Micropollutant Sorption to Membrane Polymers: 
A Review of Mechanisms for Estrogens

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Abstract

Organic micropollutants such as estrogens occur in water in increasing quantities from predominantly anthropogenic sources. In water such micropollutants partition to surfaces such as membrane polymers but also any other natural or treatment related surfaces. Such interactions are often observed as sorption in treatment processes and this phenomenon is exploited in activated carbon filtration, for example. Sorption is important for polymeric materials and this is used for the concentration of such micropollutants for analytical purposes in solid phase extraction. In membrane filtration the mechanism of micropollutant sorption is a relative new discovery that was facilitated through new analytical techniques. This sorption plays an important role in micropollutant retention by membranes although mechanisms of interaction are to date not understood. This review is focused on sorption of estrogens on polymeric surfaces, specifically membrane polymers. Such sorption has been observed to a large extent with values of up to 1.2 ng/cm² measured. Sorption is dependent on the type of polymer, micropollutant characteristics, solution chemistry, membrane operating conditions as well as membrane morphology. Likely contributors to sorption are the surface roughness as well as the microporosity of such polymers. While retention – or and reflection coefficient as well as solute to effective pore size ratio – control the access of such micropollutants to the inner surface, pore size, porosity and thickness as well as morphology or shape of inner voids determines the available area for sorption. The interaction mechanisms are governed, most likely, by hydrophobic as well as solvation effects and interplay of molecular and supramolecular interactions such as hydrogen bonding, π-cation/anion interactions, π-π stacking, ion-dipole and dipole-dipole interactions, the extent of which is naturally dependent on micropollutant and polymer characteristics. Systematic investigations are required to identify and quantify both relative contributions and strength of such interactions and develop suitable surface characterisation tools. This is a difficult endeavour given the complexity of systems, the possibility of several interactions taking place simultaneously and the generally weaker forces involved.

Keywords
Sorption, micropollutant, membrane polymer, hydrogen bonding, supramolecular interactions, nanofiltration.

1 Introduction

Micropollutants in water are a rapidly emerging global problem that seriously threatens environmental and human health. This can be attributed to the interference with hormonal functions such as behavioural development and fertility. Micropollutants are natural as well as anthropogenic persistent chemicals, such as pesticides, pharmaceuticals, personal care products, plasticizers, and many other groups such as antibiotics, hormones and endocrine disrupters. Many micropollutants accumulate in the environment due to their persistence and increasingly occur in water at measurable concentrations [1-3]. There has been much debate on the health effect of micropollutants such as the disrupting effect on the endocrine system [3-6]. Although proof of adverse effects on mammals from water sources is still being established, due to increasing regulations and for precautionary reasons the removal of those pollutants has become a priority.

Many contaminants originate from wastewater effluents where relatively high concentrations (µg/L) such as pharmaceuticals and antidepressants have been measured. This evidences an incomplete removal by conventional treatment processes [7-16]. While synthetic steroid hormones (such as contraceptive pill, menopause or chemotherapy drugs) generally only occur at trace level concentrations in wastewater effluents, in US streams concentrations of steroid hormones of more than 100 ng/L [12] and up to µg/L for pharmaceuticals, anti-depressants and hormones were measured [17]. This was attributed to effluent discharge. Wells in the vicinity of a WWTP have higher concentrations of pharmaceuticals (up to 300 ng/L) compared to other upstream wells (<50 ng/L) [15]. In a UK survey on two rivers an increase in estrone concentration was measured due to the discharge of sewage treatment works [11]. In one of the rivers the estrone concentration profile downstream clearly followed the profile of estrone concentration of the plant effluent. Further, estrogens have also been found in sediments on the ocean floor surrounding sewage outfalls [18].

Micropollutants are an increasing health threat due to the accumulation of persistent organic pollutants in the environment. The increasing abundance of a vast range of pollutants in waterways is causing concern of exposure from drinking water. In consequence, advanced treatment technologies are required to effectively remove such micropollutants. Activated carbon sorption and coagulation are generally less effective due to the low concentrations of micropollutants and competitive sorption between natural organic matter and micropollutants [19, 20]. Other alternatives are advanced oxidation, although those processes produce an array of unknown by-products with an often equal or higher toxicity [1, 21, 22]. Membrane technology is used predominantly for micropollutant control in water and wastewater treatment as well as in water reuse applications. Nanofiltration (NF) and reverse osmosis (RO) are the most suitable membrane processes for micropollutant control while more porous processes such as microfiltration (MF) and ultrafiltration (UF) cannot retain such small molecules. However, NF and RO removal of micropollutants is reported as erratic and not predictable from molecular weight of micropollutants [23-39].

In the last decade micropollutant breakthrough curves have been reported in the NF literature [23-25]. The important role of micropollutant sorption to polymeric materials used in water treatment has become apparent. This paper provides a state-of-the art review of the mechanisms and parameters responsible for micropollutant retention and sorption to membrane polymers in water treatment applications. Limitations of current knowledge and potential new approaches to find such interaction mechanisms are outlined. Better understanding of these interactions will enable the reduction of adsorption onto polymeric membranes if it is an unwanted


2 Micropollutant Characteristics: the Group of Estrogens

The molecular structure and other characteristics of estrogens are summarised in Table 1. While to date no correlation between a single micropollutant characteristic and membrane retention and sorption could be identified, the characteristics contribute to various interaction mechanisms. Estrone, estradiol and estriol are natural estrogens which are derived from cholesterol and commonly found in excreta of humans and animals. Testosterone and progesterone, also manufactured by a mammal body are steroid hormones. There are several non-steroidal chemicals synthetically manufactured which can interact with estrogen receptors such as ethinylestradiol, mestranol, diethylstilbestrol. Endocrine disrupting chemicals (EDCs, also referred to as hormonally active agents), are substances that disrupt the physiological function of endogenous hormones by acting like hormones in the endocrine system [26]. Examples of EDCs are contraceptive pill compounds, plasticizers, pesticides, and many other chemicals.

Chemical characteristics ultimately determine treatability and sorption of micropollutants. A major difficulty in removing such micropollutants from water is not only the small concentration in which they occur but also their small size or molecular weight (MW). The MW of the hormones is very similar, varying between 268 and 315 g/mol. According to their MW these compounds are expected to be retained by NF and RO while they are too small for retention by MF and UF. The $pK_a$ shows the acid dissociation constant at which the hormones lose a hydrogen atom and become negatively charged. The hormones that have a phenolic hydroxyl group all dissociate in the same pH range; between 10.2 and 10.5. At the pH above the $pK_a$ charge repulsion between the negatively charged hormone and the negatively charged membrane is expected to occur.

The Log $K_{OW}$ parameter measures the hydrophobicity of the hormones by partitioning between octanol and water. As a general rule of thumb, compounds with Log $K_{OW}$ >2.5 are expected to accumulate in solid phases instead of being soluble in the aqueous phase. The Log $K_{OW}$ values for the hormones described in Table 1 are above 2.5 (up to 5.1). Therefore hormones are expected to interact with the membranes by hydrophobic interactions [27, 28].

Estrogen solubility in water is reasonably low (0.3 to 441 mg/L) with significant variability in published data. Dipole moments give an indication on the polarity of the molecules and vary from 1.6 to 4.6 Debye. The molecules with larger difference between positive and negative electrical charges have a higher dipole moment values [29]. Dipole moments of the molecules are important considering that considerable attractive interactions may occur because of the alignment of one dipole molecule with another [30].

Steric Exclusion is a first mechanism that is essentially a sieving principle (Figure 2A) determined by micropollutant size. Pollutants larger than the membrane pore size are normally retained because of a sieving effect which is traditionally more obvious for larger pore sizes and particles [17, 24, 31, 47-53]. While this mechanism is thought to be well established in membrane filtration, unexpected results have been observed with retention of some micropollutants considerably lower than expected based on molecular weight [34, 54]. Some have attributed such variation to molecular length and shape [37, 55, 56] although Van der Bruggen et al. [31] concluded that correlation of retention with size parameters other than MW (e.g. Stokes diameter) was only a marginal improvement. This mechanism is applicable for charged micropollutants only and hence speciation is very important. Speciation is micropollutant specific and can change depending on water characteristics as well as solute-solute interactions that result in ligand formation and complexation. Most estrogens that have a phenolic hydroxyl (OH) group dissociate above pH 10.25 to 10.5. In consequence those estrogens are uncharged at neutral pH and their retention is inversely related to pH. An increase of molecular size (such as molecular width, molecular mean size, and molecular weight) for alcohols and saccharides. However in a later study [36] this clear trend with molecular width was only obtained for one of the NF membranes used and not for the other 3 membranes. Molecular shape can be exploited to prepare molecular imprints in polymers to create specific sorption characteristics.

Proton donor and acceptor characteristics are further characteristics that may affect interaction with polymers, in particular the ability to form hydrogen bonds. H-bonding has been attributed to play a predominant factor in the transport of estrogens in biological systems [37-42]. The hormones such as E1, E2 and DES all possess a phenol group which is electron-rich [43] and can therefore have the potential to form π-π bonding with electron deficient phenyl groups [30] of the polymers. Such micropollutant characteristics affect the retention and sorption by membranes and this will be examined in the following sections.

3 Retention of Micropollutants by Polymeric Membranes

The retention of micropollutants such as estrogens varies significantly with membrane process type, membrane characteristics, operating conditions, specific micropollutant characteristics and membrane fouling. In MF and UF micropollutants such as estrogens are not usually retained due to the small molecular weight. However, retention can be increased through association of micropollutants with retained matter or hybrid processes such as powdered activated carbon coupled with MF or UF [44-46].

In NF and RO retention of estrogens can vary from 0 to near 100% depending on the membrane (see Figure 1). Such variation invites a thorough investigation of retention mechanisms to achieve a more reliable and predictable performance.

Both size and charge are important and the mechanisms of micropollutant removal can be summarised as illustrated in Figure 2. Any non-retained micropollutants will penetrate into the polymer matrix, while those retained are accumulating in the boundary layer (membrane surface).

Charge and Donnan exclusion are further mechanisms of exclusion of solutes by membranes. Those describe the repulsion between a charged solute and a charged membrane (Figure 2B). Naturally, this process is well understood for inorganic salts, while organic acids, macromolecules and micropollutant behaviour needs to be better understood. Micropollutants of similar or smaller size than the membrane pores can be retained due to charge repulsion between the membrane polymer and the micropollutant [23, 24, 31, 53, 57-62]. This mechanism is applicable for charged micropollutants only and hence speciation is very important. Speciation is micropollutant specific and can change depending on water characteristics as well as solute-solute interactions that result in ligand formation and complexation. Most estrogens that have a phenolic hydroxyl (OH) group dissociate above pH 10.25 to 10.5. In consequence those estrogens are uncharged at neutral pH.
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Solute-solute interactions and fouling can make the determination of actual retention mechanisms difficult and adsorption in particular is often confused with membrane deposition formation or concentration polarization phenomena. During filtration the deposits of retained material are generally high and as fouling changes the membrane surface and hence possible charge, steric and sorption interactions. In addition, changes in retention over time or in different water matrices may occur due to solute-solute interactions (Figure 2E) as well as micropollutant-fouling layer interactions (Figure 2F). Such phenomena can, for example, induce micropollutant retention by ultrafiltration membranes [45, 46, 69] or cause desorption of adsorbed micropollutants making retention mechanisms in real waters a very complex affair.

Given that adsorption is a very common feature, no observable observation in membrane filtration of micropollutants this mechanism will be investigated systematically in this review to gain a better understanding. In the following section transport models will be summarised before returning to adsorption in more mechanistic detail.

4 Micropollutant Transport Models for Membrane Filtration

Descriptions of solute transport in RO membranes were originally given by the irreversible thermodynamic model [70, 71]. The membrane was treated like a black box, no membrane structural or electrical parameters were acquired and scarce information about the transport mechanisms inside the membrane could be obtained [72].

The solution-diffusion model was proposed where it considers that each permeant dissolves in the membrane and is transported by diffusion due to its gradient in chemical potential through a non-porous membrane [72]. The solute flux is independent of permeation pressure while the solvent flux increases proportionally to it. Retention must therefore increase with pressure. This was confirmed for metals, some ions and saccharides, namely uranium, raffinose, sodium, magnesium and calcium [68, 73, 74].

For NF membranes, there is some debate about the existence of discrete pores. In this case the solution-diffusion model is incomplete and a convection term should be included that takes account of solute transport through membrane pores. The retention of uncharged solutes in NF membranes can be described with the hydrodynamic model [75] previously described. The transport takes into account diffusion and hindered convection, caused by the difference between solute size and pore size. For charged solutes such as ions or organic acids, the addition of the membrane and ion electrochemical potential derives in the extended Nernst-Planck equation [73]. This last model not only allows determining the same parameters as the hydrodynamic model but also allows the determination of the effective membrane charge density [54, 76, 77].

Generally, both the solution-diffusion model and the hydrodynamic model describe an increase of retention for solutes with pressure. However, for some micropollutants the opposite trend is observed, e.g. with hormones [50, 78], pesticides [53, 61], volatile organic carbon (VOC such as chloroform) [47], endocrine disrupting chemicals (EDCs) such as nonylphenol (NP) [79] and pharmaceuticals [61] where retention decreases with pressure. It is thought that the interaction of micropollutants with the membrane polymer plays an important role [54] and contributes to the reduced retention at higher pH. However this phenomenon is not directly linked with the ratio between the solute and pore radius (λ=Rsolute/Rpore). It could be argued that for λ<1, the solute can penetrate the membrane and be less retained. However, for nanofiltration of Na2SO4, glycine and glucose as examples of non-adsorbing compounds with λ<1, retention increases with increase of pressure [73, 80]. This trend is not always verified for micropollutants with λ>1 [78]. When pores physically exist the issue of steric hindrance or size exclusion is obvious. However, considering a pure steric hindrance model is not accurate in the case of dense materials and adsorbing solutes [54]. Solute retention depends not only on solute size but also on adsorption and chemical organic characteristics such as hydrophobicity, as well as convection and diffusion mechanisms [81].

Adsorption of micropollutants to the membrane polymer is usually not taken into account in micropollutant retention models [54, 58, 59, 82]. In consequence, retention, permeate
concentration and mass flux are therefore often wrongly determined. Retention, in particular, is commonly overestimated when based on size. The interaction that exists between adsorbing micropollutants and the membrane was incorporated in the hydrodynamic model for NF using an affinity approach. Retention was predicted well and flux increase with permeate flux for the adsorbing contaminants, for other contaminants, retention decreased with increase of flux [78]. Furthermore, a simplified approach to model the retention of several micropollutants in NF has been developed [82]. For some micropollutants, such as xeno-estrogens, high membrane adsorption occurred and in consequence no permeate concentration was measurable. This prevents the application of this model, which does not take adsorption into account, for solutes that interact with membranes. For other solutes, diffusion only transport closely matched the measured retention. In another study the irreversible thermodynamic model was used as a basis to understand if convection or diffusion were the predominant contributor in the solute (DBP and halogenated solvents) permeate flux for NF and RO membranes [84]. This proved problematic for adsorbing compounds and the membranes had to be presaturated to achieve steady state. When reaching steady state proved to be impossible as for the case of trichloroethene, no conclusions could be drawn.

Interestingly, adsorption has been considered in a modified sorption-diffusion model for RO that added adsorption induced flux decline to pressure [85]. Results confirm flux decline due to the adsorption of the organic compounds on the membrane polymer through specific adsorption (e.g. hydrogen bonding). Organics may compete with water for adsorption sites and decreasing water content on the membrane and flux. Further, this model described the transient permeate concentration behaviour more adequately that the previous model which considered steady state conditions of water and solute flux across the membrane, by assuming adsorption-diffusion transport of organics in the membrane polymer. Shortfalls of this model remain (i) the inapplicability to NF due to a missing convection element, and (ii) the common absence of a flux reduction element due to micropollutant sorption [85, 86]. This outlines the need for retention models that are solute – and no concentration - specific and consider possible solute-membrane interactions. Some attempts have been made in this direction using artificial neural networks (ANN) and component analysis method (quantitative structure relations or QSR) have been developed to obtain a model that describes retention as a function of the contaminants most important variables (e.g. molecular width and depth) by nanofiltration membranes [55, 56] and the NF membrane characteristics such as roughness or active layer thickness [32]. Limitations of such models are the validity for certain boundary conditions only, and while simple in nature, they cannot replace the understanding of fundamental mechanisms.

A further complexity that is not yet theoretically predictable is the behaviour of micropollutant mixtures. In real waters many micropollutants are found together with other organics such as effluent or natural organic matter. This can result in solute-solute interactions [87]. When organic matter is present in solution enhanced retention is generally obtained for micropollutants [45, 52, 58, 61, 78, 88-91] due to partitioning of the micropollutants into the retained organics [92, 93]. Higher adsorption is obtained, possibly on both membrane and organic matter layer that is formed on the membrane surface [62, 63, 88, 89, 94]. According to some studies, the presence of a humic acid fouling layer renders the membrane more hydrophobic, enhancing estrone adsorption [63, 89]. However, this increased sorption may be attributable to interactions between humic acid and micropollutants more so than increased hydrophobicity. In contrast, a decrease in micropollutant adsorption may occur when natural organics and micropollutants compete for sorption sites [57, 92, 95-99]. Competition for sorption sites occurs often between micropollutants or between organics and other organics at much higher concentrations and increased with permeate flux for the adsorbing contaminants, for other contaminants, retention decreased with increase of flux [78]. Consequently, the close relationship between adsorption phenomena and retention of micropollutants. Several models to predict the amount adsorbed on a membrane for mixtures based on the amount adsorbed with only one compound has also been developed [101].

While solute retention in NF and RO is reasonably well understood, the retention of adsorbing micropollutants cannot currently be adequately described. Results obtained with pristine and saturated membranes often show diametrically opposed results making the interpretation of literature difficult. Understanding of adsorption mechanisms and transport of adsorbing solutes is instrumental to fully incorporate adsorption phenomena into membrane models successfully. In consequence this adsorption will be investigated below.

5 Micropollutant Sorption in Membrane Filtration

Sorption by membrane polymers occurs across the range of available processes and polymers. In this section a number of examples are provided from pressure driven membrane processes. Observation of micropollutant sorption is a recent phenomenon. This is presumably due to the development of analytical techniques that facilitate the detection of molecules in nanogram quantities of pollutants of very low concentration. However, such sorption would be a very common occurrence for many pollutants albeit often not measurable. Sorption of organics is well recognised as a conditioning film for subsequent biofilm attachment. Micropollutants accumulate in biofilms. However, the understanding of the impact of estrogens on growth of such biofilms or their degradation by biofilms is not yet established [102, 103].

While porous membranes such as MF and UF do not retain micropollutants, the polymer surface adsorbs significant amounts. This has resulted in the removal of estrone by a 0.2 µm MF polypropylene membrane of more than 95% [104] which can only be attributed to adsorption. Other examples showed >34% of 17β estradiol adsorption on an ultrafiltration polyamide UF membrane [105] whereas 38% and 33% of bisphenol A was observed in other studies [46, 106]. UF membranes were used to recover 6-n-propyl-2-nitrosamine from cell suspensions, and 27% and 31% of hormone was adsorbed on two different MWCO UF polysulphone membranes [107]. Jermann et al. [69] have shown low estradiol retention by a hydrophilic UF membrane, while a hydrophobic membrane showed very high retention with a gradual decrease as the polymer saturated with estradiol. Higher retention was attributed to organic material fouling while Neale and Schäfer quantified the contribution of organic matter – micropollutant interactions in the absence of significant sorption for a hydrophilic membrane [108]. This illustrates the complexity of such interactions.

Naturally, the majority of micropollutant sorption results have been published in NF, while comparison can be very interesting. High adsorption of the hormones estradiol, progesterone and testosterone on both a UF (sulphonated polyethersulfonate coated with polyimide) and NF (polyamide) membranes was observed, while surprisingly estrone did not adsorb [96]. Adsorption of estradiol was lower for NF than UF; for a delivered mass of estradiol of 1 ng/mL, the UF membrane adsorbed about 0.5 µg/cm² and the NF adsorbed about 0.2 µg/cm² [95]. Adsorption occurs on different membrane layers and alters if static adsorption (no pressure/filtration) as compared to filtration conditions. For example, adsorption of several hormones to NF200 polyamide membrane was studied in a stirred cell system without pressure. Adsorption of all hormones varied between 0.20 and 0.35 ng/cm² for a feed concentration of 10 µg/L [52]. Adsorption of 100 ng/L estrone to two NF membranes made of cellulose acetate (CK, MWCO 560 g/mol) and polyamide (DL, MWCO 490 g/mol) resulted in a decrease in feed concentration due to the adsorption-diffusion transport of organics in the membrane polymer. Shortfalls of this model remain (i) the limitations of such models are the validity for certain boundary conditions only, and while simple in nature, they...
Figure 4
Adsorption is lowest for the membrane with highest retention (X20) indicating that 'pore size' may play an important role in adsorption. In order to investigate the relationship between such 'pore size' and adsorption, a number of membranes were characterised in terms of molecular weight cut off (MWCO) and pore radius. The pore radius and the ratio membrane active layer thickness/porosity was determined for each membrane using the hydrodynamic model [75, 76] with neutral solutes (methanol, dioxane, xylose and dextrose). This model assumes perfect cylindrical pores of identical pore radius, solutes of spherical shape and that retention of the solutes only occurs through steric exclusion. The mentioned parameters are obtained by curve fitting the hydrodynamic model to the real solute retention variation with permeate flux. The same methodology described by Nghiem et al. [54] was adopted for the BW30, NF90 and NF270 characterisation using a cross-flow system. The TFC-SR2 and TFC-SR3 characteristics were determined with the same method in stirred-cells [112]. The active surface area (membrane surface area including pore surface area) was estimated with an average of active layer thickness of the membranes from literature [113-117] and summarised in Table 2. With the membrane active layer thickness, porosity can be obtained and therefore the internal surface area of the membrane active layers can be calculated. Since no active layer thickness has been published for the TFC-SR3 membrane an average value of reported thicknesses for the TFC-S and TFC-SR2 membranes was determined [113, 118-120].

Table 2
The equivalent sphere radius of estradiol was calculated with the Stokes-Einstein equation. Crossflow experiments were carried out with the same system as described for Figure 3. Retention decreased with increasing pore radius above the estimated radius of estradiol of 0.4 nm from about 80% to 30%. Mass adsorbed increased with pore radius for both the membrane area (as per sheet size) as well as per estimated total membrane area available to sorption. Sorption is lower when regarded as per available internal surface area suggesting that adsorption occurs internally and increases with increasing available area. It should be noted here that this area only considers the internal area of the active layer (polyamide) and not the polysulphone supporting layer. More work is required to differentiate between these materials systematically.

Figure 5
Sorption to membrane polymers is not unique to NF and RO. In fact, sorption to electrodialysis (ED) membranes can be significantly higher than for other membranes. Pronk et al. [121] used polyethersulphone electrodialysis membranes with an effective surface area of 49 cm² per sheet in an ED stack of two cell pairs to recover salts from urine containing ethinylestradiol (EE2). The result showed that approximately 230 µmole of EE2 was adsorbed on the membrane when 400 µmole of the hormone is added in initial urine solution at a high concentration of 10 μM (about 3 nL) [121]. Taking into account the molecular weight of ethinylestradiol the adsorption was estimated as 139 µg EE2/cm² where the initial EE2 mass added into solution was as high as 119 mg. Banasick [122] has measured the adsorption of different hormones to electrodialysis membranes (see Figure 6) at a concentration of 100 ng/L. The experiments showed an adsorption as high as 1.2 ng/cm².

[Figure 6]
Such enhanced adsorption can be attributed to very thick membranes in ED as compared to an active layer thickness in NF or RO. In addition, the effective area is very high due to the internal porosity observed in ED. Electrodialysis membranes can be classified in three groups regarding their size of clusters in swollen state. These groups are homogeneous, microheterogeneous and heterogeneous. The 'pore size' of homogeneous Nafion ED membranes is about 1 nm whereas Nafion 117 has a pore diameter of about 6 nm [123]. Eurodia/Neosepta electrodialysis membranes have a very low molecular weight cut off (350 Da MWCO) [124]. Khulbe et al., states that dialysis membranes have a pore diameter changing between 2 and 5 nm [125]. In contrast, several hollow fibre electrodialysis membranes were imaged by AFM and TEM and the results showed that pore diameter at the inner surface was 10.5 nm and 12.9 nm for polyester-polymer alloy (PEPA) and polysulphone polyvinylpirrolidone (PS-PVP) materials, respectively [126]. This indicates a nanoporous structure throughout the membrane with a thickness of hundreds of μm, which illustrated the role such an internal area plays for micropollutant adsorption- or absorption.

6 Micropollutant Sorption by active Polymer Surface Area

The mechanisms of micropollutant sorption to membrane polymers is to date not well understood. Steinle-Darling et al. [127] described two mechanisms of micropollutant sorption; a first one being adsorption to the membrane surface, and a second being internal absorption into the membrane pore structure. Solvation in the membrane and diffusion within are processes that lead from adsorption to absorption. While this process is conceptually reasonable, the reality in various membrane processes may be more complex. In porous membranes, for example, the available membrane surface area will extend into the material and it becomes debatable where adsorption ends and absorption starts. A further complication is the material characteristics of composite membranes that consist of support layers and active layers of different material, thickness, pore size and porosity. This will alter the available surface area considerably even without considering the heterogeneity of such materials. It is difficult, if not impossible, to determine the internal polymer surface area available for micropollutant sorption.

To investigate this effect of surface area systematically, adsorption of estrone (E1) to polystyrene nanoparticles separated by UF membranes was investigated (see Figure 7). Regenerated cellulose ultrafiltration (UF) membranes with a polypropylene support layer of 1, 3, 5 kDa MWCO supplied by Millipore (Bedford, US) were used. Those membranes were chosen as sorption is minimal and there does not occur at those small MWCO [128-130] for the chosen nanoparticles during the given experiments. Polystyrene nanoparticles with a size range of 46 nm to 3 µm were purchased from Polysciences, Inc. (Eppelheim, Germany). The experiments were conducted with stainless steel stirred cells in which solution operated at 300 rpm with a magnetic stirrer. Radiolabelled [2,4,6,7-3H] estrone (2.45 TBq/mmol) with a radioactive concentration of 37 MBq/mL was purchased from Perkin Elmer (Beaconfield, UK). Prior to the experiments, the membranes were compacted for 30 minutes and pure water flux determined. 15.7 mg/L of
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Results indicate that adsorption of oestrone (E1) decreases sharply with increase of particle size due to the reduced surface area of larger particles. Surface normalised sorption increases with particle size which indicates that the available surface is not saturated. Increased sorption with the lower MWCO membranes can be attributed to a longer contact time between micropollutants and the retained nanoparticles due to the lower flux. Clearly, sorption can be attributed to surface area when such a surface area can be calculated accurately which is the case for such spherical nanoparticles. Sorption is directly related to the available surface area and this has direct implications to sorption of membrane polymers. However, for generally very heterogeneous polymers, the determination of the actual surface area of a membrane polymer is very difficult if not impossible to determine accurately.

To evaluate such surface variability, the internal membrane surface area has been estimated as a function of pore size of cylindrical pores (Figure 8A-C) and voids between spherical grains (Figure 8D) with varying thickness and porosity. A membrane surface area of 100 cm² was considered and equation (1) was used for perfectly shaped cylindrical pores to determine surface area from pore size, porosity and active layer thickness.

\[
\text{Total Area} = \text{Surface Area} + \text{Internal Area} = WL(1 - \varepsilon) + \frac{2LWd_\varepsilon}{r_p}
\]

(1)

Where \( W \) and \( L \) are the membrane width and length (10 cm) respectively, \( \varepsilon \) is the membrane porosity, \( d_\varepsilon \) is the active layer thickness and \( r_p \) is the pore radius.

For membranes made from spherical grains which is the case for some MF, UF and ED membranes, a cubic close packing of spherical grains was used and equation (2) shows the relationship between the surface area, active layer thickness and sphere radius.

\[
\text{Surface Area} = \frac{16WLd_p r_\text{sphere}^2}{(2r_\text{sphere})^2}
\]

(2)

Where \( r_\text{sphere} \) is the sphere radius. This indicates a rapid increase of internally available surface area with decreasing pore size at similar porosity and a linear increase of this surface area with membrane thickness.

![Figure 7](image1)

Membrane surface roughness can be quantified by AFM [136-138]. Values for average roughness between 0.4 and 5 nm were reported, while some membranes show much higher values, 28 nm for NF90 [139] and >60 nm for BW30 [140]. Surface roughness for cellulose acetate membrane supports have been reported as high as 17 nm [138]. Using such values AFM can be used to estimate the surface area of membranes, where for a projection area of 100 μm² surface areas between 150 and 180 μm² were reported for an average surface roughness between 40 and 85 nm [141]. It is possible that such figures are an underestimate when the internal membrane structure is considered accurately, the likely range of which is evident from Figure 8. Ultimately such values will remain averages that are prone to be biased to properties visible from the surface of the membrane while properties within the material remain unknown.

![Figure 9](image2)

Where such calculations can be carried out for conceptual or ideal membrane characteristics, the characterisation of pore size, membrane thickness and porosity (and in consequence internal pore area) of real membranes, in particular composite membranes used for NF is very difficult, if possible at all.

A range of characterisation tools exists for membrane characteristics such as porosity, pore size and active layer thickness. Active layer thickness can be measured by SEM [115, 131, 132], Rutherford Backscattering Spectrometry [131], TEM [133], as well as Impedance Spectroscopy [134]. Thickness of the active layer has been determined by Freger et al. [114, 133, 135] to be in the order of 10-200 nm for NF and 200-350 nm for RO membranes of polyamide active layer. Uranyl nitrate staining of the active layer followed by transmission electron microscopy was used. The work illustrated how highly non-uniform polymer density and charged surface groups are distributed across the active polyamide layer. The densest part of the layer may be covered by an extensive surface roughness which makes the accurate determination of surface available for sorption extremely difficult. Surface roughness for three thin-film composite NF membranes – with polyamide active layers – is shown in Figure 9. This image implies a very high surface roughness for TFC membranes.

Positron annihilation spectroscopy (PAS) can be used to determine the top layer porosity [115]. A difference between the pore size of the top layer and support layer can be obtained indirectly, although no physical value of porosity was published. An evident increase in porosity is observed at the transition between the active layer to the more porous sub-layer. Porosity can however be determined experimentally. Several authors have used the hydrodynamic model [75] by filtering neutral organic and inorganic solutes to obtain the pore radius, active layer thickness to porosity ratio [54, 76, 77, 142]. With the knowledge of the thickness of the active layer (e.g. by using TEM), one can calculate the active layer porosity. Pore size distribution on the other hand can be used to determine the number of pores and the pore radius of several commercially available membranes [143, 144].

Attempts to identify a discrete pore size of NF membranes by AFM resulted in estimates from 0.1 to 2 nm [139, 145]. While such methods are limited to pores visible from the membrane surface and the existence of discrete pores in nanofiltration is subject to ongoing controversy, the results obtained are in the same order of magnitude as effective pore sizes determined by other methods. As previously mentioned the hydrodynamic model can also be used to determine the membrane pore radius. As an illustration the pore radius obtained for the NF270, TFC-SR2 and NF90 were 0.42, 0.52 and 0.34 nm respectively (Table 2).

In addition to physical parameters of the membrane such as internal surface area and roughness, chemical characteristics of the micropollutant and of membrane polymers alter adsorption behaviour.

7 Micropollutant Sorption by different Polymer Materials

The observation of micropollutant sorption to polymeric materials is not new and early observations were made of interactions with laboratory equipment. For example, Petri dishes (PVC) were found to adsorb significant amounts of hormones and results were verified with grinded PVC [146]. One study established that polystyrene plastic ware adsorbed 38% and 43% of 17β-estradiol and progesterone, respectively [147], while another study reported that the majority of parathyroid hormone sorbed to borosilicate glass tubes, polycarbonate and cellulose nitrate.

Membrane surface roughness can be calculated for conceptual or ideal membrane characteristics, the characterisation of pore size, membrane thickness and porosity (and in consequence internal pore area) of real membranes, in particular composite membranes used for NF is very difficult, if possible at all.

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In addition to physical parameters of the membrane such as internal surface area and roughness, chemical characteristics of the micropollutant and of membrane polymers alter adsorption behaviour.
Micropollutant sorption to membrane polymers, Advances in Colloid and Interface Science, 'Membrane Separation and Colloid Science’ invited special issue paper (accepted 09/2010).


Polypropylene (PP) marine resin pellets collected from the Japanese coast was reported to vary from 4-117 ng/g, 0.16-3.1 ng/g, 0.13-16 µg/g for PCB, DDE and NP, respectively. Determination of the specific surface area of PP pellets was estimated as 25 cm²/g and surface specific adsorption results were 4.7 ng/cm², 0.12 ng/cm², 0.36 pg/cm² for PCB, DDE and NP, respectively [151]. Significant sorption of hydrophobic endocrine disrupting compounds to porous polysulphone beads was reported [152].

Sorption has also been observed for filters used in sample preparation resulting in significant losses of analytes. Different types of filter materials were tested for estradiol adsorption and the results showed that cellulose acetate and cellulose nitrate adsorbed the most estradiol compared to glass fibre and paper materials [149]. Adsorption of up to 50% of feed estradiol concentration on a cellulose acetate filter was observed [153].

Sorption in samples is exploited for analytical purposes which is commonly the case in chromatography as well as sample preparation. Solid phase extraction (SPE) is used for the concentration of analytes in samples. The most widely used SPE sorbents for micropollutants are alkyl-bonded silicas (C18 silica, C2 silica), copolymer sorbents such as cross-linked polystyrene divinylbenzene, and hydrophilic-lipophilic balanced polymers. Each has specific contaminant applications [154, 155]. C18 resins and other polymeric sorbents have been used in several studies separate or in combination for purification and determination of pesticides, estrogens and progesterones with SPE [156-158]. Solid phase micro-extraction (SPME) sorbs a fraction of the analyte and can be used for the quantification of both analyte as well as analyte interactions with other dissolved molecules. Polyacrylate has been used for the detection of estrogens in water and their interactions with organic matter [87, 159]. Polydimethylsiloxane (PDMS), divinylbenzene (DB), polyacrylate (PA), as well as Carbobox (CAR; a carbon molecular sieve) and Carboxaw (CW; polyethylene glycol) are other commonly used coating polymers for SPME of organics [160].

Similar sorption phenomena are observed in other water treatment applications that involve polymer interfaces. For example, magnetic ion exchange resin (MIEX) developed for enhanced natural organics removal, sorbs significant amounts of uncharged micropollutants such as estrogens [161]. The resin has a macroporous polyacrylate shell with quaternary ammonium functional groups for ion exchange.

These results highlight an affinity of certain organic solutes for polymeric materials and a strong material dependence on interactions. While it is no surprise that membrane polymers absorb micropollutants, the mechanisms of micropollutant adsorption onto polymers are to date scarce not well understood and hence a systematic investigation is required. For this reason a range of polymers (see Table 3) commonly used for membrane materials has been selected for preliminary investigation and the very novel results are subsequently presented in this review.

Table 3

<table>
<thead>
<tr>
<th>Membrane Material</th>
<th>Adsorption (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>500µm</td>
</tr>
<tr>
<td>PP</td>
<td>500µm</td>
</tr>
<tr>
<td>PSu, PP, HDPE, PA, PS, PEN and PES</td>
<td>purchased from Goodfellow (Huntingdon, UK) in the form of 2-3 mm granules. PUs UDEL and PVDF were obtained from Solvay (Brussels, Belgium) in granular form and CEL, PMMA and PPO were purchased from Sigma Aldrich (Gillingham, UK) in powder form. Membranes were similarly cut to a size of ~500µm, and used as ground material for sorption studies.</td>
</tr>
</tbody>
</table>
of C, O and N can be obtained by using X-ray photoelectron spectroscopy XPS [134]. Hydrophobicity of polymers is measured as contact angle [162] while for micropollutants hydrophobicity is expressed as octanol water partition coefficient (K_{OW}).

In general the more hydrophobic a compound is, the more it is expected to adsorb onto a surface in contact with water because this requires less free energy compared to forming a ‘cavity’ in the water phase [163]. In the case of membrane polymers higher the hydrophobicity has also been attributed to more adsorption [58, 60, 95, 111, 164]. For example, Boussu et al. [164] obtained a clear trend of increasing adsorption with increasing hydrophobicity of the organic compound such as phenylalanine. Two of the more hydrophobic PES membranes adsorbed much higher quantities compared to the phenylalanine membrane. However, some exceptions exist where highly hydrophobic micropollutants adsorbed very little onto NF polyamide or polyethersulphone membranes.

In the specific case of hormones, Dudiak and Bodzek [165] showed that adsorption and retention was not related with hydrophobicity for two different NF membranes (polyamide and cellulose acetate). DES, the most hydrophobic hormone (see Table 1, log K_{OW} 5.07) adsorbed the least for both membranes studied, while the cellulose acetate membrane adsorbed less than the polyamide membrane. This can be explained by the fact that cellulose has practically no binding capacity for steroids [166, 167]. In the presence of natural organic matter a clear trend between hydrophobicity and adsorption of trace contaminants (e.g. hormones, analogics, antibiotics, etc.) on polyamide active layers is not clear either [96].

In terms of retention of micropollutants by membrane polymers, generally, higher hydrophobic hormone hydrophobicity results in lower retention [34, 164, 168]. However, several studies showed that membrane rejection of organic compounds (including hormones, pharmaceuticals, pesticides, etc.) varies greatly for similar hydrophobicities [33, 36, 91, 169]. In the case of non-phenyllic pesticides retention increased with increase of hydrophobicity for NF membranes with PA or PES active layers [100]. Comerton et al. [169] obtained a retention by a PA NF active layer for the DES hormone compared to the other hormones, despite DES being much more hydrophobic (see Table 1). Kim et al. [38] equally obtained higher retention values for more hydrophobic contaminants such as disinfection by-products and chlorinated solvents.

As can be seen in Figure 11 for contact angle and Figure 12 for log K_{OW}, this does not always correlate affinity with retention successfully. The reason being that hydrophobicity fails to identify specific material affinities between polymers and micropollutants [83]. It is therefore important to understand underlying adsorption mechanisms in more detail.

![Figure 11](image1)

![Figure 12](image2)

One of the main reasons why so little is known about membrane adsorption is the difficulty in obtaining specific material characteristics for membrane polymers. Some characterisation data is available, for example gas adsorption analysis conducted on PE showed that there was almost no internal porosity and the polymer had a small surface area compared to other particles. Nevertheless, partitioning was stated to play an important role in sorption atrazine and trichloroethene to PE which is a strongly hydrophobic polymer [150, 170]. Other authors attributed a slow diffusion of the hydrophobic compounds into PE granules to slow sorption [171].

![Figure 13](image3)

![Figure 14](image4)

Returning to characteristics summarised in Table 3 and results in Figure 10 a number of observations can be made. π-π interactions and strong hydrophobic interactions are involved in the sorption mechanisms of methylene and phenyl groups to hypercrosslinked polystyrene [180]. Davankov (2003) [179] states that π-π interactions between the hypercrosslinked polystyrene and the substances with π-systems of electrons such as aromatic rings, carboxyl groups and alike governs the retention mechanisms in HPLC application with non-polar solvents. In fact, hypercrosslinked polystyrene has a strong π-electron donating-accepting ability in non-polar organic solvents. This ability results in high sorption capacity of compounds which contain aromatic π-systems or functional groups with free electron pairs in HPLC application [181]. Sorbents used in SPE with phenyl groups (such as polystyrene divinylbenzene) have the capacity to interact with steroids through π-π interactions, results in Figure 13 illustrate. The number and positioning of phenyl groups in this phase determine the level of π-π interactions and the sorption capacity. It was suggested that the π-π interaction between the phenyl phase and the steroid occurs when the double bonds of steroid and phenyl group overlap [182]. Similar phenomena are likely when estrogen are in contact with membrane polymers which may explain the strong sorption of estrogens by polystyrene, although the main mechanism for polystyrene sorption is hydrophobic interactions (Figure 10A). The aromatic ring in polystyrene is electron neutral, while the benzene rings in estrone and estradiol are
10 Acknowledgments

Howard Colquhoun (University of Reading) and Arno Kraft (Heriot-Watt University) have contributed with useful discussions on polymer – micropollutant interactions and supramolecular chemistry. Alanna Stacey Campbell and Chris Jeffree have assisted with polymer characterisation. Laura Banasiak has provided results of micropollutant interactions with electrodialysis membranes. Bart van der Bruggen (KU Leuven) and Rudolf Graf (Berghof) have supplied membrane polymers while membrane samples were donated by Dow Chemicals, Koch, and Millipore. Nigel Staples from Retsch assisted with the loan of the Ultra Centrifugal Mill and Laura Richards is thanked for NF90 and BW30 membrane characterisation results. Funding for Andrea Semiao and Ine Akanyeti is provided through a School of Engineering/DTA stipend and a RSC/EPSRC Analytical Science Studentship, respectively.

11 References

### Table 1
Characteristics of micropollutant group of estrogens

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Formula</th>
<th>CAS No.</th>
<th>Mol Structure</th>
<th>MW (g/mol)</th>
<th>Solubility in water (mg/L)</th>
<th>pK_a</th>
<th>Log Kow</th>
<th>Dipole moment (D)</th>
<th>H bond capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estradiol E2</td>
<td>C_{18}H_{22}O_2</td>
<td>50-28-2</td>
<td></td>
<td>272</td>
<td>3.6, 92,135,10</td>
<td>10.25</td>
<td>4.01</td>
<td>2.2</td>
<td>Strong OH donor and acceptor; π weak acceptor (benzene)</td>
</tr>
<tr>
<td>Estrone E1</td>
<td>C_{18}H_{20}O_2</td>
<td>53-16-7</td>
<td></td>
<td>270</td>
<td>13, 147,134,10</td>
<td>10.34</td>
<td>3.13</td>
<td>2.1</td>
<td>Strong OH donor and acceptor; π=O acceptor; π weak acceptor (benzene)</td>
</tr>
<tr>
<td>Testosterone T</td>
<td>C_{18}H_{22}O_2</td>
<td>58-22-0</td>
<td></td>
<td>288</td>
<td>24, 68,14,17</td>
<td>17.4</td>
<td>3.32</td>
<td>3.5</td>
<td>Strong OH donor and acceptor; π weak acceptor (benzene)</td>
</tr>
<tr>
<td>Progestrone P</td>
<td>C_{18}H_{20}O_2</td>
<td>57-83-0</td>
<td></td>
<td>315</td>
<td>NA</td>
<td>3.87</td>
<td>4.50</td>
<td>4.8</td>
<td>Strong =O acceptor; π weak acceptor (benzene)</td>
</tr>
<tr>
<td>Estril E3</td>
<td>C_{18}H_{22}O_2</td>
<td>50-27-1</td>
<td></td>
<td>288</td>
<td>13, 441,13,10</td>
<td>10.25</td>
<td>1.71</td>
<td>3.22</td>
<td>Strong OH donor and acceptor; π weak acceptor (benzene)</td>
</tr>
<tr>
<td>Mestranol ME2</td>
<td>C_{18}H_{20}O_2</td>
<td>72-33-3</td>
<td></td>
<td>310</td>
<td>0.3, 3.5</td>
<td>4.10</td>
<td>1.10</td>
<td>-</td>
<td>Strong OH donor and acceptor; π=O acceptor (benzene)</td>
</tr>
<tr>
<td>Ethinylestradiol EE2</td>
<td>C_{18}H_{22}O_2</td>
<td>57-63-6</td>
<td></td>
<td>296</td>
<td>4.8, 116,10,1</td>
<td>10.25</td>
<td>3.60</td>
<td>2.6</td>
<td>Strong OH donor and acceptor; π weak acceptor (benzene)</td>
</tr>
<tr>
<td>Diethylstibestrol DES</td>
<td>C_{18}H_{20}O_2</td>
<td>56-53-1</td>
<td></td>
<td>268</td>
<td>12</td>
<td>5.07</td>
<td>1.62</td>
<td>2.2</td>
<td>Strong OH donor and acceptor; π weak acceptor (benzene)</td>
</tr>
</tbody>
</table>

### Table 2
Membrane characteristics determined experimentally and average active layer thickness obtained from the literature for five membranes used

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Pore Radius R_{pore} (nm)</th>
<th>Active Layer Porosity Ratio L/ε</th>
<th>Average Active Layer Thickness L (μm)</th>
<th>Total Estimated Surface Area of Active Layer (cm²)</th>
<th>Porosity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>BW30</td>
<td>0.32</td>
<td>6.01</td>
<td>250</td>
<td>2968</td>
<td>0.042</td>
<td>[117]</td>
</tr>
<tr>
<td>NF90</td>
<td>0.34</td>
<td>1.46</td>
<td>174</td>
<td>5529</td>
<td>0.119</td>
<td>[113]</td>
</tr>
<tr>
<td>TFC-SR3</td>
<td>0.38</td>
<td>1.59</td>
<td>114</td>
<td>1978</td>
<td>0.072</td>
<td>[118] [119] [120]</td>
</tr>
<tr>
<td>NF270</td>
<td>0.42</td>
<td>1.05</td>
<td>35</td>
<td>294</td>
<td>0.033</td>
<td>[113] [114]</td>
</tr>
<tr>
<td>TFC-SR2</td>
<td>0.52</td>
<td>2.45</td>
<td>67</td>
<td>361</td>
<td>0.027</td>
<td>[113] [115] [116]</td>
</tr>
</tbody>
</table>

*a* determined as average of TFC-S and TFC-SR2 membrane thicknesses due to absence of literature data

---

* [58], [34], [183], [184], [113], [78], [185], [186], [41], [95], [59], [187], [188], [189], [190], [52], [191], [169], [192]
Table 3 Polymer type, supplier, and selected characteristics for polymer powders used in adsorption studies

<table>
<thead>
<tr>
<th>Polymer Name</th>
<th>Supplier</th>
<th>Structure</th>
<th>Monomer Molecular Weight (g/mol)</th>
<th>Density (g/cm³)</th>
<th>Refractive Index (n)</th>
<th>Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysulfone (PSu), Polyurethane UDEL</td>
<td>Goodfellow &amp; Solvay</td>
<td><img src="image1.png" alt="Image" /></td>
<td>442</td>
<td>1.24</td>
<td>1.63&lt;sup&gt;a&lt;/sup&gt;</td>
<td>77&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Polyester; Polyethylene Teraphthalate (PET)</td>
<td>Goodfellow</td>
<td><img src="image2.png" alt="Image" /></td>
<td>192</td>
<td>1.35</td>
<td>1.58-1.64&lt;sup&gt;b&lt;/sup&gt;</td>
<td>79.09&lt;sup&gt;c&lt;/sup&gt;, 81°, 70°</td>
</tr>
<tr>
<td>Polyester; Polyethylene Naphthalate (PEN)</td>
<td>Goodfellow</td>
<td><img src="image3.png" alt="Image" /></td>
<td>242</td>
<td>1.36</td>
<td>1.65-1.90&lt;sup&gt;b&lt;/sup&gt;</td>
<td>80°</td>
</tr>
<tr>
<td>Polyamide Nylon 6 (PA)</td>
<td>Goodfellow</td>
<td><img src="image4.png" alt="Image" /></td>
<td>113</td>
<td>1.14</td>
<td>1.53&lt;sup&gt;b&lt;/sup&gt;</td>
<td>70°</td>
</tr>
<tr>
<td>Polyesulphone (PES)</td>
<td>Goodfellow</td>
<td><img src="image5.png" alt="Image" /></td>
<td>232</td>
<td>1.37</td>
<td>1.65&lt;sup&gt;b&lt;/sup&gt;</td>
<td>56°, 72°</td>
</tr>
<tr>
<td>Polyethersulphone (PES Radel A)</td>
<td>Solvay</td>
<td><img src="image6.png" alt="Image" /></td>
<td>324</td>
<td>1.37</td>
<td>1.65&lt;sup&gt;b&lt;/sup&gt;</td>
<td>127°</td>
</tr>
<tr>
<td>Polyvinylidene fluoride (PVDF)</td>
<td>Solvay</td>
<td><img src="image7.png" alt="Image" /></td>
<td>64</td>
<td>1.78</td>
<td>1.42&lt;sup&gt;b&lt;/sup&gt;</td>
<td>71°</td>
</tr>
<tr>
<td>Polystyrene (PS)</td>
<td>Goodfellow</td>
<td><img src="image8.png" alt="Image" /></td>
<td>104</td>
<td>1.05</td>
<td>1.59-1.60&lt;sup&gt;c&lt;/sup&gt;</td>
<td>91°</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>Goodfellow</td>
<td><img src="image9.png" alt="Image" /></td>
<td>42</td>
<td>0.9</td>
<td>1.49&lt;sup&gt;b&lt;/sup&gt;</td>
<td>95°</td>
</tr>
<tr>
<td>Polyethylene (HDPE)</td>
<td>Goodfellow</td>
<td><img src="image10.png" alt="Image" /></td>
<td>28</td>
<td>0.95</td>
<td>1.54&lt;sup&gt;b&lt;/sup&gt;</td>
<td>93-94°</td>
</tr>
<tr>
<td>Poly(2,6 dimethyl 1,4-phenylene oxide) (PPO)</td>
<td>Sigma</td>
<td><img src="image11.png" alt="Image" /></td>
<td>120</td>
<td>1.06</td>
<td>1.57&lt;sup&gt;b&lt;/sup&gt;</td>
<td>88°</td>
</tr>
</tbody>
</table>

<sup>a</sup> Materials Safety Data Sheet, <sup>b</sup>[193], <sup>c</sup>[194], <sup>d</sup>[195], <sup>e</sup>[196], <sup>f</sup>[197], <sup>g</sup>[198], <sup>h</sup>[199], <sup>i</sup>[200], <sup>j</sup>[201], <sup>k</sup>[202], <sup>l</sup>[203], <sup>m</sup>[204]
List of Figures

**Figure 1** Steroid retention by different NF and RO membranes. The hormones represented are: estradiol E2 (272.4 g/mol), estrone E1 (270.4 g/mol), estriol E3 (288 g/mol), ethinylestradiol EE2 (296 g/mol), progesterone P (314.5 g/mol), testosterone T (MW=288.4 g/mol), mestranol ME2 (MW=310 g/mol) and diethylstilbestrol DES (MW=268.4 g/mol). The MWCO of the membranes varied between 100 and 560, data adapted from [34, 50, 52, 57, 63, 78, 94, 109, 110, 169, 176].

**Figure 2** Micropollutant retention mechanisms in polymeric membranes A: Size Exclusion, B: Charge Repulsion, C: Adsorption, D: Sorption Diffusion, E: Solute-Solute Interactions, and F: Fouling Layer Interactions.

**Figure 3** Estradiol filtration by NF270 membrane in MilliQ water at pH 7 and 11. A: Feed and permeate normalized concentration, B: Retention (%), C: Mass adsorbed (ng/cm²) and D: Estradiol mass flux. The cross-flow conditions were 11 bar, Re 740, T 24°C, feed estradiol concentration 100 ng/L.

**Figure 4** Estrone and Estradiol sorption and retention for several NF membranes as a function of pH. Membranes were not saturated prior to experiments (data adapted from [25, 63, 109, 110]).

**Figure 5** Retention and mass adsorbed of estradiol per active (total) surface area and per membrane surface area (100 ng/L estradiol, 25°C, 11 bar and Re2800) of several polyamide on polysulphone membranes of increasing pore radius (BW30, NF90, TFC-SR3, NF270 and TFC-SR2, respectively).

**Figure 6** Estradiol (E2), estrone (E1), progesterone (P) and testosterone (T) adsorbed on Electrodialysis; Anion Exchange (AEM) (Neosepta® AMX-SB) and Cation Exchange Membrane (CEM) (Neosepta® CMX-SB) (polymer material: Polystyrene Divinylbenzene, supplied by Eurodia, Germany; manufactured by ASTOM Corporation, Japan). Initial hormone concentration was 100 ng/L in 1mMNaHCO₃, 85.5 mM NaCl, pH 7 [122].

**Figure 7** Mass estrone (E1) adsorbed by polystyrene nanoparticles with different particle size (46, 81, 465 and 3000 nm) for different MWCO UF membranes (regenerated cellulose active layer, polypropylene support layer). 1mM NaHCO₃ buffer and 20mM NaCl electrolyte, pH 7, and 5 bar for 1, 3, 5 kDa. The mass of polystyrene used was 15.7mg/L. Filtration process took about 4.5, 3.5 and 2.4 h for 1, 3 and 5 kDa membranes, respectively. (Note that sorption is time dependent due to kinetics).

**Figure 8** Total surface area of a hypothetical membrane as a function of thickness for several pore radius assuming cylindrical pores A) with 0.03 porosity, B) 0.1 porosity, C) 0.25 porosity. D) represents the surface area as a function of thickness of a membrane made of a cubic close packing formation of spheres with several sphere radius. The membrane surface area is 100 cm². The pore radius and thickness cover NF, UF and ED typical pore radius and thicknesses.

**Figure 9** Electron-micrographs of the clean NF membranes A TFC-SR, B TFC-S, and C TFC-ULP illustrating enhanced polymer surface area due to surface roughness.

**Figure 10** Estradiol adsorption to different pure and membrane polymer powders. A and B: Estradiol mass adsorbed/mass polymer, C and D: Estradiol mass adsorbed/polymer surface estimated from particle size measurements. 60 mL of 100 ng/L estradiol solution with 2.5g of Polymer, 6 ng initial estradiol mass, no background electrolyte. Filter was not saturated prior to the experiment and minimal losses were observed.

**Figure 11** Estrogen adsorption as a function of polymer contact angle. Vertical line is the boundary between low wetting affinity (contact angle<90º) and high wetting affinity (>90º), as described by Mulder [162].

**Figure 12** Adsorption of Estrone (E1), Estradiol (E2), Progesterone (P) and Testosterone (T) onto a Polyacrylate fibre and a NF270 membrane in filtration mode as a function of hormone log K_{OW} (data adapted from [54, 205]).

**Figure 13** Selected possible polymer micropollutant interaction mechanisms. A Hydrophobic interaction between the membrane surface and estrone, B Hydrogen bonding between polyanime and estrone, C π-π interaction between aromatic rings of polystyrene and estrone, D Cation-π interaction between the aromatic rings of estrone and functional group of polystyrene-divinylbenzene (Anion Exchange Membrane of electrodialysis membrane). Mechanisms adapted from [30].

**Figure 14** Possible hydrogen bonding interactions between estradiol and polyanime, polysulphone, polystyrene and polydimethylphenyleneoxide (ppo). Bold arrows represent strong hydrogen interactions while the dotted arrows represent weak interactions. The head of the arrows point to H-bonding acceptors.
Figure 1

Hormone Retention (%) vs. Molecular Weight (g/mol)

Figure 2

A Size Exclusion
B Charge Repulsion
C Adsorption
D Sorption Diffusion
E Solute-Solute Interactions
F Fouling Layer Interactions

Figure 5

![Graph showing E2 retention (%) and mass adsorbed (ng/cm²) vs. pore radius (nm).]

E2 Retention (%)

E2 Mass Adsorbed (ng/cm²)

Pore Radius (nm)

0.30 0.35 0.40 0.45 0.50 0.55

0.0 0.2 0.4 0.6 0.8 1.0 1.2

Retention (%)

Mass Adsorbed (ng/total cm²)

Mass Adsorbed (ng/cm²)

R_{E2}=0.4 \text{ nm}

Figure 6

![Bar chart showing mass adsorbed (ng/cm²) for E2, E1, P, and T.]
Schäfer, A.I.; Semião, A.; Akanyeti, I. (2011)
Micropollutant sorption to membrane polymers, Advances in Colloid and Interface Science, 'Membrane Separation and Colloid Science’ invited special issue paper (accepted 09/2010).

Figure 7

Figure 8
Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

A Hydrophobic interaction

B Hydrogen Bonding

C π-π interaction (stacking)

D Cation-π interaction

Figure 14

A Polysulphone

B Polystyrene

C Polyamide

D Polydimethylphenyleneoxide (ppo)