Evaluation of membrane technologies for drinking water treatment

Student: Gemma Moncusí Prieto

email address: gemmamoncusi@gmail.com

Master's: Science and technology of water resources

Tutor: Dr. Hèctor Monclús Sales

Institution /Company: LEQUIA

Tutor's signature:

MONCLUS SALES HECTOR - 46143303J

Digitally signed by MONCLUS SALES HECTOR - 46143303J
Date: 2024.09.04 11:14:22 -03'00'

Tutor's full name: Dr. Hèctor Monclús Sales

Institution / Company: LEQUIA

Email address: hector.monclus@udg.edu

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INDEX

RESUM

El clima mediterrani es caracteritza per episodis prolongats de sequera. Actualment, enfrontem un període de sequera que va començar en 2022, la qual cosa ha portat a la imposició de restriccions en l'ús de l'aigua i a variacions en la seva qualitat. La reducció en els volums d'aigua disponibles per a captació ha resultat en una degradació de la seva qualitat, evidenciada per un augment en la concentració de matèria orgànica i la presència de contaminants emergents derivats d'activitats agrícoles i usos quotidians. En aquest context, la implementació de tecnologies avançades, com les membranes de filtració, es presenta com una solució clau per a millorar l'eficàcia i eficiència en el tractament de l'aigua potable, garantint així una qualitat adequada per al consum humà.

Existeixen diverses tipologies de membranes de filtració, classificades en funció de paràmetres com el diàmetre de porus, la pressió d'operació, el pes molecular de tall (MWCO) i la seva composició material. L'elecció de la membrana adequada depèn de les característiques específiques de la solució a tractar i de les condicions operatives del sistema de filtració.

En el present estudi, es van avaluar les capacitats de diferents membranes per a la remoció de matèria orgànica natural (NOM) i contaminants emergents. Es van utilitzar membranes d'ultrafiltració (UF) de fibra buida fabricades en polivinilideno fluorur (PVDF) i dos mòduls de nanofiltració (NF) de fibra buida, un compost per polisulfona (PSU) i l'altre dopat amb òxid de grafè (PSU-GO). Els contaminants emergents avaluats van incloure atrazina, clorpirifos, galaxolide, tonalide i triclosàn.

Es conclou que les membranes de UF són efectives únicament en la remoció de matèria orgànica en suspensió. En contrast, les membranes de NF no sols eliminen matèria orgànica en suspensió, sinó també matèria orgànica dissolta i les seves fraccions húmiques, fúlviques i proteiques. L'eficàcia de les membranes de NF es millora en complementar-les amb materials addicionals com l'òxid de grafè (PSU-GO). No obstant això, en la remoció de contaminants emergents com clorpirifos, galaxolide, tonalide i triclosán, tots dos mòduls de NF mostren una capacitat de retenció total. Quant a la atrazina, el mòdul compost únicament per PSU presenta millors resultats que el PSU-GO, tant en matrius amb NOM com sense ella.

ABSTRACT

The Mediterranean climate is characterized by prolonged episodes of drought. We are currently facing a period of drought that began in 2022, which has led to the imposition of restrictions on water use and variations in water quality. The reduction in the volumes of water available for catchment has resulted in a degradation of its quality, evidenced by an increase in the concentration of organic matter and the presence of emerging contaminants derived from agricultural activities and daily uses. In this context, the implementation of advanced technologies, such as filtration membranes, is a key solution to improve the effectiveness and efficiency of drinking water treatment, thus guaranteeing a quality suitable for human consumption.

There are several types of filtration membranes, classified according to parameters such as pore diameter, operating pressure, molecular weight cut-off (MWCO) and material composition. The choice of the appropriate membrane depends on the specific characteristics of the solution to be treated and the operating conditions of the filtration system.

In the present study, the capabilities of different membranes for the removal of natural organic matter (NOM) and emerging contaminants were evaluated. Hollow fiber ultrafiltration (UF) membranes made of polyvinylidene fluoride (PVDF) and two hollow fiber nanofiltration (NF) modules, one composed of polysulfone (PSU) and the other doped with graphene oxide (PSU-GO), were used. Emerging contaminants evaluated included atrazine, chlorpyrifos, galaxolide, tonalide and triclosan.

It is concluded that UF membranes are effective only in the removal of suspended organic matter. In contrast, NF membranes remove not only suspended organic matter, but also dissolved organic matter and its humic, fulvic and protein fractions. The efficiency of NF membranes is improved by supplementing them with additional materials such as graphene oxide (PSU-GO). However, in the removal of emerging contaminants such as chlorpyrifos, galaxolide, tonalide and triclosan, both NF modules show full retention capacity. As for atrazine, the PSU only module shows better results than the PSU-GO, both in matrices with and without NOM.

1. Introduction

Access to safe drinking water and sanitation is a fundamental human right, recognized by the United Nations General Assembly in 2010 (United Nations General Assembly, 2010). This recognition underlines the essential importance of drinking water for human survival and well-being. In this context, RD 3/2023 defines drinking water as "water for human use, whether in its original state or after treatment, used for drinking, cooking, food preparation, personal hygiene or other domestic purposes". In addition, this Royal Decree stipulates the quality requirements that water intended for human consumption must meet, emphasizing the need to ensure that the water we consume and use daily is safe and of high quality, thus guaranteeing the health and well-being of communities.

In Catalonia (Spain), the rainfall regime is characterized by its irregularity, with prolonged cycles of water scarcity interspersed with intense precipitation events, a result of the predominant Mediterranean climate. This climatic variability leads to recurrent episodes of drought, particularly in the internal river basins, which are home to the highest population density and account for only 40% of the region's available water resources. These water resources are mainly located in reservoirs, aquifers and wells (*El portal de la sequera*, n. d.).

These drought conditions and the limited availability of water in internal watersheds not only affect water supply, but also water quality. Depending on its catchment source, water can contain a variety of contaminants, including natural organic matter (NOM), heavy metals and other chemical compounds. Overexploitation of water resources and the use of chemicals can significantly alter the composition of water, introducing contaminants that are difficult to remove with conventional treatment methods. Traditional techniques such as coagulation-flocculation, gravity filtration, and chlorination, while effective for certain types of contaminants, are often inadequate for treating dissolved organic matter (DOM) and emerging contaminants (Crittenden et al., 2012).

To overcome these limitations, membrane technologies have established themselves as advanced and effective solutions. These technologies provide superior separation capacity compared to conventional methods, more efficiently addressing the presence of difficult-to-treat contaminants and significantly improving drinking water quality (Yoon et al., 2007). Their implementation represents a crucial advance in water treatment, addressing modern pollution challenges and contributing to more effective water resource management.

1.1. Drinking water treatment plants

Water that requires treatment to become potable is processed in Drinking Water Treatment Plants (DWTP). These facilities integrate a series of physicochemical unit operations designed to produce water suitable for human consumption. The most common stages include collection, coagulation-flocculation, sedimentation, filtration and disinfection.

Since inlet water quality can vary significantly, DWTPs tailor their unit operations to the specific composition of the raw water. This may involve eliminating or incorporating additional treatment stages, such as pre-oxidation, which improves the performance of subsequent stages by oxidizing organic matter and reducing pathogens. Also, many stations have incorporated adsorption with activated carbon to improve the organoleptic characteristics of the water and reduce dissolved organic matter (DOM).

To better understand the process, it is important to analyze in detail the most common unit operations in DWTPs:

- **Catchment and roughing**

Catchment is the first stage of drinking water treatment, where water is extracted from different sources such as groundwater, surface water or seawater (Crittenden et al., 2012). The abstraction is done through infrastructures such as wells, reservoirs and rivers, and its objective is to ensure a continuous supply of water to the treatment plant. The selection of the water source and the design of the catchment system are critical steps in the water treatment process.

Before the water enters the treatment system, roughing, a preliminary process that uses screens and sieves to remove coarse solids and bulky materials from the water before it enters the treatment system, is performed to protect downstream equipment and processes from clogging.

- **Coagulation-Flocculation**

Coagulation is a physicochemical process aimed at reducing the repulsion potential of the electrical double layer of colloids by adding various coagulants. This process causes the destabilization of the colloidal microparticles, facilitating their initial grouping. Subsequently, the flocculation stage follows, where these destabilized particles agglomerate into larger flocs, facilitating their separation.

This agglomeration phenomenon involves several mechanisms, including charge neutralization, entrapment, adsorption, and complexation with the metal ions of the coagulant, resulting in the formation of insoluble aggregates (Sillanpää et al., 2018).

- **Sedimentation**

After the coagulation-flocculation process, the sedimentation stage follows, where the flocs formed during flocculation and suspended matter in the water settle to the bottom (Santiago Román, 2020). This stage facilitates a remarkable removal of color and turbidity from the water (Cortés Pinzón & Mora Fajardo, 2015). The settled particles at the bottom constitute the settler sludge, which is periodically removed by purges to the sanitation system.

- **Filtration**

Filtration is a crucial unit operation that facilitates the removal of suspended particles and flocs that have not been adequately removed in the previous stages of treatment. This process consists of the separation of solid particles from a fluid by passing them through a porous media. The most used porous media include sand filters, anthracite, garnet and magnetite, among others (de Vargas, n. d.). In addition to gravity filtration methods, there are other methods that use the pressure difference as a driving force, such as filtration membranes (Section 1.2.).

Filtration acts as a final stage of refinement, providing the ultimate polish to the treated water. There are several types of filtrations, which are classified according to the size of the particles to be separated and the direction of flow (Perez, 2008).

- **Adsorption**

According to Crittenden et al. (2012) in their book "MWH's Water Treatment: Principles and Design", adsorption on activated carbon is an increasingly common unit operation in drinking water treatment, generally implemented after the filtration stage. This process allows the efficient removal of dissolved organic matter, which can cause odor, taste and color problems in treated water. In addition, adsorption on activated carbon is effective for the removal of heavy metals (Shen et al., 2019) and emerging contaminants (Rathi & Kumar, 2021).

- **Disinfection**

Disinfection is a critical step in drinking water treatment plants, designed to eliminate pathogens and prevent biological regrowth in the water distribution system. To achieve this, it is essential to maintain a minimum disinfectant residual throughout the system.

Chlorine and its compounds are the most widely used disinfectants in drinking water treatment, mainly due to their low cost and effectiveness in maintaining a residual level that ensures continuous protection against biological contaminants. However, it is crucial to control the concentration of chlorine, as high levels can be toxic and cause problems in the treated water.

Therefore, the chlorine residual is kept within limits set by RD 3/2023 to ensure the safety and quality of distributed water (Ohar & Ostfeld, 2014).

One of the most controlled parameters of the disinfection cap is the formation of disinfection by-products (DBPs). The reaction of chlorine with NOM in raw water, results in the formation of trihalomethanes (THMs), haloacetonitriles (HANs), haloacetic acids (HAAs) and other chemical compounds. The most common classes of DBPs in chlorinated drinking water are THMs, which include chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), and bromoform ($CHBr_3$) (Mohd Zainudin et al., 2018).

1.2. Filtration membranes

In technology, a membrane is a thin film that can be made of polymeric, organo-mineral, ceramic or metallic materials with selective permeability properties. Membrane-based separation methods take advantage of this selective permeability to affect the separation of components. To function, a membrane requires two bulk phases physically separated by a third phase, the membrane, which acts as an interface between these two phases (Ho & Sirkar, 1992). The driving force for transporting materials across the membrane is a pressure difference (Berk, 2009).

Membrane technology is used for activities such as desalination, wastewater treatment, water recycling, and in general, for drinking water production (Gonzalez-Perez et al., 2018).

1.2.1. Type of membranes

There are various membrane processes with industrial applications. Depending on the pore size and pressure requirements, membranes can be classified into microfiltration (MF) (2 to 0.1 µm and 1 to 4 bar), ultrafiltration (UF) (0.1 to 0.005 µm and 2 to 7 bar), nanofiltration (NF) (0.005 to 0.0005 µm and >6 bar) and reverse osmosis (RO) (<0.5 nm and >10 bar) (Gonzalez-Perez et al., 2018).

These membranes are used for different applications depending on the type of dissolved and suspended components to be rejected (Figure 1). MF and UF are genuine filtration processes in which particle size is practically the only criterion for permeability or rejection. MF is used to remove suspended particles, while UF also can remove bacteria and viruses. In contrast, RO membranes are used to reject dissolved components such as monovalent salts, separating particles at the molecular level and basing their selectivity on the chemical nature of the particles. NF is essentially a membrane process similar to RO, but with a selectivity intermediate between UF and RO, allowing it to reject multivalent salts and sugars (Berk, 2009).

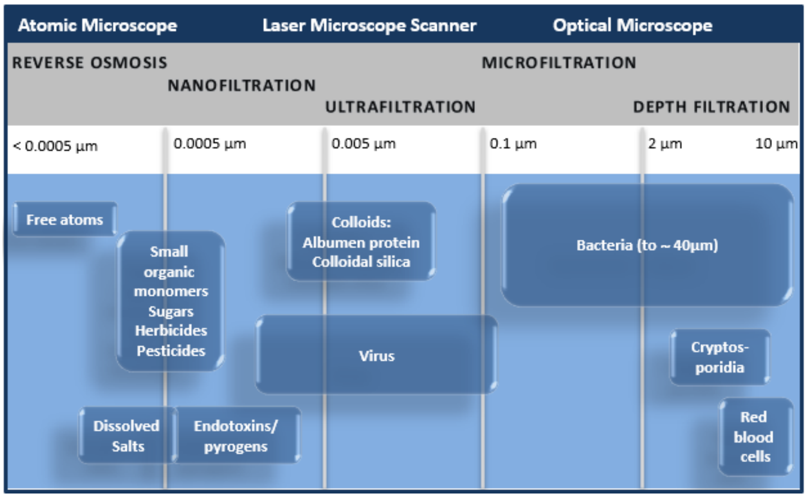


Figure 1: Membrane separation range.

Ultrafiltration (UF)

UF is a membrane separation process based primarily on molecular size exclusion and the application of pressure. Membranes used in UF have pores ranging from 100 to 1,000 Å, allowing them to retain molecules with molecular weights between 300 and 500,000 Da. Typical species retained include sugars, biomolecules, polymers and colloidal particles. Most UF membranes are described by their molecular weight cut-off (MWCO), which is defined as the lowest molecular weight of a species for which the membrane exhibits greater than 90% rejection (Ho & Sirkar, 1992).

Given the structural control of pore size on separation efficiency, UF membranes have been widely used in industrial separation and purification processes, as well as in research applications, mainly for the concentration of suspended solids, natural organic compounds, colloidal particles and macromolecular species (Kammakakam & Lai, 2023).

- **Materials for UF membranes**

From a material point of view, UF membranes are conventionally classified as inorganic membranes or polymeric membranes.

UF separation processes using inorganic membranes generally consist of materials such as ceramics, non-oxide metals, graphite, phosphates and clays. These membranes are mainly used in the dairy industry, fruit juice concentration and wastewater treatment. Although asymmetric and microporous inorganic membranes offer excellent separation properties, including moderate permeability, permeability and selectivity, as well as remarkable chemical and thermal stability, their high cost and limited reproducibility restrict their full applicability, making them less competitive in the market (Hernández et al., 1999).

On the other hand, more than 90% of UF membranes are made of polymeric materials, many of which have been successfully commercialized in various industrial applications, establishing themselves as the leading choices in UF separation processes. Polymeric membranes composed of poly(vinylidene fluoride) (PVDF), polysulfone (PSF), polyethersulfone (PES), polyacrylonitrile (PAN) and cellulose acetate (CA) have emerged as key materials in UF technology due to their excellent permeation properties, low operational footprint, large specific surface area and lower fabrication costs compared to other conventional separation techniques (Kammakakam & Lai, 2023).

In recent years, research has focused on the incorporation of nanoparticles into polymeric membranes, such as carbon nanotubes (CNTs), zeolites, and Cu nanoparticles, SiO_2, Ag, Fe_3O_4, Al_2O_3, ZrO_2, ZnO and TiO_2 (Castro-Muñoz, 2020), which are widely used in the fabrication of mixed matrix membranes.

<u>Nanofiltration (NF)</u>

NF membranes have evolved significantly since their initial recognition in the late 1980s. With properties intermediate between UF and RO, NF membranes have a typical pore size of 1 nm, corresponding to a MWCO of 300-500 Da.

Similar to RO membranes, NF membranes are effective in the separation of inorganic salts and small organic molecules. Their main features include low monovalent ion rejection, high divalent ion rejection and higher flux compared to RO membranes. These properties have enabled the application of NF membranes in various fields, especially in water and wastewater treatment, pharmaceuticals, biotechnology and food engineering (Mohammad et al., 2015).

- **Materials for NF membranes**

Nanofiltration membranes are classified according to their constituent materials into organic, inorganic and hybrid organic-inorganic.

Organic membranes are mainly made of polymeric materials such as polysulfone, cellulose acetate or polyvinylidene fluoride. On the other hand, inorganic membranes are traditionally made from ceramics such as TiO2, SiO2, ZrO2, Al2O3, TiO2-SiO2, TiO2-ZrO2 and Al2O3-SiC. More recently, inorganic nanomaterials such as graphene and carbon nanotubes have been used. Organic-inorganic hybrid membranes are prepared by mixing polymeric materials with inorganic components, which can be metals, metal oxides, or carbon-based materials (Wang et al., 2018).

Nanomaterials are excellent for fabricating a variety of NF membranes. Among the most common are metal and metal oxide nanoparticles, which are blended with polymeric matrices to improve properties such as flux and rejection (Ji et al., 2017). Carbon nanotubes (CNTs) are notable for their hydrophobic and smooth inner walls, facilitating water passage and improving separation and antifouling properties when added to mixed matrices (Zhao et al., 2016).

Graphene, a two-dimensional (2D) material with exceptional properties, has proven to be an effective building block for nanofiltration, especially in water treatment and small particle separation. Graphene is a planar monolayer of carbon atoms arranged in a honeycomb structure, which gives it high permeability and selectivity, excellent electrical conductivity, chemical stability and robust mechanical properties. These characteristics make graphene ideal for a variety of applications, including sensors and transparent conductive films (García Doménech et al., 2020).

Oxidized graphene (GO) is another 2D nanomaterial that has found wide applications in the NF. Unlike graphene, GO contains oxygen functional groups that are produced by a partial oxidation process of graphene sheets (Hu & Mi, 2013). These functional groups make GO an ideal candidate for energy and biomedical applications. GO sheets are attractive as membrane building blocks due to their facile synthesis, mechanical robustness, and scalability for industrial applications. In addition, GO membranes exhibit thermal and chemical stability, making them suitable for various nanofiltration applications (Huang et al., 2014).

Other 2D materials, similar to graphene, have also recently been used in the fabrication of NF membranes. Boron nitride (BN), known as "white graphene," is transparent, electrically insulating, chemically stable, and mechanically strong. However, it is less frequently used than other 2D nanomaterials (Pakdel et al., 2013). Transition metal dichalcogenides (TMDs), such as molybdenum disulfide (MoS2), exhibit unique physical and electronic properties. MoS2 is a semiconductor with a wide range of applications, including solid lubricants and catalysts. MoS2 membranes exhibit much higher water permeability than graphene membranes of similar thickness, as well as high chemical stability under adverse conditions, allowing for repeated use (García Doménech et al., 2020).

- **Separation mechanism:**

Nanofiltration is a complex process influenced by microhydrodynamic and interfacial phenomena present on the membrane surface and nanopores. Solute rejection in NF membranes is due to a combination of steric, Donnan and transport effects (Mohammad et al., 2015).

- Steric effect: The transport of neutral solutes is mainly through size-based exclusion, similar to the mechanism observed in ultrafiltration membranes.
- Donnan effect: This effect describes interactions between charged species and the membrane interface, influenced by the dissociation of ionizable groups at the membrane

surface and within the pores. The membrane charge can vary according to the pH of the solution and the composition of the membrane materials (Donnan, 1995).

- Ion exchange: NF membranes have a weak ion exchange capacity. Ions present in the solution can adsorb on the membrane surface, slightly altering its charge (Afonso et al., 2001).
- Obstructed transport: Solute transport in the NF is influenced by the local environment and is considered to be limited, presenting convective and diffusive components.

The precise structure and electrical properties of NF membranes are not yet fully understood due to current technological limitations, leading to debate about the exact separation mechanisms.

1.2.2. Configurations

The operating system used to operate the membranes is called modules. A module includes the membrane, the pressure support structure, and the connections for the feed inlet, as well as for the concentrate and permeate outlet. There are different module configurations based on the membrane arrangement (Ayala et al., 2006):

- **Plate and frame module:** Configuration formed by flat plates and frames that allow a uniform flow of the fluid through the membranes, optimizing filtration (Figure 2.A). They offer great ease of maintenance, thanks to the ability to disassemble and clean components individually, and their modularity, which allows the number of plates to be adjusted according to specific needs. However, they are highly complex and costly to install, as well as bulky and heavy, which may limit their use in confined spaces.

- **Spiral Wrap:** Highly efficient and compact configuration, consisting of a flat membrane wrapped around a central perforated tube (Figure 2.B). The feed flow moves parallel to the permeate flow. This design allows handling high flow volumes with low pressure loss and reduces fouling by maintaining a turbulent flow. However, it has limitations in terms of difficulty of cleaning and maintenance and can be more susceptible to fouling if adequate flow is not maintained.

- **Tubular:** Configuration formed by tubes internally lined with membranes (Figure 2.C), allowing the feed flow to pass through the inside and the permeate to percolate to the outside. This design is ideal for treating fluids with high levels of suspended solids or high viscosity, offering high resistance to fouling and ease of cleaning using clean-in-place (CIP) techniques. However, it has a smaller membrane surface area per unit volume, which can result in larger and more expensive modules, and greater complexity in manufacturing and maintenance due to the need for robust structural supports.

- **Hollow fiber:** A configuration that uses thin, hollow fibers with membranes on their surface (Figure 2.D), allowing a high surface-to-volume ratio and high treatment capacity in a small space. The feed flow can pass both inside and outside the fibers. It features high efficiency in separation and handling of high flow volumes with low pressure loss, making it ideal for space-constrained applications and easy to clean using clean-in-place (CIP) techniques. However, hollow fibers can be more susceptible to fouling and blockage, can be more complex and costly to manufacture, and their structural integrity can be compromised under extreme conditions.

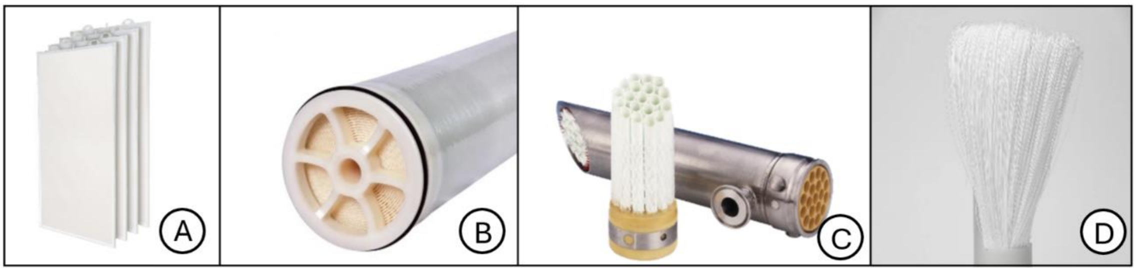


Figure 2: A) Plate and frame module configuration. B) Spiral Wrap configuration. C) Tubular configuration. D) Hollow fiber configuration.

1.2.3. Control Parameters

In order to control the state of the membranes, there are a number of key parameters that allow us to have an idea of the characteristics of the membrane at a given moment, such as permeate flux (J), transmembrane pressure (TMP) and permeability (K).

Flux (J): Volume of permeate passing through the membrane per unit area and time. This parameter is expressed in liters per square meter of membrane surface in one hour (LMH).

$$J = \frac{Q_p\ (L \cdot h^{-1})}{S_m\ (m^2)} = [L \cdot m^{-2} \cdot\ h^{-1}] \equiv LMH$$

(Eq. 1)

Where:

Q_p: Permeate flow.

S_m: Membrane surface area.

Transmembrane pressure (TMP): Difference between the pressure applied on the outside of the membrane and the suction pressure on the inside. Since liquids do not flow naturally through a membrane, it is necessary to apply a pressure for them to pass through the membrane. This pressure is not constant and varies depending on the degree of fouling of the membrane.

Permeability (K): This parameter is defined as the ratio between flux and transmembrane pressure (TMP). It is used to evaluate the state of the membrane and to check the efficiency of the cleaning process.

$$K = \frac{J}{TMP} = [L \cdot m^{-2} \cdot\ h^{-1} \cdot Bar^{-1}] \equiv LMH \cdot bar^{-1} \qquad \text{(Eq. 2)}$$

1.2.3. Membrane cleaning systems

As mentioned above, membranes act as a selective barrier to certain compounds, depending on both the characteristics of the membrane and the compound to be removed. Unwanted compounds accumulate on the membrane surface, which, if not removed, can reduce its performance, eventually rendering it unusable.

For this reason, cleaning procedures are necessary to maintain optimum membrane performance. There are different types of cleaning, such as physical cleaning, including backwashing, and chemical cleaning, which will be described below.

- **Backwashing**

Backwashing is a technique commonly used to clean filtration membranes and restore their performance. During the filtration process, unwanted particles and compounds accumulate on the membrane surface, forming a layer of solids or “cake”, which can lead to clogging of the pores, an increase in transmembrane pressure and, consequently, a decrease in permeability and separation efficiency.

Backflushing involves reversing the flow of water or solution across the membrane, i.e. in the opposite direction to normal filtration. To do this, water is taken from the ultrafiltered water tank and pumped through the membrane at a high flow rate, in the reverse direction of the filtration process. This generates a pressure that expels the particles accumulated on the membrane surface and in its pores, releasing the obstructions and cleaning the membrane.

Periodic backwashing can restore permeate flux, prolong membrane life and reduce the need for chemical cleanings. However, this technique has limited efficiency, as it is most effective for removing large, loose particles on the membrane surface, but less effective for removing contaminants that have become deeply embedded in the membrane pores (Chapinal Lázaro, 2013).

- **Chemical cleaning**

Chemical washing is a fundamental process in the maintenance of filtration membranes, designed to remove contaminants that cannot be effectively removed by physical methods such as backwashing. These contaminants, which can include organic, inorganic, biological and colloidal substances, are usually deeply embedded in the membrane pores or strongly adhered to the membrane surface.

The choice of chemical agent depends on the type of fouling present on the membrane:

- **Organic contamination**: compounds such as sodium hypochlorite, specialized detergents (e.g., Divos, Lavasol), which break down and remove accumulated organic material, are used.
- **Inorganic contamination:** Acids such as oxalic acid, ascorbic acid and citric acid are applied, which dissolve and remove mineral deposits and other inorganic scale.

The chemical washing process is generally carried out in controlled cycles, where the cleaning solution is recirculated through the membrane system for a set period. Often, a sequence of washes is employed to maximize the removal of various types of contaminants.

During chemical washing, it is crucial to control key parameters such as pH, chemical reagent concentration, temperature and contact time, as inadequate control of these factors can damage the membrane or decrease the efficiency of the process. Once the washing is completed, a rinse with clean water or a neutralizing solution should be performed to remove any remaining chemical residue, thus avoiding contamination of the permeate during normal operation (Chapinal Lázaro, 2013).

1.3. Natural organic matter

Natural organic matter (NOM) is a complex mixture of organic substances commonly found in surface and groundwater. This organic matrix originates from a variety of hydrological, biological and geological interactions. NOM can be generated within the water body through biological processes, primarily the activity of algae and microorganisms, known as autochthonous NOM, or it can enter the aquatic system from surrounding watersheds through drainage of materials resulting from the decomposition of terrestrial organisms, known as allochthonous NOM (Sillanpää et al., 2018).

Autochthonous NOM is mainly composed of humic substances, the composition of which can vary considerably depending on the geological and hydrological conditions of the ecosystem and its catchment of origin. Biological activities, which depend on the metabolism of the algal and bacterial species involved, typically generate soluble macromolecules, both extracellular and intracellular, including carbohydrates, amino acids, peptides, enzymes, and toxins (Hudson et al., 2007).

The presence of NOM in drinking water represents a significant challenge to water quality and treatment processes. Their presence can negatively affect water quality by contributing to coloration, altering taste and odor, and increasing the required doses of coagulants and disinfectants. This, in turn, results in increased sludge generation and potential production of disinfection by-products (DBP). Additionally, NOM favors biological growth in the distribution system and can increase the levels of complexed heavy metals and adsorbed organic contaminants.

In practice, the characterization of NOM is usually performed by techniques such as the measurement of Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), absorbance at 254 nm in the ultraviolet spectrum (UV254) and Chemical Oxygen Demand (COD). These analytical techniques allow the quantification of NOM, which is a determining factor in the yellowish-parched coloration of water, making color measurement a possible indirect indicator of the presence of NOM. Although these tests are rapid and do not require complex sample pretreatment or sophisticated analytical equipment, their main limitation is that they provide quantitative data on NOM, offering limited characterization in terms of its specific structure or composition.

For a more comprehensive characterization of NOM, advanced techniques such as size exclusion chromatography (SEC), liquid chromatography coupled to mass spectrometry (LC-MS), nuclear magnetic resonance (NMR) and three-dimensional fluorescence emission spectroscopy (EEM) are employed. These methodologies allow us to unravel the complexity of NOM, identifying different fractions of organic matter and providing detailed information on their origin, molecular structure and chemical reactivity (Matilainen et al., 2011).

1.4. Emerging contaminants

The increasing chemical contamination of surface and groundwater represents a significant challenge whose long-term consequences on aquatic ecosystems and human health are not yet fully understood. This phenomenon could escalate into a problem of comparable or even greater magnitude than current environmental crises. Approximately one-third of the planet's renewable freshwater is used for agricultural, industrial and domestic activities, which introduce a variety of synthetic and geogenic compounds that degrade water quality (Schwarzenbach et al., 2006).

Among the main contributors to this pollution are wastewater discharges, which significantly impair surface water quality by introducing organic pollutants that are not completely removed during conventional treatment processes (Kolpin et al., 2004). These emerging pollutants, such as pharmaceuticals, personal care products, pesticides, and industrial compounds, are of increasing concern due to their persistence in the environment, their potential for bioaccumulation, and the adverse effects they can cause on human health and aquatic life (Schriks et al., 2010).

Because many of these contaminants have been present in the aquatic environment for a long time, but could not be detected due to their low concentrations, they have not traditionally been subject to regulations limiting their presence in water. However, advances in analytical technologies, such as mass spectrometry coupled to gas and liquid chromatography, have enabled their identification.

In response to this growing concern, the European Commission established a few years ago the Watch List, which is updated every two years to include new emerging contaminants to be monitored by each Member State. These States are obliged to carry out the corresponding analyses and send the results to the European Commission, which is responsible for evaluating whether these pollutants should be incorporated into the List of Priority Substances (*Ministerio para la Transición Ecológica y el Reto Demográfico*, n. d.).

2. Hypothesis and motivation

As mentioned above, membrane technology represents a significant advance in drinking water purification processes. Membranes, particularly nanofiltration membranes, allow for tighter retention of compounds, surpassing ultrafiltration membranes in terms of efficiency, while reducing negative interactions in subsequent unit operations. When combined with materials such as graphene oxide, these membranes acquire enhanced properties that optimize their performance. In addition, they provide a highly efficient physical barrier, ensuring the stability and safety of the treated water against variations in inlet water quality, which can be induced by the effects of climate change, such as the indirect use of reclaimed water, torrential rains and scarcity of water resources.

This study is developed in the framework of a research contract with the Cicle de l'Aigua del Ter and is part of the ShERLOcK project, with the aim of optimizing drinking water treatment processes. The research seeks to advance in the monitoring and improvement of water purification treatments, contributing to the efficiency and effectiveness of these processes.

3. Objectives

The main objective of this work is to evaluate different membrane technologies to optimize the effectiveness and efficiency in the treatment of drinking water, especially in the face of alterations in the composition of the input water, which may be caused by factors such as climate change. To achieve this general objective, the following sub-objectives are proposed:

- To evaluate the organic matter removal capacity by UF and NF membranes.
- To compare the efficiency of NF with different compositions.
- To study the removal capacity of emerging contaminants by NF membranes.
- To analyze the removal behavior of emerging contaminants in the presence of organic matter through the nanofiltration process.

4. Methodology

4.1. Sampling

In order to carry out the experimental trials, it is essential to have water with characteristics representative of those found in drinking water treatment plants. For this purpose, incoming raw water was sampled at the Montfullà Drinking Water Treatment Plant (DWTP), located 7 km from the city of Girona. This facility manages a catchment flow of 1410 L/s, coming from the Pasteral II supply source (Servei d'Aigües de Girona, Salt i Sarrià de Ter S.A., n. d.). This sampling was carried out to evaluate the efficiency of the membranes in the removal of turbidity and dissolved organic matter.

In addition, a sampling of treated water was carried out at the Campdorà Wastewater Treatment Plant (WWTP), located in Girona, which processes wastewater from the municipalities of Girona, Salt, Sarrià de Ter, Sant Julià de Ramis, Aiguaviva, Vilablareix, Fornells de la Selva, Bescanó and Palol de Revardit (TRARGISA, SA, n. d.). This sampling was carried out to obtain a matrix with a high organic matter content, in order to analyze the behavior of certain pollutants under these conditions.

4.2. Ultrafiltration membranes

The ultrafiltration membranes used to study the organic matter removal capacity of water intended for human consumption are STERAPORE™ (Training) hollow fiber polymeric membranes from the Mitsubishi Chemical Group. The construction of these modules is detailed in Section 4.2.1, and their specific characteristics are described in Table 1.

According to Gan et al. (2021), ultrafiltration membrane separation technology, especially organic hollow fiber membranes, has been widely applied in WTPs due to their high efficiency in removing particulates, viruses, and bacteria.

The ultrafiltration membranes used are composed of polyvinylidene fluoride (PVDF), a polymer widely used in membrane manufacturing due to its advantages such as high purity, excellent mechanical strength and remarkable resistance to chlorine, solvents, acids, bases and heat. However, PVDF membranes are not inherently water-wettable, which limits their applicability in the filtration of aqueous solutions. In addition, they exhibit a high tendency to fouling when filtering solutions containing proteins and NOM (Pezeshk et al., 2012). Despite these limitations, PVDF-UF membranes are mainly used in three applications: water purification in DWTPs, pretreatment in desalination plants and wastewater recovery for industrial use (Ji et al., 2015).

Table 1: Characteristics of the ultrafiltration hollow fibers used.

Item	Hollow fibers STERAPORE™ (Training)
Membrane material	PVDF
Pore Size	0.05 µm
Outer Diameter	1.65 mm
Fibres lenght	0.145 m
Number of fibres	10
Total Surface area	0.0075 m^2

4.2.1. Module construction

The procedure for the manufacture of parallel ultrafiltration modules follows the following steps: First, the appropriate number of fibers required to make up the module is selected. Next, two tubes of approximately 5 cm each are cut. One end of one of the tubes is sealed and partially filled with resin, without reaching the top. The fibers are inserted into the resin before the resin dries completely, ensuring adhesion and sealing at one end. The resin is then allowed to dry completely.

The second tube is then placed at the opposite end of the fibers, allowing the fibers to protrude slightly, and resin is added to fill the tube, making sure to avoid bubble formation and to ensure that the fibers are well covered and spaced apart. Once the resin has dried completely, the end where the fibers emerge is slightly cut, verifying that none of them is obstructed by the resin, since this will be the end through which the permeate will be obtained.

Finally, a module integrity test is performed, and its permeability is calculated.

4.2.2. Integrity test

Once the modules have been manufactured, their structural integrity is verified. For this purpose, the modules are immersed in a container with water and compressed air at a pressure of 1 bar is applied inside the fibers. This test makes it possible to identify the presence of defective or poorly sealed fibers, which would be manifested by the emission of large bubbles; in such a case, the module would be discarded. If the module passes the integrity test satisfactorily, it is then subjected to a detailed characterization.

4.3. Nanofiltration membranes

Two nanofiltration membranes from MEDICA S.p.A. were used in this study, with different compositions between them (Table 2).

The first is the Medisulfone® membrane, a nanofiltration membrane composed of polysulfone (PSU), used in the field of dialysis to obtain ultrapure dialysate, and in various other applications for the retention of bacteria, viruses and endotoxins, particles/microplastics, and more generally all substances with a molecular weight greater than 15 kDa and dimensions greater than 0.005 µm.

The second is the Graphisulfone® membrane, a nanofiltration membrane composed of polysulfone and reinforced with graphene oxide (PSU-GO), capable of retaining bacteria and viruses in water, retaining in general all substances with a molecular weight greater than 15 kDa and sizes greater than 0.005 µm, as well as removing emerging contaminants such as PFAS, heavy metals, antibiotics and pesticides (*Purificazione acqua*, n. d.)

Table 2: Characteristics of the nanofiltration membranes used.

Item	Medisulfone	Graphisulfone
Number of membranas fibres	Approx. 1500	Approx. 1400
Internal diameter	0.25 mm	0.27 mm
Fibres lenght	Approx. 300 mm (U shape)	
Total Surface area	0.35 m^2	0.36 m^2
Pore size	0.005 µm	

PSU is one of the most widely used materials in membrane manufacturing due to its exceptional mechanical, thermal and chemical stability. These properties make it particularly suitable for the production of porous membranes used in processes ranging from MF to NF. In addition, PSU stands out for its remarkable ability to form uniform films, making it a preferred material in separation and filtration applications (Abdelhamid et al., 2020).

The incorporation of two-dimensional (2D) graphene-based materials has enabled the development of doped membranes that exhibit improved properties in terms of thermal and mechanical conductivity, ion exchange capacity, and arsenate removal efficiency, among other advantages, compared to their undoped counterparts (Zambianchi et al., 2022).

In particular, PSU-GO adsorbent membranes, with 5% by weight of GO, have been shown to have a high capacity to adsorb emerging contaminants in drinking water mixtures. These membranes show significant improvement in the removal of hydrophilic molecules, such as the antibiotics ofloxacin, carbamazepine and diclofenac. The polarity of the molecules to be removed plays a key role in the adsorption efficiency with GO; the higher the polarity of the compound, the higher the adsorption efficiency. However, the solubility of the compounds does not seem to significantly influence the removal efficiency (Zambianchi et al., 2017).

4.4. Filtration assembly

To perform the permeability tests of the modules and other tests, two filtration systems were established: one for ultrafiltration (Figure 3) and the other for nanofiltration (Figure 4).

The ultrafiltration system consists of immersing the membranes in a vessel containing water or the sample to be filtered. The membranes are connected to a peristaltic pump via a tube, which generates a suction force to push the water through the membrane. The permeate is collected in a beaker through the same tubing. In addition, a pressure sensor coupled to a data logger was integrated, allowing the pressure to be monitored and controlled during the tests.

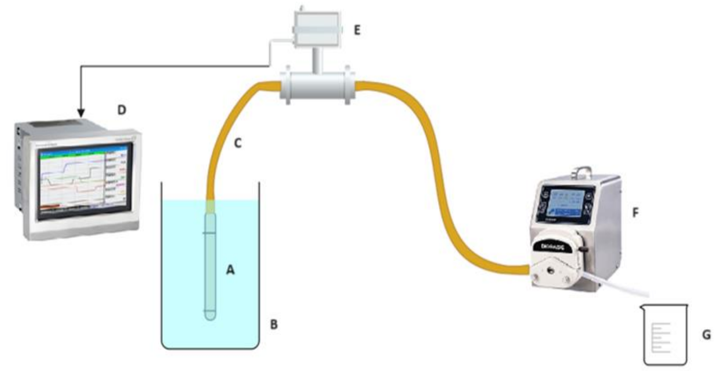


Figure 3: Schematic of the ultrafiltration setup: (A) ultrafiltration module, (B) vessel with sample to be filtered, (C) silicone tubing, (D) Memograph M RSG45, (E) pressure reader, (F) peristaltic pump and (G) vessel to collect permeate.

In the nanofiltration system, the main difference with respect to the ultrafiltration system is that the membranes are not immersed in the water or sample. Instead, the sample is pumped from a vessel to the membranes, where filtration takes place, and the permeate is collected afterwards.

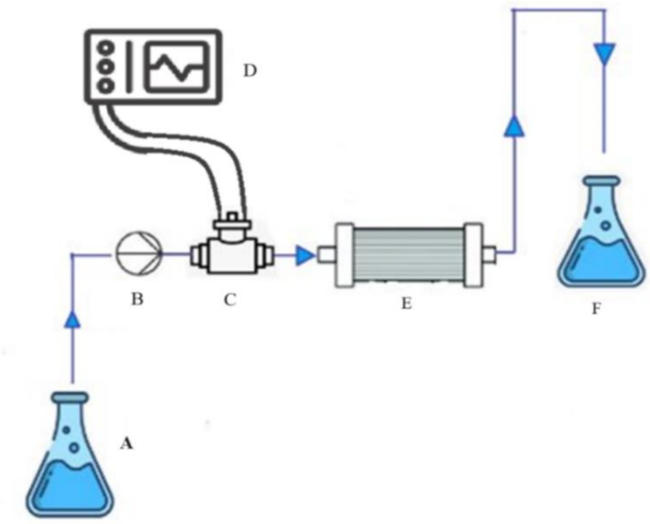


Figure 4: Schematic of the nanofiltration setup: (A) vessel with sample to be filtered, (B) peristaltic pump, (C) pressure reader, (D) Memograph M RSG45, (E) nanofiltration module and, (F) vessel to collect permeate.

4.5. Permeability test

Permeability is an essential parameter to characterize the condition of filtration membranes. To determine permeability, Milli-Q water is filtered at different revolutions per minute (rpm). The permeate flow rate (L/h) is measured and, together with the total external surface area of the membrane (m^2), the flux (LMH) is calculated. Using the transmembrane pressures (Bar) corresponding to each velocity, the pressure is plotted as a function of flux, and the trend line is drawn (Figure 5). The slope of this line represents the membrane permeability.

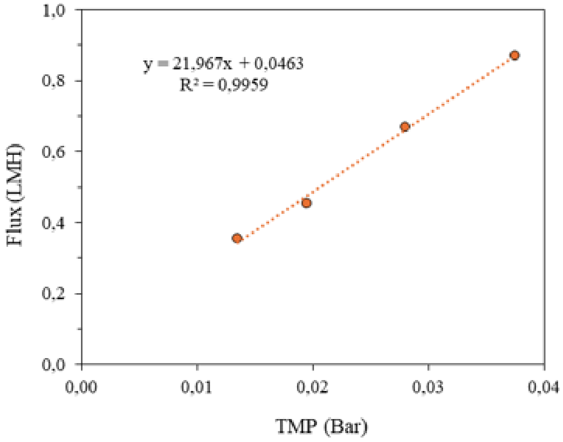


Figure 5: Example of the representation of flux as a function of transmembrane pressure, where the slope of the equation of the line corresponds to membrane permeability.

4.6. Tests performed

In order to meet the proposed objectives, four different types of tests were carried out, starting with the characterization of the membranes by calculating their permeability.

- **Organic matter removal by UF:**

In this test, a sample of raw water from the inlet of the DWTP was used. This sample was filtered using ultrafiltration modules, and the permeate was characterized at different time intervals.

- **Organic matter removal by NF:**

This test replicated the previous procedure, but employing two NF modules (PSU and PSU-GO) instead of ultrafiltration.

- **Removal of emerging contaminants by NF:**

For this assay, a solution containing 600 ppb of the studied emerging contaminants (atrazine, chlorpyrifos, galaxolide, tonalide and triclosan) was prepared in a tap water matrix. The solution was filtered through NF modules (PSU and PSU-GO), and the concentration of these contaminants in the permeate was monitored over time. Subsequently, a backwash with Milli-Q water was performed to quantify the amount of recovered compounds and to determine the fraction retained on the membrane, using a mass balance.

- **Removal of emerging contaminants in an organic matter matrix by NF:**

This test is similar to the previous one, with the difference that the matrix in which the emerging contaminants are found is composed of a mixture of treated water from the WWTP and distilled water in a 50:50 ratio.

4.7. Water characterization

4.7.1. Turbidity

Turbidity is a parameter of great sanitary importance, since it reflects the presence of colloidal, mineral or organic materials, and can be an indication of contamination (Marcó et al., 2004). To measure turbidity, an optical technique is employed using the HACH TU5200 turbidity meter, which measures light scattering caused by suspended particles and provides values in units of NTU (Nephelometric Turbidity Units).

4.7.2. Absorbance UV 254

UV absorbance at 254 nm is measured with the Agilent Cary UV-Vis Compact spectrophotometer. This technique allows the determination of absorbance, which is the amount of energy necessary for a molecule to pass from its fundamental state to an excited state, where this energy is absorbed (Díaz et al., n. d.). Absorbance is calculated as the difference between the light emitted and the light absorbed by the organic matter in the sample. This measurement is essential to determine the concentration of dissolved organic matter in water and to evaluate the efficiency of treatment processes, since dissolved organic matter (DOM) is one of the main compounds to be removed from water because it can increase microbiological and chemical risk. During the disinfection stage, the reaction of MOD with chlorinated products can form trihalomethanes, which are potentially hazardous compounds.

4.7.3. Fluorescence Spectroscopy

Another technique used to study the quality of drinking water is fluorescence emission spectroscopy, where organic matter is measured with fluorescent capabilities. This technique is performed with the Cary Eclipse Fluorescence Spectophotometre instrument of the Agilent commercial brand, and consists of the emission of a beam of light with wavelengths within the ultraviolet light range, which generates the excitation of the external electrons of the molecules, and when these return to their fundamental state, they emit energy as fluorescence.

In this case, an emission wavelength range of 250-580 nm and excitation wavelength range of 220-450 nm with steps of 5 nm in both cases (Hudson et al., 2007), and we obtain Excitation-

Emission Matrices (Figure 6) where different intensities are observed depending on the amount of organic matter with specific fluorescent capacities, in which different peaks can be identified. Peak A corresponds to the fulvic type organic matter fraction and is found in the Ex/Em lengths between 237-260 nm/400-500 nm; peak C corresponds to the humic type organic matter fraction and is found in the Ex/Em lengths between 300-370 nm/400-500 nm; finally peak T corresponds to the tryptophan type protein fraction and is found in the Ex/Em lengths between 225-237 nm/340-381 nm (Coble, 1996).

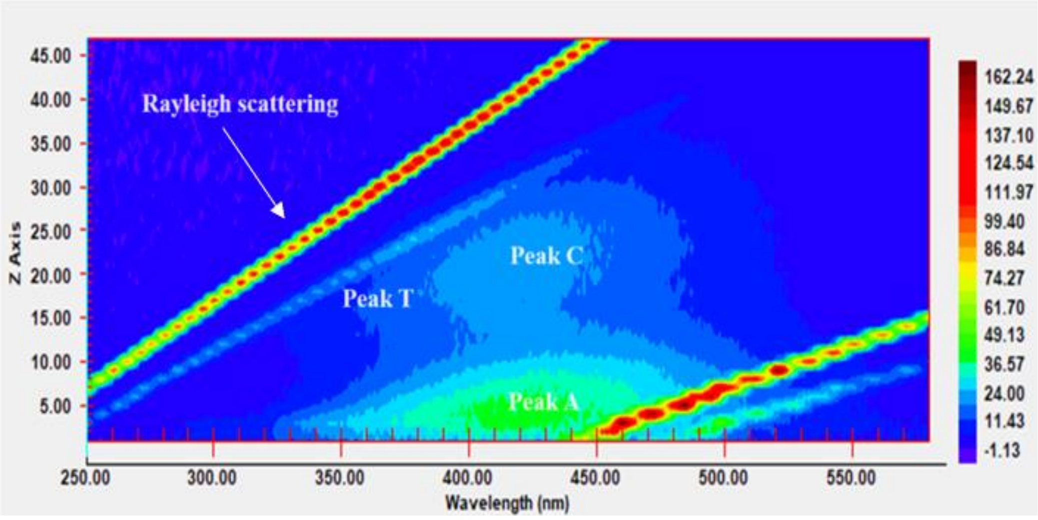


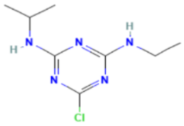
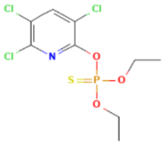
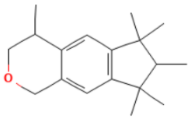
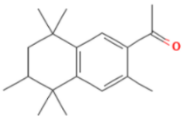
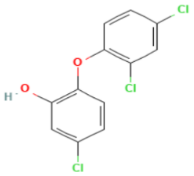
Figure 6: Excitation-Emission matrix with the different peaks identified. Peak A represents the fulvic-type organic fraction (medium molecular weight), peak C corresponds to the humic-type organic fraction (high molecular weight) and peak T to the protein organic fraction (low molecular weight). The side lines are caused by Rayleigh scattering, resulting in analysis interferences (Tan et al., 2020).

4.8. Emerging contaminants

To evaluate the performance of different nanofiltration membranes in the removal of emerging contaminants present in water intended for drinking water treatment, five semi-volatile organic compounds were selected (Table 3). These contaminants are present in a wide variety of chemicals for human use, including insecticides and pesticides applied to agricultural crops, as well as compounds present in personal hygiene products.

One of the criteria for the selection of these compounds was the ability to analyze them with the equipment and techniques present in the facilities.

Table 3: Characteristics of the organic compounds selected as emerging contaminants for testing.

Compund	Molecular formula	Molecular weight (g mol^{-1})	Boiling temperature	Chemical structure
Atrazine	$C_8H_{14}ClN_5$	215.68 g/mol	205 °C	
Chlophyrifos	$C_9H_{11}Cl_{13}NO_3PS$	350.6 g/mol	160 °C	
Galaxolide	$C_{18}H_{26}O$	258.4 g/mol	128 °C at 0.8 mm Hg	
Tonalide	$C_{18}H_{26}O$	258.4 g/mol	326 °C	
Triclosan	$C_{12}H_7Cl_3O_2$	289.5 g/mol	120°C	

Source: Pubchem

Atrazine is a triazine herbicide widely used for weed control in agriculture. Although it has low acute toxicity, it is an emerging contaminant of concern due to its persistence in water and soil, genotoxic potential, and associated environmental risks (Graymore et al., 2001). Chlorpyrifos is an organophosphate insecticide widely used in agriculture for pest control. Its persistence and toxicity make it an emerging contaminant of environmental concern (Ubaid ur Rahman et al., 2021). Both galaxolide and tonalide, polycyclic musk compounds commonly used in personal care products, persist in the environment due to incomplete removal in wastewater treatment plants. These two musks are relatively recalcitrant to degradation in the environment (Li et al., 2022). Triclosan is a chlorinated compound widely used in antibacterial and antifungal products, which acts on a specific bacterial enzyme. Its use contributes to the development of microbial resistance and poses environmental risks, as it can form toxic compounds such as dioxins (Schweizer, 2001).

4.9. Solid phase microextraction

To analyze compounds at low concentrations, it is necessary to perform a pretreatment before injecting the sample into the GC/MS. Since these are organic compounds with a certain volatility, it was decided to perform a solid phase microextraction (SPME) directly from the sample.

A SPME fiber with a fused silica core assembled with stainless steel (Fused Silica/SS) was used. The fiber cladding is 65 micrometers thick and is composed of a mixture of polydimethylsiloxane (PDMS) and divinylbenzene (DVB). This specific PDMS/DVB coating provides optimal characteristics for the extraction and analysis of volatile and semi-volatile organic compounds, due to its ability to interact with both polar and non-polar compounds.

The microextraction procedure consisted of exposing the fiber directly to the sample to be analyzed for 30 minutes, and then performing the GC/MS analysis manually.

4.9. Data processing

In order to interpret the results correctly, proper data processing is essential. Since the tests were performed with water samples taken on different days, the matrix of these samples may vary. For this reason, to compare the results of the different tests, the relative concentrations (Ct/Co) of the different parameters studied will be represented.

To evaluate the efficiency of the treatments on the different parameters and allow their comparison, the reductions (Equation 3) of these parameters in relation to the initial value of the raw water will be calculated.

$$Reduction\,(\%) = \frac{\left(\frac{Co}{Co}\right) - \left(\frac{Ct}{Co}\right)}{\left(\frac{Co}{Co}\right)} \cdot 100\%$$

(Eq. 3)

To determine whether the values obtained show significant variability, the coefficient of variation (CV) is calculated from the arithmetic mean ($\overline{x}$) and the standard deviation (S), as shown in Equation X (Vargas, V., 2007).

$$CV = \frac{S}{\overline{x}} \cdot 100\%$$

(Eq. 4)

The interpretation of the coefficient of variation is as follows:

- If CV ≤ 30%, the data are little variable or homogeneous with respect to the mean.
- If 30% < CV ≤ 70%, the data have moderate variability or are heterogeneous with respect to the mean.
- If CV > 70%, the data are highly variable or very heterogeneous with respect to the mean.

In analyzing the retention capacity of emerging contaminants by nanofiltration membranes, a mass balance will be performed for each compound analyzed to determine what portion of the compound can be recovered by backwashing the membranes and what is retained on the membranes. This will be calculated using Equation 5:

$$Recovery\ (\%) = \frac{M_{bw}}{M_i - M_p} \cdot 100\%$$

(Eq. 5)

To carry out the mass balance, the following equations will be used:

$$M_{initial} = M_{permeate} + M_{backwashing}$$

(Eq. 6)

$$M_{initial} = C_o \cdot V_{filtering}$$

(Eq. 7)

$$M_{permeate} = \Sigma_i \left[C_p(t_i) \cdot Q \cdot \Delta t \right]$$

(Eq. 8)

$$M_{bw} = C_{bw} \cdot V_{bw}$$

(Eq. 9)

5. Results and discussion

5.1. Organic matter removal capacity of UF membranes

As described in the methodology section, the ultrafiltration modules were constructed in the laboratory. Subsequently, an integrity test was performed, in which no air leaks were detected, indicating that the modules were assembled correctly. Next, the permeability test was performed to characterize the module performance, obtaining a permeability of 863.2 LMH/Bar, as shown in Figure 7. This permeability presents a correlation coefficient of 0.9996, indicating an excellent linear correlation of the flow with respect to the different pressures applied.

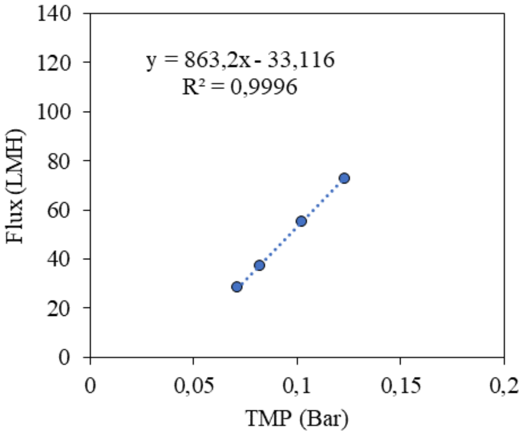


Figure 7: Relationship between the flux and the different transmembrane pressures applied, with a linear adjustment that allows determining the permeability of the ultrafiltration membrane.

Once the permeability has been determined and the value is consistent, the test is performed.

When evaluating the capacity to remove organic matter, both dissolved and suspended, present in the DWTP inlet water using ultrafiltration membranes, it has been confirmed that these membranes show limited efficiency in the retention of dissolved organic matter, although they are effective in the removal of suspended particles, which is reflected in the reduction of turbidity.

The results obtained (Figure 8) show a significant decrease in turbidity from the first sampling point, reaching a reduction of 84 % compared to the raw water, which presented an initial value of 1.21 NTU. However, with regard to dissolved organic matter, evaluated by absorbance at 254 nm and fractions differentiated by their fluorescent properties (peak C, peak A and peak T), the observed reductions were minimal. The initial values were 0.064 in absorbance at 254 nm, and 28.81, 56.9 and 35.61 in the intensity of peaks C, A and T, respectively. The greatest reduction was observed in Peak T, with 15 %, while in Peak C no reduction was detected, remaining at 0 % compared to raw water.

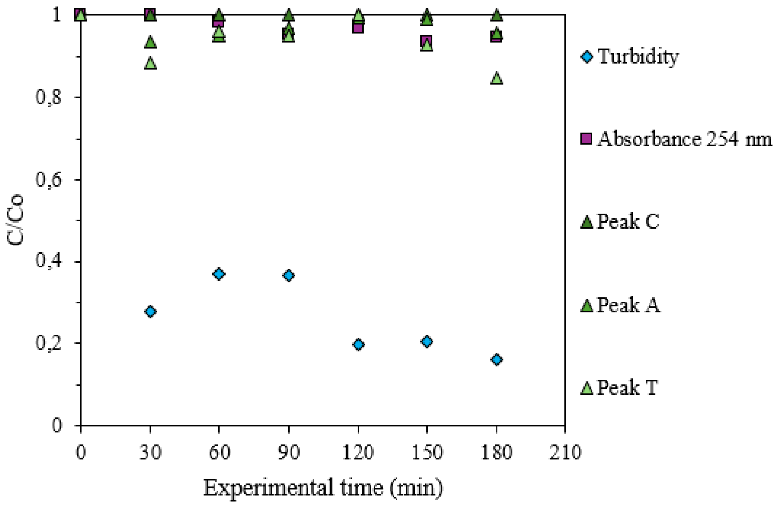


Figure 8: Relative concentrations of turbidity, absorbance at 254 nm, humic fraction (Peak C), fulvic fraction (Peak A) and protein fraction (Peak T) in the permeate obtained by ultrafiltration membranes over time.

Since no significant reduction of dissolved organic matter was achieved using ultrafiltration membranes, and only effective removal of suspended organic matter was observed, we proceeded to evaluate the removal efficiency by nanofiltration. For this purpose, two membranes of different composition were used: one of hollow polysulfone fibers and the other of hollow polysulfone fibers modified with graphene oxide.

5.2. Organic matter removal capacity of NF membranes

To study the removal of organic matter by different nanofiltration membranes, two tests were performed, in which two modules of each type of membrane were used: PSU and PSU-GO. To differentiate the modules with the same composition and the tests performed, these were labeled as “PSU X.Y”, where X represents the module and Y the test number.

Before starting the tests, the permeability of the different modules was determined to characterize their performance and evaluate possible variations between the first and second test.

It is important to note that nanofiltration membranes present permeability values of an order of magnitude lower compared to ultrafiltration membranes, evidencing a reduction of up to 96%. This is due to the fact that, having a smaller pore diameter, NF membranes require exerting a higher pressure to obtain the same permeate flux.

As shown in Figure 9, the permeabilities of the same membrane increase in the different tests, except for the PSU-GO.2 membrane, whose permeability decreases. These variations, both between tests and between modules of the same composition, may be due to the effectiveness of the cleaning process. It is possible that retained substances from previous tests have not been completely removed, which could clog the pores and increase the required pressure, resulting in a lower permeability. Alternatively, these differences could originate from human error during assembly or in the collection of data to calculate permeability.

In addition, the correlation coefficients obtained for each calculated permeability are in the range of 0.923 to 0.998, indicating that the values used adequately fit a linear model.

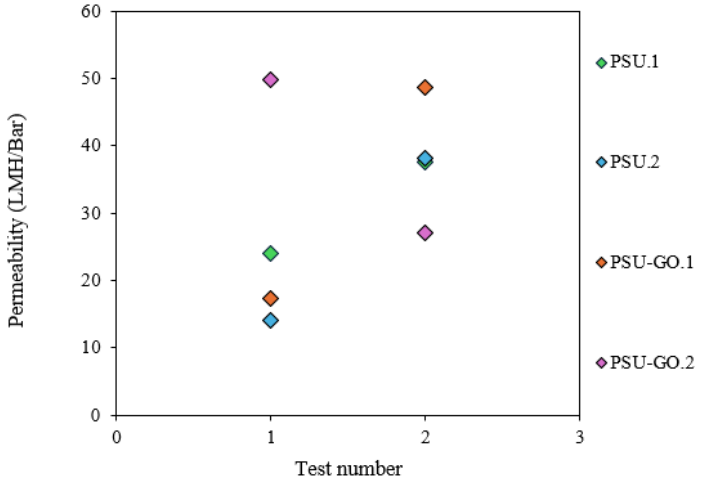


Figure 9: Representation of the permeability of the nanofiltration modules in the different tests performed.

Once the permeability of the different modules has been determined before starting the test, the organic matter of the permeates is analyzed at different experimental times.

When analyzing the fraction of undissolved organic matter, i.e., suspended solids, by measuring turbidity, a progressive decrease in this parameter is observed over the test time (Figure 10). In general, both types of NF membranes show similar behavior in turbidity reduction, with the exception of a test performed with the PSU-GO membrane, in which smaller reductions were observed. However, when considering the final reductions from an initial value of 2.06 ± 0.02 NTU, the PSU membrane achieved a turbidity reduction of 90.17 ± 0.44 %, while the PSU-GO achieved a reduction of 85.64 ± 9.12 %. The higher standard deviation observed in the PSU-GO results, as well as the difference compared to PSU, can be attributed to the particular PSU-GO trial mentioned above. If the data from that test are excluded, the results obtained are very similar to those of the PSU (90.19 ± 0.74 %). However, since this deviation was only evident in the turbidity measurement and not in other parameters evaluated, it was decided to keep the data from that test in the analysis.

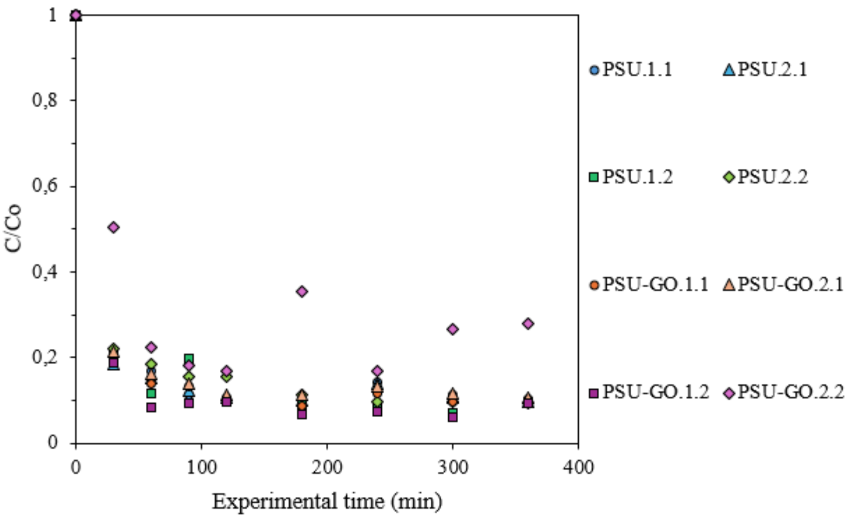


Figure 10: Representation of turbidity at different permeate times, with the different nanofiltration modules.

Regarding the removal of dissolved organic matter, evaluated by absorbance at a wavelength of 254 nm, a greater reduction is observed in all cases at the beginning of the test, which gradually decreases with time (Figure 11). Both PSU and PSU-GO membranes demonstrate the ability to reduce dissolved organic matter in water, starting from an initial value of 0.061 ± 0.003 absorbance at 254 nm. When comparing both membranes, the PSU-GO shows a higher performance than the PSU, as evidenced at the end of the test, where the PSU membrane achieves a reduction of 18.87 ± 13.04 %, while the PSU-GO achieves a reduction of 37.67 ± 8.14 %. The results obtained with the PSU modules have a coefficient of variation of 69 %, which indicates moderate variability and limits the representativeness of these results. In contrast, the values obtained with the PSU-GO membrane are highly consistent, suggesting high reproducibility.

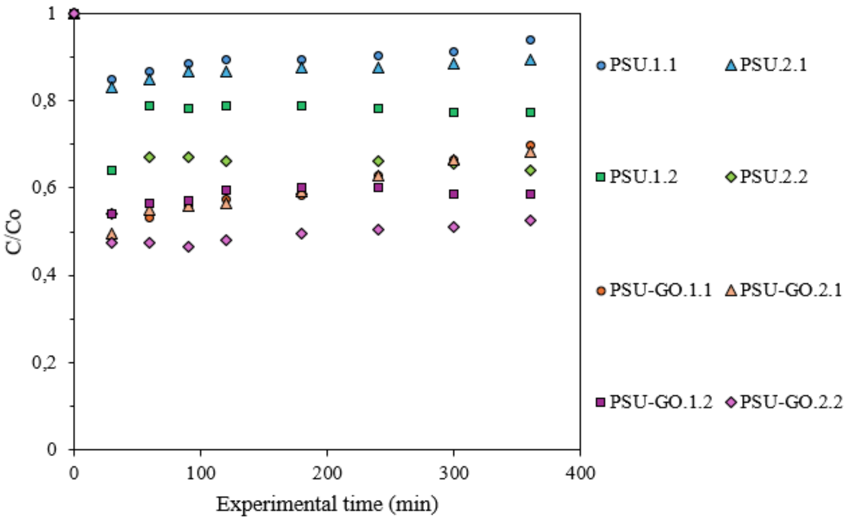


Figure 11: Representation of the absorbance at 254 nm at different permeate times, with the different nanofiltration modules.

Once the dissolved organic matter has been analyzed by absorbance at 254 nm, different fractions of it are evaluated. In relation to the humic-type organic matter fraction, identified as Peak C in the emission-excitation spectrum (EEM), significant differences are observed between the two types of membranes (Figure 12), starting from an initial value of 32.25 ± 1.78 in intensity. As expected, as in the removal of dissolved organic matter, the humic fraction shows a higher removal in the initial stages of the test. When comparing the PSU and PSU-GO membranes, the PSU-GO exhibits superior performance, with final reductions of 28.96 ± 3.12 % and 5.36 ± 7.78 %, respectively. The values obtained with the PSU-GO modules are very homogeneous, while those obtained with the PSU modules have a coefficient of variation greater than 100 %, indicating high variability and limiting the representativeness of these results.

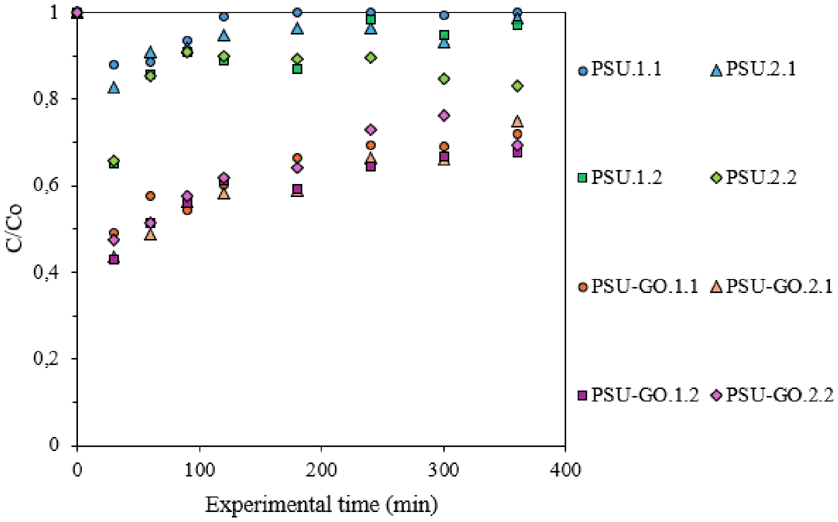


Figure 12: Representation of the humic fraction (Peak C) at different permeate times, with the different nanofiltration modules.

In relation to the fulvic type organic matter fraction, identified as Peak A in the emission-excitation spectrum (EEM), significant differences are observed between the two types of membranes (Figure 13). As in the previous results, the removal of this fulvic fraction decreases with time. In this case, the PSU membrane achieved a final reduction of 10.18 ± 4.84 %, while the PSU-GO achieved a reduction of 39.13 ± 10.36 %, starting from an initial value of 57.64 ± 1.02 in intensity. The coefficients of variation were 47 % for the PSU and 26 % for the PSU-GO, indicating that the results obtained with the PSU modules are again heterogeneous.

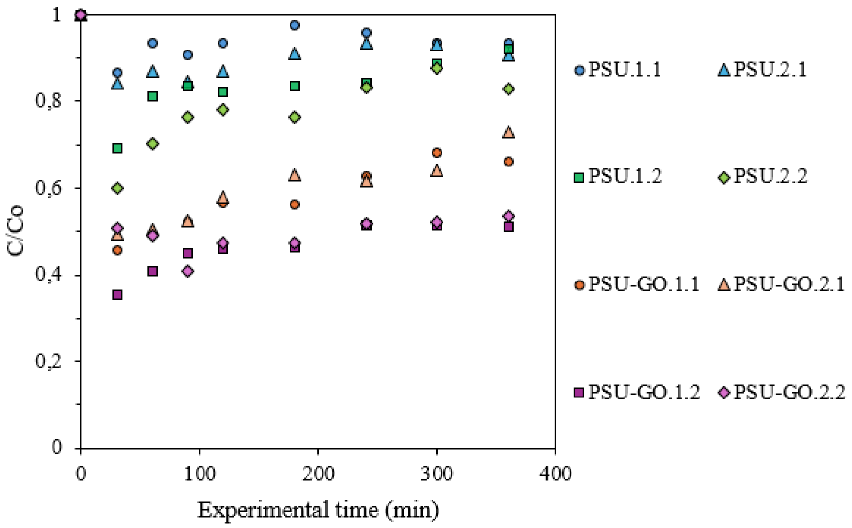


Figure 13: Representation of the fulvic fraction (Peak A) at different permeate times, with the different nanofiltration modules.

When analyzing the protein-type organic matter fraction, specifically tryptophan, identified as Peak T in the emission-excitation spectrum (EEM), a considerable dispersion is observed in the results of the different tests (Figure 14). In general terms, the values obtained with the PSU-GO membrane are predominantly located in the lower half of the graph, while the values associated with the PSU membrane are located in the upper half. In this case, it cannot be concluded that the reduction of these values decreases consistently with time, since the observed behavior is not very uniform. However, when considering the final reductions, the PSU membrane achieves a decrease of 34.74 ± 16.42 %, while the PSU-GO achieves a reduction of 49.75 ± 12.48 %, starting from an initial value of 13.16 ± 0.59 in intensity. The coefficient of variation of the results indicates that the values obtained with the PSU membrane are heterogeneous, while those obtained with the PSU-GO show greater homogeneity in relation to the median.

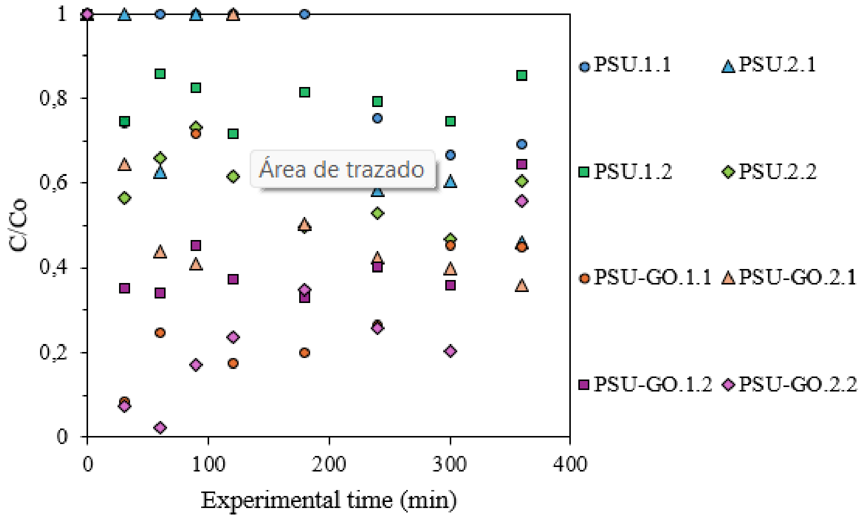


Figure 14: Representation of the protein fraction (Peak T) at different permeate times, with the different nanofiltration modules.

After characterizing the different parameters to evaluate the organic matter present in the permeate at different experimental times with the two nanofiltration modules, it can be concluded that the PSU-GO modules show a higher efficiency in the retention of dissolved organic matter. As for suspended solids, both modules show a similar capacity. In addition, the values obtained with the PSU-GO modules are more homogeneous, which makes them more robust and reliable. In contrast, the results obtained with the PSU module show greater dispersion, suggesting the need for more tests to reduce the deviation and obtain more reliable conclusions.

Since the nanofiltration modules studied have demonstrated their ability to remove organic matter present in water, their effectiveness in the removal of emerging contaminants was evaluated.

5.3. Removal of emerging contaminants by NF

After confirming that the NF membranes can remove natural organic matter, both dissolved and suspended, we proceeded to evaluate their capacity to remove specific contaminants from water. For this purpose, preliminary tests were carried out with tap water in order to characterize the behavior of the contaminants under study.

Like the previous tests, the different nanofiltration modules were characterized by determining their permeability before starting the tests (Figure 15). In this case, a single module of each type, PSU and PSU-GO, was used, obtaining permeabilities of 24.9 LMH/Bar and 22.0 LMH/Bar, respectively. The coefficients of determination indicated that the values obtained fit a linear model. It should be noted that these modules were used for the first time in this test, so no fouling effects are expected in the results, both in permeability values and contaminant removal.

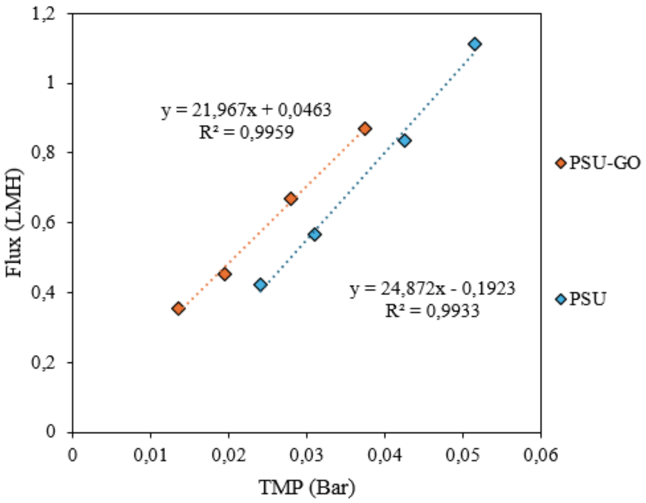


Figure 15: Relationship between flux and different applied transmembrane pressures with a linear fit used to determine the permeability of the PSU and PSU-GO nanofiltration modules used in the study of the removal of emerging contaminants from water.

When analyzing the removal capacity of the five emerging contaminants studied, as shown in Figure 16, it is observed that both the PSU membrane and the PSU-GO membrane can remove emerging contaminants from the water, although with differences between them. In general, the contaminants galaxolide, tonalide, chlorpyrifos and triclosan are removed from the first sampling time, corresponding to the first milliliters of permeate collected in both membranes. However, atrazine shows a different behavior, since its elimination decreases with time, showing significant differences between the two membranes.

Atrazine is retained more effectively by the PSU membrane, which is unexpected, since the PSU-GO, containing graphene oxide, an adsorbent material, was expected to have a greater capacity to filter and adsorb the different contaminants. In this case, both membranes show a similar reduction of atrazine in the first sampling time, but from that point on, the PSU-GO shows a 45% reduction with respect to the initial concentration, while the PSU maintains a more gradual and sustained reduction.

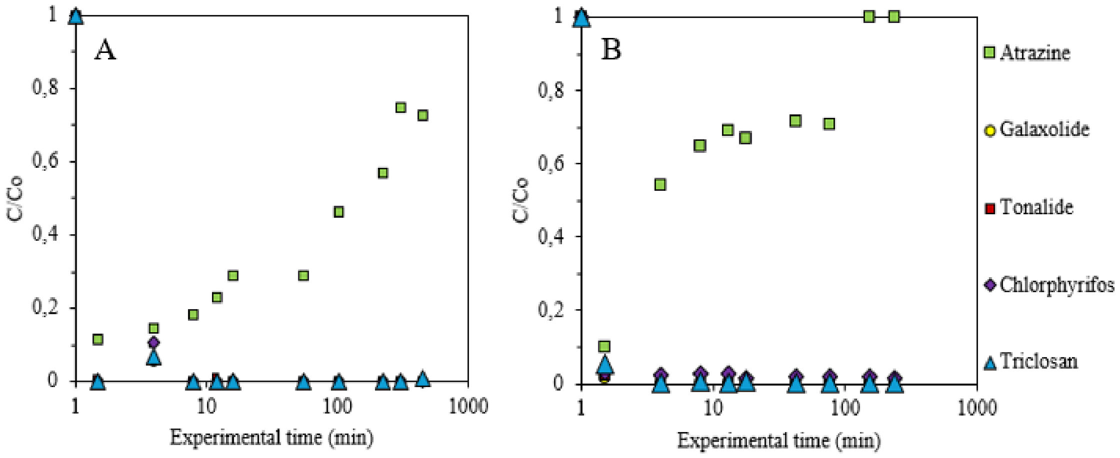


Figure 16: Relative concentration of emerging contaminants in the permeate at different experimental times using the PSU (A) and PSU-GO (B) nanofiltration modules.

Once the test was completed, a backwash with Milli-Q water was performed to eliminate as many of the compounds retained on the membranes as possible and to quantify them. For this purpose, a mass balance of each compound was performed and the percentage recovered of each one was calculated, the results of which are presented in Table 4.

Table 4: Percentage recovery of the emerging contaminants studied in the tests carried out with the PSU and PSU-GO nanofiltration modules.

	Recovery (%)	
Compound	PSU	PSU-GO
Atrazine	75.34	77.56
Galaxoline	1.96	1.65
Tonalidine	2.54	2.98
Chlorphyrifos	1.77	0.59
Triclosan	7.48	2.62

When analyzing the recovery of each compound, it is observed that atrazine shows a high recovery percentage in both modules, indicating that a significant amount of this compound was retained in the membrane fibers. In contrast, the other compounds show a very low and similar recovery percentage between the two modules.

Atrazine is distinguished from the other compounds analyzed due to its retention behavior. This difference can be attributed to the presence of nitrogen atoms in its molecular structure, which could influence its interaction with the membrane surface differently from that of the other pollutants studied.

5.4. Removal of emerging contaminants in a matrix with organic matter by means of NF

Before starting the new test, the condition of the modules was verified by evaluating their permeability values, as in previous tests.

As shown in Figure 17, there is a significant difference in permeability between the two nanofiltration modules, with the PSU module showing higher permeability compared to the PSU-GO module, which shows lower permeability. The values obtained for both modules present a coefficient of determination very close to 1, indicating that the data fit a linear model.

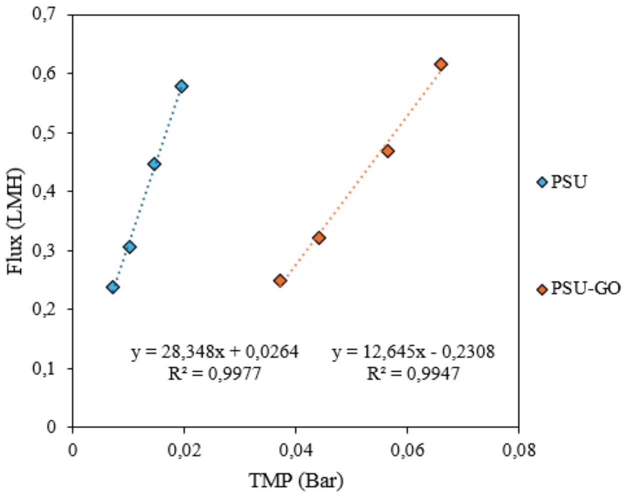


Figure 17: Relationship between flux and different applied transmembrane pressures with a linear fit used to determine the permeability of the PSU and PSU-GO nanofiltration modules used in the study of the removal of emerging contaminants in a matrix with organic matter.

When comparing these results with those obtained in the previous test (Section 5.3), it is observed that the permeability of the PSU module has increased, while that of the PSU-GO module has decreased. This variation in values could be due to differences in cleaning procedures, since each module was cleaned individually, which implies that uniform cleaning conditions were not maintained.

Since the matrix to be treated contains water with organic matter and emerging pollutants, the removal of organic matter will be analyzed first, followed by that of the pollutants. In these tests, dissolved organic matter was quantified by absorbance at 254 nm, and the different fractions were analyzed by fluorescence. Suspended matter was not evaluated due to the limited sample volume available, in addition to the fact that these modules have been shown to have a high capacity for its removal.

Regarding the removal of dissolved organic matter, evaluated through absorbance at 254 nm, differences were observed between the two modules (Figure 18). The initial value of dissolved organic matter in the raw water was 0.156 ± 0.003 absorbance units at 254 nm. In the first permeate volume, collected at 0.5 minutes, both modules showed similar removal: 52% in the PSU module and 50% in the PSU-GO module. Subsequently, the removal values began to increase until stabilization was reached. In the PSU module, an increase of 24% was observed in the second sample collected, followed by no further removal. In contrast, in the PSU-GO module, an increase in the concentration of dissolved organic matter in the permeate was also observed, but it stabilized with a reduction of 22%. When comparing these results with those obtained in previous tests (Section 5.2), it is evident that the modules presented lower removal capacities.

This phenomenon could be due to a higher concentration of organic matter in the initial water, which would have limited the capacity of the membranes.

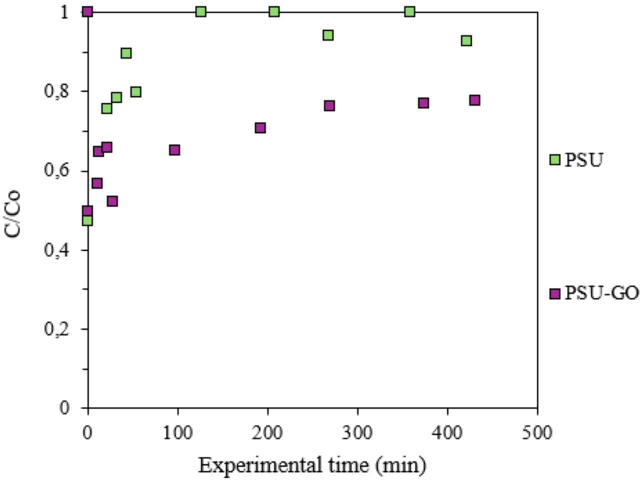


Figure 18: Plot of the relative concentration of absorbance at 254 nm as a function of permeate time in the water sample containing emerging contaminants and organic matter, using the PSU and PSU-GO modules.

In relation to the different fractions of dissolved organic matter, specifically the humic fraction (peak C), the fulvic fraction (peak A) and the protein fraction (peak T), identified in the emission-excitation spectrum (EEM) of water containing emerging contaminants and organic matter, differences were observed in the retention of these fractions among the modules used (Figure 19). The values of these fractions in the treated raw water are 196.38 ± 3.43, 183.47 ± 1.89 and 49.75 ± 3.64 intensity units, respectively.

When analyzing the fractions separately, the humic fraction is retained more efficiently by the PSU-GO module, achieving a final reduction of 32% compared to the initial water, while the PSU module shows a final reduction of 7%. Although the PSU module shows a higher initial reduction, its performance decreases with filtration time. The fulvic fraction exhibits similar behavior to the humic fraction in both modules, with better retention in the PSU-GO module. As for the protein fraction, differences are observed with respect to the other two fractions, although a greater reduction is also recorded with the PSU-GO module. In the case of the PSU module, the reduction remains constant at 50% throughout the experiment, while with the PSU-GO module, the reduction increases slightly with time, starting at 49% and reaching 60% at the end of the experiment.

When comparing these results with those obtained in the organic matter removal test by nanofiltration (Section 5.2), it is observed that the behavior of the humic and fulvic fractions is very similar. However, in the case of the protein fraction, where a high dispersion in the results had previously been observed, in this test much more consistent results have been obtained between the two modules.

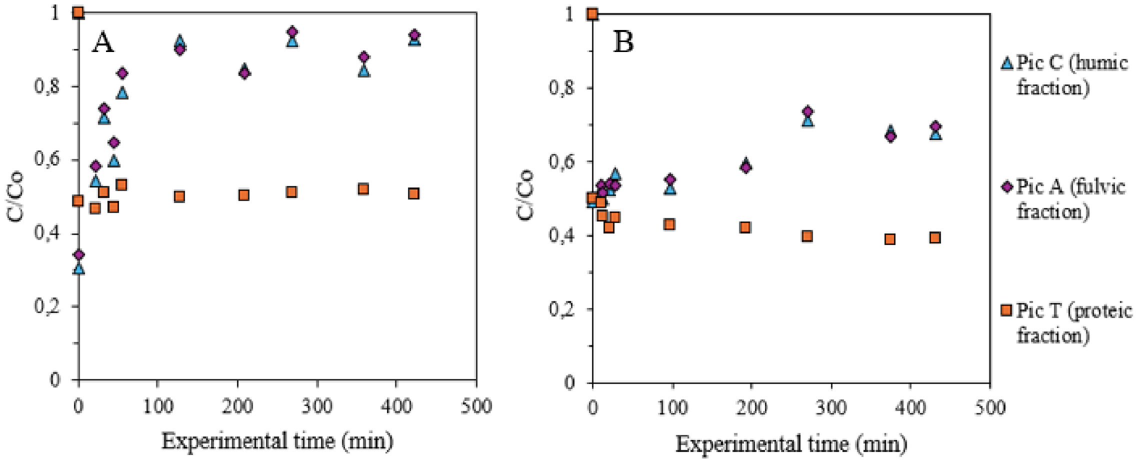


Figure 19: Representation of the relative concentration of the different fractions of dissolved organic matter, identified by emission-excitation spectrum (EEM), as a function of permeation time in the water sample containing emerging contaminants and organic matter. A) PSU and B) PSU-GO.

When evaluating the retention capacity of five emerging contaminants in a matrix with organic matter using two nanofiltration modules (Figure 20), differences between the two are observed. The largest discrepancy between the modules is found in the retention of atrazine, where the PSU module shows a higher capacity compared to the PSU-GO. In the PSU module, an initial atrazine reduction of 69% is observed, followed by a 91% reduction. Subsequently, the relative concentration increases to reach a final reduction of 34%. On the other hand, in the PSU-GO module, the maximum atrazine reduction is reached in the first time interval with 54%, gradually increasing the relative concentration until atrazine is no longer retained.

When comparing the removal behavior of these contaminants in the two modules with the results obtained in the previous test (Section 5.3), where they were not present in a matrix with organic matter, notable differences are observed in the case of atrazine. In both cases, the other compounds were retained from the first sampling time.

With both modules used, a similar behavior is evident: atrazine is retained more efficiently in a matrix without organic matter during the early stages of the experiment. However, in the long term, atrazine retention is more efficient in a matrix containing organic matter. It should be noted that, in both scenarios, the PSU-GO modules eventually lost their ability to retain the compound.

As for the other compounds, galaxolide, tonalide, chlorpyrifos and triclosan, complete retention is observed from the beginning in both PSU and PSU-GO modules.

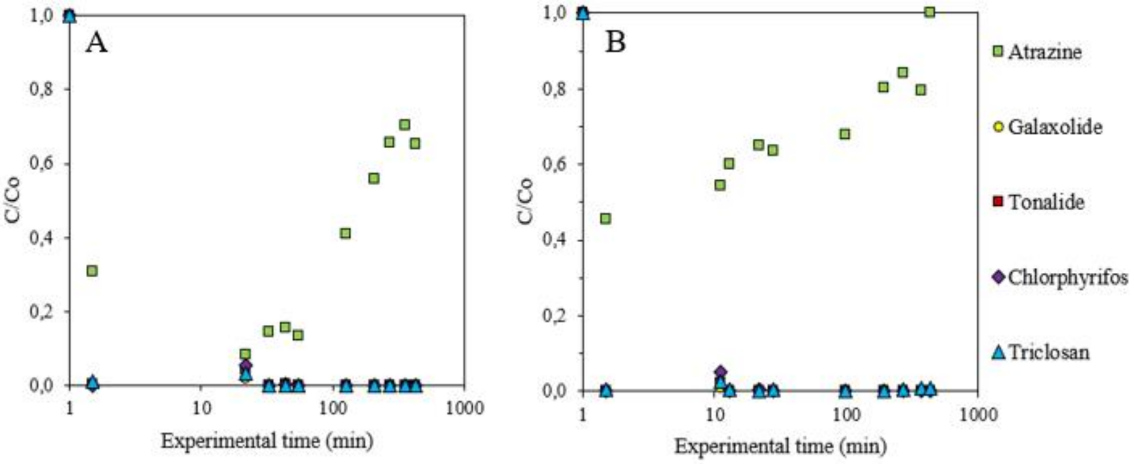


Figure 20: Relative concentration of emerging contaminants as a function of permeate time in a water sample containing organic matter and emerging contaminants using the PSU (A) and PSU-GO (B) nanofiltration modules.

By calculating the percentage recovery of each compound in the two nanofiltration modules (Table 5), it is possible to evaluate the efficiency of the post-treatment recovery process.

Table 5: Percentage recovery of the emerging contaminants studied in the tests carried out with the PSU and PSU-GO nanofiltration modules.

	Recovery (%)	
Compound	PSU	PSU-GO
Atrazine	56.97	125.37
Galaxoline	1.62	1.73
Tonalidine	1.81	1.92
Chlorphyrifos	0.73	0.77
Triclosan	2.18	2.33

In the case of atrazine, a significantly higher recovery percentage was observed in the PSU-GO module (125.37%) compared to the PSU module (56.97%). The value higher than 100% obtained with the PSU-GO module suggests an interference or overestimation during the process, indicating a significant effect of this module on atrazine recovery.

On the other hand, the compounds galaxolide, tonalide, chlorpyrifos and triclosan show very low recovery percentages in both modules, suggesting that these compounds could be being retained in the membrane.

Comparing these results with those obtained in previous experiments (Section 5.3), where the compounds were in a matrix without organic matter, it is observed that atrazine is recovered more efficiently with the PSU module in the absence of organic matter, while the opposite occurs with the PSU-GO module. For the other compounds, the recovery percentages remain consistently low in both scenarios.

6. Conclusions

Membrane filtration techniques are mainly classified according to their pore size range and, consequently, by their molecular weight cut-off. Furthermore, within each classification, membranes can be composed of different materials, which gives them distinctive properties.

In general terms, the membrane filtration techniques studied in this work show varied capacities for NOM retention. In the case of UF membranes, they have been shown to be effective in the removal of suspended organic matter; however, they are not capable of retaining dissolved organic matter or its specific fractions. Therefore, in situations where the raw water entering the DWTP contains high levels of NOM, these membranes will not provide an improvement in the effectiveness and efficiency of the treatment, since sand filters also remove suspended solids at a lower energy cost. For this reason, the performance of membranes with smaller pore diameters, such as NF membranes, composed of different materials (PSU and PSU-GO) has been investigated.

The NF membranes (PSU and PSU-GO) demonstrated a higher removal capacity for suspended organic matter, with reductions of 90.17 ± 0.44% and 85.64 ± 9.12%, respectively, compared to the UF membrane, which showed a reduction of 83.98%. For dissolved organic matter, the PSU and PSU-GO membranes also exhibited superior removal capacities with respect to UF, with reductions of 18.86 ± 13.40% and 37.67 ± 8.14%, respectively, according to absorbance measured at 254 nm, compared to the 5.51% reduction observed for UF. This pattern is repeated for the different dissolved organic matter fractions analyzed, where NF membranes presented higher removal rates compared to UF. In addition, PSU-GO showed superior performance to PSU, with reductions of the humic fraction of 28.95 ± 3.12% vs. 5.36 ± 7.78%, of the fulvic fraction of 39.13 ± 10.36% vs. 10.18 ± 4.84%, and of the protein fraction of 49.75 ± 12.48% vs. 34.74 ± 16.42%, respectively.

Since NF modules have been shown to be effective in removing a large portion of NOM, their ability to remove emerging contaminants in water was evaluated using five representative compounds (atrazine, chlorpyrifos, galaxolide, tonalide and triclosan). The results indicated that both modules have a high capacity to retain chlorpyrifos, galaxolide, tonalide and triclosan. However, in the case of atrazine, differences in removal efficiency were observed: the PSU module showed better performance over time, with a final reduction of 27%, while the PSU-GO module lost its atrazine retention capacity in the final stages of the trial.

To simulate a more representative environment, emerging contaminants were analyzed in a matrix containing NOM. The results showed that the MOD removal capacity by NF membranes was similar to that observed in the absence of emerging contaminants. For these contaminants, behaviors consistent with previous tests were observed: a total retention of chlorpyrifos, galaxolide, tonalide and triclosan, and a higher removal efficiency of atrazine by the PSU module, regardless of the presence of NOM in the matrix.

In summary, UF membranes, within the parameters evaluated, are effective only in the removal of suspended organic matter. On the other hand, NF membranes also present a significant capacity to remove dissolved organic matter but are also more efficient when doped with GO. However, atrazine is more effectively retained by the PSU module, both in matrices with and without NOM, while chlorpyrifos, galaxolide, tonalide and triclosan are consistently fully retained by both types of membranes.

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MASTER EN CIENCIA Y TECNOLOGIA DE LOS RECURSOS HÍDRICOS

HAY UN MÍNIMO DE DOS TUTORÍAS OBLIGATORIAS, FIRMADAS COMO MÍNIMO 1 MES ANTES DE LA ENTREGA DE LA MEMORIA FINAL. ADJUNTAR ESTE DOCUMENTO EN FORMATO PDF COMO EVIDENCIA AL DEPOSITAR EL TFM.

FICHA INICIAL

NOMBRE DEL ESTUDIANTE: Gemma Moncusí Prieto

NOMBRE DEL TUTOR ACADÉMICO: Hèctor Monclús Sales

EMPRESA O GRUPO DE INVESTIGACIÓN EN EL QUE SE DESARROLLA EL TFM: LEQUIA

TÍTULO TENTATIVO DEL TFM: Evaluation of membrane ultrafiltration in drinking water treatment.

BREVE DESCRIPCIÓN:
The objective of this work is to evaluate the efficacy and efficiency of ultrafiltration membranes for drinking water treatment. More specifically, how they reduce the natural organic matter in water, both suspended and dissolved organic matter.

Fecha y firma del estudiante 20/05/2024

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1ª TUTORIA

OBJETIVOS:

Learn the operation of ultrafiltration membranes.

Evaluate the performance of ultrafiltration membranes for raw water treatment:

- Removal of suspended organic matter.
- Removal of dissolved organic matter
- Reduction of trihalomethanes formation potential.
- Evaluate filtration efficiency over short-term periods.

ESTADO DEL ARTE:

Membrane technology is a very promising tool in the water purification sector, as it has a wide variety of applications.

In periods of drought, water can change its composition, increasing its organic matter content and concentration of emerging contaminants. For this reason, it is necessary to evaluate membrane filtration techniques, such as ultrafiltration, in order to improve the performance of drinking water treatment plants (DWTP).

PLAN DE TRABAJO:

Study the permeate resulting from ultrafiltration membranes, with different water matrices:

- Inlet water to the DWTP.
- Water leaving the settling tank.

Fecha y firma del estudiante y del tutor académico 18/06/2024

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2ª TUTORIA

DESVIACIÓN DEL PLAN DE TRABAJO (tan solo si procede)

After observing the results obtained with the ultrafiltration modules, we proceeded to add experimentation with two nanofiltration modules of different composition and compare the organic matter removal capacity with these modules and the ultrafiltration module. The removal capacity of certain emerging contaminants in different matrices will also be studied with the two nanofiltration modules.

By adding another membrane filtration technique, it is decided to change the title of the work to: Evaluation of membrane technologies for drinking water treatment.

In addition, the objectives of the work will also be modified.

RESULTADOS ESPERADOS

Nanofiltration modules are expected to have a higher efficiency in the removal of dissolved organic matter than ultrafiltration. In addition, among the nanofiltration modules used, the one containing graphene oxide is expected to show greater reductions than the one without, both in the removal of organic matter and emerging contaminants.

ESTRUCTURA DE LA MEMORIA

The report will have a conventional structure consisting of: introduction, hypothesis and motivation, objectives, methodology, results and discussion, and conclusions.

In the introduction we will talk about the consequences of drought, the conventional unit operations in a DWTP, membrane technology, focusing more on the two types of filtration used.

FEED BACK Y RECOMENDACIONES DEL TUTOR ACADÉMICO:

The tutor's recommendations were to first develop the results and, from them, to determine the objectives that would align with the experimental part obtained, as well as to identify the necessary information to add in the introduction to ensure a complete understanding of the work.

Fecha y firma del estudiante y del tutor académico 01/08/2024

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