Xenobiotics removal by membrane technology: an overview

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1 Introduction

1.1. Xenobiotics removal by conventional water treatment processes and natural water contamination

Xenobiotics are compounds foreign to a living organism or introduced in the environment by artificial means. The implications of xenobiotics on human health, including endocrine disruption, have been intensively debated recently [131, 149, 113]. Although studies to date are not conclusive, it is important to remove xenobiotics from wastewaters discharged to surface waters as well as protecting drinking water sources.

Concentrations of xenobiotics up to µg/L were measured in wastewater treatment plant (WWTP) effluents, showing an incomplete removal by conventional treatment processes all over the world [11, 68, 153, 120]. Batt et al. [12] measured a total concentration of active pharmaceuticals up to 3,000 ng/L in New Mexico of which carbamazepine concentration was up to 800 ng/L. Carbamazepine and paracetamol were found at high concentrations, 300 ng/L and 11.3 mg/L respectively, in the Hérault area, France [108]. High concentrations of antidepressants in Minnesota, USA [120] and pharmaceuticals in the Berlin area, Germany [50] were also measured.

These effluents are discharged into surface and groundwaters where concentrations up to µg/L were measured for pharmaceuticals, anti-depressants and hormones [62, 12]. Rabiet et al. [108] showed that wells tapped for drinking water in the vicinity of WWTPs had concentrations of pharmaceuticals up to 300 ng/L compared to other wells with <50 ng/L upstream from the plant.

The same phenomenon was found with surface waters downstream of a WWTP in the Berlin area [50]. In a UK survey on two rivers in the southeast of England an increase in estrone concentration was measured caused by a WWTP discharge [142]. Although hormones were measured at trace level concentrations in these effluents, in USA streams concentrations of more than 100 ng/L were quantified [67].

There are thousands of xenobiotics of concern most of which are small and occur at low concentrations making them very difficult to remove effectively. Due to an insufficient removal by conventional treatment processes, the applications of advanced technologies such as membrane processes have been the focus of attention since they have the potential to efficiently remove xenobiotics down to very low levels.

1.2. Target xenobiotics

Six organic xenobiotics were chosen as example compounds for this chapter due to the extensive availability of data from different types of membrane filtration studies and due to their different physico-chemical properties. This choice allows the illustration of different behaviours of xenobiotics in different membrane processes. The chemical properties of the xenobiotics are described in Table 1. The $pK_a$ and $Log K_{ow}$ represent the acid dissociation constant and the partition coefficient in octanol-water, respectively. The latter is a measure of the compound hydrophobicity. Sulfamethoxazole (SMX), estrone, bisphenol-A (BPA), fluoranthene and carbamazepine (CBZ) have approximately the same molecular weight (MW). They differ in their dipole moment, $Log K_{ow}$ and $pK_a$. They are all bipolar, with the exception of fluoranthene, meaning they can act either as a proton (H) acceptor or donor, being able to form H-bonds with other molecules [45].
Membranes are either porous, e.g. ultrafiltration (UF) and microfiltration (MF), or dense, e.g. reverse osmosis (RO). Nanofiltration (NF) membranes are considered to be between porous and dense [116]. These differences dictate how the contaminant is transported through the membrane. MF and UF membranes are characterised by the molecular weight cut-off (MWCO), an indication of the compounds size they remove, corresponding to the MW at which 90% rejection is obtained [84]. NF can be either characterised by MWCO or ionic retention of salts such as NaCl or CaCl₂. RO membranes being dense are characterised by salt rejection, although some researchers have modelled molecular retention to determine a MWCO [65]. Retention of a contaminant is defined as:

\[ R_{\text{ retention}} (\%) = 100 \times (1 - \frac{c_p}{c_f}) \] (1)

Where \( c_p \) and \( c_f \) are the permeate and feed concentrations, respectively. Other common performance parameters for membrane processes are:

\[ Q_s = Q_f + Q_p \] (2)

\[ \text{Recovery} = \frac{Q_p}{Q_f} \] (3)

\[ J = \frac{1}{A} \frac{\partial V}{\partial t} = L_p (\Delta P - \Delta m) \] (4)

Where \( Q_f, Q_p, \) and \( Q_s \) are feed, concentrate and permeate flow rates, recovery is the amount of clean water produced per feed water treated, \( A \) is the membrane area, \( V \) is the permeate volume, \( t \) is time, \( L_p \) is the membrane permeability, \( \Delta P \) is the applied transmembrane pressure and \( \Delta m \) is the osmotic pressure difference between feed and permeate.

Several types of membrane processes are available for water treatment depending on their separation principle, pore size, and driving force for separation. The different membrane processes found are pressure driven as described in Figure 1 (MF, UF, membrane bioreactor MBR, NF and RO), electrical potential driven (electrodialysis ED), thermally driven (membrane distillation MD) and due to vapour pressure differences between feed and permeate (pervaporation PV). A comparison between different membrane separation processes described in this chapter and solutes they remove is presented in Table 2. The MW range of the compounds and membrane pore sizes or particle sizes are also presented.

<table>
<thead>
<tr>
<th>Solutes</th>
<th>Membrane Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bacteria</td>
<td>MF, UF, MBR</td>
</tr>
<tr>
<td>Xenobiotics</td>
<td>MF, UF, NF, RO</td>
</tr>
</tbody>
</table>

Solute-solute interaction and retention by MF and UF

Organics in wastewater play a role in xenobiotic retention, as they interact with xenobiotics and enhance their removal [34]. This case was illustrated by Schäfer et al. [118] in a submerged UF process where higher retentions of BPA at pH 9 are obtained in the presence of natural organic matter (NOM) compared to retentions of BPA without NOM. BPA partitions into the NOM and is better retained. At pH 9 due to charge repulsion between BPA, NOM and the membrane no enhancement of BPA retention is obtained since no adsorption and partitioning of BPA to the membrane and on NOM occurs.

When adsorption of xenobiotics on the membrane is the main retention mechanism, the presence of NOM can decrease their retention. NOM possesses hydrophobic moieties [49, 150], H-bonding capacity [102] or gel formation capacity [32, 38] and therefore adsorbs onto the membrane surface and competes for adsorbing sites with the xenobiotics. Pore blockage by NOM also causes less access for adsorption sites, decreasing the rate of adsorption and therefore decreasing retention of xenobiotics. This has been shown to happen for steroid hormones, pharmaceuticals and pesticides [23, 148, 146, 29].
Solute-solute interactions of xenobiotics with organic compounds from water and wastewater are very compound and solution chemistry specific. Interaction and their effects on xenobiotic transport and removal are important. However mechanisms are to date poorly understood.

2.3. Hybrid processes on xenobiotics removal by large pore size membranes

Pre-treatment processes such as coagulation, adsorption, oxidation, complexation or precipitation enhance xenobiotic retention. The formation of larger complexes enhances the removal by large pore membrane processes.

Oxidation, pH adjustment or polymer assisted filtration can lead to the precipitation or complexation of metals and subsequent removal of the precipitate by MF or UF [19, 132, 114, 127, 71, 38].

Coagulation appears to be a poor treatment method for trace organics removal from aqueous solutions. No interaction of steroid hormones was obtained by Chang et al. [22] and Bodzek and Dudziak [16] when mixed with iron and aluminium based coagulants. The reason for this low efficiency is most likely a lack in affinity for inorganic solids as well as the low concentration of xenobiotics.

Considering sorption of steroid hormones on activated carbon (AC) is generally high [22, 16], combining MF to remove AC with the sorbed xenobiotic from solution is an option. Chang et al. [22] obtained an estrone removal as high as 96%, providing a minimum AC dosage is met.

In real life applications xenobiotics removal enhancement by hybrid MF and UF processes is a difficult task. These processes rely on an effective interaction between xenobiotics and the sorbent. This interaction depends on sorbent and xenobiotic characteristics and the solution chemistry that may both enhance or hinder the process. This makes such processes inherently complex and unlikely to function effectively for a vast number of xenobiotics or solution chemistries. A physical separation such as NF and RO is therefore an attractive option.

2.4. Xenobiotics removal using membrane bioreactors

The combination of MF/UF with biological degradation into a single process is called an MBR, considered to be a MF/UF hybrid process. Suspended solids and microorganisms responsible for biodegradation are separated from the treated water by a membrane filtration unit. In this case a biological rather than a physico-chemical process is coupled with the membrane filter. The inhibitive end product of the bioconversion by enzymes and microorganisms is continuously removed to proceed with the reaction [77, 84].

In MBR are partially effective in xenobiotics removal [60, 54]. Removal is higher when compared to conventional activated sludge processes (CASP) possibly due to a higher specific surface obtained in MBR processes [58, 76]. Kim et al. [62] obtained 95% removal of hormones and some pharmaceuticals (e.g. ibuprofen) by treating wastewater from University campus dormitories and student apartments. Xenobiotics removal can be effective if they are biodegraded after an association with the biomass in the MBR which is obtained for contaminants such as BPA, nonylphenol (NP), pharmaceuticals and endocrine disrupting chemicals (EDC) [27]. Removal is also effective when the xenobiotic adsorbs on the biomass suspended solids [59, 60] and is later separated from the treated water by MF or UF. Adsorption on the sludge is found to be the highest at lower pH where there is less charge repulsion between the sludge and the xenobiotics [117, 81]. Removal is also enhanced for xenobiotics with lower dipole moment or higher hydrophobicity [13, 54]. Due to gel formation or fouling on the membrane surface there is thought to be a shift of the membrane MWCO which can partly remove macromolecular organic carbon to which xenobiotics are adsorbed to [117, 76, 81].

However removal of compounds such as CBZ and SMX has been found to be very low or nonexistent for MBR and conventional processes due to a low sorption capacity on the sludge [27, 60, 44, 62, 109].

Xenobiotics that are not removed are discharged and in consequence often found in natural waters [50, 108] or in river, ocean and soil sediments [73, 139, 18]. Degradation of compounds into smaller, more hydrophilic, polar, persistent and sometimes more toxic molecules also occurs and is to date poorly understood [13, 44, 54]. For example Hu et al. [54] obtained higher concentrations of NP in the effluent compared to the influent concentration due to NP production from parent compounds. Although MBR processes show enhanced xenobiotics removal compared to conventional treatment processes, this removal is still insufficient and poorly understood.

3 Nanofiltration and reverse osmosis

NF pores are in the <2 nm range while RO “pores” are to be seen as non-discriminatory voids between polymer chains. Transport of a liquid through a dense membrane is described in terms of the solution-diffusion mechanism which is a function of solubility on the membrane and its diffusivity. Each permeant dissolves in the membrane material and passes by diffusion due to its chemical potential gradient [15]. In NF the transport of liquid through the membrane is considered to be between UF and RO with a contribution of both convection and sorption-diffusion.

The retention of contaminants by NF and RO membranes involves several mechanisms such as steric exclusion, adsorption followed by diffusion and electrostatic interactions. These mechanisms depend on the membrane properties such as surface charge and pore size, the xenobiotic properties such as H-bonding capacity, molecular size and polarity and the solution chemistry involved such as pH, ionic strength and the presence of NOM.

A simplified schematic of the several mechanisms involved in xenobiotics retention by NF and RO membranes is shown in Figure 3.

3.1. Size exclusion

Size exclusion mechanism is directly related with molecular size. In general it increases with increase of compound MW [14, 35, 64] and retentions are usually higher than 90% [112, 111, 138, 62, 69] for compounds with MW higher than the MWCO of the membrane [14, 136, 70] (see Figure 4A). MW has been shown to be a good indicator of the retention trend obtained by NF and RO membranes compared to other molecular sizes, e.g. Stokes diameter [136].

However, this trend is not always obeyed and deviations occur in NF and RO (see Figure 4). For NF this happens especially when the contaminant size is of the same order as the membrane pores [65] (see Figure 4A). The retention is affected by the occurrence of adsorption phenomena, charge interactions between the contaminant and the membrane material and the presence of a third component in solution such as NOM. Presence of ions such as monovalent and divalent salts also affects retention.

3.2. Adsorption

Many polymeric membranes adsorb xenobiotics. Adsorptions of pesticides, steroid hormones, volatile organic carbon (VOCs) and pharmaceuticals of up to 100% are obtained [24, 35, 66, 96, 64, 119, 65, 87, 148, 93, 106, 151, 70, 97].

Adsorption plays an important role in membrane retention. Until saturation of the membrane sites is achieved the real retention is overestimated [63, 64, 91]. While adsorption occurs, the apparent retention is often >90% but once the membrane becomes saturated this latter decreases drastically, sometimes to <10% [63, 64, 55, 56, 80]. The permeate concentration shows a
breakthrough curve similar to an AC process, with a slow increase in the initial phase until it reaches equilibrium translated in a constant permeate concentration with time (see Figure 5A). This is accompanied by a feed concentration decrease until saturation occurs. In this later phase steric hindrance and electrostatic interactions as well as solution concentration above solubility limit results in lower retention than expected for membranes with smaller pores than the compound due to diffusion of the xenobiotic through the membrane. The main difference between estrone and BPA is in their molecular structure. Estrone and BPA are bipolar, although estrone has one =O, one benzene ring and one -OH and BPA has only two -OH and two benzene rings. The =O group forms stronger H-bonds than the -OH group explaining the higher adsorption of estrone compared to BPA. This was shown by Neale et al. [85] when studying the interaction between hormones and organic matter. Estrone’s adsorption on the membrane is simply higher than the estradiol and testosterone due to their -OH groups in the molecules which are very strong H-acceptors.

Commercial membranes are usually thin film composite membranes (TFC) with a very thin active layer and a support layer made of a different material. The active layer is the selective layer with pores in the nm level and the support layer with wider pores does not give any resistance to flux. Most commercial membranes have a polyamide active layer and a polysulphone support layer although cellulose acetate active layers are also found. No comprehensive study has been made on what material adsorption occurs onto. According to McCullam et al. [80] adsorption of estradiol occurs mainly in the polysulphone layer compared to the polyamide layer. When looking at Figure 6 one can see that H-bonding between the bipolar estradiol molecule can be formed in both layers. A high adsorptive interaction between BPA, another bipolar contaminant, was also noticed by Lyko et al. [76] with a polyethersulphone membrane. Williams et al. [141] on the other hand obtained a higher adsorption of organic pollutants such as 2-chlorophenol on the polyamide layer when compared to the polysulphone layer showing that interactions are compound and membrane material specific.

3.3. Charge repulsion

The surface charge of commercial membranes becomes more negative with increase of pH [36, 25, 119, 94, 55]. Xenobiotics that dissociate, do so at the pH corresponding to their pKₐ (e.g. estrone at pH 10.3). When this occurs, charge repulsion between the membrane surface charge and the dissociated compound occurs enhancing the retention of the xenobiotic [136, 63, 94, 95, 144, 95, 145, 80]. This effect is especially pronounced with molecules smaller than the pore size of the membrane. For example, Berg et al. [14] obtained an increase in the pesticide mepropa rejection from 10% to 90% when increasing the pH from 3 to 7. Solution pH can also affect pore size due to repulsion of negatively charged groups on the membrane polymer or due to membrane structural changes which in turn affect the rejection of xenobiotics [14, 3]. CBZ retention does not vary much with pH as can be seen in Figure 7. This compound is neutral and governed by steric interactions only [94]. In the previous section it was shown that this compound does not adsorb. SMX which practically does not adsorb either on the other hand changes from neutral to negatively charged at pH 5.6. Retention increases from 20% to 100% with increase of pH due to charge repulsion between the membrane and the compound (see Figure 7). Although CBZ is smaller, when these two compounds are both neutral (pH 5.6) SMX is significantly less retained. The authors explained this due to differences in dipole moment where a higher dipole moment for the SMX causes a lower retention, as argued by other authors for different compounds [24, 135, 136, 42, 94, 95, 146]. Molecules with high dipole moment are directed towards the pore with the side of the dipole with opposite charge closer to the membrane pore, entering more easily into the membrane [24]. Kimura et al. [65] however found that a higher
dipole moment enhances retention when a cellulose acetate membrane is used instead of a polyamide membrane as Van der Bruggen et al. [136] used in their study. Retention of polar and non-polar compounds is therefore affected by the membrane material used and no generalised trend can be obtained at present. Although estrone is also negatively charged at high pH an opposite trend compared to SMX was obtained by Schäfer et al. [119]. When estrone dissociates at higher pH, retention decreases dramatically from >90% to 50%. Neutral estrone adsorbs on the membrane and gives an apparent high rejection. At higher pH when the molecule dissociates, charge repulsion occurs, decreasing adsorption and consequently retention. These results with estrone seem to contradict what Hu et al. [55] obtained, where estrone retention increases from 15% to 25% with increase of pH once the membrane is saturated in estrone (see Figure 7). This is caused by charge repulsion between the membrane and estrone. In the latter case the membrane was saturated with estrone which did not occur in the study by Schäfer et al. [119]. Another possible explanation for this discrepancy is the different membranes used. Although both polyamide they can have different properties which are propety of the manufacturer.

A decrease in xenobiotics retention as a consequence of fouling can also occur. NOM adsorption and increase in membrane negative surface charge increases the MWCO of the membrane due to charge repulsion between the functional groups on the membrane [145] resulting in lower rejection of ionic solutes. Colloidal fouling also causes a decrease in xenobiotics retention by NF and RO membranes [87, 89]. Due to the cake formed on the membrane surface, back diffusion to the feed is hindered which causes accumulation on the membrane surface and consequent diffusion through the polymer [2, 90, 97]. Other types of foulant decrease the membrane surface charge when adsorbed, decreasing the repulsion between the membrane and the xenobiotic [51, 90].

Membrane fouling decreases xenobiotics retention

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Membrane fouling affects xenobiotics adsorption

When both charge shielding and competitive adsorption effects are present, a decrease in xenobiotics retention occurs. NOM adsorption and increase in membrane negative surface charge increases the MWCO of the membrane due to charge repulsion between the functional groups on the membrane [145] resulting in lower rejection of ionic solutes. Colloidal fouling also causes a decrease in xenobiotics retention by NF and RO membranes [87, 89]. Due to the cake formed on the membrane surface, back diffusion to the feed is hindered which causes accumulation on the membrane surface and consequent diffusion through the membrane polymer [2, 90, 97]. Other types of foulant decrease the membrane surface charge when adsorbed, decreasing the repulsion between the membrane and the xenobiotic [51, 90].

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When NOM is present two main trends are found in the xenobiotic adsorption mechanism on membranes. Higher adsorption of the contaminant is obtained, possibly on both membrane and NOM layer that is formed on the membrane surface [1, 96, 145, 55, 56]. In the case of hydrophobic HA presence for example, it renders the membrane more hydrophobic, enhancing estrone adsorption [55, 56]. Jin et al. [56] found that estrone interaction with NOM depends on the NOM specific functional groups, such as the presence of phenolic groups, which enhance estrone retention by partitioning into the NOM, but do not seem to readily affect estrone adsorption on the membrane.

On the other hand, a decrease in xenobiotics adsorption also occurs when there is competition between the NOM and the contaminant for adsorbing sites [148, 103, 146, 151, 80, 89, 97]. Competition for adsorption between different xenobiotics also take place [66, 103] decreasing the retention when compared to a single xenobiotic solution.

Complexity of natural waters renders the removal prediction of xenobiotics difficult due to all the interactions that take place between the xenobiotic, the compounds in water and the membrane. Removal mechanisms are to date poorly understood. Studies on the removal of xenobiotics by membranes not involving pressure driven processes are scarcer because water treatment applications are currently dominated by pressure driven processes. From the studies presented next it can be seen though that membrane processes share some of the mechanisms of xenobiotics removal such as adsorption followed by diffusion through the membrane material amongst others. They depend on the contaminant chemical characteristics, e.g. hydrophobicity.
4 Electro dialysis

Ions or charged molecules can be removed by ED where an electrical potential difference acts as the driving force for separation. Uncharged compounds are unaffected and can be separated from charged compounds. Electrically charged membranes (cation-exchange membranes allow the passage of cations and anion-exchange membranes allow the passage of anions [84]) are alternately stacked between the positive electrode (anode) and negative electrode (cathode). Cations migrate to the cathode and anions migrate to the anode [126]. Two phases are obtained: the diluate which is purified and free from charged solutes and the concentrate where the charged solutes migrate to and concentrate.

ED studies have mainly focused on wastewater treatment of metals and heavy metals from industrial wastewaters [78, 75]. In general, high removals of metals are achieved by this process although membrane type affects metal removal [46, 134, 8, 130, 9]. Metal speciation plays an important role. In some cases the pH of the solution has to be adjusted and/or controlled since it affects the metal solubility, charge and therefore the metal mobility [46, 79, 78, 130].

Less attention has been given on the application of ED for the removal of xenobiotics, despite the fact that some deprotonate at a certain pH and could be removed. The only studies are on the applicability of ED for salts recovery from a urine solution containing xenobiotics [37, 105]. Although high removal of 17α-ethynylestradiol is obtained [37], Pronk et al. [105] showed that xenobiotics such as CBZ and propanolol readily adsorb on the membranes, where electrostatic, size exclusion and hydrophobic interactions play a role in the adsorption behaviour. More hydrophobic compounds seem to adsorb more. This adsorption governs the permeation of these contaminants through the ED membranes since both increase with time and breakthrough eventually occurs. Pronk et al. [107] studied the application of ED followed by ozonation in a pilot scale for the production of a fertiliser from urine. Whilst the conductivity decreases substantially to almost 100% removal of salts, all xenobiotics are below detection limit with the exception of ibuprofen. Ibuprofen adsors on the membrane and, after saturation of the membrane sites, significant permeation occurs.

5 Pervaporation

In PV the permeate is removed as vapour from the feed stream in contact with a dense hydrophobic membrane due to a low vapour pressure on the permeate side.

This process was first applied in the removal study of VOCs. Most xenobiotics such as EDCs have low volatility, high MW and low water solubility when compared to VOCs. Although PV does not seem to be an appropriate treatment process it has been applied for the treatment of water containing trace amounts of xenobiotics. According to Higuchi et al. [53] removal of trace amounts of EDCs is >90% and a function of the contaminant hydrophobicity. A high removal by more hydrophobic compounds was also obtained by other authors [98, 52]. Interactions between the contaminant and the membrane are crucial in the removal performance by PV [98].

However, due to the xenobiotics low vapour pressure and high MW when compared to VOCs, the driving force needs to be increased to increase removal rates [52, 133], translating into higher energy requirements.

Contrary to NF and RO, in PV the higher the interaction of the xenobiotic with the membrane the better, since the contaminant is to be removed on the permeate side. The more hydrophobic compounds permeate better, but in general xenobiotics have large MW and low vapour pressures, translating into a higher driving force, accompanied by energy costs.

6 Membrane Distillation

In a MD process two liquids at different temperatures are separated by a very hydrophobic microporous membrane. This temperature difference results in a vapour pressure gradient, the driving force for separation. Thus transport occurs by evaporation on the high-temperature side followed by transport of the vapour molecules through the membrane pores. Finally the molecule condenses on the permeate side which is either a liquid or a gas at a lower temperature [84, 30].

A significant application of MD to xenobiotic contaminated water is appealing since most xenobiotics have low vapour pressures and the solution they are found in can be concentrated, with pure water obtained on the permeate side. Wu et al. [143] studied the application of MD in the treatment of a taurine rich pharmaceutical wastewater effluent where the concentrate obtained is very rich in taurine (66% purity). Cartinella et al. [21] studied the removal of natural steroid hormones using MD. Rejections of estrone and estradiol are >99.5% without having much effect on the water recovery. Solutions containing urine and humidity contain water with traces of organic acids do not affect the performance either and rejections are maintained >99.5%. Zolotarev et al. [152] studied the removal of heavy metals from wastewater and obtained a pure distillate of water and a heavy metal selectivity of 99.8% which only decreased to 99.7% when the feed metal concentration increased. MD can therefore be used to very high concentrations of metals without losing its selectivity. However, this is accompanied with a decrease in trans-membrane flux.

MD can also be used by applying vacuum on the permeate side (vacuum membrane distillation) to remove volatile xenobiotics from the feed solution. Couffin et al. [30] and Banat et al. [10] showed that MD can be used to remove halogenated VOCs and benzene (87% removal) from water, respectively.

7 Large Scale Applications

Despite the pessimistic picture previously painted in the efficiency of xenobiotics removal by membrane processes, large scale applications have shown very good results with high water quality obtained. These applications are motivated by the need to remove xenobiotics for water treatment where the water supply is contaminated, or for water recycling where wastewater is treated to a potable water standard. Increasing water pollution awareness combined with increased water demand and water scarcity is rapidly expanding the number of large scale plants. A number of such applications will be outlined here.

- Méry sur Oise

The Méry-sur-Oise water purification plant in Paris, France, treats water for potable usage directly from the river Oise to 650,000 people with a daily maximum production of 340,000 m³.

The majority of the treated water produced (80%) originates from MF pre-treatment followed by NF treatment, while the remaining (20%) originates from conventional biological treatment. The NF area used is 340,000 m², corresponding to 9,120 modules of Dow Filmtec NF 200 membranes (polyamide on a polysulphone support and polypropazine as an ultrathin top layer). The choice of the membrane technology was due to its high removal of organic carbon and pesticides when compared to conventional processes [137, 31].

The Oise generally has very high concentrations of pesticides (e.g. >1.6 µg/L in May, June and August of 2007 [123]). The highest concentrations were measured for glyphosate and the water composition (AMPA) ranging from 0.2 µg/L to 0.9 µg/L. Removal of pesticides remains very high with single pesticide concentration lower than 0.1 µg/L and 0.5 µg/L for total pesticide concentration in the treated water. In 2007 the atrazine and desethylatrazine concentrations in treated water were always lower than the detection limit of 50 µg/L [124].

The total organic carbon (TOC) removal is also very high with a drinking water concentration of about 2 mg/L. Disinfection by-products (DBP) such as trihalomethanes are removed in the process to concentrations lower than 90 µg/L. Metals such as aluminium have concentrations lower than 12 µg/L in the treated water [124].

- NEWater

The NEWater facilities in Singapore are advanced water reclamation plants designed to produce a total of 75,000 m³/day of water [129] with MF followed by RO and UV disinfection. The water influent originates from a clarified secondary effluent with CASP. This treated water can be
Further high grade industrial water (e.g. microelectronics industry) or for indirect potable reuse applications. For a typical input of 12 mg/L of TOC removals higher than 99% were achieved in 2000 [121]. Sample analyses from 2000 to 2002 showed concentrations of pesticides in the treated water lower than 0.1 µg/L and of DBP lower than 75.9 µg/L [125].

- Water Factory 21 (WF21)

WF21 in California, USA, was built to treat and purify water from the Orange County District to drinking water standards. This treated water was then injected into the groundwater basin [100] that supplies drinking water to a population of more than 2 million people. Groundwater is protected from seawater intrusion by injecting up to 19,000 m³/day of treated reclaimed water to be blended with deep-well water into coastal aquifers. A RO treatment with Hydranautics ESP2.6 polyamide membranes was added to reduce salts and organics, with MF as a pre-treatment process. DBP such as N-Nitrosodimethylamine (NDMA) were detected in several drinking water wells in California [20]. The presence of this compound in the injected water from WF21 forced the interruption of the plant in 2000-2001, reducing water treatment by more than 85% [83]. The levels of NDMA in the discharged water were higher than 20 µg/L [82, 20]. A UV treatment was subsequently installed to remove the NDMA. According to a study by Plumlee et al. [104], the RO process in WF21 removes NDMA between 24-56%, depending on the sampling season. With the addition of UV treatment the overall removal increases up to 75%. As expected MF does not remove any of the NDMA. On the contrary, due to chlorination pre-treatment to avoid MF fouling the NDMA concentration decreases in the MF influent.

Metals and heavy metals concentrations in 2003 were below 5 µg/L, organic carbon was below 0.7 mg/L and trihalomethanes were below 2.7 µg/L [140]. WF21 has stopped working since 2007 to be replaced by an improved and larger water purification plant [47, 101].

- Luggage Point Water Reclamation Plant

The Luggage Point Water Reclamation Plant (LPWRP) was built to convert effluent from a WWTP into high quality reclaimed water for industrial reuse (e.g. BP refinery cooling towers) with MF pre-treatment followed by BW30 RO membranes from Dow Filmtec (polyamide on polysulphone support). Its maximum production is 10,600 m³/day [5].

According to a study by Al-Rifai [4] in 2006 the MF process does not reject any of the studied xenobiotics. The removal of acidic pharmaceuticals (e.g. ibuprofen) by the RO membranes on the other hand is high and varies between 30% and 100% and increases with the increase of compounds log Kow and pKaz. Rejection of neutral pharmaceuticals (e.g. CBZ) ranges from 63% to 100%. For EDCs (e.g. BPA) removal varies greatly between 0% and 100%. No relationship with the compounds characteristics was found for the latter two classes of compounds.

Other membrane plants applying NF and RO processes have reported good removal of xenobiotics to very low concentrations. In the Debben Road Plant UK, pesticide concentration is lower than 0.1 µg/L in the permeate [41]. According to Khan et al. [61] RO shows the best results in removing hormones and pharmaceuticals compared to NF, UF and MF in a water recycling demonstration plant in Queensland, Australia.

Despite the high removal percentages of xenobiotics by NF/RO processes, some compounds are not readily removed and show high concentrations in the treated water (e.g. NDMA and BPA) meaning that removal by membrane processes is insufficient. Furthermore the concentrate stream obtained in these processes which is very rich in xenobiotics poses a disposal problem that needs to be addressed. Disposal of the washing solutions for both MF/UF and NF/RO processes can also present a problem since polymeric membranes are capable of adsorbing high rates of xenobiotics, which desorb under certain backwash conditions such as acidic and alkaline washes.

8 Conclusions

Xenobiotics removal by NF and RO has progressed to full scale applications in water and wastewater treatment with particular interest in water recycling applications. The key advantage of membrane filtration for xenobiotics removal is the fact that treatment is a physical process that does not result in new unwanted by-products. Removal of many xenobiotics by membrane filtration is effective albeit compound and membrane specific. In fact, removal mechanisms for each process are governed by xenobiotics characteristics, membrane type, water matrix and solution chemistry (such as the presence of other xenobiotics or organics, pH and ionic strength) and operational parameters (such as pressure, feed flow rate). This makes removal prediction of specific compounds for a specific water difficult. Long term phenomena such as membrane fouling further affect xenobiotics retention which means that removal can vary with time as well as season. The underlying mechanisms for xenobiotics removal are size exclusion, adsorption followed by diffusion and charge repulsion. These mechanisms are currently not understood well enough to allow prediction of removal of xenobiotics. Different waters require a tailored process with requires individual design and pilot testing.

9 References


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### Table 2 - Membrane processes and contaminants dimensions (adapted from [6, 7, 77, 84, 115])

<table>
<thead>
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<th>Molecular Weight (g/mol)</th>
<th>Ionic Range (µm)</th>
<th>Molecular Weight Range (µm)</th>
<th>Micrometer Range (µm)</th>
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<td></td>
<td></td>
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<tr>
<td>pesticides, etc.</td>
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</table>

| Membrane Separation       |                  |                             |                       |
| Processes                 |                  |                             |                       |
| Electrolysis              |                  |                             |                       |
| Reverse osmosis           |                  |                             |                       |
| Nanofiltration            |                  |                             |                       |
| Ultrafiltration           |                  |                             |                       |
| Permeation                |                  |                             |                       |

### Figures

**Figure 1** – Pressure-driven membrane schematic with pore size $d_p$ (microfiltration, ultrafiltration, nanofiltration and reverse-osmosis)

**Figure 2** – Retention mechanisms by MF and UF membranes
Figure 3 – Retention mechanisms by NF and RO membranes

Figure 4 – Xenobiotics retention by NF (A) and RO (B) membranes as a function of MW – the shaded area corresponds to the MWCO of the NF membranes (adapted from [24, 14, 35, 66, 65, 88, 70]) with EDC: Endocrine Disrupting Chemicals, Pharm: Pharmaceuticals, VOC: Volatile Organic Carbon, DBP: Disinfection By-products and the membrane used specified in [ ]

Figure 5 – BPA, estrone (A), SMX and CBZ (B) feed and permeate concentrations progress with time in NF (A and B adapted from [93, 56] and [94] respectively)

Figure 6 – H-bonding between xenobiotics and polyamide and polysulphone membranes

Figure 7 – SMX, estrone, BPA and CBZ retention as a function of pH (adapted from [93, 94, 55, 97])