

# FS-TER-005

**TECHNICAL SHEETS  
FOR EFFLUENT TREATMENT PLANTS  
IN TEXTILE INDUSTRY**

## **MEMBRANE FILTRATION AND REVERSE OSMOSIS**

***SERIES: TERTIARY TREATMENTS***

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# INDITEX



**MEMBRANE FILTRATION AND REVERSE OSMOSIS**

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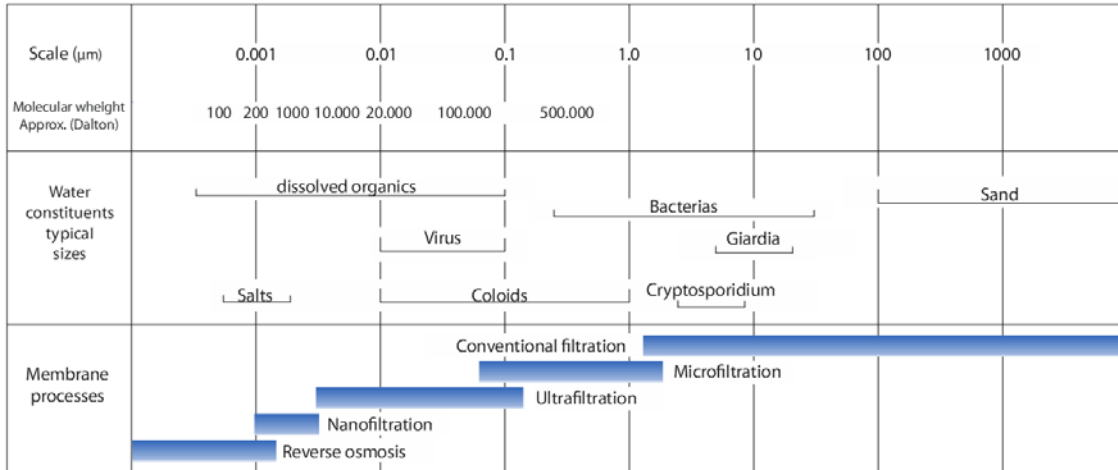
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**1.- INTRODUCTION**

A membrane can be defined as a thin film that separates two phases and acts as a selective barrier to mass transport (AWWA, LdE, & WRC, 1996). Membrane processes are designed to perform physical and physical-chemical separations; processes that in recent decades are experiencing an important development in the treatment applications for domestic and industrial water supply and wastewater treatment (Judd, 2003a). Membrane filtration systems receive different names depending on the pore size of the membrane (and therefore the size range of rejected particles). In Figure 1, general ranges for various membrane filtration techniques are indicated.



**Figure 1.- Pressured membrane filtration processes application guide (mod. from Bergman, 2005)**

The use of membranes has advantages over other treatment techniques. The separation occurs in the same phase, which is energetically favorable with regard to distillation. In membranes, no accumulation occurs (or occurs at low scale), so the unit can operate continuously without requiring regeneration cycles, in contrast to adsorption processes. In addition, reagents use in membrane systems is required to a very small extent, unlike conventional clarification processes, usually requiring the addition of coagulants and flocculants.

Considering that most of the processing operations in the textile industry are in batch, wide variations are normally found in the effluent quality. The selection of the right strategy to reduce effluent pollution is problematic and should be addressed on a case by case basis. However, there are some commonalities (Judd, 2003b):

Water reuse is facilitated by the segregation of wastewater streams

Membrane technologies offer the best guarantees of all possible candidates in order to obtain good effluent quality regardless of the quality of water supply.

**Table 1. Membrane processes (mod. from CITME, 2006)**

<b>Membrane processes</b>	<b>Main objective</b>	<b>Driving force</b>
Microfiltration (MF)	Suspended solids removal, including microorganisms	transmembrane pressure difference
Ultrafiltration (UF)	Elimination of long dissolved molecules and colloidal particles	
Nanofiltration (NF)	Removal of selectively multivalent ions and certain charged or polar molecules	
Reverse osmosis (RO)	Inorganic ions removal	
Pervaporization (PV)	Selective extraction of gaseous molecules and/or volatile solutes	
Gas transfer (GT)	Transfer of gas molecules into or out of water	
Electrodialysis (ED) and dialysis (DIA)	Selective extraction of ions from the water and/or concentration level rise of ionic pollutants in the reject water	transmembrane electric potential difference

**2.- MEMBRANE CLASSIFICATION**

The membranes can be classified according to various parameters, providing information on their structure, nature, form, composition, work pressure, etc. The following are some of the most common classifications:

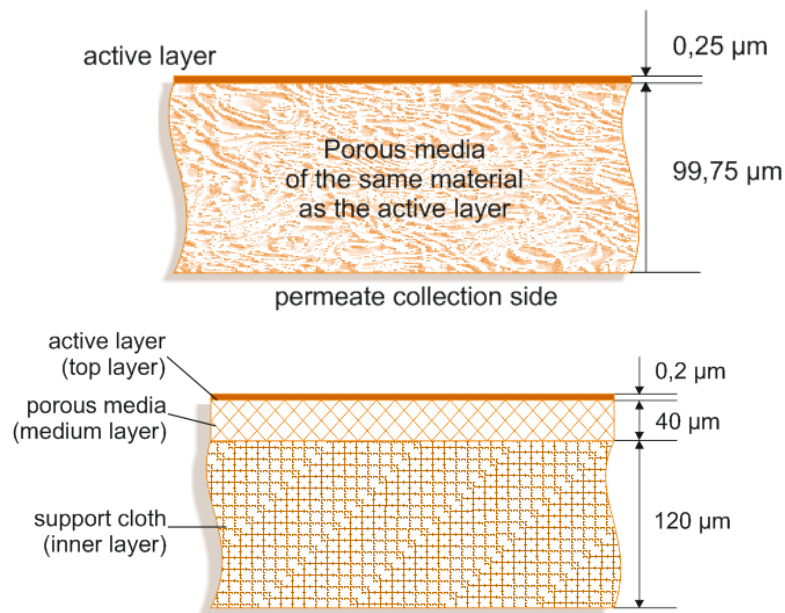
**According to the separation mechanism:** Membranes are divided in porous membranes, which are separated by size differences; non-porous, also called dense membranes; and ion exchange membranes which, in turn, can be subdivided into cation exchange (negatively charged surface) or anionic (positively charged surface).

**According to its structure:** A distinction can be drawn between isotropic membranes (symmetric), with a uniform structure; or anisotropic membranes, which tend to add an extremely dense layer on the side that faces the water flow.

**Depending on their nature:** Anisotropic membranes can be made of the same material with different porosities, or they can also be made of various materials, receiving the names of integral or composite anisotropic membranes, respectively.

**According to its shape:** Three types are basically considered: Flat membranes, tubular membranes (with internal diameter of 3 mm or higher), and tubular hollow fiber membranes (internal diameter lower than 3 mm).

**According to its surface charge:** There are membranes with cationic or anionic ends in the membrane structure, where components with the same electric charge are excluded during separation.



**Figure 2.- Snapshot of an integral asymmetric membrane –up- and a thin layer composite membrane –down- (mod. from Fariñas I., 1999)**

### 3.- MEMBRANE MODULES AND CONFIGURATIONS

The operating unit in which the membranes are installed is called a **module**. This work unit consists of membranes, pressure support structures, water supply and concentrate outlet valves and permeate extraction points (AWWA et al., 1996).

Many different modules have been developed until present with regard to required applications. Some of the most common are described below:

#### 3.1.- Membrane cartridge filters

Where membranes, suitably folded, are wound around a permeate collector, being packaged inside a case of, as an example, 25 cm in length and 6 cm in diameter (Figure 3). This typology is suited for in line filtration (see epigraph 4.1), where contaminants are retained inside the membrane, generating a purified effluent (permeate). These layouts provide superficial areas in the order of 0.3 m<sup>2</sup>. Membrane cartridges are disposable.

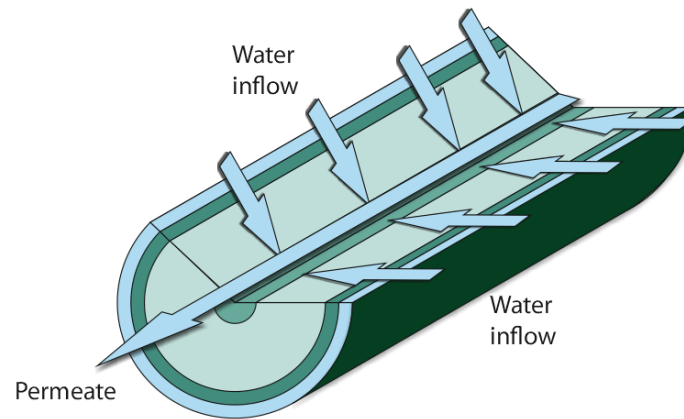


Figure 3.- Cartridge membrane scheme

### 3.2.- Flat sheet membrane modules

In this typology, membranes are arranged in racks separated by plates. Pumped water circulates between the membranes of two adjacent plates, getting more concentrated on contaminants as permeate flows through the walls of the membranes (Figure 4). The specific surface of the flat sheet modules is  $100\text{--}400\text{ m}^2/\text{m}^3$ . The plates provide mechanical support to the membrane and, at the same time, drain permeate. The plates must be corrugated on the water feed side so as to increase the mass transfer. Their arrangement makes possible to perform circulation in parallel or in series, reaching an area of  $100\text{ m}^2$ . They are easily removable for cleaning and replacement (AWWA et al., 1996; CITME, 2006).

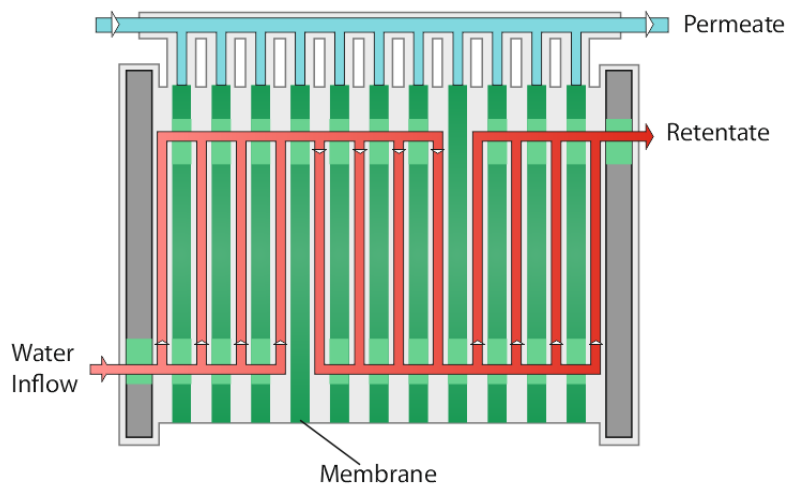


Figure 4.- Flat sheet membrane module scheme (modified from CITME, 2006)

### 3.3.- Tubular membrane modules

Tubular membrane modules consist of stainless steel or PVC cylindrical case, which contain a variable number of tubular membranes (3 to 151). Water feed is pumped through the interior of the membranes, producing side permeate flow through the walls. Membrane module is provided with suitable devices to collect the permeate and the concentrate flows with up to 19 channels of parallel flow devices. Tubular membranes comprise a porous paper or glass fiber support media where the filter surface is deposited. They can also be built in ceramic material.

The tubular modules typically have lengths of 13 cm - 20 cm, with 4-6 membranes of 0.5 cm-4 cm in diameter, disposed therein. The rate of feed flow through the membranes is 2 m/s - 6 m/s, which results in pressure losses of 14 to 21 kPa per module. The energy consumption of plants using these modules is about 0.8 - 2.5 kWh/100 permeate L. The membrane modules have a total surface area of 0.2 to 7.4  $\text{m}^2$ . These modules do not require fine prefiltration and are easy to clean. They are particularly well suited for the treatment of highly viscous fluids. Their main disadvantage is their low compacted density, which increases the investment cost.

### 3.4.- Spiral wound membrane modules

Structure made of two flat membranes enclosing a porous flexible sheet (permeate collector), sealed on three edges. The open edge is connected and wound onto a perforated pipe carrying permeate flow. The outer walls

of the spiral membrane are separated by hollow structures (spacers) which allow water feed to flow through while permeate flow crosses laterally the membrane walls. These modules typically have 20 cm diameter and 100 cm long (up to 30 cm diameter and length 150 cm) with several wound membranes which provide a membrane surface of 1-2 m<sup>2</sup> (Figure 5). In one cylindrical pressure vessel several elements (two to six) can be installed. These are much more compact (700 to 1000 m<sup>2</sup>/m<sup>3</sup>) and produce a pressure drop lower than the flat-sheet membrane modules. The spiral wound module is, however, sensitive to clogging due to the spacer and cannot be used directly in turbid water without pretreatment.



Figure 5.- Spiral wound membrane (mod. from CITME, 2006)

### 3.5.- Modules type hollow fiber membranes

There are hollow fiber modules on the market of very different sizes, with lengths which range from 30 to 210 cm and diameters between 63 and 250 mm keeping up to 4,400,000 hollow fiber membranes (Johnson & Busch, 2009). The hollow fibers are tubular structures typically of 85-4200 microns in outer diameter and 40-900 microns in internal diameter (Fariñas I., 1999; Simpson Env. Corp., n.d.). Most of them are anisotropic and the structure responsible for the separation is located in the outer or inner surface of the fiber. The packing density is inversely proportional to diameter, so that these units are very compact. There are basically two configurations, considering that water feed can enter from the inside or the outside of the fibers. The pressure drop in these modules is 0.7 bar - 70 bar, depending on the type of application (CITME, 2006).

Table 2 presents some of the most significant features of this type of provision.

Table 2. Membrane modules significant characteristics (mod. from CITME, 2006)

Parameter	Hollow fibers	Capillar fibers	Spiral wound	Flat-sheet	tubular
Polarization – clogging control	Poor	Good	Moderate	Good	Very good
Pressure drop through membrane	High	Moderate	Moderate	Low	Low
High work pressure behavior	Yes	No	Yes	Yes	Low
Specific membrane materials	Yes	Yes	No	No	No

### 4.- MEMBRANE PROCESS FUNDAMENTALS

The permeate flux (L/m<sup>2</sup>/h) is defined as the water flowing through the membrane per unit of membrane surface. The rejection coefficient ( $R_i$ ), of a component  $i$  to be removed from the permeate is a way to estimate the degree of separation achieved by the membrane. It is defined as the difference respect to 1 of the ratio between the concentrations of component  $i$  in the permeate ( $C_{ip}$ ) and in the feed ( $C_{if}$ ) flows.

$$R_i = 1 - \frac{C_{ip}}{C_{if}}$$

The variation of pressure between both sides of the filter membrane is called transmembrane pressure ( $\Delta p$ ), or osmotic transmembrane pressure where appropriate. This parameter, along with the temperature ( $T$ ) and saline feed concentration ( $C_{if}$ ), determines the main variables of the process: the water flow ( $J_w$ ) and the rejection coefficient ( $R$ ). Typically, considering a selected salt concentration, the increase of transmembrane pressure has a

linear relation with the increase in water flow. Transmembrane pressure rise also implies an increase in rejection rate although in this case the increase of  $R$  tends to an asymptotic value.

The surface area is defined as the area available for liquid feed and membrane contact. It is the parameter that, together with the transmembrane flow, allows to extract the number of membrane modules required.

The recirculation ratio is defined, in cross-flow filtration systems, as the ratio between the feed and the permeate flows inside a membrane module.

The temperature bears a complex relation with the membrane processes characteristics. Its increase is related with a decrease in rejection coefficient and with permeate flux flow rise (CITME, 2006).

#### 4.1.- OPERATION MODES

##### 4.1.1.- In line filtration (Dead-end filtration)

Membranes are arranged at the flow line of the water to be treated (feed), remaining the particulate contaminants retained inside the membranes and generating a purified stream (permeate). The membranes used are of deep filter type, arranged in cartridges (Figure 6).



Figure 6.- In line filtration scheme (mod. from CITME, 2006)

##### 4.1.2.- Cross-flow filtration

The effluent to be treated is circulated tangentially to the membrane. The contaminants remain on the surface of the membrane, being washed by the main flow, avoiding membrane fouling. This operation mode generates two streams coming from the feed flow: concentrate, with a greater concentration of contaminants than in the feed and permeate, with contaminants levels which enable its discharge or reuse. The membranes used are sieve or dense types (Figure 7).

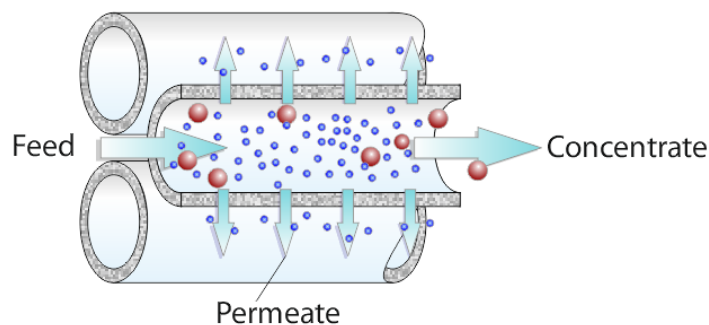


Figure 7.- Cross-flow filtration (mod. from CITME, 2006)

#### 4.2.- Factors hindering the performance of the membranes

##### 4.2.1.- Concentration polarization

It takes place in those processes operating in cross-flow filtration, such as reverse osmosis and ultrafiltration. In working conditions of these processes it is difficult to prevent feed rejected components accumulation on the membrane surface. The result is the creation of concentration gradients (concentration polarization) on the supply side, what can hinder the separation efficiency of the membrane and permeate flow. Figure 9 shows a situation where a component  $i$  in the feed, which is rejected by the membrane, gets accumulated on the surface, creating a concentration gradient located in a  $\delta$  thickness film, next to the membrane.



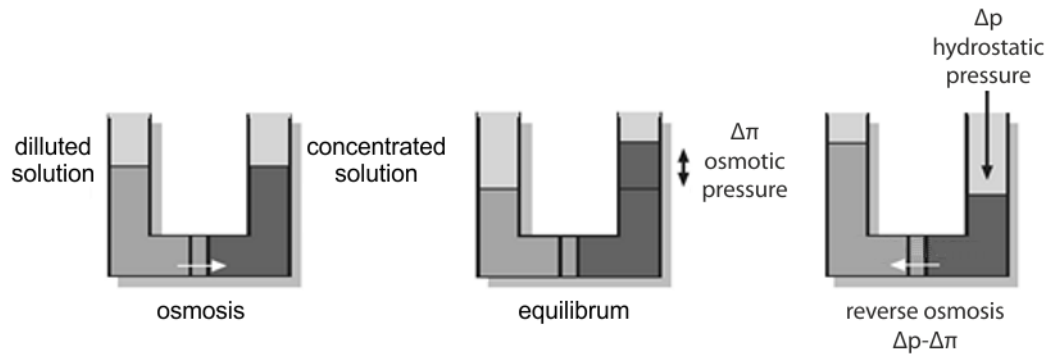


Figure 9.- Concentration gradient generation (mod. from CITME, 2006)

A high **polarization** level also increases the osmotic pressure in the supply side, which would also contribute to a reduction of permeate flow. Also, if the concentration ( $c_m$ ) is high, diffusion component  $i$  through the membrane will be favored, which leads to a lower rejection coefficient. Thus, malfunction of the membrane depends on the operating conditions more than membrane using time. The simplest way to avoid polarization is increasing the **feed flow velocity** rate, so that the generated turbulence can remove substances deposited on the surface of the membrane.

#### 4.2.2.- Membrane fouling

Membrane fouling is due to the presence of substances in wastewater supply which can interact with it, getting adsorbed and/or precipitating on the surface. There can also be substances that penetrate in the interior of the membrane, in which case they are adsorbed on the walls of the pores reducing the pore size. The consequence of contamination is a lower permeate flow due to increased resistance of the membrane. A progressive increase of transmembrane pressure difference, in order to keep the permeate flow, normally accelerates the fouling process reaching a state of irreversible clogging of the membrane, which would require replacement.

This type of malfunction is dependent on the working time of the membrane. How to correct it depends on the fouling characteristics. Thus, in the case of surface fouling, a change in the flow direction by defined time intervals or by pulses may be sufficient to eliminate the problem. In other situations like fouling inside of the membrane or persistent deposits on the surface, it will be necessary to use cleaning chemicals.

The best way to delay the fouling problems is to foresee them identifying the causes. Sometimes this is possible with small changes in operation, and optimizing work differential pressure in order to slow down pores clogging. The operating pressures should be lower than those of maximum flow but sufficient to maintain an advantageous ratio permeate flow-time. It is also recommendable to determine whether adsorption processes are pH dependent, and if the case, optimizing working pH; the type of pretreatment that could be made to improve the membrane fouling behavior, etc.

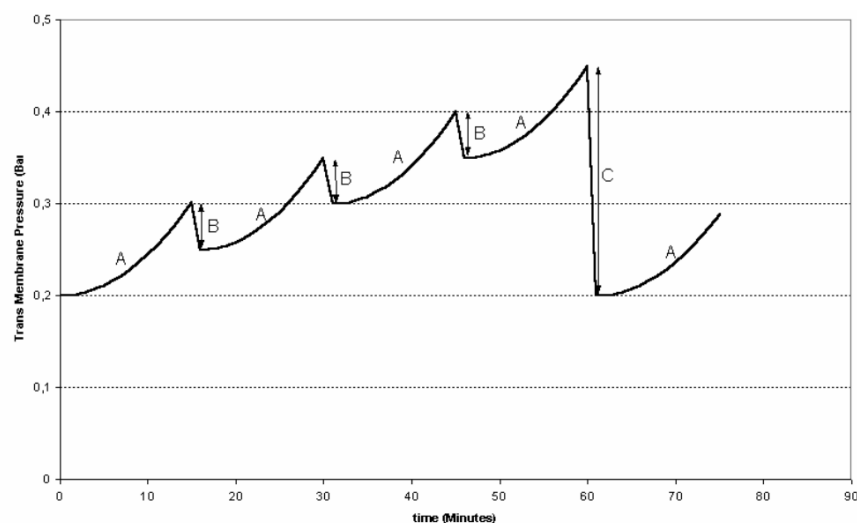


Figure 10.- Working cycle (A), backflush (B) and backflush with chemical cleaning reagents (C) in a UF membrane (Futselaar, Schonewille, & Dalfsen, 2003)

It is also possible to improve fouling by acting on the configuration of the membranes, it has been found that membranes of hollow fibers of small diameter, arranged in vertical orientation and low packing density have better fouling behavior, or that in membranes with high porosity and large pore diameter the reduction in permeate flow occurs sooner (CITME, 2006).

### 5.- Microfiltration (MF) and Ultrafiltration (UF)

In these two technologies membranes act as molecular sieves. The relation between pollutants size/pore size distribution allows the exclusion of contaminants in permeate. Thus, substances bigger than the larger size of the pores will be totally rejected by the membrane, and substances whose size is between the largest and smallest pore size will be partially rejected.

Although the processes of ultrafiltration and microfiltration are based on the same principle as the classical filtration: mechanical separation of particles through a sieve, it must be outlined that this is only applicable to suspensions, while in microfiltration and ultrafiltration, the exclusion of particles by membrane takes place in the case of colloidal dispersions and solutions.

#### 5.1.- Microfiltration process fundamentals (MF)

Microfiltration uses transmembrane pressure difference values in the range 100 - 500 kPa, being able to separate particle sizes within the range: 0.1 microns-10 microns, of different natures: suspended solids, fine particles, colloids, algae and microorganisms as bacteria, Giardia lamblia, etc.

Microporous dead-end membranes are used arranged in cartridges which are installed in line. There are also membrane modules allowing cross-flow configurations. For industrial applications, microfiltration membranes are made from polyvinylidene fluorides, polyamides, polyolefins and ceramics (AWWA et al., 1996; CITME, 2006).

Table 3 shows the characteristics of the operations involving microfiltration membranes.

**Table 3. Micropore membranes main characteristics (mod. from CITME, 2006)**

<b>Dead-end Microfiltration</b>	<b>Cross-flow Microfiltration</b>
Low capital cost	High capital costs
High operating costs	Low operating costs
Membranes should be replaced after each process	Membranes life can be extended through proper cleaning program utilization
Simple process without moving parts	Complex operations: cleaning cycles required
Use in the case of effluent with low concentration of particles: membranes replacing increases with increasing particle concentration in the feed	Use in the case of effluents with high concentration of particles: costs relatively independent of particle concentration in the effluent to be treated
Typical Applications: - Sterilization by filtration - Clarification and sterilization of beer	Typical Applications: - Recovery and recycling of microorganisms in membrane bioreactors - Water treatment with dispersed colloidal oil

#### 5.2.- Ultrafiltration process fundamentals (UF)

Ultrafiltration uses differences in **transmembrane pressure (TMP) from 100 to 800 kPa**, with a range of pore size of 10 Å - 1000 Å, and can perform separations of microsolute as colloids and macromolecules. The usual way of classifying these membranes is by **molecular weight cut-off (MWCO)**, defined as the molecular weight of protein, globular type, that the membrane can separate by a 90%. The range of molecular weight cutoff ultrafiltration membranes is 10 kD - 900 kD.

When choosing the most suitable membrane, MWCO must be taken into account along with certain physical characteristics of the macromolecules as linearity and rigidity. Flexible linear macromolecules may cross membranes with a MWCO well below their molecular weight. The pH of the medium is another factor that may also change the process of ultrafiltration. Polyacrylic acids, at pH 5 and above, are ionized, forming rigid structures that repel one another and are easily rejected by ultrafiltration membranes. However, at pH 3 or lower they stop being ionized by adopting a more flexible conformation which can pass through the membrane hindering their separation process.

The most commonly used UF membranes are anisotropic Loeb-Sourirajan type where a thin layer of small pore diameter is attached without interruption to a thicker and microporous layer. The materials commonly used in the

manufacture of such membranes are: polyacrylonitrile, polymers polivinilchloride/polyacrylonitrile, polysulfones, polyvinylidene fluoride, aromatic polyamide, cellulose acetate and ceramic materials (oxides of titanium, aluminum and silicon).

The average length of ultrafiltration membranes is of the order of 2 - 3 years. Membranes are usually arranged into modules of flat-sheet, tubular, spiral wound membrane or hollow fiber types. The lower costs of spiral wound membrane modules or hollow fiber type have displaced others. However, in applications where significant fouling problems exist, tubular modules, due to the bigger diameter of the membranes, are of choice and can compensate in this case the higher cost and higher energy consumption, and operating costs due to cleaning and replacement of membranes reduction. The flat-sheet modules can be a less expensive option but with higher fouling problems than tubular modules.

Because in UF relatively large particles like macromolecules and colloids are separated, with relatively small diffusion coefficient values ( $D_i$ ); the relation  $C_{im}/C_{iB}$  may vary between 20 - 50, which means that high values of concentration polarization can be reached, creating an adjacent gel to the membrane in seconds that can reduce permeate flow from 1 cm<sup>3</sup>/cm<sup>2</sup>·min, for clean water, to 0.1 cm<sup>3</sup>/cm<sup>2</sup>·min in the case of a colloidal suspension.

Elimination of substances that usually foul the ultrafiltration membrane like residues colloidal dispersions and gelatinous materials is performed by cleaning cycles with a frequency and duration that depends on the separation operation being carried out. The steps of a standard cleaning cycle could be: i) membrane rinsed with hot water and high flow velocity, ii) washing with acid or base, depending on the nature of the membrane, iii) flushing the system with hot detergent and iv) system rinsed with water to remove detergent residue.

### 5.3.- Microfiltration and ultrafiltration systems design

The design of water treatment systems with MF and UF membranes involves communication with suppliers or those who are familiar with the product (Bergman, 2005). Many systems have particular design elements that the supplier must know (Bergman, 2005). Given this fact, the following guidelines are adapted, if not to all, to most of MF and UF systems.

The **permeate flow** ( $J_w$ ) is estimated from the Poiseuille equation.

$$J_w = \frac{\varepsilon d^2}{32\mu L} \Delta p$$

$\Delta P$ : the TMP difference

$d$ : the pore diameter

$\mu$ : water viscosity

$L$ : pore length

$\varepsilon$ : porosity of the membrane

According to the average pore diameters ratio: MF (1 micron  $\ll$  10000 Å) 100 times greater than UF (100 Å) filtering flows per unit pressure may have a large variation, which will condition the industrial use of these technologies. Transporting substances,  $i$ , through the membrane is due to the convective flow ( $J_i$ ) inside the pores. The estimation of this flow may be performed by Darcy equation.

$$J_i = K C_i \frac{\Delta p}{\Delta x}$$

$\Delta p/\Delta x$ : transmembrane pressure gradient

$A_x$ : membrane width

$c_i$ : concentration of substance  $i$  in the medium

$K$ : coefficient which takes into account the characteristics of the membrane

The clean membrane resistance varies from one type to another. The resistance increase may be due to the deposition of materials on the membrane surface, the polarization effect, pores clogging and the membrane absorption. The "cake" formed can improve membrane performance until the time when it is removed by backwashing and starts to regenerate in the next cycle.

#### 5.3.1.- Configuration

There are two basic types of MF and UF processes used in water treatment: pressurized systems where the membranes are encapsulated in pressure chambers and vacuum systems including membranes submerged in tanks. There are significant differences in facilities for these configurations; therefore, selecting the configuration before giving a detailed design of the facility is a common practice. The chosen equipment is often determined by a comparative process considering investment costs and life cycle based on criteria drawn from pilot scale tests (Bergman, 2005).

## 5.4.- General applications for UF and MF systems

### 5.4.1.- Microfiltration applications

Table 4 shows common filtered water volumes per membrane unit  $m^2$  in different applications.

**Table 4. Permeate volumes for different microfiltration applications (CITME, 2006)**

Origin	Permeate volume ( $m^3/m^2$ )
Well water	1000
Electronics industry process water	500
Drinking water	200
Wine	50
Pharmaceutical industry process water	50 – 10
Fruit juice	2
Sera (7% protein)	0.6

Microfiltration applications are conditioned to the development of cross-flow filtration systems that allow a longer duration of treatment membranes and flow of water with a higher concentration of contaminants.

### 5.4.2.- Ultrafiltration applications

As unique technology it is used in the treatment of wastewater streams, especially in cases such as hot water treatment and proteins recovery in the food industry; recovery of paint particles from water in industrial parts painting processes; recovery of oils present in the process water in the metal industry, etc. In all cases the dual purpose of recovering a valuable product and/or reusing water arise.

Depending on the intended objectives, the savings due to wastewater treatment by UF can be estimated as (CITME, 2006):

- **Water reuse**, reducing the cost of water consumption from the municipal supply network in 0.25 to 0.5 US  $\$/m^3$  of water reused.
- **Hot water treatment** in such waters where the temperature can be up to 50 °C, the UF treatment is possible without pre-cooling. The savings can be 1 US  $\$/m^3$  of water reused, as well as saving energy, lower fouling problems will lower the costs for membranes replacement.
- **Industrial wastewater treatment cost reduction**, water reuse avoids largely effluent discharge to public sewerage and to the same extent, treatment costs related to compliance with the regulations on discharge limits. Based on food and automotive industries and supply (bodywork painting) savings can be estimated at 0.25 - 2.5 US  $\$/m^3$  of water reused.
- **Product recovery**: UF allows recovery of valuable products that can be recycled in the production process. The influence of this application in the economics of the process will depend on the value and quantity of product recovered. Using UF technology on a larger scale it is determined by the high operating costs due to the problems of membrane fouling.

## 5.5.- Microfiltration and ultrafiltration applications in textile effluent treatments

Microfiltration has **limited application in the treatment of textile wastewater**, due to its proximity to conventional filtration processes. It is mainly used for the removal of suspended particles and colloidal dyes in exhaustion dyeing processes and in washing flows rejection from dyeing processes. However, it allows auxiliary substances as dissolved, reactive organic contaminants and other soluble contaminants to escape with permeate. Therefore, microfiltration has a relatively low use, as an isolated treatment technique in wastewater as complex as textile effluents. Thus, it is mainly used as a pretreatment system in combined systems in order to complement other processes that correctly remove dyes and other soluble pollutants, but fail to remove colloids and suspended solids (Dasgupta et al., 2015).

Wool degreasing produces a high BOD effluent (6000 mg  $O_2/L$ ) containing detergent, suspended solids, fats and oils that can be subjected to biological treatment and/or dissolved air flotation. Using ultrafiltration, with working pressures between 8-10 bar, it allows a substantial concentration for most of the pollutants in the retentate stream. The concentration factor is typically  $\sim 7$ , producing a high organic concentrate (10-35% in COD weight). The largest UF plant for wool degreasing is in Norway. This UF plant is operational since 1989, obtaining COD removal efficiencies of  $>80\%$ , although obtaining an effluent which COD level is still not suitable for reuse (Judd, 2003b).

Ellouze, Tahri, & Amar (2012) compared the performance of textile wastewater treatment using coagulation/flocculation/nanofiltration and microfiltration/nanofiltration systems, noting that for the same volume reduction factor (VRF) close to 8, the NF permeate flow obtained by microfiltration (34 L/h.m<sup>2</sup>) was considerably higher than that obtained using coagulation/flocculation (14 L/h.m<sup>2</sup>). This observation was attributed to significant color retention, COD, turbidity and salinity provided by microfiltration pretreatment as opposed to the presence of large amounts of colloidal material in the feed coming from the pretreatment by coagulation. Colloidal matter present aggravated NF membranes fouling. The study established therefore the superiority of microfiltration over coagulation-flocculation as nanofiltration pretreatment in textile wastewater. Microfiltration can also be used as a posttreatment.

**Table 5. Summary of some MF studies in textile effluent treatment (mod. from Dasgupta et al., 2015)**

Process description	Membrane Specification	Effluents present	Component(s) removed	Permeate Flux
Advanced oxidation process (AOP)/ microfiltration (MF)	Fabricated (average pore size of 0.31 µm)	Crystal violet aqueous solution	100% dye removal and dispersed particles	–
Cross flow microfiltration (CMF)	Ceramic Membrane Tubular multichannel configuration	Garment processing industry discharge: sulphur black dye, turbidity (5912 NTU) and COD (3910 mg/L)	SST: 51% Dye: <50% COD: 22-24% Turbidity. and dye: >99%	1 h flow at 1 kg/cm <sup>2</sup> TMP: 100 L/m <sup>2</sup> /h
Biosorption/CMF	Filtration Area: 0.045 m <sup>2</sup>		SST: 98-99% COD: 80% Turbidity and dye: >99% SST: >94-98% COD: 80%	1 h flow at 1 kg/cm <sup>2</sup> TMP: 130 L/m <sup>2</sup> /h 1 h flow at 1 kg/cm <sup>2</sup> TMP: 150 L/m <sup>2</sup> /h
Coagulation/CMF			Turbidity and dye: >99%	

(Bhattacharya, Dutta, Ghosh, Vedajananda, & Bandyopadhyay, 2010)

Recently, there have been attempts to make modified microfiltration membranes to provide a direct treatment of textile effluents. For this reason, asymmetrical tubular microfiltration membranes made of mineral coal and thermostable resin have been created. These membranes could successfully treat textile industrial effluents, reaching satisfactory permeate flow and removal efficiencies, providing a 50% removal of COD, with a retention of 30% salinity; while turbidity and color were almost completely eliminated.

The ultrafiltration membrane processes, like microfiltration, have limited applications in the textile industry, mainly because the molecular weights of the dyes present in the textile industry highly colored effluents are much smaller than the molecular weight cut-off (MWCO) provided by UF membranes. Consequently, rejection of dyes provided by a UF single process does not exceed 90%, although there have been good results in dye and COD removal in the case of hydrophobic UF membranes, as polyether-sulfone and polyvinylidene fluoride (PVDF). UF reused water can be used only in subsidiary textile processes as rinses and washes. However, it is not qualified water to other applications like primary dyeing of fibers processes, which require a soft, clean water supply. UF is usually employed as a pretreatment step in systems requiring a high level of purification; followed by other processes such as nanofiltration or reverse osmosis to meet the needs of process quality.

Some innovative measures have been evaluated in order to improve the capabilities of the UF treatment in textile wastewater. For example, Marcucci et al. (2001) created modules configured to adapt submerged flat-sheet UF membranes for this purpose. Another example found in Srivastava et al. (2011) examined changes in the surface of PVDF membranes at varying concentrations of styrene acrylonitrile (SAN). These membranes were used to remove color and COD (84.6-96.9%) dyes RB5 and CR (removal of up to 70% and 97% respectively) aqueous solutions, resulting suitable to improve the performance against fouling. Annex 1 includes additional information on other ultrafiltration applications in textile effluents.

However, conventional polymeric membranes often fail when coping with test conditions due to their low resistance to chemicals such as organic solvents, high working temperatures or acidic/caustic medium (Barredo-Damas, Alcaina-Miranda, Iborra-Clar, & Mendoza-Roca, 2012). Furthermore, the progressive fouling with the consequent reduction in permeate flow is common, what can lead to significant economic losses over the full lifecycle. This causes the need for combined processes where UF is preceded, for example, by a flocculation process.

## 6.- Reverse osmosis and nanofiltration

RO and NF can be described as processes where ions mass transfer through the membrane is diffusion controlled. Accordingly, these processes can lead to the removal of salts, pathogens, turbidity, disinfection by products precursors (DBPs), synthetic organic compounds (SOC), pesticides and most drinking water contaminants known today.

Most dissolved gases such as hydrogen sulfide (H<sub>2</sub>S) and carbon dioxide (CO<sub>2</sub>) along with some pesticides pass through the NF and RO membranes. However, membrane technology may be used to treat a greater number of contaminants in drinking water, more than any other treatment technology (AWWA, 1996).

RO is able to reject contaminants or particles with diameters as small as 0.0001 microns, while the NF may do the same with pollutants as small as 0.001 microns.

### 6.1.- NF and RO process characteristics

The performance of nanofiltration technology lies between UF and RO. It utilizes membranes with molecular weight cutoff of 150 D - 1000 D and sodium chloride rejection coefficients of 0.2 to 0.80%. NF is applied to water treatment with a salt concentration of 200 mg/L - 5000 mg/L with pressures of 5 - 10 bar, the reason why it is also called low pressure reverse osmosis. It allows a small retention of monovalent ions, which improves its behavior in the rejection and reuse of low salinity solutions, while it provides close to 100% removal rate of multivalent ions, resulting in a high selectivity of solutes. Nanofiltration substance rejection is primarily governed by steric and charge repulsion. Other advantages attributed to NF include its high permeability to solvent, retention of neutral solutes as organic molecules bigger than 150 Da, modular construction (what facilitates scaling), ease of chemical cleaning and ability to withstand high temperatures up to about 70 °C, which reduces power consumption in industrial water supply reuse (CITME, 2006; Dasgupta et al., 2015).

**Reverse osmosis** process consists in generating, through a water permeable membrane, an aqueous solution with low salt content from another with high salt content. It is the technology used to produce desalinated water from seawater. As in MF and UF, the cause that generates the driving force to achieve separation of the salt is transmembrane pressure (TMP). However, in RO the separation process is conducted by the different solubility and diffusivity in the membrane of the aqueous solution components. Operating TMP values and solution concentration are 7-70 bar and from 200 to 30,000 ppm, respectively (CITME, 2006).

#### 6.1.1.- Osmosis and nanofiltration membranes

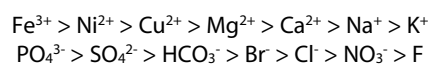
Dense anisotropic membranes are used in RO and NF, in spiral wound configuration, with modules size around 20 cm - 30 cm in diameter and 100 to 150 cm long; which are disposed 5 - 7 number inside plastic housings reinforced with fiberglass. Hollow fiber membranes type of 100 mm in diameter, arranged in modules containing 1000 units (Table 6), are also used. The type of membrane depends on the characteristics of the water to be treated, considering that hollow fiber membranes configuration has higher fouling problems than spiral configurations (CITME, 2006).

**Table 6. Reverse osmosis membranes materials and typologies (CITME, 2006)**

Material	Membrane	Reject coefficient (%)	Work pressure (bar)	Permeate flow (L/m <sup>2</sup> .h)
CA Celulose acetate (40% acetate)	Loeb Sourirajan	95-98	50-90	15-30
Aromatic polyamide	Loeb-Sourirajan	>99,5		0.5 - 1.34
NTR (nanofiltration)				
Polisulfones/polyvinyl alcohol	Loeb-Sourirajan	20 - 80	3.5 - 14	Acceptable
NS100				
Poliethylenamine/toluene	Composite	>99	100	8
FT-30/SW-30	Composite	99.3 - 99.5	55	
Phenylendiamine/chlorure de trimesoyl		>99	15	11

The performance of the RO membranes used can be summarized in the following points:

- Multivalent ions are retained better than monovalent. From a rejection coefficient view, they can be classified as:



Dissolved gases as ammonia, carbon dioxide, sulfur dioxide, oxygen, chlorine and hydrogen sulfide have good permeability. Acids and weak bases rejection is higher at pH values where they are in ionized form.

The rejection of neutral organic molecules increases with compounds molecular weights. As an example, compounds above 100 D exhibit high rejection coefficient values. The nature of the membrane material has an

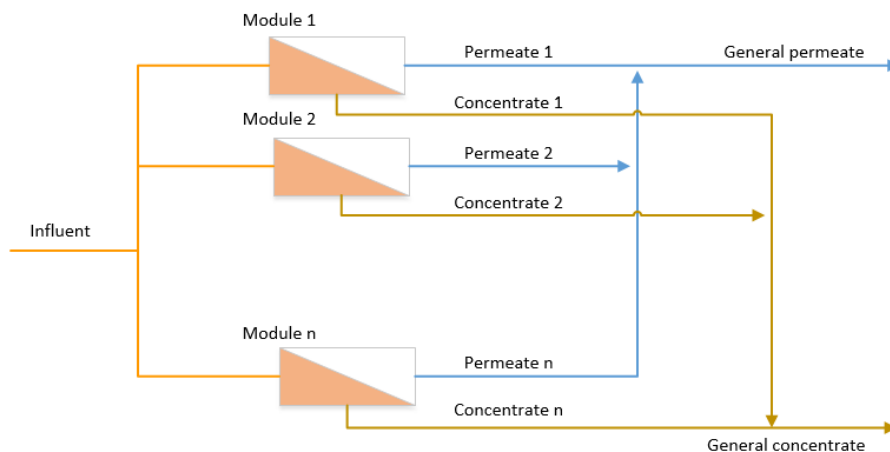
important influence on the value of this parameter. Negative values of rejection coefficient for solutes like phenol and benzene were observed in cellulose acetate membranes (CITME, 2006).

### 6.1.2.- Nanofiltration and reverse osmosis modules

Required permeate flow rate rarely matches that of a particular module, while it is often quite superior. Therefore, a set of modules should be used to achieve the desired flow.

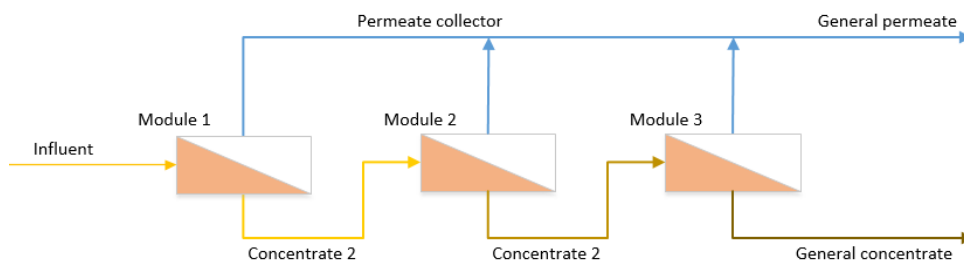
The modules of a reverse osmosis system can be grouped in two ways: in series or parallel.

In parallel: Water inlet, together with permeate and concentrate outlets, are respectively connected to general pipes, as shown in Figure 11. This configuration is used to produce permeate flow  $n$  times higher than that provided by a single module. Since the maximum rejection coefficient for the full system is the same as that of a single module. It is important that, when several modules are working in parallel, membranes aging should be similar. Otherwise imbalances will take place in individual streams, what would make newer units to work with higher flows, leading to rapid clogging phenomena (Fariñas I., 1999).



**Figure 11.- Membrane modules arranged in parallel (Fariñas I., 1999)**

In series: The concentrate flow of each module enters as the inlet of another membrane unit and so on, as showed in Figure 12. Membrane modules permeate is collected in a common collector. This configuration is used to reduce polarization phenomena at high permeate flows or at high conversion performance.



**Figure 12.- Membrane modules arranged in series (Fariñas I., 1999)**

### 6.1.3.- Specific fouling problems

Due to the high values of rejection in RO processes, fouling is the most important malfunction of the membranes. The most common causes of fouling are due to:

- Surface crusts or scales deposit on the membrane surface composed by calcium carbonate, calcium sulfate, complex silicates, barium, strontium sulfate, calcium fluoride, sulfate etc., depending on the feed composition and as a consequence of salt levels in the concentrate flow that may exceed the solubility of the salt.
- Sediment particles as colloids, corrosion products of iron pipes, iron hydroxide precipitates, algae, etc.
- Biofouling due to microbial growth on the surface of the membrane, as some membrane materials, such as cellulose acetate or polyamide, can be an useable substrate by microorganisms
- Fouling from organic compounds such as oils or fats present in industrial wastewater.

The way of cleaning the membranes will **depend on the feed water characteristics, the membrane type and nature of fouling**, as a general guideline the plant operator can proceed to alternate periods of membrane rinsing by circulating the cleaning solutions at high speed over the surface of membranes, with periods where the membranes are submerged in the cleaning solutions.

**Cleaning agents** commonly used are i) hydrochloric, phosphoric or citric acids and chelating agents such as EDTA, to remove precipitated salt crusts, and oxalic acid to remove sediment iron ii) combined alkalis with surfactants to kill microorganisms, sediments and organic compounds iii) sterilization of the membranes with solutions of chlorine to kill microorganisms.

Successive cleanings eventually degrade the membranes. Depending on the application, the lifetime guaranteed by the manufacturer is usually 1-2 years. With a good cleaning program membrane life can be extended to 3 years, with improbable life periods of 5 years (CITME, 2006).

The use of recirculation system allows the generation of high flow velocity on the surface of the membranes, reducing significantly the polarization phenomena and contamination risks, at the cost of increased pumping power consumption. It is a solution which can be appropriate with high salinity water (Fariñas I., 1999).

## 6.2.- General applications of NF and RO systems

### 6.2.1.- Nanofiltration

It is used to purify drinking water in small communities, elimination of water hardness and as a pretreatment for ultrapure water.

### 6.2.2.- Reverse osmosis

General applications for installed RO plants are desalination of seawater and brackish water; production of ultrapure water in electronics industry, pharmaceutical and energy production industries; decontamination systems of urban and industrial wastewater (CITME, 2006).

#### Brackish water desalination

The salinity of this type of water ranges between 2000 mg/L-10000 mg/L. 14 - 21 bar pressure levels are employed in order to achieve rejection ratios above 90%, obtaining water with salt concentrations lower than 500 mg/L, which are recommended by WHO as a requirement in potable water. Treatment plants use spiral wound membrane modules. It is estimated that the capital costs of these plants are in the range of 0.25 US \$/L treated water/day, with operating costs in the same order of magnitude.

#### Wastewater treatment

This application of the RO is constrained by high operating costs due to membrane fouling problems. In the case of industrial wastewater, the RO is used in industries where it is possible to improve process economy by means of valuable components recovery that can be recycled back into the production process like in electroplating industries, painting of metal structures or where the reuse of treated water means a significant reduction of water consumption (textile industry).

In the case of urban water, the RO is a process indicated as tertiary treatment, being possible to obtain water with a quality that would make it ready for consumption, with a cost of 0.5 to 0.75 US \$/m<sup>3</sup>. The main problem for the consolidation of this type of treatment is the social controversy. However, in areas of Japan and California, where there are extreme water shortages, RO plants are being used to treat wastewater from the biological treatment, using RO treated water to recharge aquifers (CITME, 2006).

## 6.3.- Nanofiltration and reverse osmosis applications in textile effluent treatment

### 6.3.1.- Nanofiltration

NF technology has an increasing popularity through the years as a simple and effective technology for textile effluent treatment, what can be attributed to several benefits in terms of pollution prevention, rejection of contaminants, recovery and reuse of textile dyes, divalent salts and other auxiliaries; brine recovery and reuse. Furthermore, permeate flow quality allows reuse in the main processes of dyeing and finishing lines (Dasgupta et al., 2015).

Yu et al. (2012) examined the behavior of submerge NF in aqueous solutions of anionic dyes through hollow fiber membranes composed of a thin layer of sodium carboxymethylcellulose (CMCNa)/polypropylene. Hollow fiber membranes are generally preferred over flat-sheet membranes, due to the improvement in energy efficiency along



with a high surface/volume ratio. Moreover, submerged membrane filtration technology provides advantages as relatively smaller energy and cleaning requirements than cross-flow filtration. The rejection rate of dye (Congo Red and Blue methyl), salt rejection and water flux in an aqueous solution of 2000 mg/L of dye and 10,000 mg/L NaCl were 99.8%, less than 2.0% and 7.0 L/m<sup>2</sup>.h.bar respectively. The electrostatic repulsion between dye molecules and the negative charged surface of this new type of membranes was considered as the immersed nanofiltration main process mechanism of the dye aqueous solution.

In another study, Bes-Pia et al. (2010) evaluated the behavior of six spiral wound membrane modules, namely TFC-SR2, ESNA, NF270, DS-5 DK, DS-5 DL and Duraslick in textile secondary effluent treatment. The performance of the six NF membranes was investigated for a wide range of volume-concentration factor (VCF) examining the resulting trends in membrane fouling and permeate characteristics. The results showed that for all membranes, the normalized flow went down proportionally to the increase in VCF. The NF membrane load has a significant influence on solute rejection and reuse of treated effluent. However, most commercial NF membranes are negatively charged in normal operating conditions with low values of the pH isoelectric point (Cheng et al., 2012).

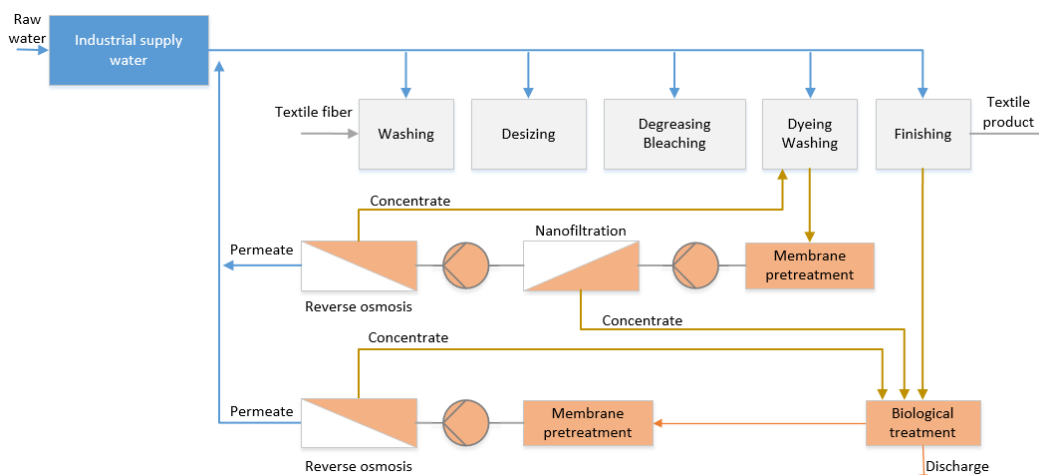
A summary table about different studies of nanofiltration treatment of textile effluents is included in Annex 1.

### 6.3.2.- Reverse osmosis

Reverse osmosis is effective in removing macromolecules as well as the textile discharge ions. The effluent obtained is usually colorless and has low salinity. However, the use of dense polymer membranes and the osmotic pressure rise due to high salt concentrations becomes a constraint to permeate flux, and can sometimes lead to high fouling levels, which affects the performance of the membrane. Thus, in RO systems with pressures above 2000 kPa, it is necessary to maintain a reasonable flow level, which is again an impact from the process economical point of view (Dasgupta et al., 2015).

Two of the studies (Marcucci et al., 2001; Sójka-Ledakowicz et al., 1998), which incorporated tests of reclaimed water for dyeing process, concluded that RO step was required in order to obtain water ready to reuse. The effluent from dyeing line is typically high in dissolved solids and low in suspended solids, including color from the exhaust dyeing. It is recommendable to retain dissolved reagents to remove color at very low levels. The ultrafiltration membrane processes allow a selective recovery of sparingly soluble dyes such as indigo, but a process of reverse osmosis is normally required downstream to remove soluble dyes.

In an example given in Fariñas I. (1999), the effluent from the dyeing and washing tanks are conducted, after pretreatment, to a nanofiltration system which retains the dye and allows the passage of salt water. The nanofiltration permeate is then sent to RO modules and the reject is led to biological treatment. High rejection RO membranes require high pressure avoiding the pass of salts contained in water, so that they are recovered in the reject, with a concentration of 70 g/L, being returned to the dye bath. The permeate from the reverse osmosis has high water quality, being reused in the process. The effluent from biological treatment, after a preliminary pretreatment, is sent to a second RO system. The permeate from this second osmosis is reused in the process again while rejection is returned to the biological treatment (Fariñas, 1999).



**Figure 13.- Dyeing process effluent treatment scheme using NF and RO membranes (Fariñas I., 1999)**

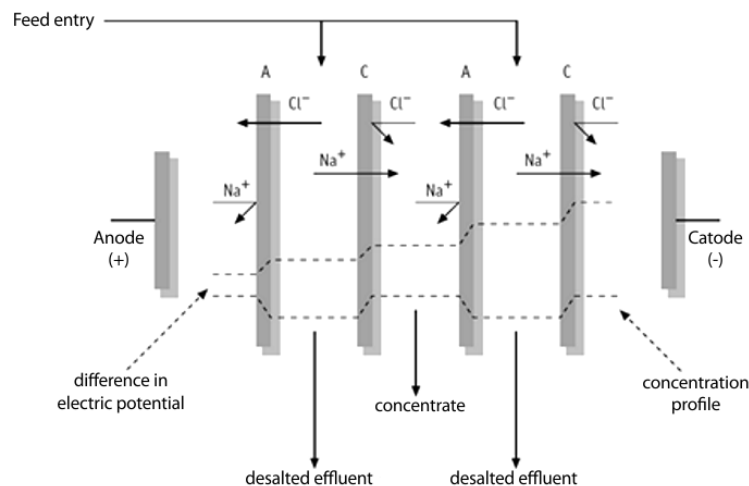
Liu et al. (2011) conducted a comparison of the efficiency showed by NF and RO in textile effluent processing from biological treatment, based on the evaluation of the permeate quality obtained with each technique. The tests were conducted using NF90 flat RO membranes and BW30 NF membranes in a wide range of concentration ratios and different hydrodynamic conditions. Treated effluents were satisfactory in both cases as reuse water with adequate quality for textile processes, such as dyeing and washing, what allows savings in energy and water as well as in the treatment necessary to water discharge.

## 7.- Electrodialysis (ED)

Separation processes based on electrodialysis employ membranes where groups with electrical charges are introduced, in order to restrict ions present in an aqueous solution crossing through them. In these processes the driving force responsible for the flow of ions through the membrane is an electric potential difference (CITME, 2006).

### 7.1.- Electrodialysis process fundamentals

An electrodialysis equipment is formed by a set of cation and anion membranes arranged alternatively and separated by spacers or plates, in a configuration similar to a filter press. Spacers which prevent turbulences cause materials deposition on the surface of the membranes and homogenize concentration. Figure 14 shows a scheme of this arrangement.



**Figure 14.- Electrodialysis equipment (CITME, 2006)**

The water to be treated (feed) flows in longitudinal direction to the membranes, and the electric field created by the potential difference causes a transverse flow of positive ions towards the cathode and the negative ions towards the anode. The anion exchange membranes (A), which are positively charged, allow the passage of negative ions and retain the positive, similarly to cationic membranes (C), which are negatively charged, allowing only the passage of positive ions. The number of cells (pairs of anionic and cationic membranes) that are contained in the electrodialysis equipment is variable and usually greater than 100.

Thus, due to alternating cationic and anionic membranes, aqueous influent (feed) is separated into two effluents, one with higher concentration of salt (concentrate) and other desalted.

The voltage across each cell is 1 - 2 V and the values of the current density of about 40 mA/cm<sup>2</sup>. For a standard equipment of 200 cells with 1 m<sup>2</sup> of membrane surface, the voltage potential is 200 to 400 V and intensity of 400 A. The electrodialysis needs continuous power, so process economics is based on the optimization of consumed electricity in the separation of concentrate and desalted effluent.

The relationship between separation requirements: molar concentration difference between feed and desalted effluent ( $\Delta c$ ) is related to the intensity of the current flowing through the system, using the following equation:

$$I = z \cdot \Delta c \cdot F \cdot Q$$

Where  $I$  is the intensity of electrical current,  $z$  the salt valence,  $F$  the electrical charge of one mole of electrons (faraday - 96500 coulombs) and  $Q$  the flow rate. The electrical energy consumption ( $E$ ) is expressed as a function of  $I$  by:

$$E = I^2 R = I \cdot R \cdot z \cdot \Delta c \cdot Q \cdot F = V \cdot Z \cdot \Delta c \cdot Q \cdot F$$

Where  $R$  is the resistance of the system to the flow of electric current and  $V$  the potential difference of work. It is estimated that the theoretical energy consumption in the case of electro dialysis water of 200 to 40.000 mg/L and coefficients rejection of 80% - 95% are in the range 1 - 13 kWh/1 m<sup>3</sup> of demineralized water (CITME, 2006).

### 7.1.1.- Membranes used in the electro dialysis process

There is a variety of membranes developed by each producer for the specific requested applications. They are classified into homogeneous and heterogeneous membranes, considering the fact that electrically charged groups are homogeneously distributed in the matrix of the membrane or in certain places. Both types of membranes may present problems of malfunction due to swelling derived from water absorption by polar groups. Homogeneous membranes are made from polymers of styrene/divinylbenzene or perfluorocarbon polymers. Heterogeneous membranes are manufactured from polypropylene or polyvinyl chloride (CITME, 2006).

### 7.1.2.- Causes of malfunction: concentration polarization

In working conditions, the concentration of ions in the spaces between membranes is not homogeneous, producing a decrease in the concentration of ions close to the membrane, which leads to concentration polarization, as indicated in Figure 15, in the case of a cationic membrane.

Following the concentration polarization in the vicinity of the membrane, the concentration difference ( $c_i^+ - c_m^+$ ) is greater than the concentration difference operation  $\Delta c = (c_c^+ - c^+)$ , which means a larger membrane potential drop and therefore a higher energy ( $E$ ) consumption, which can be 5 to 10 times greater than estimated.

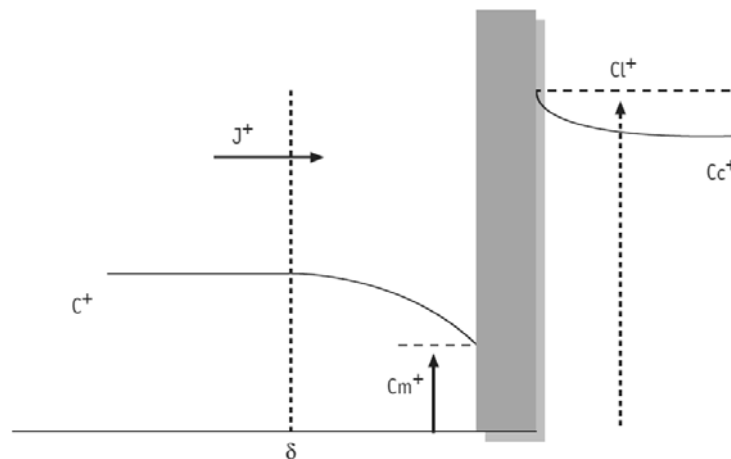


Figure 15.- Cationic membrane polarization (CITME, 2006)

Furthermore, because of the concentration profile, the flow of positive ions ( $J^+$ ) has two addends: diffusive and electrolytic transport:

$$J^+ = D^+ \frac{(c^+ - c_m^+)}{\delta} + \frac{I}{F} t^+$$

Where  $D^+$  is the diffusivity of the cations,  $(c^+ - c_m^+)$  is the difference in concentration of the cations in the feed and in the vicinity of the membrane,  $\delta$ , the width of the film next to the membrane where the cation concentration change takes place and  $t^+$  is the transport number of the cations or the cations ratio in the total charge flow.

Furthermore, the flow of cations in the membrane can be approximated to  $I/F$ , since being a cationic membrane, the entire electrolytic current will be due to the positive ions.

At steady state and combining the two equations

$$I = \frac{F D}{(1 - t^+)} \delta (c^+ - c_m^-) \xrightarrow{c_m^+ \rightarrow 0} I_{lim} = \frac{D^+ F c^+}{\delta(1 - t^+)}$$

$I_{lim}$  is the current limit reached when the concentration in the vicinity of the membrane becomes zero. Its value must be determined experimentally. The excess current over the limit value is not used in the separation operation,

but in other processes such as anion transport across the cation membrane or dissociation of water molecules. The way to avoid concentration polarization, and thus to minimize both the problem of the current limit intensity and the energy consumption increase, is the use of spacers with specific designs to cause turbulence concentrations which homogenize the flow circulation through the membranes (CITME, 2006).

Other malfunction causes can be:

- Certain membrane permeability to ions having the same charge
- Transport of water through the membrane due to the solvation of ions or osmotic processes
- Fouling problems.

### 7.2.- General electro dialysis systems application

The most important ED applications are desalination of brackish water and brine production, with an emerging presence in the food industry and industrial water treatment.

#### *Brackish water desalination*

It is the technology of choice, against RO, in the case of aqueous solutions with 500 mg/L - 2000 mg/L of salt as operating costs are lower. Power consumption is directly proportional to the salt concentration of the feed, ranging from 1 kWh/m<sup>3</sup> for influent with 1000 mg/L of salt until 10 kWh/m<sup>3</sup>-15 kWh/m<sup>3</sup> in the case of salt concentrations influent with 5000 mg/L (CITME, 2006).

### 7.3.- Electrolysis process applications in textile effluents treatment

Electrolysis is quite common in the textile industry, in removing pollutants from wastewater. ED is highly functional in removing chloride, which is particularly effective in complying with textile industries discharge legislation, where large bulk amounts of NaCl are used. Additionally, ED with bipolar membranes (EDBM) has increased the interest in the technique due to its high energy efficiency and in terms of cost compared to reverse osmosis processes, more energy intensive (Dasgupta et al., 2015).

ED can also be employed to reduce the volumetric load on evaporator processes, by concentrating the reject stream from RO units. The efficiency of the ED membranes process to achieve desirable concentrations from RO discharge was evaluated by Praneeth et al. (2014). The possibility of generating a concentrate with salt level 6 times higher than RO rejection was explored using a system with five pairs of membranes. Limiting current densities for feed flows varying between 18-108 L/h were observed in the range 2.15 - 3.35 A/m<sup>2</sup>; operating cost was about an eighth of which would be required using isolated evaporation process. Moreover, the percentage of inorganic constituents in the digested product was improved from 4.35% to about 24%. The ED has been found to be particularly applicable in RO rejection treatment with low COD concentrations. The diluted stream may be recycled to the RO plant for later reuse as process water.

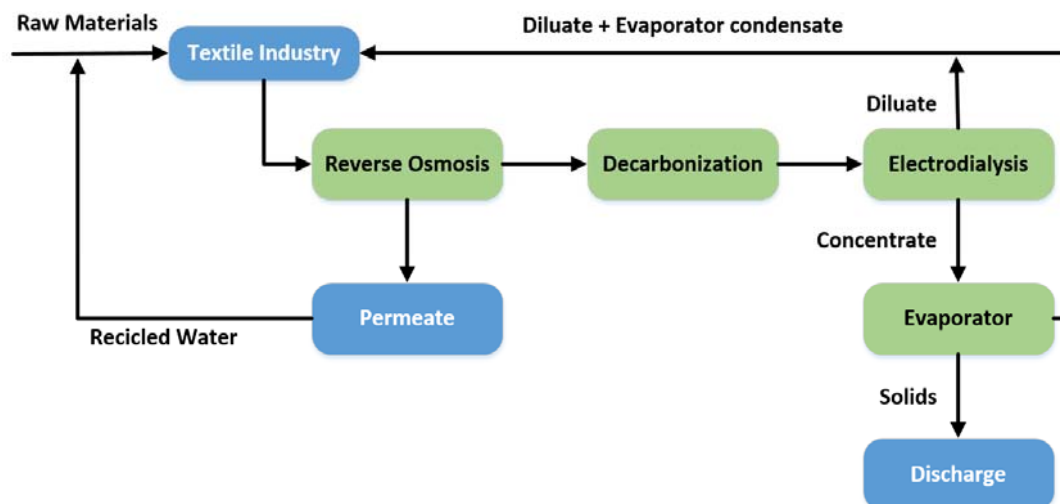


Figure 16.- Integrated process flowchart for the RO rejection stream with ED (mod. from Singhal & Gupta, 2009)

## 8.- Membrane concentrate management and coupling with other treatments in textile effluent treatment

The use of the right technology depends on the material of the membrane, and certain mechanical properties such as thermal and chemical resistance and susceptibility to fouling; furthermore, the pore size, which determines the substances that can be effectively retained by the membrane and the membrane morphology, indicating its potential to resist clogging.

Additionally, the management of the concentrate flow, with contaminants from the water feed and other reagents that have been added during the treatment, is also a challenge when using membrane processes in textile effluents. Concentrate flow treatment has to be explored in terms of cost, energy efficiency and reduced impact on the natural environment.

Thus, the direct discharge of NF and RO concentrate in exhaust dyeing lines is not an environmentally appropriate choice given the complex reactivity of the concentrate compounds, organic materials (dyes and additives such as deforming agents) and inorganic salts. The reuse of this highly colored flow directly is impossible given the heterogeneity of its constituents, usually modified by reactions like hydrolysis.

Bioremediation of rejected dyes with activated sludge systems is often not effective due to recalcitrant dyes presence; in those cases, an anaerobic degradation used in association with membrane processes can be a viable option. Other options, such as ozonation and other advanced oxidation techniques, can also be effective in color removal, though being intensive in terms of cost. The bio-decoloring or biosorption, coupled with degradation by enzymatic catalysis, are other effective treatment options.

However, due to the inflexibility of these techniques of biological treatment, membrane distillation (MD) of NF and RO concentrates, followed by incineration of MD concentrates, is currently seen as the most promising scenario, due to the associated benefit/cost ratio of 3.58. The success of the ZLD approach in such configurations is governed by the membrane distillation process providing the 70-90% of the ratio. The distillate is used in the finishing process, while the value-added energy recovery from the subsequent incineration process is used in other stages of textile effluents treatment (Dasgupta et al., 2015).

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# ANNEX 1

## COMMERCIAL MEMBRANE PRODUCTS INFORMATION

**Table A1a. Summary of different research studies in textile effluent nanofiltration treatment (Dasgupta et al., 2015).**

Process description	Membrane specification	Effluents present	Component(s) removed	Permeate flux
Ultrafiltration (UF) nanofiltration (NF)	UF stage: spiral-wound polyethersulfone (PES) MWCO: 1 kDa NF stage: commercial spiral-wound (2), NF270 and Duraslick NF	Raw effluents (textile finishing industry)	High color, COD and turbidity removal (NF) 71% salts rejection 54% conductivity (Duraslick NF)	Maximal permeate flux (UF) at pH 11 No significant effect of on NF permeate flux. Flux (NF270) > (30%) (Duraslick NF)
Textile wastewater reclamation	Three flat sheet NF membranes: Desal-5, 70 and TS-40	Textile effluent (dyeing facility)	>99% dye removal Rejection (NE-70) > rejection (Desal-5) Turbidity, hardness, TOC and color removal: <0.2 NTU, 60 mg/L as CaCO <sub>3</sub> , 10 mg/L and 5 HU, respectively.	Flux (NE-70) twice flux (Desal-5)
Direct NF and UF/NF	Membranes (NF): NF90, NF200 and NF270 Set up: pilot plant Flat-sheet module Membrane: NF90-2540 Spiral-wound module	Secondary textile effluent (cotton thread factory). Effluent COD: 200 mg TDS: 5000 mg/L	99 % COD reduction. Maximum (95e97%) salt rejection (NF90). Permeate conductivity (NF90) < 500 mS/cm. UF pre-treatment: 40% reduction COD retentions: 80e100% (UF and NF). Conductivity rates (80%) and Decolorization rates >90% (NF).	Flux trend: J (NF270) > J (NF200) > J (NF90). UF pre-treatment: NF permeate flux increase (50%)
Fouling tendency examination	Membrane: NF90-2540 Spiral-wound module	Reactive azo dyes: Everzol Black, Everzol and Everzol Blue. Raw textile effluents (rinsing baths)	Dye rejection: 99.4e99.9%. Electrolyte retention: 63 e73%. Organics retention:	Affected by effluent complexity
Ultrafiltration (UF) nanofiltration (NF). Transmembrane pressure range UF: 2e7 bar NF: 4e15 bar. Reactive dye printing compounds by nanofiltration (NF). Cross-flow velocities: 0.4, 0.6 and 0.8 Pressures (2e15 bar). Dye wastewater	NF: commercial (NF200 NF270). UF: polyethersulfone (10 kDa and 1 kDa) NFT-50 membrane. Plate and frame module.	Reactive dyes: C.I. Red 24, C.I. Reactive 12, C.I. Reactive Blue 19, Reactive Black 5	Dye rejection: 99.4e99.9%. Electrolyte retention: 63 e73%. Organics retention:	50% Permeate flux (adsorption and concentration)
1. Comparison tertiary treatment processes: nanofiltration (NF) and reverse (RO) 2. UF/NF and UF/RO Nanofiltration using novel fabricated membranes.	Nanofiltration polyamide (PA) composite MWCO: 500 Da. 1. NF membrane: HL (flat sheet). 2. NF membrane: (spiral-wound) MWCO: 150e300 Da. 3. RO membrane: AG2514TF Configurations: dead end and cross-flow UV-photografting p-styrene sulfonate monomer on polysulfone UF membrane. MWCO: 1200e1300 Da	Separate aqueous of 5 different dyes: Red 75, 80 and 81. Direct Yellow 8 and 27. Model dyeing Direct Red 75, PVA, NaCl and Na <sub>2</sub> SO <sub>4</sub> Raw effluents (denim dyeing factory)	Almost 100% dyes Retention efficiency improvement after coagulation (alum) pre-treatment NF permeate quality relatively superior. COD < 90 mg/L. 60% TDS rejection above 9 bar. Permeate hardness: 70 mg/L 97% dye retention (0.4 MPa). Fouling tendency (photografted membrane) < fouling tendency (commercial polyamide membrane Desal SDK	20% flux improvement coagulation (alum) pre-treatment 11 bar pressure: 9% permeate yield (NF) < permeate yield (RO) 0.23e0.28 m <sup>3</sup> /m <sup>2</sup> day (0.4 MPa)

**Table A1b. Summary of different research studies in textile effluent nanofiltration treatment (II) (Dasgupta et al., 2015)**

Process description	Membrane specification	Effluents present	Component(s) removed	Permeate flux
Colour and COD rejection	Spiral wound MPS 31 (MWCO: not available) NF 45 (MWCO: 200 Da) DK 1073 (MWCO: 300) Cross-flow configuration	Waste waters: 1. Yellow 3 RS, Remazol Red 3 BS 2. Remazol BTE Blue, RN Special Remazol, BTE BS 3. Remazol Black, BTE Red 3 BS Salts: NaCl, CaCl <sub>2</sub> , Na <sub>2</sub> SO <sub>4</sub>	99% color rejection (DK 1073 and NF 45). 87% COD reduction (DK 1073) Fouling tendency (all the test membranes)	30.5e70 L/h m <sup>2</sup>
Textile dye (polyamide based nanofiltration membrane)	Membrane: Desal 5DK MWCO: 150e300 Da	High molecular weight Direct dyes: direct red direct yellow 8. Anionic dyes: acid orange 10, red 4 Cationic dye: Basic blue 3 Disperse dye:	~100% dye rejection Rejection (pH 3) (pH 6) (anionic dyes) Rejection (pH 6) < (pH 3) (cationic dyes)	Declining flux profile (fouling)
Color removal and reduction	Membrane: organic membrane (unstirred batch and rectangular mode) MWCO: 400 Da	Disperse blue 56 Reactive dye: Reactive orange 16 Reactive black dye (Cibacron Black B), Reactive red dye	94 and 92% dye (reactive black and reactive red dye COD reduction	Flux profile: (i) rise with increase in trans-membrane pressure (ii) with time and increasing feed concentration
Cross flow nanofiltration	Flat sheet polysulfone based thin film composite (TFC-SR2)	CI reactive black 5 Sydney), Salt: NaCl	Average dye rejection: Average NaCl rejection: <14%	Average flux at 500 59.58e78.4% Mean waterflux recovery:99%
Nanofiltration	UV-photografted nanofiltration MWCO increases with increasing hydraulic permeability	Direct red 80 (DR80), disperse blue 56 (DB56), acid red 4 (AR4), reactive orange 16 (RO16) and blue 3 (BB3)	Dye retention: >96% at 0.4 MPa	Hydraulic permeability: 0.48e0.56 m <sup>3</sup> /m <sup>2</sup> day
Nanofiltration	1. Negatively charged polypiperazine (phthalazinone ether sulfone ketone) NF membrane 2. Positively charged quaternized poly (phthalazinone ether sulfone ketone) membrane	Synthetic Sulfur Black B wastewater	QAPPESK NF membrane better than PIP/PPESK NF membrane 92.3% dye Rejection 10% salts rejection at 60 °	Flux: 14.5 L/m <sup>2</sup> h (QAPPESK at 60 °C



## ANNEX 2 GRAPHICAL DESCRIPTION OF UNIT PROCESSES

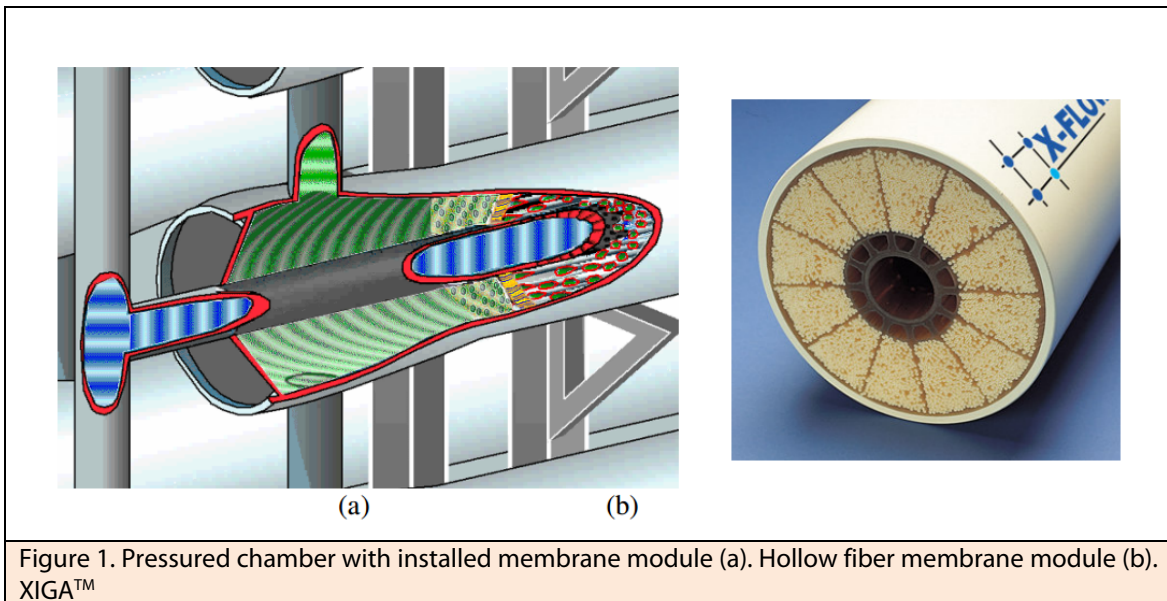


Figure 1. Pressured chamber with installed membrane module (a). Hollow fiber membrane module (b). XIGA™

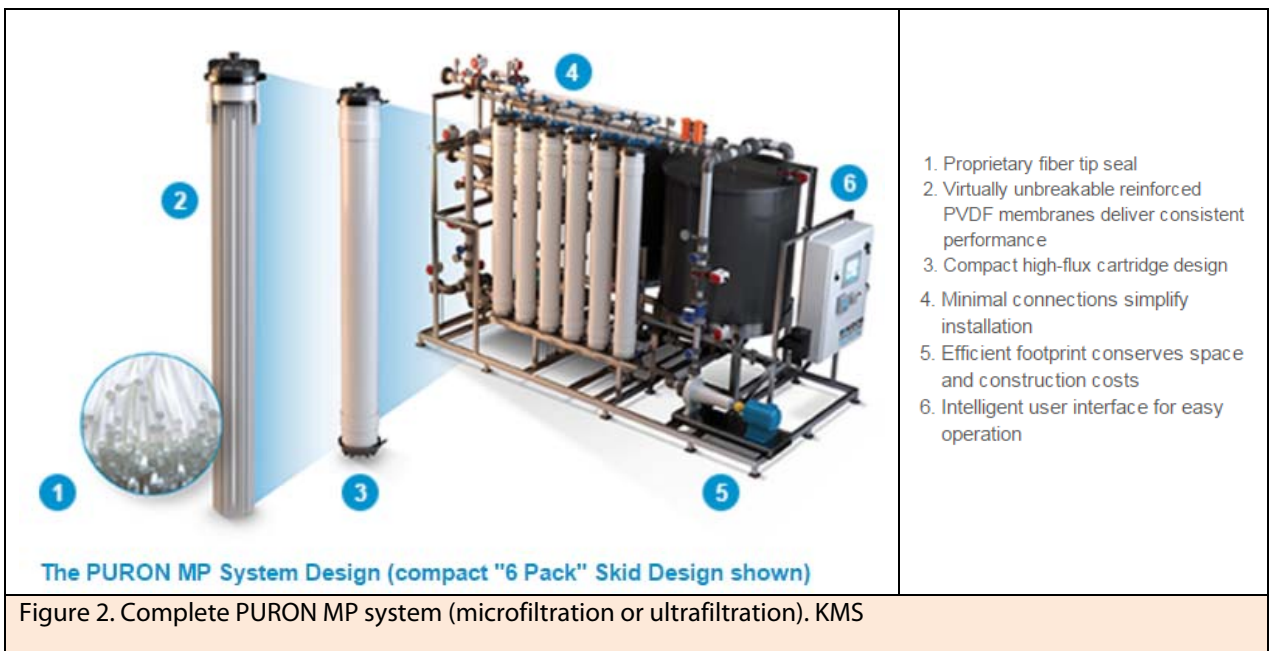


Figure 2. Complete PURON MP system (microfiltration or ultrafiltration). KMS

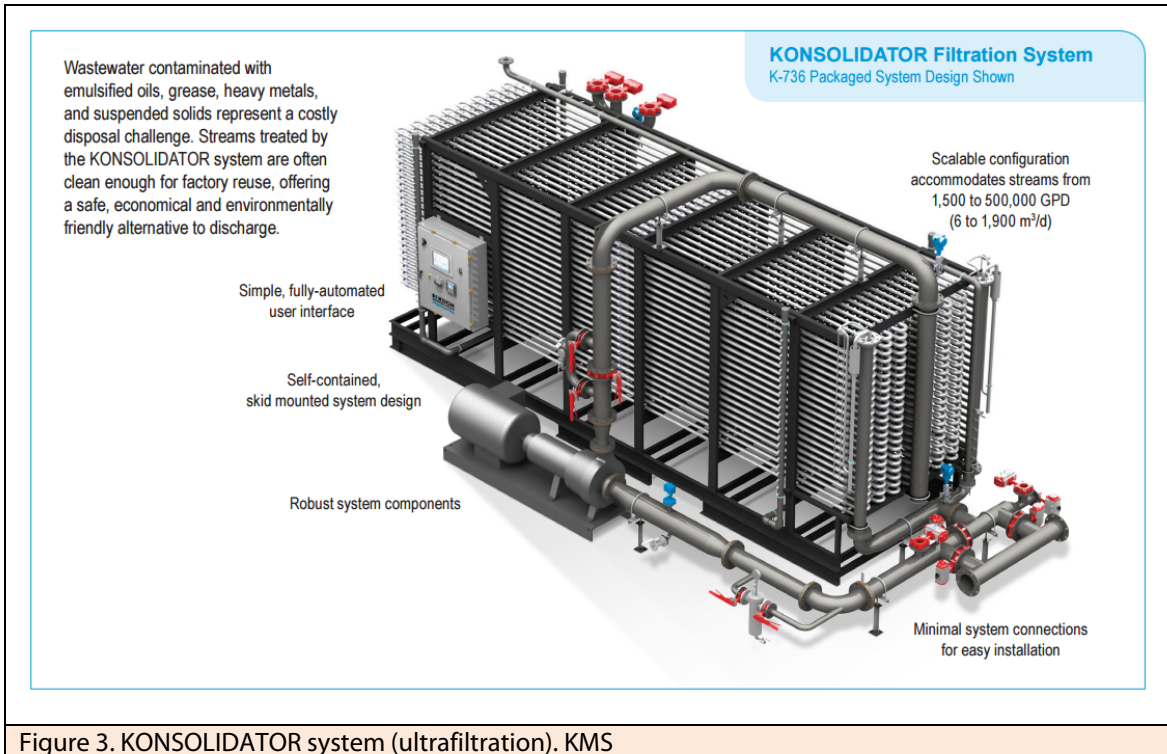


Figure 3. KONSOLIDATOR system (ultrafiltration). KMS

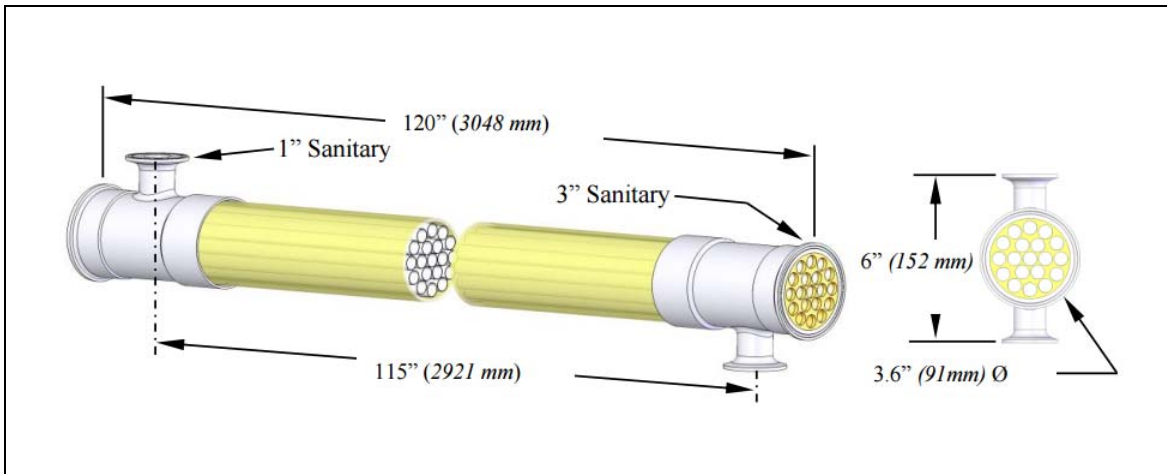


Figure 4. Microfiltration module SUPER-COR®. KOCH membrane systems

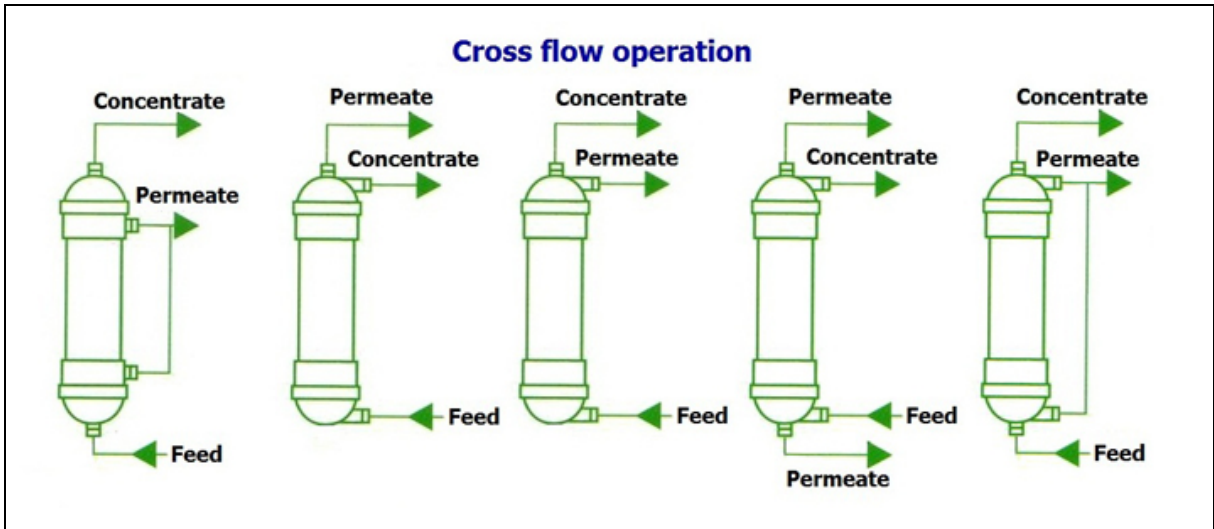


Figure 5. Crossflow operation examples

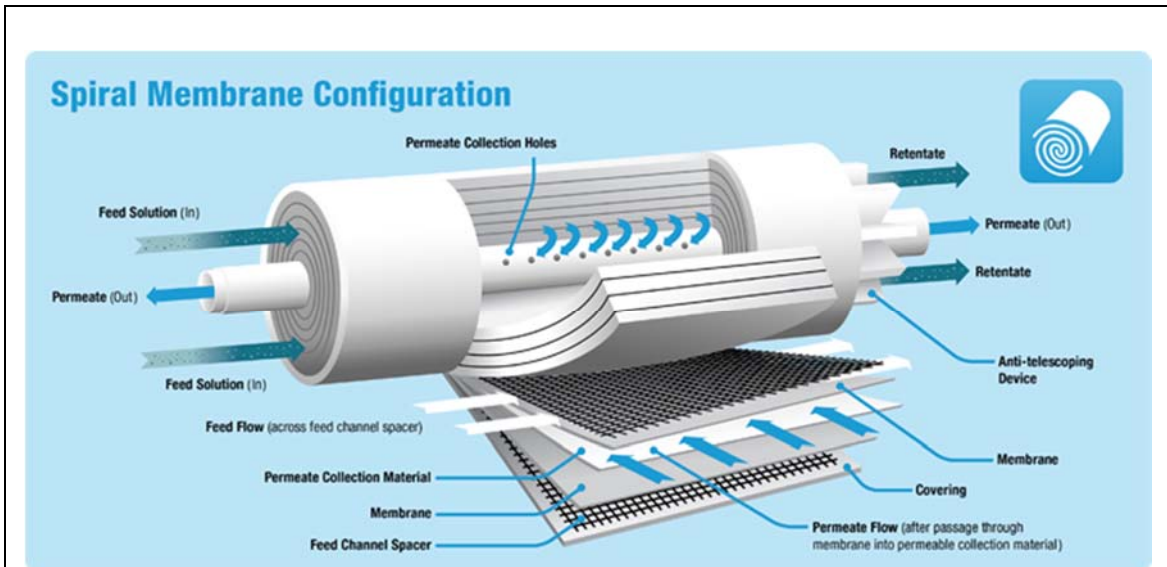


Figure 6. spiral membrane module. KMS



Figure 7. LIQTECH. Ultrafiltration system for a 70 m<sup>3</sup>/h flow. Textile ETP (Egipt).



Figure 8. PANDA water tech. Nanofiltration system applied to textile industry.

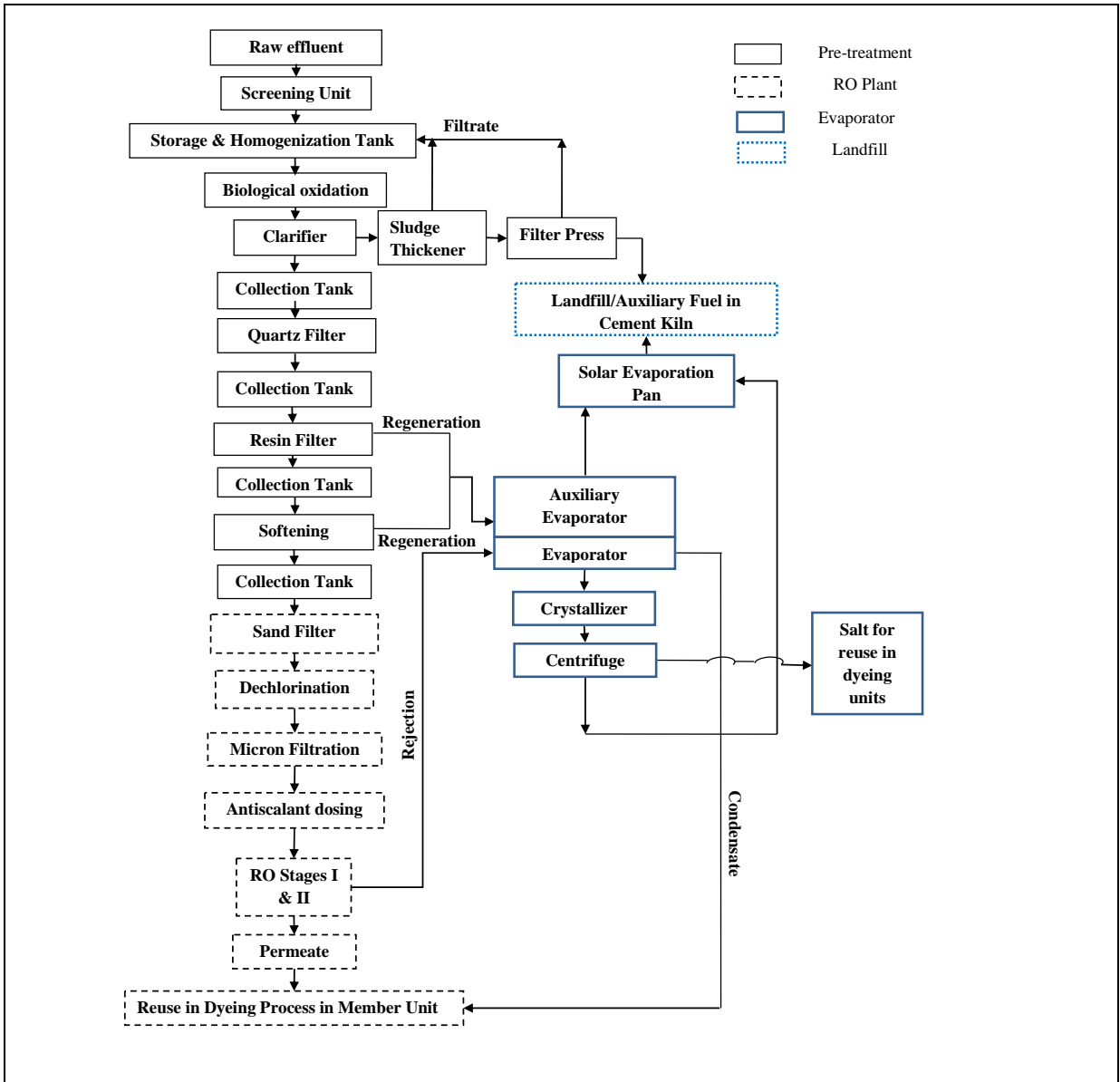


Figure 9. General water flow line in a CETP of Arulpuran (India)



Figure 10. Nanofiltration and reverse osmosis systems in a Zero Liquid Discharge CETP in Angeripalayam, with high contribution of textile effluents, in Tirupur (India).



Figure 11. United Envirotech. Reverse osmosis modules