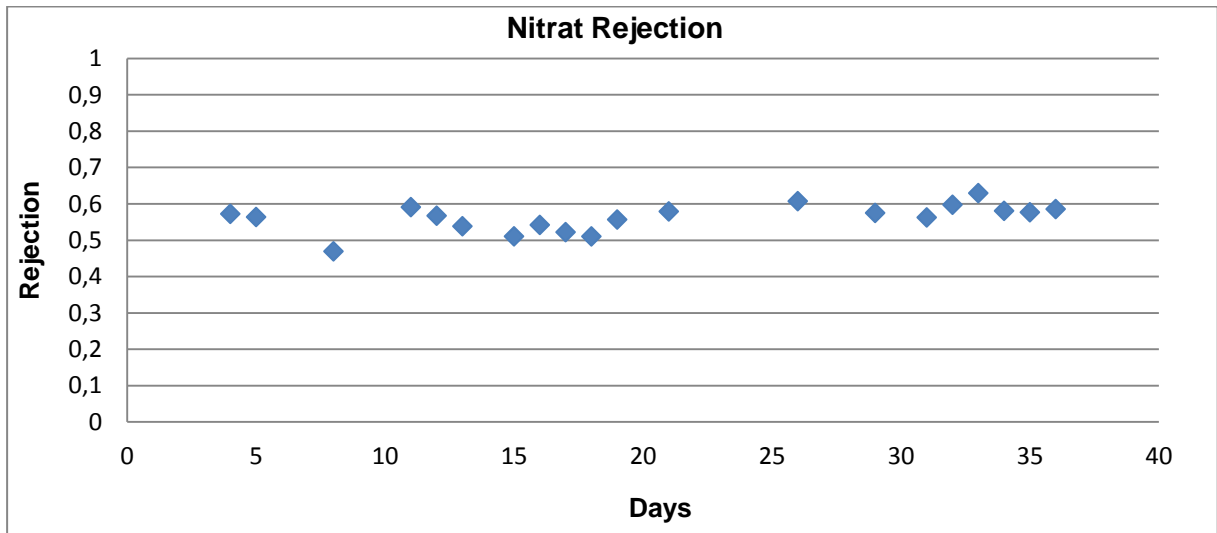


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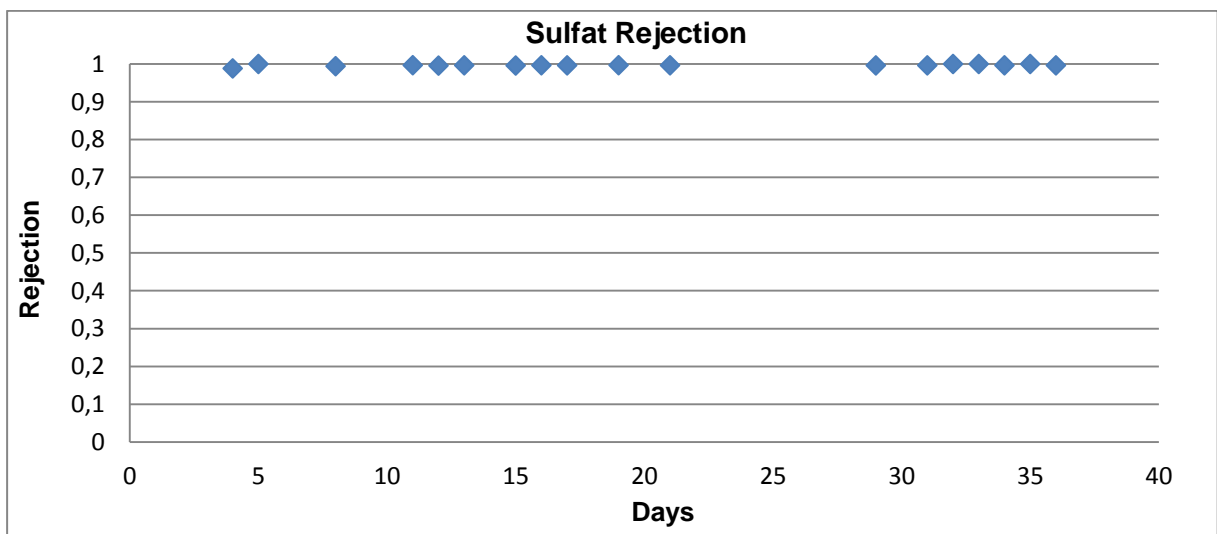


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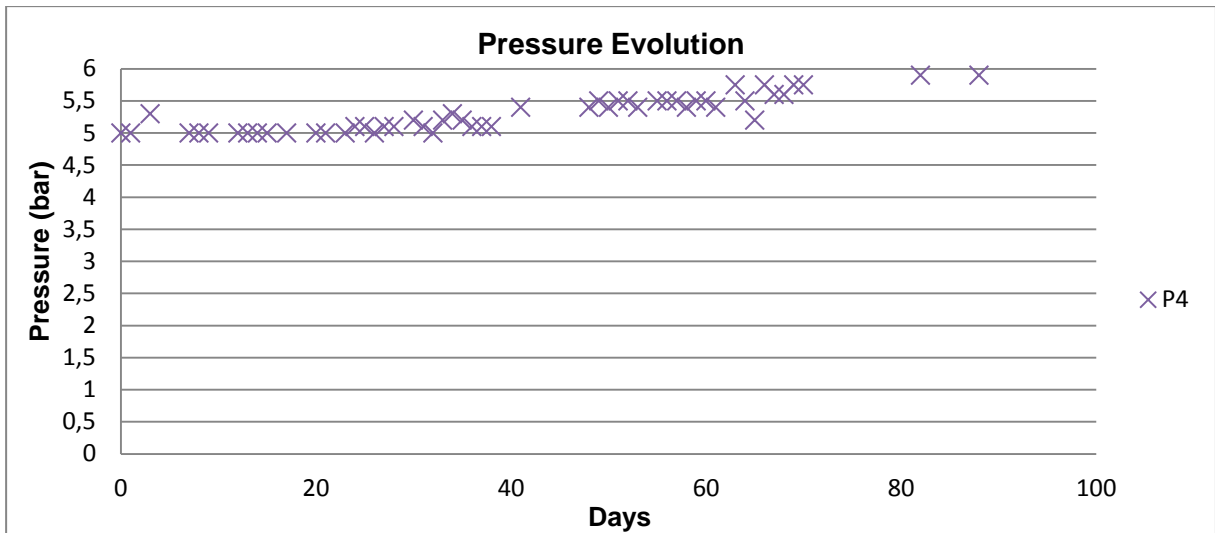


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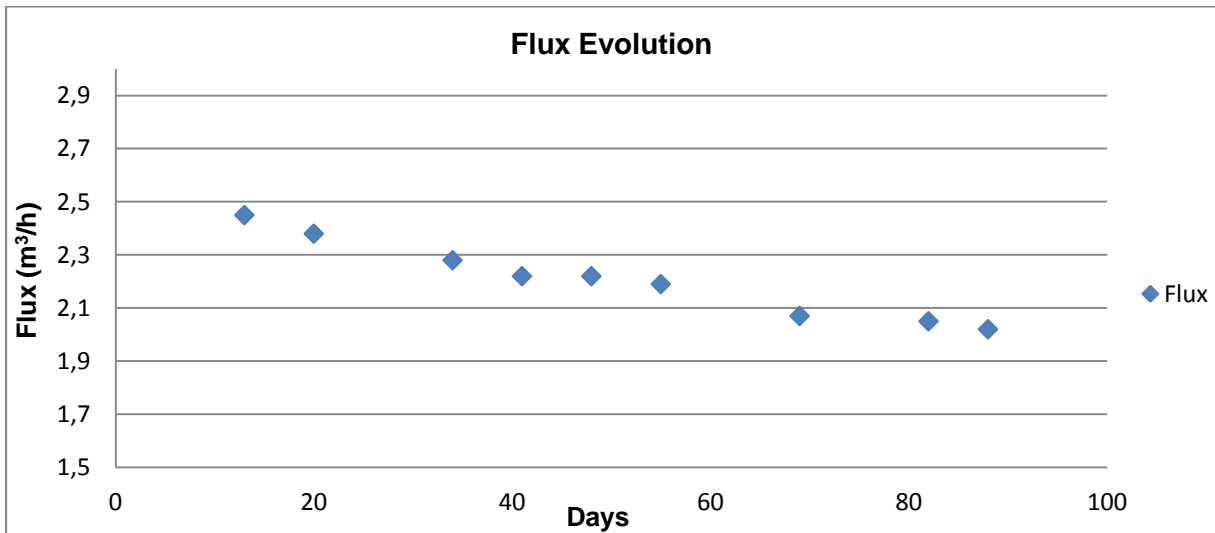


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