

Introduction

Phytoestrogens	< 1 x 10 ⁻³	[67]
4-Butyl phenol	1.6 x 10 ⁻⁴	
4-Nonyl phenol	0.9 x 10 ⁻⁵	
Kepone	1 x 10 ⁻⁶	[68]
DDT	1 x 10 ⁻⁶	

Being excreted by humans, such steroid hormones are ubiquitous in aquatic environments receiving sewage effluent. They are frequently detected in wastewater treatment plants (STP) discharge effluent or fresh water bodies receiving sewage effluent around the world within the lower ngL⁻¹ range [17, 69-74]. Estradiol concentrations of up to 200 ngL⁻¹ in STP effluent have been also reported [61]. The performance of conventional wastewater treatment plants with regards to removal of steroid estrogens varies greatly and, as a consequence, concentrations of some steroid estrogens in secondary effluent often remain sufficiently high to harm wildlife such as fish [75]. This is particularly true for steroid estrogens as only 1 ng/L of 17β-estradiol may cause distinctive effects on fish [54]. In spite of the magnitude of this problem, research on the removal of EDCs (particularly steroid hormones) in water and wastewater has been limited to date due to their relatively low concentration and the associated analytical difficulties but has attracted significant interest in recent years in particular in Europe where large projects such as POSEIDON and PTHREE are addressing those issues in great detail [69].

Given the potential impacts of EDCs such as estrone and 17β-estradiol, and inadequate and inconsistent performance of conventional wastewater treatment with regard to such compounds, NF and low-pressure RO membranes are likely to play an important role in removal of these compounds. Retention of estrone and 17β-estradiol using several NF/RO membranes reported by several recent studies are summarised in Table 6.

Table 6: Retention of estrone and 17β-estradiol using various NF/RO membranes.

Membrane	Compound	Feed Conc.	Retention (%)	Reference
TFC-SR2	Estrone	100 ng/L	13	[76]
	17β-estradiol	100 ng/L	21	
TFC-S	Estrone	100 ng/L	76	
	17β-estradiol	100 ng/L	82	
X-20	Estrone	100 ng/L	87	[77]
NF-90	Estrone	100 ng/L	89	
	17β-estradiol	100 ng/L	86	
NF-270	Estrone	100 ng/L	85	[77]
	17β-estradiol	100 ng/L	85	
UTC60	Estrone	50 µg/L	80	[78]
	17β-estradiol	50 µg/L	72	

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NTR7250	Estrone	50 µg/L	57	[79]
	17β-estradiol	50 µg/L	58	
PES10	Estrone	100 µg/L	40	
	17β-estradiol	100 µg/L	50	

The results in Table 6 indicate that the retention of natural hormones estrone and 17β-estradiol also varies over a large range depending on the membrane type. However, the highest retention reported is 89% and hence not a complete retention of those compounds can be achieved. This phenomenon will be explained in more detail in the later mechanisms section.

3.5 Pharmaceutically active compounds (PhACs)

Pharmaceuticals are administered to humans and animals for a variety of benefits including prevention and treatment of various types of disease. Given the variety of compounds in use and their widespread distribution and persistence in the environment, there are potential unanticipated consequences of pharmaceutical residues and their metabolites [80-82]. Most (if not all) pharmaceuticals administered to humans and animals are excreted to various degrees and discharged directly to the sewage system, depending upon the physiochemical properties of the compounds. Although some of the compounds are biodegradable, most xenobiotics are persistent to the conventional biological sewage treatment process. Consequently, in investigations carried out in many countries including Austria, Brazil, Canada, Croatia, England, Germany, Greece, Italy, Spain, Switzerland, The Netherlands, Australia and the U.S., more than 80 pharmaceuticals and their metabolites, have been detected in aquatic environments at concentrations in the µg/L range or lower [20, 83-88]. Reported compounds include pharmaceuticals with a wide range of applications: analgesics, anti-inflammatory compounds, beta-blockers, lipid-regulators, antiepileptics, β₂-sympathomimetics, antineoplastics, antibiotics, X-ray media contrast agents and contraceptive drugs. Molecular structures of several PhACs frequently detected in the aquatic environment are shown in Figure 4.

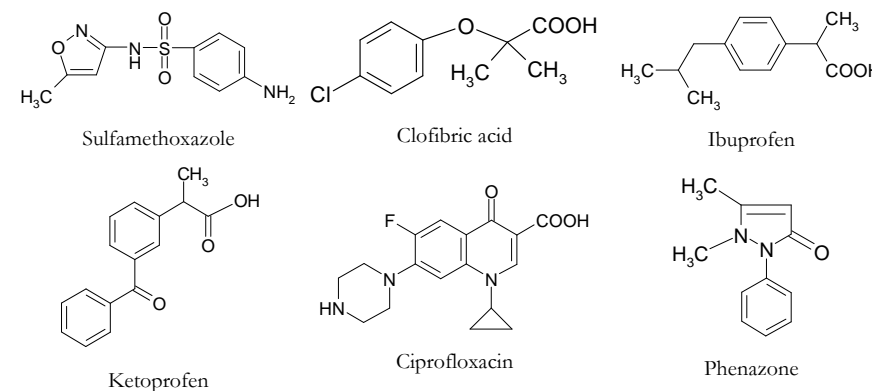




Figure 4: Structures of several PhACs most frequently detected in aquatic environment.

As pharmaceuticals are designed to be biologically active, their potential to affect a large variety of non-target organisms for a wide range of physiological consequences is inherent. The potential for induction [89] or proliferation of antibiotic resistance [89-91] due to low concentrations of antibiotic agents in the environment is of increasing concern to scientists.

Several studies have shown that some PhACs are not eliminated completely in the conventional sewage treatment plants and are, thus, discharged as contaminants into the receiving waters [84, 85, 92]. Removals of some PhACs by municipal wastewater treatment plants are listed in Table 7. Under effluent recharge conditions, residues of PhACs such as clofibric acid, carbamazepine, primidone or X-ray contrast agents may also leach into groundwater aquifers [93]. PhACs occurrence has been reported in ground and drinking water samples from water works using bank filtration or artificial groundwater recharge downstream from municipal wastewater treatment plants [94].

Table 7: Removals of some PhACs in municipal wastewater treatment works.

Compound	Reference	Raw sewage (ng/L)	Effluent (ng/L)	Removal (%)	Treatment process	Remark
Diclofenac	[87]	N/A	N/A	4	Flocculation	Lab scale
Clofibric acid		N/A	N/A	13		
Bezafibrate		N/A	N/A	None		
Ciprofloxacin	[95]	313	68	79	STP	Switzerland
Ciprofloxacin		447	62	86		
Norfloxacin		255	51	80		
Norfloxacin		435	55	87		
Topamidol	[96]	4300	4700	None	STP	Germany
Diatrizoateb		3300	4100	None		
Ioxithalamic acid		170	160	None		
Ibuprofen	[97]	1000	600	52	STP	Australia, predicted by quantities of use & fugacity model
Carbamazepine		2000	1000	39		
Diclofenac		400	300	30		
Sulfamethoxazole		1000	900	27		
Naproxen		8000	4000	58		

STP: Sew treatment plant; N/A: data not available

The results reported in Table 7 vary from zero to 87%, depending on the PhAC, the location and most likely the local treatment plant design and operating conditions including the type of biomass. While several research groups now focus on the biodegradation mechanisms of trace contaminants and the optimisation of conventional treatment processes towards the removal of such contaminants, it is unlikely that high removal of all compounds can be achieved.

On the other hand, several researchers have reported almost complete removal of all PhACs using NF/RO membranes in their studies (see Table 8) [1, 8, 98, 99].

Table 8: Removal of some PhACs using RO membranes.

Membrane	Compound	Feed Conc. (µg/L)	Retention (%)	Reference	Remark
ESNA	Phenacetine	100	19	[99]	Lab scale
	Primidone	100	87		
	Diclofenac	100	93		
NF-270	Sulfamethoxazole	700	96	[98]	Lab scale
	Carbamazepine	700	84		
RO membrane	Carbamazepine	0.43	>99.8	[1]	Pilot scale
	Clofibric acid	0.33	>99.7		
	Diclofenac	0.329	99.7		
	Naproxen	0.038	95		
RO membrane	Clofibric acid	7.4	89	[8]	Pilot scale

Table 8 shows that the retention of pharmaceuticals is high in RO processes. Recent studies show that PhACs are retained to a much higher extent than hormones despite a comparable or even lower molecular weight. This illustrates that there may be significant differences in how these compounds are removed and such possible mechanisms will be addressed in the following section.

4 TRACE ORGANIC REMOVAL MECHANISMS IN NANOFILTRATION

Following the reported variations of trace organic retention in NF (see Table 4, Table 6, and Table 8) in the previous section, the reasons for such variations will be explored. Hence, a more detailed discussion of trace inorganic contaminant removals in membrane filtration processes is provided. Although focusing mainly on NF, this section will go beyond the boundary of NF to include ultrafiltration (UF) and reverse osmosis (RO) membranes to a limited extent to place removal mechanisms into proper context in this often ill-defined spectrum of processes.

As NF membranes spans the gap between UF and RO membranes, while separation is thought to be accomplished via size exclusion or charge repulsion, sorption diffusion mechanism can also contribute to the separation process [2, 100]. Depending on the physicochemical characteristics of the solute and the membrane, separation can be achieved by one or several mechanisms. The word 'physicochemical' explicitly implies that separation can be due to physical selectivity (charge repulsion, size exclusion or steric hindrance) or chemical selectivity (solvation energy, hydrophobic interaction or hydrogen bonding).

Consequently, the separation process of some low molecular weight trace organics can be strongly influenced by their physicochemical interactions with the membrane polymer and/or with water. All of the mechanisms mentioned above can contribute to the separation process. These interactions are complex and the transport of organic trace organics across the membrane is an interesting topic, which is to date not fully understood. Hence this section will provide an overview of existing parameters of importance, current mechanisms and models and their applicability to organic trace contaminant removal.

4.1 Molecular compound characteristics and groupings

Characterisation of trace contaminants is very important in understanding the fate of such compounds in the environment and to some extent in treatment systems [101]. Some generalities can be drawn by classifying organic compounds into groups based on their physical state in solution such as dispersion, aggregation and volatility [102]. In an early study, Hindin *et al.*, found that high retention was achieved for those chemical species existing primarily in the colloidal, aggregate, micelle or macromolecular form [102]. Lower retention was observed for chemical species that exist as both an aggregate in dispersion and a discrete molecule in true solution. They also stated that volatile and low molecular weight compounds were poorly retained by the membrane. Molecular structure and conformation are also important. Reinhard *et al.* [8] for example studied the removal of a number of trace organics that can be encountered in wastewater reclamation processes, including trihalomethanes (THMs), aromatic hydrocarbons, chlorobenzenes and benzoic acids using two pilot RO systems. Both membranes rejected branched, complex molecules but varied greatly in their retention characteristics for smaller compounds such as chlorinated solvents. They also concluded that the latter group passed through cellulose acetate membranes while being retained to some extent by polyamide membranes.

From the above it is clear that the characteristics of the contaminants are critical in the prediction of removal. While experimentation and monitoring of each contaminant of interest is not feasible, there is significant relevance in grouping contaminants into suites of similar characteristics. Besides molecular structure and electrokinetic properties, physicochemical properties especially important in understanding the separation process of trace organics in membrane nanofiltration include, but are not

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limited to, polarity, dissociation constant, hydrophobicity, solubility, and volatility. Details of these parameters are described below. It should be noted that values of these physicochemical parameters reported in the literature should be used with some caution, as methods and conditions used in determining them can vary widely.

Many organic molecules are electronically neutral having no net charge, neither positive nor negative. However, certain bonds in the molecule, especially bonds of the functional groups, are polar. Bond polarity results in an unsymmetrical electron distribution within the molecule. Polar organics are more reactive than non-polar ones. They may be ready to participate in chemical reactions with the membrane polymers, known as polar interactions [103]. The measure of a net molecular polarity is a quantity called the dipole moment, which is defined as the magnitude of a unit charge q times the distance r between the polar centres [103].

$$\mu = qr \quad (1)$$

where q is electric charge in electrostatic units (esu), r is distance in angstroms ($\text{\AA} = 0.1 \text{ nm}$), and the dipole moment μ is a vector expressed in Debye units (D).

A number of trace organics possessing ionisable functional groups and can be ionised to become negatively charged (acid) or positively charged (base). The degree of ionisation depends on the solution pH and the solute dissociation constant value (pK_a for acid and pK_b for base), which describe the equilibrium relationship between ionised species and non-ionised species in an aqueous system. For example, since bisphenol A (BPA) has an pK_a value of approximately 10.1, at pH above 10.1 exists mostly as negatively charged species, while at pH lower than 10.1 most BPA are neutral species. pK_a (or pK_b) value of a compound is also related to its polarity as they both involve in the distribution of electrons within the compound.

Partitioning of trace organics to the membrane substrate or particulates and organic matters in the feed water can be understood and predicted to some degree based on the compound hydrophobicity, which is usually quantified as the relative partitioning between the liquid octanol and water (octanol-water partitioning coefficient - K_{ow}) and water solubility. In literature, the value of K_{ow} is commonly presented in a log scale and defined as [104]:

$$\text{Log}K_{ow} = \log \frac{C_{oc}}{C_w} \quad (2)$$

where C_{oc} is the concentration of the solute in octanol and C_w is the concentration of the solute in water at equilibrium. Water solubility is defined as the maximum solute concentration in an aqueous solution at a given temperature.

Henry constant (H) for chemical equilibrium between gaseous and aqueous phases is usually used to present the volatility of an organic compound. Similar to K_{ow} , H is a partition coefficient between water and the atmosphere:

$$H = \frac{\text{concentration in gas (air)}}{\text{concentration in water}} \quad (3)$$

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4.2 Size Exclusion

Size exclusion is a simplified retention model that is based on the physical size of a contaminant. In size exclusion, solutes larger than the pore size of the membranes are retained due to size. This is comparable to a sieving phenomenon except that in membrane filtration, pores neither have a uniform pore size nor are the solutes of a uniform size. Solutes of varying structures are not easily represented by equivalent spheres due to different shapes and molecules are flexible in size and shape as a function of stress and solution chemistry.

Many researchers consider size exclusion and sieving phenomena as an identical retention mechanism. The process can be described using a number of simplified assumptions. It is usually assumed that the membrane consists of a bundle of cylindrical capillaries with the pore size being the internal capillary diameter, and that solutes are spherical in shape. An average pore size and an estimated equivalent sphere diameter of solutes can be used to model the separation process. While this process is particularly useful for the retention of colloids and particulates by membranes, it can also be used for the retention of salts where the hydrated ion radius needs to be considered.

In the case of organics there is a likely deviation of shape from a sphere and molecules may also change configuration due to changes in solution chemistry or interactions with other molecules or surfaces. Retention of trace organics due to a size exclusion mechanism is illustrated in Figure 5.

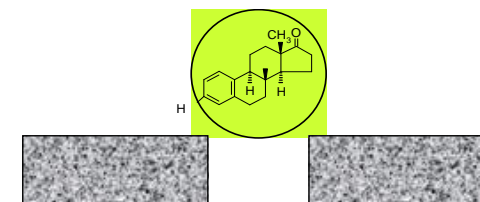


Figure 5: Size exclusion mechanism.

A number of models using this approach have been developed such as the friction model and the pore model [105] to elucidate the separation process of organics using NF membranes. Having included some empirical formulae, these models are relatively simple and powerful. Prediction of solute retention can be obtained based on available physical parameters such as pore size, molecule size and pure water flux. These models have been verified using a number of non-polar neutral organics such as carbon hydrates [105, 106].

Although size exclusion is usually the prevalent retention mechanism, in many cases, the separation process is not solely based on this mechanism. Consequently, application of such size exclusion models to trace organics is limited for a number of reasons. Firstly, the presentation of organic molecules as equivalent spheres is one of the major limitations of these models. Furthermore, the geometry of organic molecules can vary significantly as a function of solution chemistry. For instance, some larger NOM molecules are known to form coils when the molecules are uncharged (at low pH) and fold out into more linear chains at high pH due to charge repulsion as described by Braghetta *et al.* and shown in Figure 6 [107]. Trace contaminants may also alter in conformation. More importantly they also interact with other molecules such as NOM [6, 7], which can have important implications on retention. Finally, as some trace organics can also interact with the membrane polymer (for example via hydrogen

bonding or hydrophobic interaction), which subsequently results in adsorption that is not accounted for in the steric hindrance models.

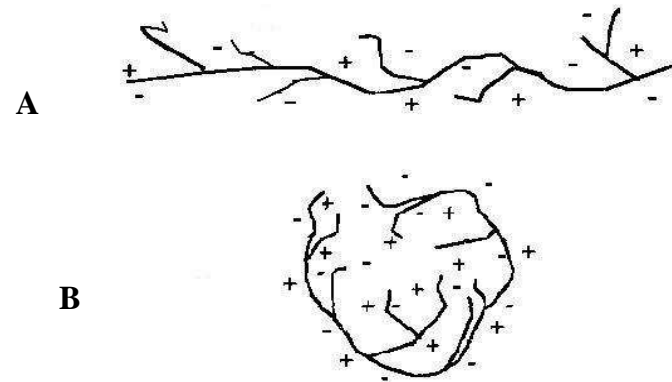


Figure 6: Variation of molecular dimension and shape for the example of natural organics. A: high pH, low ionic strength, low solution concentration. B: low pH, high ionic strength, and high solution concentration [107].

Adsorption may have a strong influence. Given that surface diffusion is significantly faster than sorption diffusion, the transportation of trace organics across the membrane may be enhanced if the membrane pore is larger than the size of the trace organic. The extent of such influences on trace organic retention depends on the membrane pore size and distribution. It has been illustrated that, depending on the pore size, size exclusion, adsorption or both contribute to the retention of the trace organic estrone [104].

There are several models relating molecular weight and size of contaminants. Molecular weight is the most easily accessible parameter that indicates the size of a molecule. Many studies have subsequently focused on molecular weight to obtain information about retention of neutral organics by NF. The molecular weight cut-off (MWCO), the molecular weight of a solute that corresponds to a retention of 90%, is commonly used by most membrane manufacturers as a measure of the retention properties of NF membranes.

However, molecular weight cut-off does not provide information on the retention of organics having a molecular weight smaller than the MWCO [108]. In addition, as dimensional parameters of the molecule are not taken into account, retention of organics with a similar molecular weight but different molecular structure may differ. It is hence desirable to be able to use a structural parameter to estimate retention. Consequently, the Stokes radius is often regarded as a better parameter to describe molecule size, when the molecule is assumed to be spherical in shape. The Stokes-Einstein radius of a molecule is defined as:

$$r_s = \frac{kT}{6\pi\eta D_s} \quad (4)$$

where k is the Boltzmann constant (J/mol.K), η is viscosity (kg/m.s), T is temperature (K) and D_s is diffusion coefficient (m²/s).

As the equation indicates, the Stokes radius is essentially related to the diffusion coefficient, which is not available for many organics. Fortunately, the diffusion coefficient can be estimated from molecular weight using several different methods as summarised in Table 9. However, the variation between different methods can be up to about 125% [109].

Table 9: Summary of methods to estimate diffusion coefficients [109].

Method	Equation
Wilke-Chang	$D_s = 1.193 \cdot 10^{-7} \frac{M_s^{1/2} T}{\eta \cdot V_s^{0.6}}$ (5)
Worch	$D_s = 3.595 \cdot 10^{-14} \frac{T}{\eta \cdot M^{0.53}}$ (6)
Tyn-Calus	$D_s = 8.93 \cdot 10^{-8} \frac{V_w^{0.267} T}{V_s^{0.433} \eta} \left(\frac{\sigma_w}{\sigma_s} \right)^{0.15}$ (7)
Scheibel	$D_s = 8.2 \cdot 10^{-8} \left(1 + \left(\frac{3V_w}{V_s} \right)^{2/3} \right) \frac{T}{\eta V_s^{1/3}}$ (8)

Some size parameters other than Stokes radius worth mentioning include the equivalent molar diameter [108] where the molecule is also assumed to be spherical, and STERIMOL parameters [52] where both molecular width and length are calculated taking into account Val der Waals effects. However, there is usually a good correlation between these parameters and the Stokes radius.

An organic molecule can also be presented as a cylinder whose height and diameter are determined following an energetic optimization procedure, which can be carried out using a computer program such as HyperChem [108].

Further studies are essential to take into account such influences on trace organics retention with a rigorous approach coupled with grouping of contaminant characteristics. While size is an important factor, the impact on retention is also influenced by the charge of the molecules that may enhance attraction or repulsion from the membrane.

4.3 Charge Interaction

Wang *et al.* [110] have proposed a model to describe the transport of an organic electrolyte across a NF membrane by combining the space-charge and steric-hindrance pore physical phenomena. The model was consequently named the electrostatic and steric-hindrance (ES) model. It indicates that both electrostatic and steric-hindrance can contribute to the retention of organic electrolytes by NF membranes. Based on this model, solute retention is a function of the ratio of charge density of the membrane to ionic concentration, solute radius to pore radius of the membrane, and the relative mobility between cations and organic anions. As a result, one would expect that retention of these trace organics can be influenced by solution chemistry such as pH and ionic strength. Braghetta [111] has

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illustrated schematically the effect of solution pH and ionic strength on the “apparent” pore size of the membrane as in Figure 7. Such variation of membrane structure as a function of solution chemistry usually manifests itself with a variation of flux and salt retention.

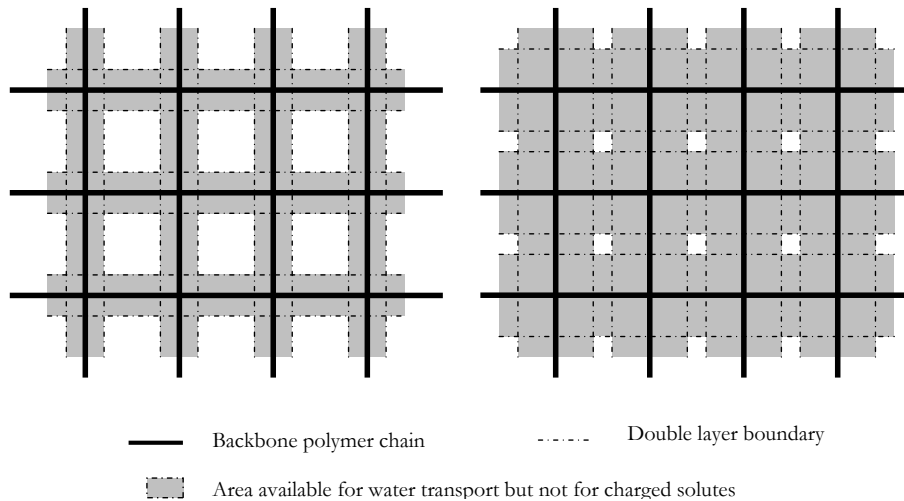


Figure 7: Schematic effect of solution pH and ionic strength on membrane properties. Left: low pH and low ionic strength. Right: high pH and high ionic strength (adapted from Braghetta [111]).

Some trace organics can possess a negative or positive charge when the molecules dissociate at high or low pH. For example, p-aminobenzoic acid has a negative charge at pH higher than 4.8 (pKa of carboxyl group) while it has a positive charge at lower pH (amine pKa = 4.6). Negatively charged organics often experience higher retention than uncharged organics with the same size, which can be attributed to electrostatic repulsion between the molecules and the negative functional groups of the membrane. On the other hand, positively charged organics are poorly retained by the negative membranes. Berg *et al.* [48] reported a significant increase in retention of the negatively charged organic, mecoprop, by five different negatively charged membranes at high pH. Williams *et al.* [112] also showed that the retention of p-aminobenzoic by negatively charged membranes resembles its speciation as a function of pH with an increase of retention as charge repulsion increases (see Figure 8). Although electrostatic interaction dominates the separation process, steric hindrance also appears to influence the retention of such solutes [48].

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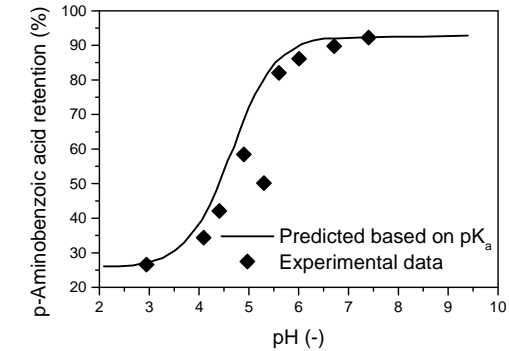


Figure 8: Effect of pH on retention of p-aminobenzoic acid by a negatively charged NF membrane (adapted from [112]).

The pH value of the feed solution can also affect characteristics of the membrane; hence, their retention properties. Most significant is the membrane surface potential, which is often measured as zeta potential. Figure 9 shows the surface zeta potential of several NF membranes as an example. In general, zeta potential of the membrane surface can change from a positive to a negative value as the solution pH increases. Subsequently, electrostatic interaction between an ionic compounds and the membrane surface can also vary according to the solution pH.

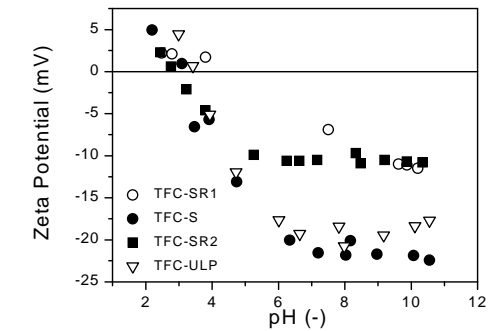


Figure 9: Surface zeta potential of several NF/RO membranes as a function of pH ([113]).

In addition to the change in zeta potential of the membrane surface, Childress and Elimelech [114] have also illustrated the dependence of membrane pore size on the pH of the feed solution using polyamide NF membranes. At high or low pH, functional groups of the membrane polymer can dissociate and take on positive or negative charge fractions. Repulsion between these fractions in the membrane polymer reduces or "closes up" the membrane pores. At the pore surface point of zero charge (or the isoelectric point), membrane functional groups are minimal in charge and hence the pores open up, as the absence of repulsion force contributes to the widening of the membrane pores.

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This was confirmed experimentally when a drop in salt retention (corresponding to a peak in permeate flux) at this pH compared to low or high pH was observed [114]. On the other hand, Braghetta reported a decrease in retention due to charge repulsion between the polymer chains, and hence increased pore size [107]. However, this phenomenon in trace organics retention has yet to be examined and one would expect that the effects of pH on trace organic characteristics and membrane pore size cannot be easily separated.

4.4 Interactions due to polarity

Separation of polar organics by NF membrane is, in general, even more complex as the process is not only governed by charge repulsion and size exclusion but is also influenced by other physicochemical interactions between solutes and the membrane polymer. These polar interactions can influence the partitioning of solute between bulk solution and the membrane pores, sorption of solute into the water-membrane interface and even sorption of solutes into the membrane polymer. Van der Bruggen *et al.*, have successfully combined size exclusion and polarity effects to explain the retention of four pesticides [51]. Consequently, the polarities of both trace organics and the membrane polymers are of importance in predicting the retention of a trace organic. In addition, it is necessary to identify chemical parameters that contribute to the polarity of trace organics.

While the dipole moment can be experimentally determined, it is not practical to measure dipole moments of all trace organics, given the large number of contaminants that exist. Sourirajan and Matsuura [100] have identified a number of parameters indirectly related to the polarity in their magnificent work in the early 1970s. The main quantifiable parameters related to polarity are:

- Hydrogen bonding ability of the solute as represented by its $\Delta\nu_s$ (acidity) relative shift in the OH band maximum in the IR spectra of the solute in CCl_4 and ether solutions),
- Taft (δ^* or $\Sigma\delta^*$) or Hammett (δ or $\Sigma\delta$) numbers for the substituted group in the solute molecule with reference to a given functional group,
- pKa value of solute.

However, while the pKa value is commonly reported in literature, the use of the other two parameters is limited due to their complexity and unavailability.

In addition to these indirect polarity parameters, several researchers have attempted to relate retention and $\log K_{ow}$ (logarithm of the n-octanol/water partition coefficient) or hydrophobicity of the membrane surface in examining the separation process of trace organics [52, 115-117]. Nevertheless, none of them has conclusively reported any characteristic correlations. Note that some researchers refer to this parameter as log P and log P and $\log K_{ow}$ are indeed identical. Since these parameters are an indirect measure of the molecule polarity, they are uniquely related to each other [100].

Similar to the dipole moment, data on the values of these parameters are not available in the literature for many trace organics. Comparison between organics of similar structure but different in functional groups or vice versa can be made given the hydrocarbon skeleton and composition of the compounds. Based on a reference organic, the chemical characteristics of other organics can be qualitatively and quantitatively predicted. For example, a method to estimate the pKa value of an organic based on the pKa value of other organics similar in structure has been described by Perrin [118]. Several commercial computer software packages such as HyperChem and Pallas have been developed to predict these

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parameters. However, when using such software, one should be caution that the database of referenced structures can be limited and they may fail to give a close estimation in some situations.

Seeing the difficulty in quantifying the chemical characteristics of some contaminants, the relationships between chemical characteristics such as polarity and NF retention remain unavailable. Consequently, there are no universal indicators for the retention of such polar trace organics using NF. Membrane supplier information such as MWCO and salt retention are clearly not appropriate as salt retention often fails to serve as an indicator for trace organics removal [115] and MWCO should only be applied to non-polar neutral organics with caution as discussed earlier. It is hence not surprising when Kiso *et al.* [52] showed a poor correlation between the retention and molecular weight of 11 different aromatic pesticides as illustrated in Figure 10.

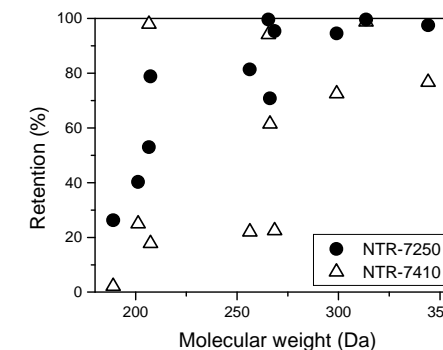


Figure 10: Retention of 11 aromatic pesticides by NF membranes as a function of molecular weight [52].

Sourirajan and Matsuura [100] examined the relevancy of these polarity parameters as described earlier to retention, using 65 organic compounds with different functional groups. Experimental results showed that there is a unique correlation between $\Delta\nu_s$ (acidity) and retention of monohydric alcohols and phenols, which exist essentially as unionized molecules in aqueous solutions. Similarly, an excellent correlation has been found between the Taft number ($\Sigma\delta^*$) and the retention of mono and polyhydric alcohols.

Sourirajan and Matsuura subsequently explained these correlations using a sorption-capillary flow mechanism; where the sorption of solute with higher polarity to the membrane-water interface is favourable, solute transport across the membrane is enhanced, hence decreasing retention [100]. These results establish the relevance of polar parameters to retention of these alcohols and phenols. More importantly, Sourirajan and Matsuura reported that while retention is positive for solutes whose acidities (or Taft numbers) are less than that of water $\Delta\nu_s$ (acidity of water) = 250 cm^{-1} ($\Sigma\delta^*=0.49$), retention can be negative, zero or positive for those solutes (such as phenols) whose acidities or Taft numbers are higher than that of water, depending on filtration conditions. Sourirajan and Matsuura have illustrated this finding using phenol and p-chloro-phenol and several different membranes [100]. In general, for such solutes retention decreases as the driving force transmembrane pressure increases.

This separation phenomenon is distinctive for polar organics as it is in fact in contrast with the separation process of other solutes such as colloids, salts and neutral non-polar organics.

While polarity is an important factor, again it is not the only factor influencing the separation process. Different correlation curves obtained between retention of ethers, ketones, aldehydes, esters and alcohols and their acidities and Taft numbers [100] clearly indicate that factors other than polarity can also influence the separation process. Identifying and including all of these factors in a mechanistic model to understand and predict retention of trace contaminants would be a complicated task and one that much more dedicated efforts should be devoted to in future research.

4.5 Adsorption

Adsorption (or partition) of trace organics to membrane materials is an important aspect of trace organics removal using NF. Many researchers have observed significant adsorption of some trace organics into the membrane polymer [27, 28, 52, 99, 112, 119, 120]. In fact, adsorption is recognized as the first step in the transport mechanism of water and in some cases solutes across the membrane in the well-known sorption-diffusion model [112, 121]. Trace organics, which can adsorb to the membrane, usually have high log K_{ow} or hydrogen bonding capacity and are sparingly soluble in water.

According to the sorption-diffusion model, water flux across the membrane is thought to be greatly dependent on its ability to form hydrogen bonds with the hydrophilic groups of the membrane polymer; while specific adsorption due to hydrogen bonding can reduce water permeation. Possible formation of hydrogen bonding between the membrane polymer and a trace organic (in this case the steroid hormone estrone, the compound that showed the breakthrough phenomena in Figure 12) are illustrated in Figure 11. This indicates the likelihood of hydrogen bonding playing a major role in retention by NF. This premise is supported by an earlier study, in which Williams *et al.* [81] reported significant adsorption of benzene with no hydrogen bonding capacity but negligible water flux drop. On the other hand, there was a 60% drop in flux due to adsorption of 2,4-dinitrophenol, a compound with a high hydrogen bonding capacity, to an aromatic polyamide membrane. This can be attributed to the competition between 2,4-dinitrophenol and water for hydrogen bonding sites. Adsorption can also be accomplished via hydrophobic interaction. Kiso *et al.*, besides showing a poor correlation between molecular weight and retention as was shown in Figure 10 also investigated the relationship between log K_{ow} versus retention and adsorption of eleven aromatic pesticides using NF membranes [52]. While there was no significant correlation between retention of these pesticides and log K_{ow} , there is a good correlation between adsorption of these pesticides and log K_{ow} . Hydrogen bonding and hydrophobic interaction can act independently or together. In the later case, it is often difficult to separate the effect between them.

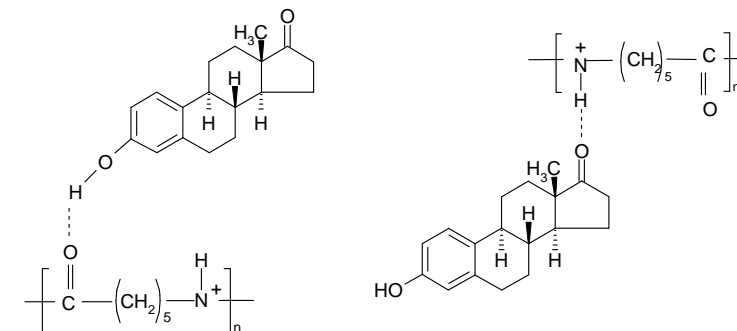


Figure 11: Hydrogen bonding between membrane polymer (polyamide) and natural hormones estrone [120].

Adsorption of trace organics to the membrane has two important implications. It may result in the accumulation of trace organics, which can lead to several deteriorative problems. In addition, a concentration gradient built-up as a result of adsorption (or partition) followed diffusion can reduce the membrane effectiveness to some extent.

Trace organics can accumulate in the membrane to a considerable amount and changes in operation conditions may be able to cause a shift in adsorption/desorption equilibrium, and subsequently release some of the accumulated contaminants [122]. For example, the concern of estradiol release during membrane cleaning has been raised, where alkaline solutions at pH 11 are commonly applied [123]. At this pH, estradiol dissociates and becomes negatively charged. Subsequently, desorption of estradiol occurs due to charge repulsion between the negatively charged estradiol and the negative membrane surface. Figure 15 shows approximate amounts of the steroid hormone estrone that can be adsorbed by spiral wound membrane elements. It is necessary to emphasise that steroid hormone such as estrone can be endocrinologically active to fish at only about 1 ng/L [65].

Table 10: Estimated estrone adsorption on full scale modules [120]

Steroid Hormone	NF-270			NF-90		
	2.5'' Module (μg)	4'' Module (μg)	8'' Module (μg)	2.5'' Module (μg)	4'' Module (μg)	8'' Module (μg)
Membrane Area (m^2)	2.6	7.6	53.0	2.6	7.6	53.0
Estrone	184	538	3737	169	493	3425
Estradiol	100	292	2027	82	239	1657
Testosterone	111	325	2259	54	158	1098
Progesterone	231	674	4681	232	679	4718

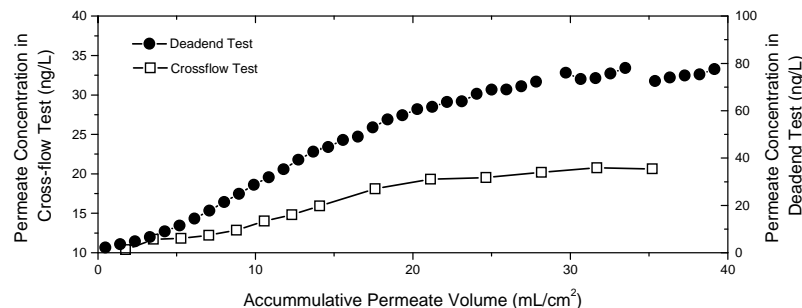


Figure 12: Permeate concentration of estrone as a function of accumulative permeate volume [123].

Although adsorption contributes to an initial retention, lower retention is often observed when the membrane media has been saturated. When investigating the long-term effect of adsorption on retention of steroid sex hormone estrone, Nghiem *et al.*, [123] observed a clear breakthrough curve for a NF membrane (see Figure 12).

This phenomenon can be explained by the sorption-diffusion model, where solutes adsorb (or partition) into the membrane and transport across the membrane by diffusion. Adsorption itself occurs due to hydrophobic interaction or the formation of hydrogen bonding between the membrane polymer and trace organics. Diffusion in the dense polymeric phase can possibly be accomplished by a series of successive jumps from one equilibrium position to another, which usually involve the formation and breakage of secondary bonds [124]. Such “make-and-break” action can be the result of switching between two bonding sites or between a hydrophobic bond to a substrate and a hydrogen bond to water [125, 126]. It has been previously observed that compounds with hydrogen bonding capacity are usually retained less [121]. Several researchers have used the term “solute membrane affinity” to cautiously refer to this phenomenon [99, 115]. In another study, Nghiem *et al.*, showed that retention of several natural hormones were slightly lower than predicted based poorly on a steric hindrance pore transport model [77].

4.6 Concluding remarks

This section demonstrates the complexity of trace organic retention by a nanofiltration process. Retention is mainly governed by three factors including steric hindrance, electrostatic interaction, and solute membrane affinity. Such factors can act dependently or together in a complex fashion. In the later case, they may enhance or diminish one another effect on retention. In addition, they are strongly influenced by physicochemical characteristics of not only the solute but also the membrane. Polarity, hydrophobicity and hydrogen bonding capacity are amongst the most important ones. These characteristics are again strongly dependent on operational parameters, particularly the solution chemistry such as pH and ionic strength as repeatedly illustrated through out the section. Therefore, to understand the retention of trace organics, one must fully understand this rather complex and interwoven matrix of many dependent components. Although recent years have seen many fruitful and dedicated studies particularly focusing on trace organic retention, much work is still needed to fully

understand the complexity of each phenomenon and creating a model that adequately describes such truly complex systems.

5 REMOVAL OF INORGANIC TRACE CONTAMINANTS BY NANOFILTRATION

NF has traditionally been more prominent for the removal of inorganic trace contaminants due to the presumably high charge of NF membranes. This has reflected in a large amount of work on heavy metals, for example. This is covered in more detail in Chapter 19 of this book.

In this chapter the focus remains on trace inorganic contaminant removal mostly focuses, again, in drinking water provision. As such, groundwater from deep wells is an excellent water source, which is relatively free from pathogens and organic contaminants. However, underground waters may contain some undesirable inorganic contaminants at trace levels like arsenic, uranium, fluoride, and boron. Nitrates has also been identified as compounds of interest, although its maximum concentration in drinking water is much higher than what would be classified as trace level.

Arsenic is a naturally occurring element, which can occur at considerable concentrations in inorganic form, particularly in ground water supplies. Inorganic arsenic has been identified as a toxic and carcinogenic agent that causes skin and various forms of internal cancer [127-129].

Naturally occurring uranium is a mixture of three isotopes, of which U-238 is the most abundant and the other two isotopes U-234 and U-235 only account for less than 1% (see Table 11). Surprisingly, no radiological effects of natural uranium have been reported to date, although practically it is radioactive. This is possibly due to very low radiation doses involved. However, ingestion of natural uranium can lead to kidney and liver failure.

Table 11: Isotope composition and their half-life of natural uranium.

Nuclide	Percent by weight (%)	Half-life (years)
²³⁸ U	99.2836	4.47 x 10 ⁹
²³⁵ U	0.7110	7.04 x 10 ⁸
²³⁴ U	0.0054	2.45 x 10 ⁵

Fluoride concentrations in fresh water depend on the geochemistry of soil and minerals through which the water drains. Fluoride concentrations in deep aquifers can be up to about 10 mg/L if the rock formations are fluoride rich. Regular consumption of water with fluoride concentrations above 1.5 mg/L may lead to dental fluorosis and above 4 mg/L may progressively increase the risk of skeletal fluorosis [130].

Continuous ingestion of high boron doses may lead to several health effects such as gastrointestinal disturbances, skin eruption and depression [130]. Boron can be present in drinking water resources through the natural leaching of boron rich minerals processes, due to seawater intrusion or unsatisfied boron removal in seawater desalination processes.

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Although nitrate is a naturally occurring oxide of nitrogen, intensification farming practices and sewage effluent disposal to streams have led to elevated concentration of nitrate in fresh water bodies, particularly in groundwater. Since nitrate can be reduced to nitrite, which can then disrupt the normal biological function of haemoglobin, high concentration of nitrate can have a particularly detrimental effect to infants. Consequently, most water authorities restricted nitrate concentration in drinking water to 50 mg/L.

Given the human health effects of such contaminants, their maximum contaminant levels in drinking water have been regulated in most countries. Summary of the most recent drinking water guidelines for these inorganic contaminants by several water authorities around the world is shown in Table 12. Occurrences of these contaminants at excessive levels are sometimes encountered in groundwater with high or moderate salinity. In such circumstances, NF can be considered as a feasible treatment option, which can reduce salinity and remove these trace contaminants at the same time.

Table 12: Drinking water guideline values (in mg/L) for the inorganic contaminants of interest by several authorities

Contaminants	US-EPA [18]	WHO [131]	Australia [130]	Canada [132]
Arsenic	0.01	0.01	0.007	0.025
Uranium (as ²³⁸ U)	0.03	0.009	0.02	0.02
Boron	not regulated	0.5	4	5
Fluoride	4	1.5	1.5	1.5
Nitrate	10	50	50	45

5.1 Characterisation of inorganic trace contaminants

Most if not all of inorganic trace contaminants exist in aqueous environment in ionic form. In an aqueous solution, each ion bound strongly with a number of water molecules by electrostatic interactions with the positive (or negative) pole of the H₂O dipole (see Figure 13). Energy of such interactions is known as the solvation energy, as it is so great that it suffices to overcome the hydrogen bonding of the water. Consequently, it is important to note that the effective (hydrated) size of an ionic solute can be considerably larger than its ionic size (see Table 13). Interestingly, ions with small ionic radius can have a larger hydrated radius, as it binds strongly to more water molecules. For example, the hydrated radius of F⁻ is larger than that of I⁻, even though it has a much smaller ion radius. The hydration of an ionic compound can be seen as a special case of complexation, where water plays the role of the ligand. Complexation can significantly enhance retention due to an increase in the apparent size of an ion (see Chapter 19 for more detail). Furthermore, different species of the same element can be greatly different in hydrated radius. Readers are encouraged to refer to Chapter 7 for more detail on speciation and complexation of compounds. It is important to note that trace inorganics will often be found in the environment in complexed forms, with again compounds like natural organic matter (NOM) playing a key role [133].

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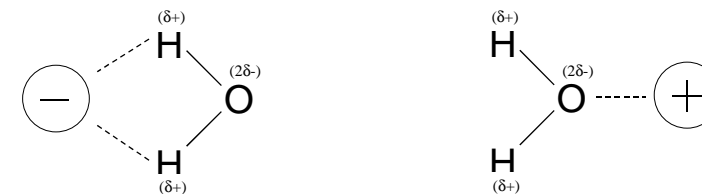


Figure 13: Electrostatic interactions between an ion with the positive (left) or negative (right) poles of the water dipole.

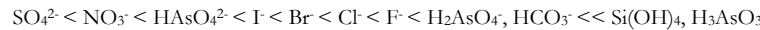
Table 13: Ionic and hydrated radius of several selected ions.

Ions	Ionic radius (nm)	Estimated hydrated radius (nm)	Reference
Na ⁺	0.095	0.280	[134]
K ⁺	0.133	0.230	
B ⁺	0.082	not available	
U ⁴⁺	0.103	not available	
AsO ₄ ³⁻	not available	0.400	[135]
I ⁻	0.205	0.331	
Br ⁻	0.180	0.330	
Cl ⁻	0.164	0.332	
F ⁻	0.116	0.352	
NO ₃ ⁻	0.179	0.340	

However, the issue is complicated in a nanofiltration process as hydrated radii are not consistently and fully documented for comparative purposes [134]. Furthermore, the membrane often carries fixed charge groups, which can compete with water, or in another word ions are transported through the membrane in an ion-exchange process [136]. This phenomenon is more profound in RO and ion exchange membranes. Even when ion exchange plays a minimal role, it has been hypothesized that transmembrane pressure can reduce the hydrated layer of the membrane pores or of the solute ions [137]. Mukherjee and Sengupta argued that hydrated radii are unreliable to access the retention of polyatomic ions such as NO₃⁻, AsO₄³⁻, AsO₃³⁻, etc. [136]. They proposed to use ion exchange selectivity as a surrogate to access the relative retention of ions and reported a characteristic correlation between ion exchange selectivity and retention of ionic solutes (higher ion exchange selectivity ions are retained less). Indeed, ion exchange selectivity can be seen as an analogue to the term “solute membrane affinity” as discussed in the previous section for trace organics. Ion exchange selectivity can be easily determined using ion chromatography or batch isotherm techniques. Although, this finding can provide a powerful method to predict the retention of inorganic trace contaminants, the premise is not always

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true and it must be applied with caution. Reviewing available data of ion exchange selectivity in the open literature provides the following order of ionic compounds retention by RO/NF membranes:



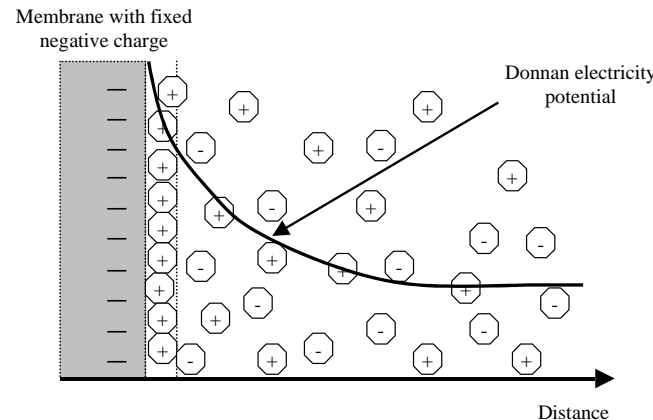
While this sequence is correct for halide series (see Figure 20), it contradicts current experimental results where retention of arsenic species is reported to be in the opposite order: $\text{H}_3\text{AsO}_3 < \text{H}_2\text{AsO}_4^- < \text{HAsO}_4^{2-}$ [138-140]. It appears that this model can only be used for ionic compounds of the same charge number and when diffusion is the dominant transport mechanism.

5.2 Retention Mechanisms

In neutral NF membranes, solutes are transported across the membrane by two mechanisms:

- i. Convection: they are carried by the solvent stream and larger solutes are better retained (physical selectivity).
- ii. Sorption-diffusion: they are transported across the membrane due to diffusion under a chemical potential gradient. Their transportation is influenced by chemical selectivity such as ion exchange selectivity and diffusion coefficient.

However, most available NF membranes are negatively charged and the presence of the fixed charge can also influence ion transport in the membrane. Such influence can be described by two central principles: Donnan equilibrium and the Nernst-Planck equation. When a negatively charged NF membrane is in contact with an electrolyte solution, ions with the same charge as the fixed ions in the membrane are excluded and cannot pass through the membrane. This is known as Donnan exclusion effect. In a polyelectrolyte solution, ions with lower or higher permeability can modify the permeability of the others, since electrostatic neutralisation must be maintained on both sides of the membrane. For example, Seidel *et al.* found that arsenate (as HAsO_4^{2-}) removal by loose nanofiltration membrane can be enhanced by the presence of HCO_3^- [138]. Since HCO_3^- is more permeable through the membrane than HAsO_4^{2-} , HCO_3^- is transported through the membrane instead of HAsO_4^{2-} . A Donnan equilibrium is formed at the membrane surface where fixed negative charge of the membrane is neutralised by positively charged ions of the electrolyte solution. This is schematically shown in Figure 14. Consequently, there is an electrical potential built-up at the membrane – solution interface.



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Figure 14: Schematic illustration of the ionic distribution at the membrane solution interface for a membrane contains fixed negatively charged groups.

The electrical potential caused by Donnan effect can be calculated using a simple equation:

$$E_{don} = \frac{RT}{z_i F} \ln \left(\frac{c_{i,m}}{c_i} \right) \tag{9}$$

where F , E_{don} , R , and T are Faraday constant, Donnan potential, gas constant, and temperature (in Kelvin), respectively. The symbols z_i , $c_{i,m}$, and c_i are charge number, solute concentration in membrane and aqueous phase of component i , respectively.

Apart from convective and concentration differences, the ionic solute is also subjected to a force caused by an electrical potential difference. Assuming minimal steric hindrance interactions and ideal conditions, combination of these three forces results in an equation known as the Nernst-Planck equation:

$$J_i = J_{i,diff} + J_{i,conv} + J_{i,elec} \tag{10}$$

where J_i is the total solute flux; and $J_{i,diff}$, $J_{i,conv}$, and $J_{i,elec}$ are solute flux of component i due to diffusion, convection, and electrical potential, respectively.

In absence of coupling phenomena, the Nernst-Planck equation can be given as:

$$J_i = -D_{si} \frac{dc_i}{dx} + \frac{z_i F c_i D_{si}}{RT} \frac{dE_{don}}{dx} + c_i J_v \tag{11}$$

where D_s and x are diffusion coefficient distance from the membrane surface of component i , respectively.

The Nernst-Planck equation is an improvement over the Donnan equilibrium model as it takes into account the effects of convective and diffusive fluxes. Although both Donnan equilibrium model and Nernst-Planck equation are being used extensively to model the transport of ions in nanofiltration membranes (see Chapter 6 for further details), specific studies addressing such processes of trace inorganic contaminants are still limited. Work done by Elimelech, Urase, and co-workers are amongst the few who have applied to explain the removal of arsenic and nitrate by nanofiltration membranes [138, 139, 141].

5.3 Arsenic

Arsenic can occur in the environment in various forms and oxidation states (-3, 0, +3, +5) but in natural waters is mostly found in inorganic forms as oxyanions of trivalent arsenite [As(III)] or pentavalent arsenate [As(V)]. The speciation of arsenic depends on the oxidizing conditions; arsenate is predominant in surface water while arsenite may dominate in some groundwaters. Arsenic toxicology and carcinogenicity depend on their chemical forms. Inorganic arsenic is more toxic than organic arsenic, and arsenite is more toxic than arsenate [142].

The concern over occurrence of arsenic in groundwater resources has increased exponentially followed the recognition of the largest mass poisoning of a population in history in Bangladesh. It is estimated that between 33 and 77 million Bangladeshis were at risk due to arsenic contamination of their drinking

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water supplies [143]. High levels of arsenic in water resources in many countries including Bangladesh, India, Taiwan, Northern China, Thailand, Argentina, Chile, Mexico, Hungary, the South-Western USA and most recently Vietnam are well documented by Smedley and Kinniburgh [129]. In response to the mounting evidence for the chronic toxicological effects of As in drinking water, recommended and regulatory limits of many authorities are being reduced. The current WHO guideline value for As in drinking water is 10 µg/L; however, this value should be substantially lower based on standard risk assessment [129]. A limit of arsenic levels in drinking water of 50 µg/L within the United States was established in 1942. However, its adequacy was questioned by early studies in 1968 relating arsenic exposure and skin cancer [140]. This limit has been reduced to 10 µg/L since early 2002 [144]. The Australian and Japanese limits for drinking water are 7 and 10 µg/L, respectively, while the interim maximum acceptable for Canadian drinking water is 25 µg/L [132].

Treatment of arsenic in water supplies has been the subject for a considerable quantity of research. Amongst the many viable treatment technologies, the potential of membrane filtration to comply with the most stringent limit is unarguable. Performance of NF to reduce the arsenic health risk of drinking water has been demonstrated by a number of researchers [138-140, 145, 146]. The separation process of arsenic using NF is an interesting topic as its various speciation forms depend greatly on the solution chemistry. Both As (III) and As (V) occur in several protonated forms. At typical pH conditions of natural water (pH 6.5-8), As (V) exists as an anion, while As (III) remains as a neutral molecule. Consequently, these two As species are subjected to different separation mechanisms. Brandhuber and Amy [140] studied the removal of arsenic using negatively charged membranes and showed that under environmental conditions, retention of As (III) is due mainly to a sieving mechanism whereas the retention mechanism for As (V) it is predominantly due to charge repulsion (or Donnan effect). This is illustrated in Figure 15.

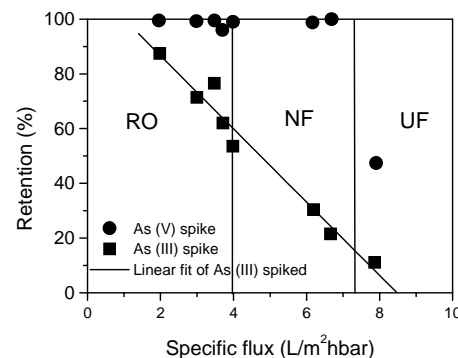


Figure 15: Relationship between specific flux and As(III) (squares) and As(V) (circles) retention for different negatively charged membranes. Mean arsenic concentration of test solution is 25.5 and 18.5 µg/L for As(V) and As(III), respectively, pH near neutral (Adapted from [140]).

As the speciation of both As(III) and As(V) depends strongly on pH (see Figure 16), one would expect that retention of arsenic can be pH dependent. As can be seen from Figure 17, retention of As (III)

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increases sharply from 55 to 85% as As (III) changes from an uncharged species (H_3AsO_3) to a charged species ($H_2AsO_3^-$) when pH increases from 7 to 10 (-o- symbol). A slight increase in As(V) was also observed presumably due to the charge enhancement (negative) of both membrane and As(V) (speciation of As(V) changes from monovalent ($H_2AsO_4^-$) to divalent ($HAso_4^{2-}$) forms as pH increases) (-□- symbol). In fact, when investigating the retention of arsenic using another NF membrane (-▲- symbol), Elimelech *et al.* [138] reported a more significant increase in retention of As(V) when pH increased from 4.7 to 8.5 (see Figure 17). With a more porous negatively charge NF membrane, retention of As(V) relies mainly on charge repulsion [138].

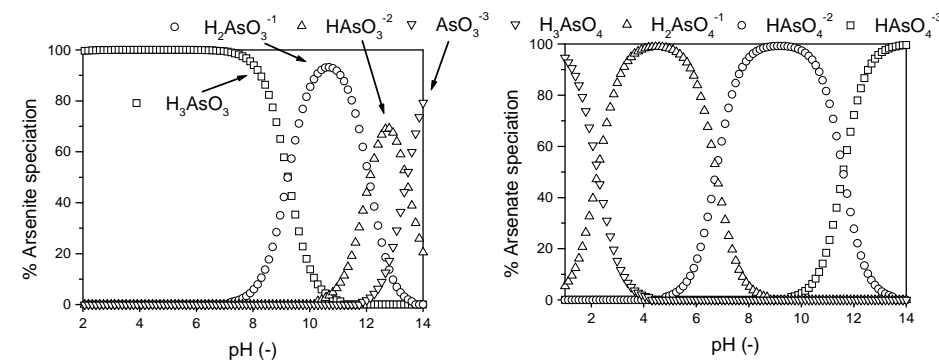


Figure 16: Speciation of arsenite (left) and arsenate (right) as a function of the solution pH.

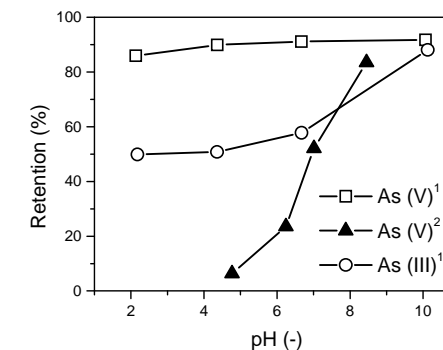


Figure 17: Effect of solution pH and membrane on arsenic retention (¹[139], ²[138]).

When using NF for the removal of inorganic trace contaminants, it may be desirable to operate at high pH to enhance arsenic retention and high recovery for economic reasons. However, high recovery at high pH with the presence of scalants such as Ca^{2+} or Mg^{2+} may result in severe scaling.

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Therefore, it may be necessary to have several stages in series, where a high recovery at low pH stage to reduce salinity and eliminate scalants can be followed by a low recovery at high pH stage to target arsenic and minimize the risk of scaling.

5.4 Uranium

Uranium is a naturally occurring element, which can be found at very low levels in almost all rocks, soils, and waters. Higher levels (in the range of 50-300 mg/kg) of uranium can be found in phosphorous rocks, lignite or monazite sands. Amongst three natural isotopes, only U-234 can be used as fissile material in nuclear warheads or conventional nuclear reactors. However, U-234 makes up a very small fraction in natural uranium. The enrichment process of U-234 subsequently leads to the accumulation of a massive amount of non-fissile, low radioactive uranium by-product, known as depleted uranium. This amount of depleted uranium is reaching a million tons globally, which is currently in storage in the form of UF₆ [147].

Although there have not been many reports about natural contamination of uranium in the environment, extensive mining activities, massive storage of depleted uranium (DU) and recent use of hundreds of tons of DU ammunition during military actions in the Gulf (1991 and 2003) and Balkan (1994 and 1999) regions mean localised contamination has already occurred in many places [147]. Natural uranium and DU (which has been fired during military action) are usually in the form of uranium oxide such as UO₂, which is insoluble in water and body fluid. However, in an oxygen rich and weak acidic environment, they are readily oxidised further to form soluble uranyl species, which can then threaten to contaminate groundwater aquifers and water supplies.

The uranyl ion easily forms complexes, particularly with carbonate in natural water (see Figures 8 & 9 in Chapter 7 for detail). Similar to arsenite and arsenate, retention of uranyl in natural water also depends on the solution pH. Highest retention in the range of 95-100% was found for a variety of nanofiltration membranes at pH near neutral where UO₂(CO₃)₂²⁻ is the dominant species. At lower pH, the retention is slightly lower but overall, retention remains high [148]. Size exclusion is probably the predominant retention mechanism for uranium by nanofiltration membranes. In fact, uranium retention is much higher than that of Na⁺ or Ca²⁺ [149].

5.5 Boron

The boron content in saline and seawater is often higher than the drinking water limit (WHO: 0.5 mg/L). For example, concentrations of boron in Canadian coastal marine waters is in the range of 3.7 to 4.3 [150]. Concentration can be even higher in boron rich mineral aquifers and concentrations in the range of 5 to 15 mg/L have been reported in western USA [151]. The impact of boron on human health is controversial and drinking water guidelines for boron hence vary greatly amongst government authorities throughout the world. While the maximum boron concentration in drinking water was not regulated by the US-EPA [18], it was set at 4 mg/L and 5 mg/L for Australia [130] and Canada [150], respectively. In contrast, the World Health Organisation provides a guideline value of 0.5 mg/L [131] and the Japanese authority current sets a maximum value of 1 mg/L in drinking water [152]. However, it is clear that vegetation and crops are much more sensitive to boron than humans. For instant, boron concentration in irrigation water of more than 0.5 mg/L can cause obvious damage to lemon and cherry [150].

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Nevertheless, there have been a number of studies focusing on boron removal in drinking water treatment using membrane technology. However, most of these studies used RO membranes [152-156]. Boron exists in natural water in the form of boric acid, and the dissociation of boric acid also strongly depends on the water pH (see Figure 18). At low or near neutral pH, boric acid that is quite small in size is undissociated. Consequently, it is conceivable that most NF membranes poorly retain boron.

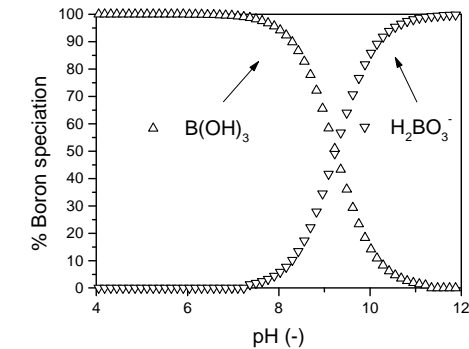


Figure 18: Speciation of boric acid in an aqueous solution as a function of the solution pH.

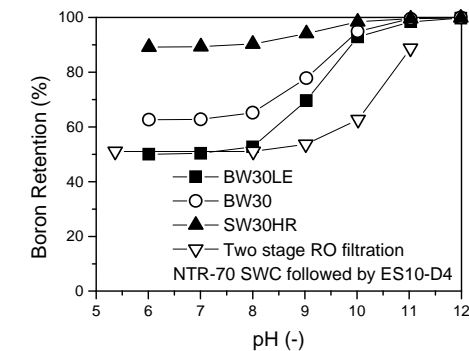


Figure 19: Boron retention by several RO membranes as a function of the solution pH (adapted from [153] and [154]).

The transport mechanism of boric acid in a nanofiltration membrane is thought to be sorption diffusion. There was no significant dependence of retention on concentration when Magara *et al.*, varied the boron concentration from 2 to 30 mg/L [153]. An increase in transmembrane pressure (or recovery) can enhance boron retention. However, as discussed above with arsenic, NF operation at high recovery can result in scaling caused by other cations such as Ca²⁺ and Mg²⁺ in the feed water. Raising the solution pH can also enhance boron retention. As boric acid dissociates at pH 9.24, it

becomes a negatively charged species, which exhibits some Donnan exclusion effect and would be repelled by the negatively charged membrane. Boron retention by several RO membranes as a function of pH is shown in Figure 19. pH modification adds more complexity to the process as the permeate water pH also needs to be readjusted. Unfortunately, these two methods cannot be applied in the same stage, as scaling would be much more severe at high pH. Consequently, a multi-stage approach incorporating high recovery and low pH stages with low recovery and high pH stages has been suggested by several researchers. The first desalination plant with a capacity of 100 Million m³/day utilising this multi-stage approach is currently under construction in Askelon, Israel [155].

5.6 Fluoride

Fluoride is an element essential to dental health at low concentration (between 0.4 and 1.0 mg/L) but it is known to cause dental or bone fluorosis at higher concentration (more than 1.5 mg/L). Consequently, while many water supply plants include a fluoride dosing system in their treatment process, in some rare circumstances, fluoride must be reduced to meet the drinking water standard. Since there are no ion exchange resins or specific electrodialysis membranes for fluoride [157] and conventional water treatment is not effective in removing fluoride, NF appears to be the most attractive process to reduce fluoride concentrations.

Although fluoride has the smallest ionic radius, its hydrated radius is larger than that of other halides (see Table 13). Therefore, it is not surprising when Lhassani *et al.* reports that retention of fluoride is the highest amongst all halides despite its very small molecular weight, particularly at low transmembrane pressure where diffusive transport is significant. Halide retentions as a function of transmembrane pressure are represented in Figure 20 [157]. However, the difference in retention between chloride and iodide cannot be explained by their hydrated radii, nor by the Nernst-Planck equation as these halides have similar hydrated radii and charge. In this case, it appears that ion exchange selectivity also contribute to high fluoride retention. Indeed, when pressure increases; the transport mechanism of these halides shifts from diffusion to convection, the difference in retention between chloride and iodide subtly reduces as the effect of ion exchange selectivity diminishes.

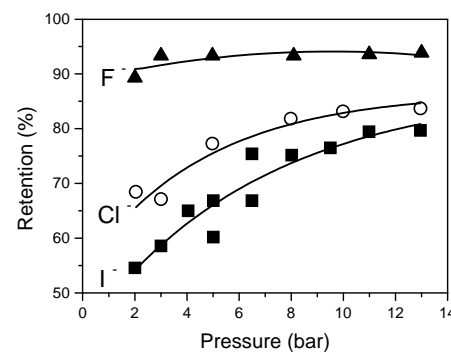


Figure 20: Retention of sodium halides as a function of pressure in single solution (NF-70 membrane, feed concentration of each halide was 5.67 mM) [157].

It is important to note that retention of fluoride and chloride by a looser NF membrane can be in a reversed order. When investigating retention of a co-ion mixture by NTR 7450 membrane, Choi *et al.*, found that chloride retention was 55-70%, while fluoride retention was much lower, in the range of 10-15%. Perhaps, in this case the Donnan effect plays a much larger role as the NTR 7450 membrane has a high negative surface potential [158].

5.7 Nitrate

As groundwater sometimes contains excessive levels of calcium and magnesium that cause hardness and render the water unfit for human consumption, NF membrane has long been employed to soften groundwater. Recent years have seen many groundwater aquifers being polluted by nitrate due to intensive and unsustainable farming or poor sewage disposal practices. Accordingly, there have been a considerable number of studies, investigating the removal of nitrate by nanofiltration membrane [141, 158-162]. Although, nitrate does not have the ability to speciate and poorly complexes with other species, the variety number of co-ions exist in raw water and complicated interactions between nitrate and the membrane substrate make the task of predicting the performance of a nanofiltration membrane in removing nitrate a difficult one.

Based on the extended Nernst-Planck equation, one can predict that negative retention of nitrate is possible given that co-ions of higher charge exist in the feed solution. This has been confirmed with experimental data reported by Choi *et al.* [158]. On the other hand, the presence of counter-ions such as Ca²⁺ and Mg²⁺ can significantly enhance nitrate retention, although the phenomena is much more complicated by the fact that such cations can shield the fixed negatively charge groups of the membrane, reducing electrostatic repulsion force between ionic solutes and the membrane, and hence the retention [3].

The hydrated radius of nitrate is slightly higher than that of chloride and both have similar charge. However, chloride is usually better retained by the membrane, a phenomenon that cannot be explained solely base on size exclusion mechanism or the extended Nernst-Planck equation. By taking into account the “solute membrane affinity”, which is essential equivalent to the ion exchange selectivity as mentioned earlier, Ratanatamskul *et al.*, were able to explain this phenomenon [159]. It appears that sorption diffusion also play an important role in the transport of nitrate in nanofiltration membrane.

5.8 Concluding remarks

As discussed in this section, size and charge are the two key factors influencing the retention of trace inorganics by nanofiltration membranes. These factors can be incorporated into the extended Nernst-Planck equation. Trace inorganics in the form of high charge ionic compounds such as H₂AsO₄⁻ or complexes such as UO₂(CO₃)₂²⁻ are rejected by nanofiltration membranes to a much greater extent. In addition to Chapter 6, this is a further emphasis on the importance of acid based transformation and complexation of trace inorganic species. Retention of several trace inorganic species strongly depends on the solution pH. In contrast, trace inorganics in the form of a neutral species such as B(OH)₃ or those that have small hydrated radii such as NO₃⁻ are often poorly rejected by nanofiltration membranes. In addition to size and charge, ion exchange selectivity appears to play an important role in a diffusive flux, where the extended Nernst-Planck equation is unable to predict the relative retention order of same charge species. Although much more work is still needed, the inclusion of speciation and

complexation has set a positive outlook for the quest for a sound model that is capable of predicting trace inorganic retention.

6 CONCLUSIONS

This chapter describes the relevance of NF as a notable approach to remove trace contaminants, both organic and inorganic, in aquatic environments. A variety of trace contaminants, their occurrences in various water bodies, their health effects, and the perspective in their removal by NF has been summarised. Some insights into retention mechanisms have also been discussed.

Retention is generally governed by three factors including steric hindrance, electrostatic interaction, and solute membrane affinity for trace organics or ion exchange selectivity for trace inorganics. While the first two factors often dominate the separation process, the latter factors play a subtle but not less critical role. All of these factors depend strongly on the physicochemical characteristics of the solute, which may be influenced by its environment. Since trace contaminants often exhibit distinct physical and chemical characteristics, the retention of trace contaminants in nanofiltration (as in other processes) can be very compound specific.

An attempt to fully document research work relevant to trace contaminant removal in nanofiltration has been made. However, the variety of operational parameters used in those studies has rendered a conclusive interpretation to some extent. The chapter illustrates the influence of many inter-dependent factors on trace contaminants retention in seemingly simple nanofiltration processes. Much more dedicated work is needed to fully appreciate the complexity of trace contaminant separation processes in nanofiltration and allow the development of adequate predictive models. Future studies should pay particular attention to both physical and chemical properties of trace contaminants, and their interactions with the membrane polymer and other entities in the solution.

Trace contaminant removal is however an important feature of nanofiltration. It is this characteristic that has driven nanofiltration into the water market and will continue to do so with an increased emphasis on trace contaminant regulation. A thorough understanding of mechanisms will assist the development of membranes that are able to remove targeted compounds at higher and higher efficiency. We are looking forward to watching and contributing to this progress.

7 SYMBOLS

c	concentration (g/L)	c	concentration in solution (g/L)
D _s	solute diffusion coefficient in water (m ² /s)	c _m	concentration in membrane phase (g/L)
E _{don}	Donnan potential	J	flux
F	Faraday constant (96 500)	q	electric charge (esu)
M	molecular weight (g/mol)	r,x	distance (m)
R	gas constant	z	charge number
T	temperature (°K)	η	viscosity (cP)
V _w	water molar volume (cm ³ /mol)	δ _w	water surface tension (N/m ²)
V _s	solute molar volume (cm ³ /mol)	δ _s	solute surface tension (N/m ²)
		μ	dipole moment (D)

8 GLOSSARY

DBPs	Disinfection by-products	PCBs	Polychlorinated biphenols
DOC	Dissolved organic carbon	PhACs	Pharmaceutical active compounds
DU	Depleted uranium	POPs	Persistent organic pollutants
EDCs	Endocrine disrupting chemicals	STP	Sewage treatment plant
HAAs	Halogenated acetic acids	SOCs	Synthetic organic compounds
MCLs	Maximum contaminant levels	THMs	Trihalomethanes
MW	Molecular weight	THMFP	Trihalomethanes formation potential
MWCO	Molecular weight cut-off		Molecular weight
NOM	Natural organic matter	TOX	Total organic halide
PAHs	Polyaromatic hydrocarbons	TOXFP	Total organic halides formation potential

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