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Membrane Treatment of Potable Water for Pesticides Removal

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1. Introduction

Over the last 50 years, plant protection products (PPPs), which are commonly referred to as "pesticides" (a term used henceforth in this chapter), are indispensable agents for the sustainable production of high quality food and fibres. The significant role of pesticides in controlling weeds (herbicides), insects (insecticides) and plant diseases that interfere with the growth, harvest, and marketability of crops has rendered the pesticide industry a significant economic player in the world market. At the same time, the widespread use of pesticides for agricultural and non-agricultural purposes has resulted in the presence of their residues in various environmental compartments. Traces of these products are frequently detected in surface water and in some cases in groundwater, which is the major source of drinking water around the world (Novotny, 1999; Martins et al., 1999; Loos et al., 2009). The frequent detection of many types of pesticide residues (including herbicides) in natural waters is of great concern to the public, to authorities and to all those involved in potable water production, wastewater treatment, and water reuse applications, due to potentially adverse health effects associated with these compounds even at very small concentrations (pg/L to ng/L). Specifically, potential health risks identified in toxicological and epidemiological studies include cancer, genetic malformations, neuro-developmental disorders and damage of the immune system (Skinner et al., 1997; Sanborn et al., 2004; McKinlay et al., 2008).

Regarding the potential for exposure of humans to pesticides residues, a strict regulatory framework is in force today. To ensure a high level of protection of both human and animal health and of the environment, the European Union (EU) developed and implemented a Thematic Strategy for Pesticides lately. The strategy is comprised of four elements:

- the Regulation (EC) 1107/2009, concerning the placing of plant protection products on the market (repealing Council Directives 79/117/EEC and 91/414/EEC),
- the Directive 2009/128/EC, establishing a framework for Community action to achieve the sustainable use of pesticides,
- the Regulation (EC) 1185/2009, concerning statistics on pesticides, and
- the Directive 2009/127/EC, regarding the equipment for pesticide application.

Moreover, EU implemented the Regulation (EC) No 396/2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin, in order to control the end of the life cycle of such products. Regarding the quality of water intended for human consumption, the Drinking Water Directive (98/83/EC) sets a limit of 0.1 μg/L for a single active ingredient of pesticides, and 0.5 μg/L for the sum of all individual active ingredients detected and quantified through monitoring, regardless of hazard or risk. In contrast, the residue limits and guideline levels set by the World Health Organisation (WHO) or the U.S. Environmental Protection Agency (USEPA) depend on the toxicity of the active substances and are determined using a risk-based assessment. The broad spectrum of legislation makes clear that pesticides are amongst the most thoroughly controlled substances in use today.

In parallel with appropriate regulatory controls and best pesticide-use practices, there is an urgent need for determination and removal of pesticides from potable water sources. These are in themselves difficult tasks, which are further complicated by the fact that a very large number of these synthetic chemical compounds are spread in the environment for crop protection. Conventional methods for potable water treatment, still widely employed, comprising particle coagulation–flocculation, sedimentation and dual media filtration, are ineffective for removing pesticide residues. The addition of more advanced final treatment steps (usually involving oxidation by H_2O_2 or O_3, and granular activated carbon – GAC – filtration) is generally considered to be effective, although significant problems still arise, mainly related to saturation of activated carbon, and to toxic chemical by-products, which may develop in the GAC filters under some conditions.

In view of the problems inherent in presently used processes, for removing various pesticides as well as the multitude of other synthetic organic micropollutants frequently encountered in drinking water sources (e.g. persistent organic pollutants-POPs, pharmaceutically active compounds-PhACs, endocrine disrupters-EDCs, etc), significant research effort has been invested to develop effective treatment methods, based on pressure-driven membrane processes. The growing interest in such processes is justified on account of the high and stable water quality they can achieve, although their cost effectiveness needs improvement. Therefore, influenced also by social and legislative pressure for more stringent potable water quality regulations, membrane processes, such as nanofiltration or low pressure reverse osmosis, are under development for broad applicability. To underpin these efforts, special attention is required for clarifying the attributes and limitations of membrane processes for pesticides removal as well as for prioritizing related R&D.

In view of the above considerations, the scope of this chapter is to review our current understanding and knowledge, gained from laboratory research, pilot and industrial-scale activity, regarding pesticides removal by membrane based processes. A fairly thorough discussion of pesticides retention by membranes will be provided, highlighting the prevailing mechanisms and the main factors involved. Particular attention will be paid to the role played by the dissolved organic matter (DOM), commonly present in the raw feed-water. The relevant physico-chemical properties of typical herbicides, of DOM, and of the active membrane surface will be assessed in an effort to clarify the significant membrane – organic species interactions. For a better understanding of the terminology used for membranes and membrane processes, some fundamental relations describing the function of a membrane and the basic principles of membrane processes will be briefly reviewed. Finally, future R&D needs for trace organic contaminants removal from potable water will be discussed, both at the scientific and the technological level.

2. Membrane technology – A short review of potable water treatment

2.1 Membrane processes in water treatment

Since the early 1990's membrane filtration has gained momentum and is now considered mainstream technology for removing a broad spectrum of contaminants from water and effluents. Advances in materials science and membrane manufacturing technology have shaped this trend, together with the increased regulatory pressures as well as an increased demand for drinking water originating from water sources of inferior quality (surface water, other). Moreover, membrane technologies have emerged as a very attractive option, in the production of clean and safe drinking water, due to their significant advantages over the conventional water treatment methods. Specifically:

- membrane treatment takes place at ambient temperature without phase change; this explains, for example, the success of reverse osmosis for water desalination;
- membrane separations occur without accumulation of substances inside the membranes; thus, membranes are well adapted to be ran continuously without a regeneration cycle as, for example, in ion-exchange resin operations;
- membrane separations do not involve addition of chemical additives; this affords advantages regarding the quality of treated water and leads to reduced environmental load;
- most membrane systems are compact (with reduced plant footprint), modular in nature, allowing retrofitting of existing processes;
- membrane processes are often technically simpler and more energy efficient than conventional separation techniques and are equally well suited for large-scale continuous operations as for batch-wise treatment of very small quantities,
- advances in polymer chemistry have led to the development of low pressure membranes, less prone to fouling, which are associated with reduced energy requirements, reduced chemical cleaning frequency, longer membrane life, and thereof, reduced operating costs.

A disadvantage of membrane processes is the usually required costly feed-water pre-treatment to avoid membrane fouling caused by various species. Furthermore, membranes are structurally not very robust and can be damaged by deviations from their normal operating conditions. However, significant progress has been made in recent years, especially in seawater reverse osmosis desalination, in developing membranes which have not only significantly better overall performance but also exhibit better chemical and thermal stability and are less sensitive to operating upsets.

The technically and commercially established membrane processes, for water treatment, are reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). Although there is no sharp distinction, these processes are defined mainly according to the pore size of the respective membranes, and to a lesser extent by the level of driving force for permeation, i.e. the pressure difference across the membrane (Table 1). With decreasing porosity (i.e. from MF to UF and NF to RO) the hydrodynamic resistance of the respective membranes increases and consequently higher pressures are applied to obtain required water fluxes. MF and UF systems generally operate at a pressure of ~25 to ~150 psi, while some operate under vacuum at less than 12 psi. These systems can be operated in dead-end or cross-flow mode. The dead-end mode resembles conventional sand filter operation, where the feed solution flows perpendicular to the membrane surface. Unlike crossflow filtration, there is normally no reject stream, only a feed and a permeate stream, as shown in

Fig. 1. The crossflow system, which has gained wider acceptance in recent years, operates in a continuous manner where the feed solution flows tangentially across the membrane surface, thus generating a continuous exiting stream (defined as "retentate" or "concentrate") capable of partly sweeping the rejected substances, away from the membrane surface (Fig. 1). NF and RO operate almost exclusively in the crossflow mode and the operating pressure depends on the type of membrane used and the required water quality characteristics. Typical operating pressure for a NF system ranges from 100 to 200 psi, while for RO the pressure may vary between 100 and 400 psi, depending on ionic strength. For seawater desalination, RO plants operate at even higher pressures, between 800 to 1000psi.

Membrane process	Typical pore size (nm)	Pressure (bar)	Permeability ($Lm^{-2}h^{-1}bar^{-1}$)
Microfiltration (MF)	50-1000	0.1-2.0	> 50
Ultrafiltration (UF)	10-50	1.0-5.0	10 – 50
Nanofiltration (NF)	< 2	5.0-20	1.4 – 12
Reverse Osmosis (RO)	< 1	10-100	0.05 – 1.4

Table 1. Comparison of pressure-driven membrane processes (Mulder, 1998; Singh, 2006)

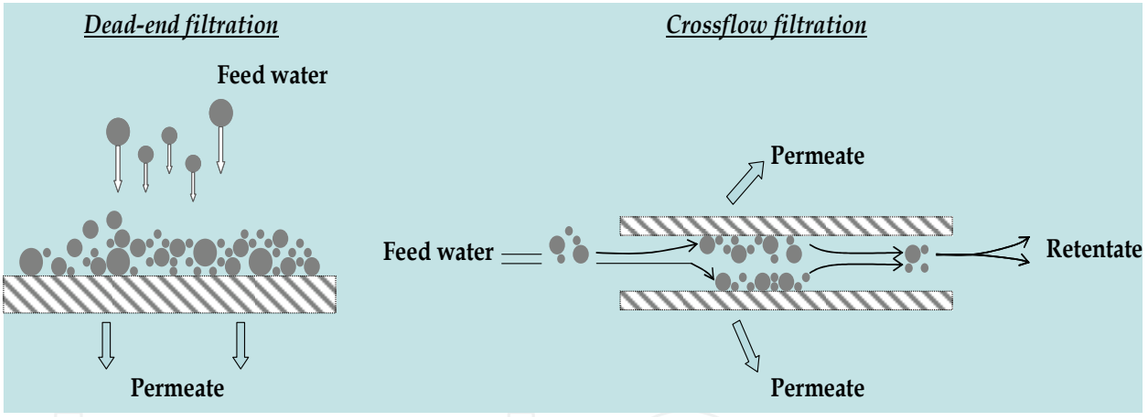

Fig. 1. Dead-end versus crossflow filtration

The porous MF and UF membranes are characterized by the molecular weight cut-off (MWCO), which is expressed in Dalton indicating the molecular weight of a hypothetical non-charged solute that is 90% rejected (Mulder, 1996). NF can be characterized either by MWCO or ionic retention of salts such as NaCl or $CaCl_2$; RO membranes being dense are characterized by salt retention, although some researchers have modeled molecular retention to determine a MWCO (Kimura et al., 2004). The percentage retention (R%) of species in solution is defined as:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) x100 \quad (1)$$

where C_p and C_f are the permeate and feed concentration, respectively. Other common performance parameters are the permeate recovery and flux, given as follows:

$$\text{Recovery} = \frac{Q_p}{Q_f} \tag{2}$$

$$J_w = L_p\,(\Delta P - \Delta\pi) \tag{3}$$

Recovery is defined as the ratio of permeate production rate Q_p over the feed flow rate Q_f. J_w is the permeate water flux, L_P the membrane permeability, ΔP the applied transmembrane pressure and $\Delta\pi$ the osmotic pressure difference between feed and permeate.

From Table 1 it is evident that the selection of a particular membrane type mainly depends on the contaminant size to be removed. MF is usually applied to separation from an aqueous solution of particles of diameter greater than 100nm (usually 0.05-1μm), while UF to separation of macromolecules (of size down to 30nm), with molecular weights varying from about 10^4 to more than 10^6. Examples of species that can be removed with MF and UF processes include assorted colloids (frequently referred to as "turbidity"), iron and manganese precipitates, coagulated organic matter, and pathogens such as *Giardia* and *Cryptosporidium* cysts. UF membranes are also capable of removing viruses. RO membranes are used to remove from the feed stream even smaller species, of diameter as small as 0.1nm, such as hydrated ions and low molecular weight solutes. On the other hand, NF, also called "loose RO", lies between RO and UF in terms of selectivity of the membrane as it is designed for removal of multivalent ions (typically calcium and magnesium) in water softening operations and for organic species control. The feed water to NF plants can be any non-brackish, ground or surface water. For treatment of brackish water, nanofiltration is usually not the most suitable process, since Cl^- and Na^+ are among the ions with the lowest retention rates. A simplified decision tree for selecting the suitable membrane process for treatment of potable water is shown in Fig. 2.

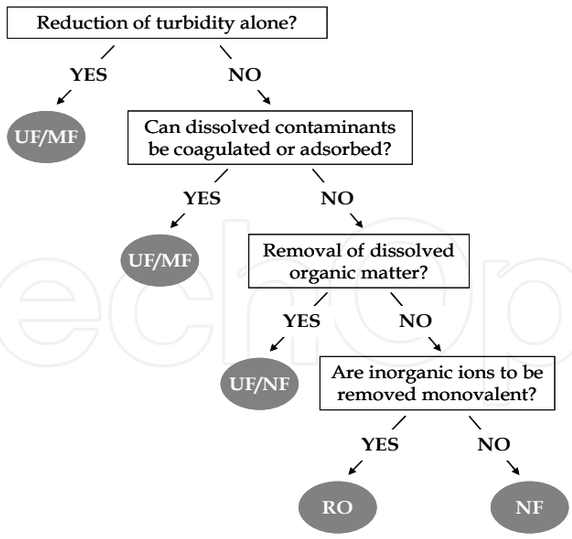

Fig. 2. Simplified decision tree for selecting a membrane process for treatment of potable water.

Taking into consideration that the majority of the compounds categorized as pesticides have molecular weights (MW) greater than 200 Da and a size in the range of ions (close to 1 nm), reverse osmosis and nanofiltration are promising options for their removal from

contaminated water sources. However, RO is generally more expensive, regarding both investment and operating costs, due to the required greater pressures (lower permeability membrane). For these reasons scientists and all those involved in potable water production have turned their attention to the application of NF and ultra low-pressure RO membranes (ULPRO). Related R&D has resulted in the development of an advanced type of NF/ULPRO membranes, the so called thin film composite membranes (TFC or TFM) which have been successfully applied for the removal of pesticides in past 10-20 years (Hofman et al., 1997; Wittmann et al., 1998; Bonné et al., 2000; Cyna et al., 2002).

TFC are multi-layer membranes comprising a very thin and dense active layer (of cross-linked aromatic polyamide) which is formed in situ on a porous support layer, usually made of polysulfone (Fig.3). Their broad applicability is attributed to their unique characteristics such as the high salt retention capacity, the good chemical stability and mechanical integrity as well as to the fact that they can achieve high specific water fluxes at lower operating pressures (AWWA, 1996; Filteau & Moss, 1997). A list of the TFC membranes studied for the removal of pesticides from potable water is given in the Appendix, together with their retention performance and their characteristic surface properties (MWCO).

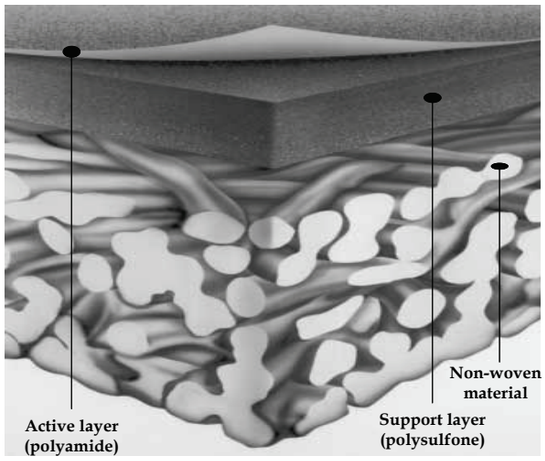

Fig. 3. Schematic representation of a thin film composite (TFC) membrane (Dow, 2010)

2.2 Examples of water treatment plants using NF/ULPRO membranes

A list of significant water treatment plants using nanofiltration or ultra-low pressure RO membranes is shown in Table 2. An outstanding example of nanofiltration for the removal of pesticides and other organic residues, for the production of drinking water, is the Méry-sur-Oise plant in the northern part of Paris, in France. The Méry-sur-Oise plant has been successfully producing water from the river Oise, using NF technology, since 1999. Its performance indicators are very satisfactory, especially with regard to the two main objectives; i.e., elimination of organic matter and of pesticides, which renders nanofiltration a very successful technology (Ventresque et al., 2000).

The design of a membrane water treatment plant may vary depending on the feed water conditions, the required final water quality, the water recovery ratio, the membrane module configuration (spiral wound, hollow fiber, tubular) and the material of membrane active surface layer (asymmetric cellulosic or non-cellulosic membranes, thin film ether, or amidic composite membranes). In general, a conventional NF/RO treatment system includes

Location	Capacity (m^3/d)	Application	Reference
Boca Raton, Florida, US	152,000	Groundwater softening	Suratt et al., 2000
Méry-sur-Oise, Paris, France	140,000	Pesticide removal for drinking water supply	Cyna et al., 2002
Heemskerk, Holland	~57,000	Surface water treatment for drinking water supply	Kamp et al., 2000
Bajo Almanzora, Andalusia, Spain	30,000	Groundwater softening	Redondo & Lanari, 1997
Debden Road, Saffron Walden, England	3,000	Pesticide removal for drinking water supply	Wittmann et al., 1998

Table 2. Case studies of water treatment plants using NF/ULPRO membranes

pre-treatment, membrane filtration and post-treatment, as schematically shown in Fig. 4. Pretreatment of the feed is required to protect the membranes and to improve their performance, while post-treatment includes several unit operations common to drinking water treatment such as aeration, disinfection, and corrosion control. The pre-treatment should be carefully designed, mainly to cope with the fouling propensity of the feed water and aims to (Redondo & Lomax, 2001):

- reduce suspended solids and minimise the effect of colloids
- reduce the microbiological fouling potential of the feed water
- condition the feed by adding chemicals (antiscalant, pH adjustment)
- remove oxidising compounds in the feed if required (to protect the membranes)

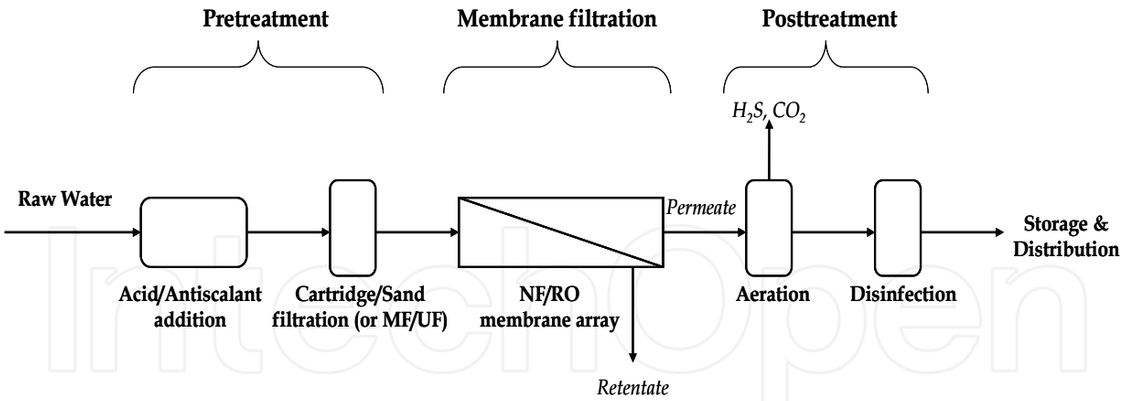

Fig. 4. A typical NF/RO membrane water treatment process.

In the case of the Méry-sur-Oise plant, the full scale facility consists of the following treatment steps (Ventresque et al., 2000):

- ACTIFLO® clarifiers (coagulation using polyaluminium chloride and an anionic polyelectrolyte at pH 6.9, flocculation)
- Ozonation
- Dual-media filtration (two-layer sand and anthracite bed, preceded by a second injection of coagulant)
- Cartridge filtration (6 µm micro-filters, back-washable and chemically cleanable)

- Nanofiltration
- CO_2 stripping (degassing towers)
- UV disinfection

Pretreatment plays a critical role in the performance, life expectancy and the overall operating costs of NF/RO systems. R&D in this direction includes studies on new technologies and/or new design concepts on feed pretreatment, membrane washing and chemical cleaning (to restore membrane fluxes) and extensive studies on membrane performance improvement, focused on development of low fouling membranes. More information on these matters can be found in various publications, in scientific articles as well as in technical reports issued by several membrane manufacturers (Tanninen et al., 2005; Al-Amoudi & Lovitt, 2007; Dow, 2010). In the following, for the sake of completion and to facilitate the discussion in sub-section 3.5, a brief introduction to fouling is presented and of the related phenomena occurring at the membrane surface.

2.3 Membrane fouling

Membrane performance can be negatively affected by a number of species whose concentration and/or presence in the feed water must be controlled. As indicated in Fig. 5, these species are divided in two categories: substances capable of damaging the membranes and species with potential for membrane fouling or scaling. The discussion is concentrated on fouling, which is the major problem faced in any membrane separation. Membrane fouling, if not controlled, is detrimental to the overall process efficiency because of the increased energy requirements, reduced plant productivity and increased cost of chemicals due to cleaning as well as the shorter lifetime of the membranes, which also lead to an increase of the total production cost. Moreover, membrane fouling may alter the surface characteristics of NF/RO membranes, which in turn could potentially influence the removal of undesirable dissolved species, including pesticides.

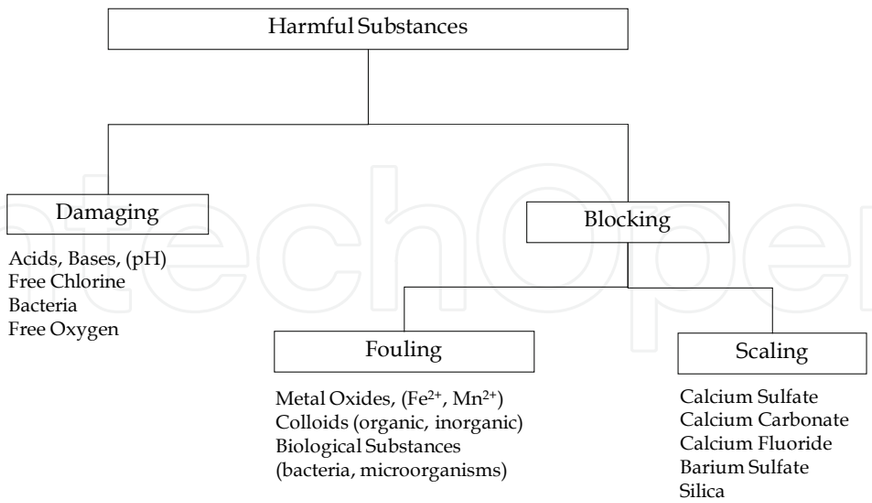

Fig. 5. Substances potentially harmful to membranes (Rautenbach & Albrecht, 1989)

The main fouling categories are organic, inorganic, particulate and biological fouling. Metal complexes and silica are also important. In operating plants all types of fouling may occur (Yiantsios et al., 2005), depending on the feed water composition. Research on

understanding fouling and applying appropriate control strategies are important endeavours aiming at improvement of NF/RO membrane processes. Among the different kinds of fouling, emphasis is given here to fouling by organic matter, naturally occurring in source waters in concentrations ranging from 2 to 40mgC/L, which are roughly 10,000 times greater than pesticide concentrations encountered in surface waters.

Extensive research on fouling of NF membranes by natural organic matter (NOM) has shown that it can be influenced by membrane characteristics, including surface structure as well as surface physico-chemical properties, composition of feed solution including ionic strength, pH and concentration of divalent ions, NOM properties, including molecular weight and polarity, as well as hydrodynamic and operating conditions including permeate flux, pressure, concentration polarization, and the mass transfer properties of the fluid boundary layer (Al-Amoudi, 2010). The effect of the aforementioned factors on NOM fouling is summarized in Table 3. The significant role of feed-water chemical composition (ionic strength, pH, divalent cations) on NOM fouling, as well as the fouling mechanisms involved in the case of humic substances (Hong & Elimelech, 1997) are illustrated in Fig. 6.

	Value	NOM fouling rate	Cause
Ionic strength concentration	Increased	Increased	Electrostatic repulsion
pH	High pH Low pH	Increased Increased	Hydrophobic forces Electrostatic repulsion
Divalent cations	Presence	Increased	Electrostatic repulsion and bridging between NOM and membrane surface
NOM fraction	Hydrophobic Hydrophilic	Increased Decreased	Hydrophobicity
Molecule or membrane charge	High charge	Increase	Electrostatic repulsion
Concentration polarization	High	Increased	
Surface morphology	Higher	Increased	"Valley" blocking
Permeate flux (high recovery)	Higher	Increased	Hydrophobicity
Pressure	Higher	Increased	Compaction

Table 3. Factors affecting natural organic matter fouling of NF membrane (Al-Amoudi, 2010)

The term concentration polarization (CP) mentioned earlier describes the process of accumulation of retained solutes in the membrane boundary layer where their concentration will gradually increase. Such a concentration build-up will generate a diffusive flow back to the bulk of the feed, but after a certain period of time steady-state conditions will be established. The consequences of CP can be summarised as follows (Mulder, 1996):

- Flux will be reduced.
- Retention of low molecular weight solutes, such as salts, can be reduced.

- Retention can be higher: this is especially true in the case of mixtures of macromolecular solutes where CP can have a strong influence on the selectivity. The higher molecular weight solutes that are retained completely form a kind of second or dynamic membrane. This may result in a higher retention of the lower molecular weight solutes.

Concentration polarization is considered to be reversible and can be controlled in a membrane module by means of velocity adjustment, pulsation, ultrasound, or an electric field. Most membrane suppliers recommend a minimum feed flow rate (i.e. minimum superficial velocity at the retentate side) and a maximum allowable water recovery rate to minimize the effects of CP. Membrane fouling, on the other hand, is more complicated in that it is considered as a group of physical, chemical, and biological effects, which lead to irreversible loss of membrane permeability (Sablani et al., 2001).

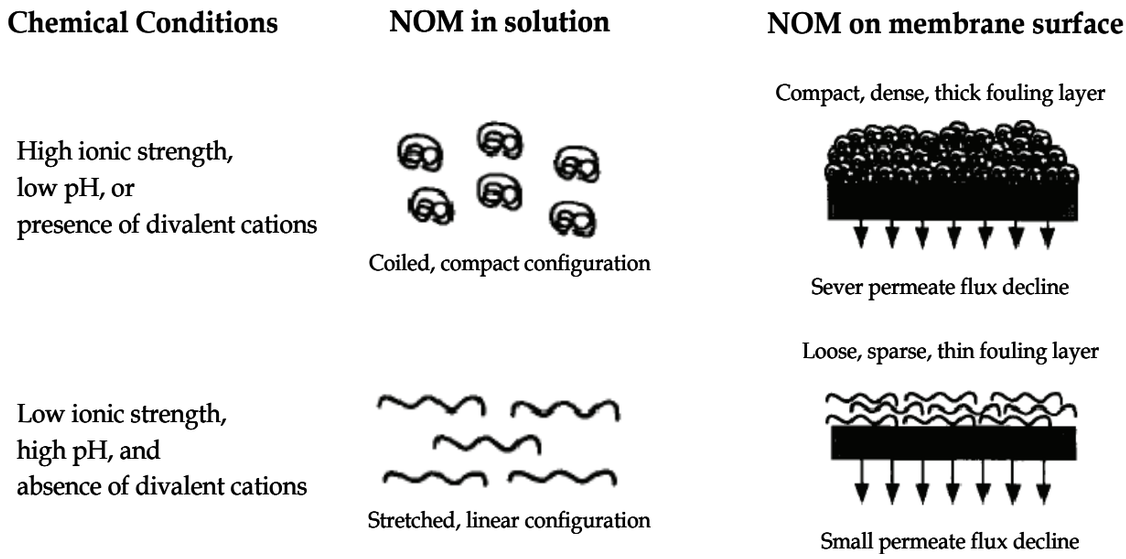

Fig. 6. Schematic description of the effect of solution chemistry on the conformation of NOM macromolecules in the solution and on the membrane surface and the resulting effect on membrane permeate flux. The NOM fouling described in the diagram is applicable for permeation rates above the critical flux. The difference, between the two chemical conditions shown, becomes less clear at very high permeate flux. At low permeate flux (below the critical flux), no significant fouling is observed for both conditions (adapted from Hong & Elimelech, 1997)

2.4 Retention mechanisms in NF/RO processes

There is a great deal of published work on the basic retention mechanisms and the various applications of NF/RO processes (Mulder, 1996; Scott, 1998; Nghiem & Schäfer, 2005). In general, the separation process involves several mechanisms such as size exclusion or charge repulsion. Moreover, a sorption-diffusion mechanism can also contribute to the separation process, attributed to hydrophobic interactions or hydrogen bonding between the contaminants and the membrane surfaces (solute-membrane affinity) (Nghiem & Schäfer, 2005). Depending on the physicochemical characteristics of the contaminant and the membrane, separation can be achieved by one or several mechanisms. The word 'physicochemical' implies that separation can be attributed either to physical selectivity

(charge repulsion, size exclusion or steric hindrance) or to chemical selectivity (solvation energy, hydrophobic interaction or hydrogen bonding). Consequently, the separation process can be strongly influenced by the physicochemical interaction between the solute and the membrane polymer and/or with water (Nghiem & Schäfer, 2005). In the case of trace organic contaminants, like pesticides, such interactions are complicated and their transport across the membrane is still a topic of extensive research.

For non-charged solutes, the distribution at the boundary layer/membrane interface is considered to be determined by a steric exclusion mechanism. Steric exclusion is not typical for nanofiltration but applies to ultrafiltration and microfiltration, where solutes larger than the pore size of the membranes are retained. This is comparable to a sieving phenomenon except that in membrane filtration, neither pores nor solutes have a uniform size. For instance, dissolved organic species may change their configuration due to changes in solution chemistry or interactions with other molecules or surfaces. For example, the combined nanofiltration of triazine herbicides and naturally occurring humic substances facilitates the formation of complexes with triazines resulting in an increased steric congestion or reduction of the diffusivity of the NOM–triazine pseudo-complex (Plakas & Karabelas, 2009).

For charged solutes, an additional mechanism can be recognised, the Donnan exclusion, which has a pronounced effect on the separation by NF. Due to the slightly charged membrane surface, solutes with an opposite charge compared to the membrane (counter-ions) are attracted, while solutes with a similar charge (co-ions) are repelled. At the membrane surface, a distribution of co- and counter-ions will occur, thereby influencing separation. The relative importance of Donnan exclusion in solute retention by NF membranes is still debated in the scientific community since steric hindrance appears to be capable of significantly influencing such retention. For instance, Van der Bruggen et al., (1999) suggest that the charge effect can be important when the molecules are much smaller than the pores; when the molecules have approximately the same size as the pores, charge effects can exert only a minor influence, as the molecules are mainly retained by a sieving effect.

In the case of polar organic species, separation by NF/RO membranes is even more complicated as the process is not only affected by charge repulsion and size exclusion but it is also influenced by polar interactions between solutes and the membrane polymeric suface. Research in this direction has led to the conclusion that retention may be negatively affected by the polarity of a molecule (Van der Bruggen et al., 1999; Agenson et al., 2003; Kimura et al., 2003a). A possible explanation for this behaviour is related to electrostatic interactions; specifically, the dipole can be directed towards the charged membrane in such a way that the side of the dipole with the opposite charge is closer to the membrane (Van der Bruggen et al., 1999). The dipole is thus directed towards the pore and enters more easily into the membrane structure; moreover, once the molecule is in an open (straight-through) pore, it will follow the permeate. The polarity effect is expected to be the same for positively and negatively charged membranes, since the only change occurring is the direction of the dipole (Van der Bruggen et al., 1999).

Adsorption of organic species to membrane materials is an important aspect of trace organic matter removal using NF/RO. Organic contaminants, which can adsorb onto the membrane, are usually hydrophobic (high $\log K_{ow}$) or present high hydrogen bonding capacity. In addition, experimental results have shown that the adsorption of hydrophobic compounds is significant for neutral compounds and for ionizable compounds when

electrostatically neutral (Kimura et al., 2003b). Also, operating conditions such as the permeate flux can have a significant effect on the degree of compound adsorption (Kimura et al., 2003b). Although adsorption contributes to an initial retention, an increased surface concentration as a result of adsorption, favouring species diffusion through the membrane, can reduce process effectiveness to some extent (Nghiem & Schäfer, 2005). Moreover, adsorption, resulting in the accumulation of organic molecules on the membrane surfaces, can cause several problems leading to overall performance deterioration.

3. Factors affecting the removal of pesticides by NF/RO treatment

3.1 Introduction

The idea of applying membrane processes for the removal of pesticide residues from potable water is not new. It originates back in the late '60s when Hindin et al. (1969) studied the removal of a few chlorinated pesticides, including DDT, TDIE, BHC, and lindane, by reverse osmosis using an asymmetric cellulose acetate (CA) membrane. The initial results of their study have shown that RO filtration, employing a CA membrane, is a promising treatment process for producing water low in organic substances, including pesticides. The excellent performance of RO membranes in removing a variety of pesticides, including chlorinated hydrocarbons, organophosphorous, and miscellaneous pesticides, was also shown in an early study by Chian et al. (1975) in which a number of non-cellulosic membranes, such as aromatic polyamide and cross-linked polyethylenimine membranes exhibited far better performance in pesticides removal and resistance to pH than conventional CA membranes. Because of this advances in membrane technology, RO has been gradually finding applications in the treatment of a variety of domestic, industrial, and hospital wastewaters.

In the past three decades, the need for a complete assessment of the RO, and of the later developed NF process, regarding removal of pesticide residues from various aquatic matrices, led to an extensive research effort in many laboratories (Berg et al., 1997; Devitt et al., 1998a; Van der Bruggen et al., 1998, 2001; Kiso et al., 2000, 2001a, 2002; Košutić et al., 2002, 2005; Zhang et al., 2004; Causserand et al., 2005; Bhattacharya et al., 2006; Plakas et al., 2006; Sarkar et al., 2007; Plakas & Karabelas, 2008, 2009; Ahmad et al., 2008a, 2008b; Comerton et al., 2008; Caus et al., 2009; Benítez et al., 2009; Pang et al., 2010; Wang et al., 2010), pilot (Baier et al., 1987; Duranceau et al., 1992; Agbekodo et al., 1996; Berg et al., 1997; Hofman et al., 1997; Wittmann et al., 1998; Bonné et al., 2000; Boussahel et al., 2000, 2002; Chen et al., 2004) as well as to industrial scale experiments (Agbekodo et al., 1996; Wittmann et al., 1998; Ventresque et al., 2000; Cyna et al., 2002). A fairly large number of commercially available NF/RO membranes have been tested for the removal of an even larger number of herbicides, insecticides, fungicides and miscellaneous pesticides from various water matrices. The results of the respective literature review are summarized in the Appendix, in which the NF/RO membranes employed are listed together with their pesticide rejection performance.

A critical review of the rejection mechanisms and of the main parameters involved in pesticide removal by NF/RO processes is made in the following. Specifically, the findings of a comprehensive literature review are reported together with the results obtained from the experimental work performed by the authors.

3.2 The role of membrane characteristics

The success of pesticides removal from potable water by membrane processes is strongly related to the type of membrane selected. Important aspects to consider when choosing an appropriate membrane are MWCO, porosity, degree of ionic species rejection, surface

charge and membrane type (polymer composition). The significance of each parameter on pesticides removal is directly related to the solute properties (molecular weight, molecular size, acid disassociation constant-pKa, and hydrophobicity/hydrophilicity-logK_{ow}) which determine the strength of the pesticide-membranes physicochemical interactions.

Membrane molecular weight cut-off

Based on the molecular weight of the majority of the pesticide residues detected in potable water sources (usually greater than 200Da), membranes with a MWCO varying from 200 to 400Da are promising options for the successful removal of such solutes from water. These are reverse osmosis and tight nanofiltration membranes which are characterized by pore sizes close to those of pesticides (<1nm). It is evident that the larger the pesticide molecule the greater the sieving effect, resulting in greater retention. On the other hand, the retention of small pesticide molecules by wider pore membranes can be influenced not only by the sieving parameters (pesticide and membrane pore size) but also by the physicochemical interactions taking place between the pesticides and the membrane surfaces. For example, in pilot studies (Boussahel et al., 2000; 2002), among the two membranes tested, Desal DK membranes achieved the best retention results for all pesticides and water matrices tested due to their lower MWCO value (150-300Da) compared to NF200 (300Da) membranes. The low MWCO of Desal DK membranes provided an explanation for the similar percentage removal for all pesticides (except from the polar diuron), something that was not observed in the case of NF200 membranes, for which the retention capacity was found to be dependent both on the size and the polarity of the pesticide molecules (Boussahel et al., 2000). In a recent work (Zhang et al., 2004), the retention of two triazine herbicides (atrazine and simazine) by four nanofiltration membranes was also related to their MWCO. Specifically, the smaller MWCO of UTC-20 (180Da) and UTC-60 (150Da) membranes resulted in significantly greater removal than that achieved by DESAL 51 HL (150-300Da) and DESAL 5 DL (150-300Da) membranes (Table 5).

Some deviations from the aforementioned trends have been also reported. For instance, in a study by Van der Bruggen et al. (1998), the MWCO of the employed NF membranes was poorly correlated with the removal of two classes of herbicides; i.e. triazines (atrazine, simazine) and phenyl-ureas (isoproturon, diuron). Specifically, the NF70 membrane, with a MWCO 200Da, presented greater retention capability than the seemingly somewhat tighter UTC-20 membrane (MWCO 180Da). On the other hand, a NTR-7450 membrane exhibited the worst performance (<20% retention) due to the larger pore sizes, indicated by its high MWCO (600-800Da) (Van der Bruggen et al., 1998). Similar observations were also made in another study (Mohammad & Ali, 2002), where the rejection of uncharged solutes and salts did not conform to the expected trend of reduced rejection with increasing MWCO of the NF membranes used.

Membrane porosity

The above results support the commonly held belief that the characterization of NF and ULPRO membranes by a nominal MWCO value may be convenient in practice, but it is questionable on physical grounds since the molecular weight of a model compound, used to determine MWCO, cannot be representative of all molecular species (i.e. the pollutants to be separated) of the same molecular weight but differing in conformation and in other physical properties, which affect molecule-membrane interaction and permeation; thus, MWCO provides only a rough estimate of the membrane capability to retain dissolved uncharged

compounds. However, other quantities such as the nominal pore size of a membrane, which refers to the smallest pore size in the membrane matrix, and the porosity, expressed as pore density, pore size distribution (PSD), or effective number of pores (*N*) in the membrane top layer (skin) have been regarded as representative parameters for predicting the rejection of different organic compounds or particles (Van der Bruggen et al., 1999; Lee et al., 2002; Košutić et al., 2002, 2005, 2006). For instance, the rejection of uncharged pesticide molecules was positively correlated with membrane porosity parameters (PSD and *N*) (Košutić et al., 2002, 2005). The apparent sensitivity of rejection, to accurate characterization of the membrane porosity, is in itself an indication of the dominant role played by the sieving mechanism; this is also consistent with findings that the membrane pore size is a crucial parameter for pesticide removal by a specific membrane (Van der Bruggen et al., 1998). It should be pointed out that, although in these studies the physicochemical effects on the rejection of pesticides may be of lesser importance, they cannot be neglected as they can contribute to final rejection achieved for specific membrane-pesticides systems. This issue is subsequently discussed.

Degree of membrane desalination

The separation capability of tight NF and RO membranes is commonly characterized by their salt rejection performance, rather than by MWCO which is often not reported by the manufacturers. The desalination degree of a membrane is usually reported as the stabilized salt rejection of a 2000 mg/L sodium chloride or magnesium sulfate solution, and/or a 500 mg/L calcium chloride solution. The desalination degree can be a useful parameter in roughly estimating the rejection of pesticides, because the MWCO of a membrane is often unknown and manufacturer-specific, whereas PSD and porosity determination require the performance of specific filtration experiments or the application of special analytical techniques (atomic force microscopy, bubble point, gas adsorption/desorption, thermoporometry, etc). The usefulness of salt rejection has been demonstrated in studies (Kiso et al., 2000, 2001a) where the rejection of aromatic and non-phenylic pesticides was positively correlated with the desalination degree of commercial NF membranes; indeed, rejection was greatest in the case of the highest desalting membranes. Specifically, the order of rejection followed that of the nominal salt rejection capability of the membranes; i.e., NTR-729HF > NTR-7250 > NTR-7450 > NTR-7410, with 92%, 60%, 51% and 15% NaCl rejection, respectively. It is interesting to notice that only the highest desalting membrane was found to reject effectively almost all pesticides. However, rejection was again found to be strongly influenced by the pesticide properties (hydrophobicity, charge), regardless of the membrane salt rejection performance. In general, the reliability of the membrane desalination degree as an accurate indicator for assessing the removal of hydrophobic organic micro-pollutants is doubtful.

Membrane material

Membrane material is also identified as an important factor of the system pesticide-water-membrane that affects the membrane rejection performance through physicochemical interactions in that system. For example, a number of studies confirm that composite polyamide (PA) membranes exhibit far better rejection performance for several mixtures of micropollutants, including pesticides, compared to the cellulose acetate (CA) membranes (Chian et al., 1975; Hofman et al., 1997; Causserand et al., 2005). This behavior has been

attributed to the higher polarity of CA membranes which is responsible for the poor rejection of the highly polar pesticides (Chian et al., 1975). On the contrary, the relatively nonpolar aromatic PA membranes exhibit better rejection performance as well as high water fluxes attributed to the very small thickness characterizing their effective active layer (skin), which varies between 10nm and 500nm for various TFC NF and ULPRO membranes. It has been also reported (Kiso et al., 2000, 2001a) that membranes made of sulfonated polyethersulfone display lower rejection of pesticides compared to poly(vinyl alcohol)/ polyamide ones, even though their desalination capabilities are similar.

Membrane charge

The majority of the commercial TFC membranes is characterized by a negative charge which tends to minimize the adsorption of negatively charged foulants present in membrane feed waters and to enhance the rejection of dissolved salts (Xu & Lebrun, 1999; Deshmukh & Childress, 2001). The electrostatic repulsion of negatively charged pesticides (pH>pKa) at the membrane surface is expected to enhance the overall rejection performance. This is in agreement with results obtained by Berg et al. (1997) where the rejection of the negatively charged mecoprop (at neutral pH) was greater than the one measured for non-charged herbicides of the same size. Specifically, rejection experiments with mecoprop in dissociated and undissociated form were conducted with five different NF membranes; in this study, it was estimated that less than 10% of mecoprop was dissociated at pH 3. Mecoprop, in the dissociated form, was rejected more than in the undissociated form, by all five NF membranes at levels between 10% and 90%. The rejection of the undissociated form of mecoprop was comparable to the uncharged diuron which is of similar size, providing additional evidence that rejection of undissociated organic molecules is due to steric effects.

3.3 Effect of pesticides properties on retention

According to the preceding discussion, the selection of an appropriate membrane is primarily made on the basis of key pesticide parameters, like the molecular weight, the molecular dimensions (length and width), the polarity (dipole moment), the hydrophobicity /hydrophilicity ($\log K_{ow}$), and the acid dissociation constant (pKa). Several research groups have systematically studied the role of one or more of the aforementioned pesticide parameters on membrane rejection, and their results are summarised here.

Pesticide molecular weight and size

Researchers agree that size exclusion is the most important mechanism of pesticide retention. Various size parameters used in the literature to correlate pesticide rejection include the molecular weight (MW), the Stokes diameter (d_s), the diameter derived from the molar volume (d_m), the molecular length and molecular width (calculations based on molecular STERIMOL parameters), and the diameter which is calculated from the molecular structure by using special computer software (HyperChem, ChemOffice) (Van der Bruggen et al., 1998, 1999; Kiso et al., 2001a; Agenson et al., 2003; Chen et al., 2004). Typical values of size parameters for selected pesticides are listed in Table 6, where it is clearly shown that the dimensions of a pesticide are not directly related with its MW. Small MW pesticides can be characterized by a larger molecular length and/or width compared to other pesticides of larger MW. This is attributed (Chen et al., 2004) to the structure and the small range of molecular weights of the specific pesticides (198-286Da).

Pesticide	Molecular weight (gr/mol)	Molecular length (Å)	Molecular width (Å)
Atrazine	215	10.36	8.02
Bentazone	240	9.31	5.42
Cyanazine	240	10.38	8.33
Diuron	233	9.19	4.87
Mecoprop	214	9.43	4.88
Metribuzin	214	10.43	4.43
Pirimicarb	238	10.30	7.93
Simazine	201	10.34	7.49

Table 4. Size of selected pesticides; calculations using the HyperChem software (Chen et al., 2004)

Since MW is the most easily accessible parameter (though only indicative of molecular size), in the majority of studies attempts are made to relate the retention of uncharged pesticides to this quantity. It has been reported (Chen et al., 2004) that a positive correlation exists between the rejection of eleven pesticides with their molecular weights, from which a MWCO of 200Da was determined for the membrane tested (Dow Filmtec NF70). In pilot studies (Boussahel et al., 2002), the higher rejection of atrazine and cyanazine was attributed to their molecular weight, which is larger than the one characterizing the other three herbicides tested (DEA, simazine and isoproturon). Significant efforts were also made (Van der Bruggen et al., 1999) to correlate the rejection of miscellaneous organic molecules with their molecular weight values as well as with other size parameters with physical meaning (d_s, d_m, molecular diameter calculated with the HyperChem software). Interestingly, it was found that the correlation of retention was only slightly improved by employing size parameters, as compared to correlation with MW; this implies that MW is a useful indicator for correlating retention (Van der Bruggen et al., 1999). Nevertheless, MW cannot be recommended for modeling efforts, since it is not representative of the geometry of the molecules that affects their rejection or transfer through the membrane.

Molecular length and molecular width are also reported in the literature to be realistic measures of molecular size and good parameters for predicting the rejection of different groups of organic compounds by NF/RO membranes. For example, the rejection of aromatic pesticides was found (Chen et al., 2004) to be best correlated with their molecular length rather than their molecular width (theoretical calculations by HyperChem based on their structures and orientation). The molecular length in this case represented the cross-sectional diameter due to structural orientation. On the other hand, the molecular width (MWd) was suggested (Kiso et al., 2001b) as a useful descriptor of the steric hindrance effect on the rejection of alcohols and carbohydrates. In addition to MWd, Kiso et al. (2001b) developed another molecular size parameter which correlated the rejection of alcohols and carbohydrates better than the MWd or the Stokes diameter; specifically, they calculated a mean molecular size (MMS) by taking half of the length of the edge of the cube encompassing the molecule (Kiso et al., 2001b). Better correlations with MMS where observed for high MWCO membranes (>500Da), while for low MWCO membranes (<250Da) MWd was found to be a better descriptor than MMS (which is the case for most pesticides) (Kiso et al., 2001b).

Regarding the aromatic (phenylic) and the non-phenylic pesticides, it was found (Kiso et al., 2000, 2001a) that rejection cannot be correlated solely with a molecular size parameter. This is attributed to the sorption capacity of these molecules on the membrane polymer which

together with the molecule planarity (size) explain the solute permeability through the nanofiltration membranes. In an effort to combine steric hindrance effects with adsorption, Kiso et al. (2001a) developed an alternative molecular width parameter (P-MWd) which was used in the statistical processing of their experimental results. A regression analysis showed that the permeability of an aromatic compound through a membrane can be reduced due to both its sorption capacity and its molecular width. Similar observations were also made for alkyl phthalates and mono-substituted benzenes (Kiso et al., 2001b) with the rejection being strongly affected by their hydrophobic properties. These results indicate the significance of the solute-membrane affinity on rejection, and that solute transport predictions should not be based only on steric exclusion effects (Verliefde et al., 2009a).

Pesticide hydrophobicity/hydrophilicity

The significance of adsorption on the rejection of pesticides during membrane applications has been first reported by Chian and his coworkers (Chian et al., 1975). They claimed that the interaction between the hydrocarbon (nonpolar) segments of pesticide molecule and membranes is due to hydrophobic bonding. Since then, many researchers have reported significant adsorption of pesticides and of other organic micropollutants onto the membrane polymer (Kiso et al., 2000, 2001a; Nghiem & Schäfer, 2002; Agenson et al., 2003; Kimura et al., 2003a, 2003b; Comerton et al., 2007; Plakas & Karabelas, 2008). A literature review shows that except from the hydrophobic interactions, adsorption may also take place through hydrogen bonding between the organic molecules and the hydrophilic groups of the membrane material (Nghiem et al., 2002). Hydrogen bonding and hydrophobic interactions can apparently act either independently or together. In the latter case, it is often difficult to distinguish the two effects. Regarding pesticides, the literature review suggests that the hydrophobic interactions are mostly responsible for pesticide adsorption onto membrane surfaces, which is considered to be the first step of the rejection mechanism. This observation led researchers to the conclusion that the rejection of hydrophobic compounds should be experimentally evaluated after the tested membrane is saturated with the target compounds; otherwise, the rejection is likely to be overestimated, with adsorption misinterpreted as some kind of high initial rejection (Kimura et al., 2003b).

A measure of solute hydrophobicity/hydrophilicity is the octanol/water partition coefficient ($\log K_{ow}$ or logP), while the hydrophobic nature of a membrane is characterized by its contact angle value (Mulder, 1998). $\text{Log}K_{ow}$ values of trace organic molecules vary between -3 and 7, with the higher values characterizing hydrophobic compounds (usually for $\log K_{ow}>2$). Kiso et al. (2000, 2001a, 2002) systematically investigated the relationship between $\log K_{ow}$ versus retention and adsorption of a number of aromatic and non-phenylic pesticides, using flat sheet and hollow fiber nanofiltration membranes. While no significant correlation was identified between retention and $\log K_{ow}$, there was a rather good correlation between the adsorption and the characteristic $\log K_{ow}$ values of the pesticides tested (Kiso et al., 2000, 2001a, 2002). Moreover, it was found that the presence of a phenyl group in a molecule increases its adsorption capacity (aromatic pesticides), while alkyl groups can have negative effects on the interaction between a phenyl group and the membrane (Kiso et al., 2001a). In a recent study (Comerton et al., 2007), static adsorption experiments with 22 endocrine disrupting species and pharmaceutically active compounds (including the pesticides alachlor, atraton, metolachlor, DEET), and UF, NF and RO membranes, showed that adsorption was strongly correlated with compound $\log K_{ow}$ and membrane pure water permeability, and moderately correlated with compound solubility in water. Kimura et al.

(2003b) reported also the negative effect of solute charge on adsorption, since adsorption was found to be greater for electrostatically neutral hydrophobic compounds.
Finally, in a systematic study on the effect of coexisting herbicides on rejection (Plakas & Karabelas, 2008), a competition was identified for adsorption sites on the membrane surfaces between the different solutes present in the feed-waters. This phenomenon resulted in different rejection values, since herbicides were better rejected in single solute solutions than in mixed solute systems. This effect was particularly pronounced in the case of tight membranes (NF90, XLE), since the more porous membrane (NF270) showed an increased retention of the herbicides atrazine and isoproturon when treated together with prometryn or in triple-solute solutions (Table 5). A pore restriction effect, due to the larger prometryn molecule, could be responsible for this trend, which seems to positively influence the retention of the smaller molecules (Plakas & Karabelas, 2008).

Membrane	Herbicide	Single solute system	Double solute system			Triple solute system
			A	I	P	
NF270	Atrazine	78.9 (18.8)	-	73.2 (20.2)	86.1 (16.5)	81.2 (17.1)
	Isoproturon	73.1 (25.0)	63.8 (26.0)	-	85.0 (15.1)	82.4 (17.0)
	Prometryn	90.8 (23.7)	87.7 (27.5)	82.7 (33.6)	-	83.1 (32.5)
NF90	Atrazine	99.3 (21.1)	-	93.1 (19.2)	86.2 (30.5)	87.5 (26.8)
	Isoproturon	95.1 (25.6)	93.1 (23.1)	-	91.8 (25.3)	92.1 (23.2)
	Prometryn	99.8 (28.3)	96.6 (26.2)	96.8 (29.0)	-	96.3 (27.3)
XLE	Atrazine	97.6 (24.8)	-	88.2 (27.0)	94.9 (23.0)	90.1 (22.5)
	Isoproturon	96.6 (5.1)	83.2 (11.3)	-	84.1 (8.2)	87.0 (9.0)
	Prometryn	98.1 (31.2)	95.5 (29.5)	94.0 (32.4)	-	94.9 (31.3)

Table 5. Herbicide retention results (%) and percentage adsorption data (values in the brackets) in the case of single and multi-solute nanofiltration experiments; A, I and P designate solutions with Atrazine, Isoproturon and Prometryn, respectively (Plakas & Karabelas, 2008).

Pesticide polarity

One of the most important physicochemical criteria governing nanofiltration and reverse osmosis separation of trace organic compounds in aqueous solution is the "Polar Effect" of the solute molecule (Matsuura & Sourirajan, 1973). As outlined in paragraph 2.4, the passage of polar organic molecules to the permeate side is facilitated by the polar interactions with the membrane charge, which leads to a reduced solute rejection. Van der Bruggen et al. (1998) have successfully combined size exclusion and polarity effects to explain the retention

of four pesticides. Specifically, the retention of the two phenyl-urea derivatives, diuron and isoproturon, was lower than the one measured for the two triazine compounds, atrazine and simazine (Van der Bruggen et al., 1998). Diuron and isoproturon are not smaller than the two triazines, but they have a higher dipole moment (a measure of polarity) which favors the sorption, and consequently the diffusion of these molecules into the membrane polymer. The effect of the dipole moment was also confirmed by comparing the retentions of the two polar herbicides with those measured for a series of non-polar carbohydrates. The filtration results showed that a greater dipole moment leads to a lower retention (Van der Bruggen et al., 1998). In general, it has been concluded that solute polarity is important for membranes with an average pore size that is larger than the size of compounds to be retained (Van der Bruggen et al., 1999, 2001; Košutić et al., 2002).

3.4 Effect of the feed water composition

Membrane filtration experiments with real or simulated raw waters (i.e. solutions containing salts, organic matter and pesticides) have shown that pesticide rejection can vary greatly, depending on the feed water composition. Specifically, pH, ionic strength, and the presence of organic matter are identified as having an influence on pesticide rejection. The respective literature results are discussed next.

Influence of water pH

The role of pH on pesticide rejection is related mainly to the changes taking place in the membrane surface structure and charge. It has been determined that pH has an effect upon the charge of a membrane due to the dissociation of functional groups. Zeta potential for most membranes has been observed in many studies to become increasingly more negative as the pH is increased and functional groups deprotonate (Childress & Elimelech, 1996; Deshmukh & Childress, 2001; Afonso et al., 2001). Moreover, pore enlargement or shrinkage can occur depending upon the electrostatic interactions between the dissociated functional groups of the membrane material (Freger et al., 2000). In a study performed by Berg et al. (1997) the rejection of uncharged organic compounds (atrazine, terbuthylazine) at pH 3 and 7 was relatively constant. However, higher pH values resulted in reduced rejection rates together with an increased permeate flux. This was attributed to the pore enlargement at higher pH values.

Experiments with the uncharged simazine molecule showed that rejection attained the highest value at pH 8, and consistently lower values at pH 4 and 11 (Zhang et al., 2004). These results were attributed to ion adsorption on the membrane surface; specifically, at higher pH, OH^- ions adsorption increased, resulting in an increase of the membrane charge. Polar components such as pesticides exhibit a reduced rejection with increasing membrane charge, because such molecules tend to preferentially orient themselves so that the dipole with a charge opposite to that of the membrane charge is the closest to the membrane surface. Consequently, this preferential orientation results in an increased attraction, an increased permeation and thus a lower rejection. At lower pH, the same effect might occur with H^+ ions (Zhang et al., 2004).

Finally, it was recently reported (Ahmad et al., 2008b) that increasing the solution pH led to enhanced atrazine and dimethoate rejection, but degraded the permeate flux performance for NF200, NF270 and DK membranes. However, the NF90 membrane exhibited relatively consistent performance in both rejection and permeate flux, regardless of the solution pH (Ahmad et al., 2008b).

Influence of solute concentration

Filtration experiments with atrazine and prometryn in different concentrations (10–700 μg/L) showed small variations in rejection by NF/ULPRO membranes (Plakas et al., 2006; Plakas & Karabelas, 2008). Specifically, the differences in retention values varied between 7 and 13%. This is in agreement with observations made by other researchers (Agbekodo et al., 1996; Van der Bruggen et al., 1998; Zhang et al., 2004; Ahmad et al., 2008a), in that herbicide concentration does not significantly affect their retention. The fact that the filtration of fluids with smaller feed concentrations led to a slight reduction of triazine retention (especially in the case of a ULPRO membrane) could be attributed to the amount of triazines adsorbed on the selected membranes; more specifically, the smaller triazine concentration may be associated with a slightly smaller adsorption, in comparison to the results obtained with greater feed concentrations, something that was more pronounced in the case of the less tight NF membrane (Plakas et al., 2008).

Influence of the ionic environment

A number of studies have shown that the retention of pesticides can be moderately influenced by the presence of dissolved salts in the feed solution due to the interactions taking place between the ions and the membrane surfaces. Specifically, it has been suggested (Yoon et al., 1998) that, at high ionic concentrations, there may be a reduction in the electrostatic forces inside the membrane (i.e. reduced repulsion) which may cause a reduction of the actual size of the pores, leading to a reduced membrane permeability; consequently, a better rejection of pesticides accompanied by a reduced water flux could be observed. Based on these considerations, an explanation can be also provided for the higher rejection of pesticides by nanofiltration membranes with ground water (Van der Bruggen et al., 1998), tap and/or river water (Zhang et al., 2004). It should be noted, however, that the presence of natural organic matter in the natural water samples employed may have also positively affected the rejection of pesticides (Zhang et al., 2004).

In an earlier study (Boussahel et al., 2002), the presence of divalent cations (calcium) in the feed solution appeared to exercise little influence on pesticide rejection, whereas rejection was found to be related to the membrane type. Specifically, an improvement in pesticide rejection by approx. 5% (in the presence of $CaCl_2$) and 10% (in the presence of $CaSO_4$) was reported for a NF200 membrane, while for the Desal DK membrane very little change was noted, i.e. a slight drop in the percent removal (5%) for DEA and simazine with $CaCl_2$ (Boussahel et al., 2002). These results are in agreement with those from a recent study (Plakas & Karabelas, 2008), where a moderate influence of calcium ions on herbicide retention was obtained; this influence, was either positive or negative depending on the membrane type. For example, the effect of calcium ions on pesticide removal by relatively dense and neutral NF/ULPRO membranes was found to be negative. This was not observed in the case of dense and negatively charged membranes which were not significantly influenced by the presence of calcium. On the other hand, the retention of pesticides by relatively porous NF membranes was found to increase with the presence of calcium ions, possibly due to the mechanism of pore blockage described earlier (Plakas & Karabelas, 2008).

In the case of elevated ionic strength, due to the presence of sodium chloride in the feed solution, rejection was reduced for all herbicides and membranes tested (Plakas & Karabelas, 2008). This was explained by the reduction of the hydrodynamic radius of herbicides in the presence of NaCl, especially of the hydrophobic triazines, with a likely

contribution of concentration polarization on the membrane surface. Regarding the effect of herbicides on salt rejection, there was an increase observed in sodium chloride rejection only for the wide-pore NF membranes, something that was not observed in the case of calcium ion retention which remained constant. However, the calcium retention was reduced somewhat, by approximately 7% and 13% for the tight NF90 and XLE membranes, respectively. Furthermore, the presence of calcium ions had no influence on herbicide adsorption on all membranes tested, as also observed by previous researchers (Boussahel et al., 2002).

Pesticide retention in the presence of organic matter

A number of studies performed with either NF/RO membranes (Agbekodo et al., 1996; Berg et al., 1997; Devitt et al., 1998a; Boussahel et al., 2000; Zhang et al., 2004) or dialysis membranes (Devitt & Wiesner, 1998b; Dalton et al., 2005) have shown that the retention of pesticides is significantly influenced by the presence of natural organic matter (NOM) in water. This fact is of considerable importance since a large percentage of pesticide residues is present in surface and ground waters together with organic matter; i.e. humic and fulvic acids, polysaccharides, etc. (Kulikova & Perminova, 2002). In general, humic substances (HS) are a ubiquitous component of natural water systems that may function as an auxiliary phase to alter the speciation and transport behaviour of other xenobiotic compounds present in water (Wersaw, 1991). Thus, organic micropollutants, like pesticides, may exist either as free dissolved species or as a complex with HS.

A literature review on the effect of NOM on pesticide retention by membranes, suggests that there is a dependence on the type of NOM present in the water. NOM is composed of an extremely diverse group of compounds, including humic acids, carbohydrates, alcohols, amino acids, carboxylic acids, lignins, and pigments, whose origin greatly influences its character and behaviour. The majority of the published works agree on the fact that the retention of pesticides in membrane-based systems tends to increase in the presence of NOM (Agbekodo et al., 1996; Devitt et al., 1998a, 1998b; Zhang et al., 2004; Dalton et al., 2005), which is generally attributed to a variety of factors; e.g., the size, shape, and surface chemistry of compounds involved. On the other hand, the use by various researchers of NOM of different origin, and the inadequate information regarding their physicochemical properties (elemental analysis, functional groups), hinder the systematic comparison of experimental results as well as the correlation of the pesticide/NOM membrane retention with the characteristic properties of the organic matter naturally occurring in water.

To identify the variability introduced by the different properties of humic substances on pesticide rejection, Plakas & Karabelas (2009) performed systematic studies with well-characterized HS in order to improve the understanding of mechanisms of NOM–pesticide retention by membranes. Specifically, they used four different types of HS; i.e. three of them were typical water-born HS (humic acid, fulvic acid, and a mixture of NOM) whereas the fourth one was a HS surrogate (tannic acid). The results of this study show that the combined nanofiltration of triazines (atrazine, prometryn) and naturally occurring humic substances facilitates the formation of complexes with triazines which in turn enhance their removal by nanofiltration (Fig. 7). This complexation appeared to be related not to the characteristic acidity (phenolic, carboxylic) of the HS used, but rather to their molecular conformation (Plakas & Karabelas, 2009). More specifically, a preferential binding was observed between triazines and low molecular weight fractions of humic compounds

(especially of fulvic acid and tannic acid), which resulted in higher retention values for the two triazines. Under all conditions, tannic acid exhibited the greatest effect on triazine retention, among the four standard HS compounds used, leading to an almost complete removal of the two triazines (95–100%) for all three membranes tested (Fig 7).

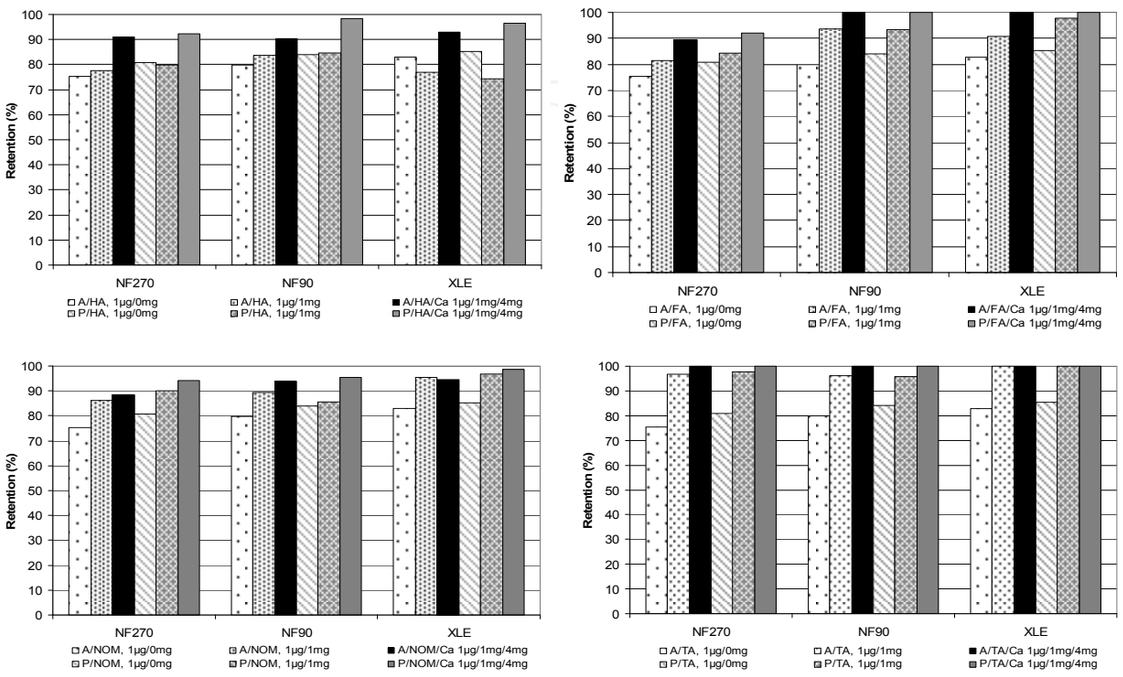

Fig. 7. Retention of atrazine (A) and prometryn (P) by three NF/ULPRO membranes in the absence or presence of humic substances (HA, FA, NOM, TA) and/or calcium ions (Plakas & Karabelas, 2009)

Moreover, triazine retention was found to increase with increasing HS concentration, to a degree depending on the type of HS; additionally, removal of triazines was improved in the presence of calcium which displayed a tendency to enhance the interaction between HS and triazines (Plakas & Karabelas, 2009). In parallel, it is noted that a number of studies with dialysis membranes (Devitt et al., 1998a, 1998b, Dalton et al., 2005) have reported reduced values of atrazine retention when divalent calcium is present together with naturally occurring organic matter, including the NOM surrogate, tannic acid. According to Devitt et al. (1998a, 1998b), this trend is due to the reduced association of atrazine and NOM, as a result of the occupation of interaction sites by calcium and/or the reduced access of atrazine to NOM sites due to changes in molecular conformation. However, gel permeation chromatography experiments (Plakas & Karabelas, 2009) have shown that this is not the case, since the presence of calcium had the tendency to increase the interaction of humic substances with triazine compounds. These conflicting results could be attributed to the different types of membranes and filtration techniques used. In particular, the use of cellulose ester membranes, as well as the experimentation on batch dialysis systems by Devitt et al. (1998a, 1998b), where concentration and osmotic pressure difference serve as the driving force for solute transport (absence of hydrodynamic forces), may justify the seemingly different calcium effect on triazine retention.

3.5 Effect of membrane fouling

The significant number of parameters affecting pesticide retention is indicative of the complicated interactions taking place, which can be further influenced by the changes occurring in membrane surface properties as a result of fouling. This is especially true in the case of the organic micropollutants (EDCs, PhACs, pesticides, etc), since their retention is determined by electrostatic, steric and hydrophobic/hydrophilic solute-membrane interactions, which can be modified due to foulants depositing on the membrane surface. The effect of fouling on organic micropollutant retention has been the subject of rather extensive research in the past decade (Ng & Elimelech, 2004; Xu et al., 2006; Plakas et al., 2006; Steinle-Darling et al., 2007; Agenson & Urase, 2007; Nghiem & Hawkes, 2007; Bellona et al., 2010; Nghiem & Coleman, 2008; Verliefde et al., 2009; Yangali-Quintanilla et al., 2009). Systematic investigations on the influence of colloidal and/or organic fouling on various trace organic species suggests that solute retention can be distinguished in two different cases, depending on the relative solute selectivities of the fouling layer and the membrane. First, if the membrane rejects solutes better than the deposited layer, hindered back diffusion of solutes (by the fouling layer) would cause solute accumulation near the membrane surface. This cake-enhanced concentration polarization results in greater concentration gradient across the membrane and, hence, a decrease in solute retention. Second, if solutes are rejected better by the deposited layer than the membrane, the fouling layer controls solute retention which tends to improve.

The literature review suggests that membrane fouling may significantly affect the retention of low MW organic compounds depending on the concentration and characteristics of the foulants, the membrane properties, and the chemical composition of feed water. Regarding pesticides, it has been shown (Plakas et al., 2006) that the differences in retention between fouled and virgin membranes are related to the diffusion capacity of herbicides across the membranes. When a rather loose humic layer is formed on the membrane surfaces, especially when membranes are fouled by humic substances alone, in the absence of calcium ions, herbicides retention can be reduced due to their increased diffusion through the membrane polymeric matrix, which is further facilitated by the cake-enhanced concentration polarization effect. In the case of rather dense fouling layers formed through HS-Ca complexation, herbicide retention may improve; indeed, these layers can serve as additional barriers which enhance the sieving effect, resulting in higher retention values (Plakas et al., 2006).

3.6 Influence of the operating parameters

Rejection of pesticides is also found to be influenced by operating parameters, such as the water flux and the feed-stream velocity in the cross-flow mode of filtration. In a study conducted by Chen et al. (2004) rejection of pesticides was shown to be dependent on operating flux and recovery. In particular, the highest percent rejection occurred at high flux and low recovery, whereas the lowest percent rejection took place at low flux and high recovery, which is in accord with the solution-diffusion theory (Chen et al., 2004). This finding is in agreement with the work performed by Ahmad et al. (2008a), where the retention of both dimethoate and atrazine was found to be better when the pressure was increased from 6 to 12×10^5 Pa (increased water flux).

It is interesting to note that in an early study (Chian et al., 1975), the effect of pressure on pesticide separation was negligible in the case of a high-desalting membrane. However, it

was anticipated that rejection of the more polar molecules would increase somewhat with increasing pressure, especially for membranes exhibiting inferior rejection performance (Chian et al., 1975). Finally, in a pilot study (Duranceau et al., 1992), no effect on pesticide mass transfer was observed for varied feed-stream velocity, which was estimated to vary between 0.07 and 0.16m/s. This is in agreement with the crossflow experiments performed by the authors (paper in preparation) where the cross-flow velocity had a minimum effect on atrazine and prometryn rejection by a relatively porous NF membrane. It will be added that ongoing work in the authors Laboratory, shows that an increase in applied pressure results in a more pronounced increase in herbicides retention.

Finally, a cascade of NF stages was recently proposed (Caus et al., 2009) to attain high removal of organic pollutants, combined with low salt rejection; to achieve the latter, loose commercial nanofiltration membranes were selected (Desal51HL, N30F and NF270). Through modelling, it was shown that the separation could be significantly improved by a design involving cascade of NF membrane stages. Moreover, researchers have suggested the use of a Desal51HL membrane for an almost complete pesticide rejection combined with moderate salt passage (Caus et al., 2009).

3.7 Summary

By reviewing the literature, one is led to the conclusion that pesticides removal by nanofiltration and low-pressure reverse osmosis membranes is a complicated process in which several membrane and solute parameters, including feed water composition and process conditions play a role. In general, there is ample evidence that size exclusion (sieving) by the membrane pores is one of the main mechanisms determining the retention of pesticides; the pesticides molecular mass, in comparison to the MWCO of the membrane used, appears to be a very rough, albeit frequently convenient, criterion for assessing the effectiveness of the separation process. For the relatively small size uncharged pesticides, molecular mass in combination with the hydrophobic character of the molecules (commonly characterized by $\log K_{ow}$) seem to determine the retention. For instance, hydrophobic pesticides (with a large value of $\log K_{ow}$) are not well retained by nanofiltration membranes; this is attributed to the increased adsorption on the membrane surfaces that promotes their subsequent diffusion to the permeate side. For charged pesticides, both size exclusion and electrostatic interactions appear to control the degree of separation. In the case of polar pesticides, rejection may be reduced due to polar interactions with the charged membranes; this is especially true for membranes with an average pore size larger than the compounds to be retained. In general, pesticides characterized by increased affinity for the membrane tend to be rejected to a lesser extent than those of a similar size but with reduced tendency for adsorption on the membrane.

The aforementioned results can form the basis for recommending general rules for selecting membrane type for efficient separation of pesticides, taking also the composition of feed-water into account. In principle, a nonpolar membrane surface would be preferable for improved, overall, pesticides rejection. However, it should be recognized that the presently widely employed polyamide NF/RO membranes are characterized by surface hydrophilicity (desirable as it resists organic fouling) and by rather small negative charge. Regarding porosity, dense membranes are definitely preferable, for effective removal of even small pesticides molecules. However, membranes characterized by reduced porosity and polarity are associated with reduced flux, thus requiring increased operating pressure (and energy expenditure) to achieve a given clean water production rate.

Another aspect to be considered in purification of water from organic micro-pollutants, like pesticides, is membrane fouling. Systematic studies on the effect of organic fouling on pesticide rejection have shown that fouling alters the membrane surface properties and, as a consequence, rejection of pesticides can drastically change in comparison with virgin membranes. Therefore, it is of paramount importance in membrane applications to identify the type of foulants with potential to deposit on the membrane surface, in order to predict the influence of these deposits on membrane surface properties and thus on rejection. In this direction, an adequate characterisation of the membrane surface as well as of the composition of the feed water is necessary.

4. Current trends and R&D needs for removal of trace organic contaminants from potable water

Regarding the design and operation of modern water treatment processes, to remove toxic pollutants including pesticides, there are two major issues with very significant technological, economic and (above all) environmental and human health impact, that have to be successfully addressed by the scientific community : (a) Production of safe potable water. This target entails the design of effective, environmentally friendly and economically attractive processes capable of meeting the stringent drinking water standards, even in cases of feedwater with variable load of pollutants (including pesticides) of uncertain type and concentration. (b) Elimination or disposal of liquid and solid wastes from the water treatment process, after appropriate treatment to render them safe for humans and the environment; this problem is especially acute due to the high concentration of pollutants retained in the wastes. It is evident that development of *integrated processes*, successfully coping with the above problems should be pursued, and that R&D activities should support these efforts.

Considering the first issue, as discussed in this chapter, NF has emerged as a reliable operation that provides the basis for developing effective potable water treatment processes. However, in general NF may not be possible (and perhaps should not be assigned) to handle alone the water purification task. Indeed, NF has to be combined with other complementary operations, in the context of an effective integrated design. The main considerations and current trends regarding the design of such integrated processes, taking advantage of the NF attributes, should be stressed:

- NF alone can achieve three technical objectives, on the basis of its characteristics; (i) partial hardness removal (i.e. water conditioning) by reducing the concentration of Ca and Mg salts, (ii) practically total removal of NOM and of assorted colloidal species, with the unavoidable penalty of membrane fouling, (iii) removal of pesticides and of other toxic compounds, to a rather high degree depending on many factors.
- The currently favored approach of coping with pesticides and the multitude of toxic substances, at very small concentration, is to incorporate in an integrated process sequential operations (akin to successive "lines of defense"), ensuring adequate final removal of all these pollutants. The key role of NF in this scheme is to perform as best as possible, and at least to remove most of the toxic pollutants, so that a final purification can be achieved in one or two subsequent steps; e.g. by employing granular activated carbon. This approach affords significant advantages over the currently employed conventional treatment processes, which tend to rely mostly on activated carbon.

In view of the above considerations, it appears that priority should be mainly given to the following R&D areas:

- To maximize the rejection of pesticides (and of other micro-pollutants) by the NF membranes. Particular attention deserve the improved understanding of the physico-chemical interactions between pesticides (and other such species) and various types of NF and LPRO membranes, as well as the clarification of the interaction between common organic matter (humic and fulvic acids, polysaccharides, etc) and the micro-pollutants. As the latter cannot be avoided, it may have to be facilitated (possibly by adjusting conditions) to maximize pesticides removal.
- In connection with the above areas, further investigation of the role of membrane fouling layers on the adsorption and/or rejection of pesticides.
- Development of processes for pesticides degradation that may be combined with, and complement, NF for optimum overall performance. Typical cases currently studied include Advanced Oxidation Processes (AOP); photo-catalytic and electro-Fenton processes, belonging in this category, need further study as they may offer significant advantages in conjunction with NF.
- Design of novel integrated process schemes, including NF; e.g. a combination of NF and AOP with final activated carbon treatment, could be pursued for developing optimum solutions. Structural (flow-sheet) and parameter optimization of these processes is necessary. One of the design objectives of the integrated processes should be the minimization of liquid and solid wastes, thus reducing the load of the following waste treatment stage. It should be pointed out that, due to social and legislative pressure, major stake-holders in the water treatment sector are very concerned about this waste treatment problem, and are taking steps to address it at the R&D and demonstration levels [e.g. Bozkaya-Schrotter et al., 2009].

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Appendix

Membrane	Specifications	Remarks	Pesticides	Retention (%)	Reference
YC 05	Amicon MWCO 500Da	Lab scale (dead-end)	Atrazine	~10	Devitt et al., 1998a
HR95PP	Dow Filmtec	Lab scale (crossflow)	Atrazine MCPA Propham Triazimefon	99.0 93.6 96.8 82.9	Košutić et al., 2002
NFc	Dow Filmtec	Lab scale (crossflow)	Atrazine Diazinon Dichlorvos Triadimefon	80-85 86-94 56-62 63-67	Košutić et al., 2005
NF45	Dow Filmtec MWCO 300Da	Lab scale (dead-end)	Atrazine	~31	Devitt et al., 1998a
		Lab scale (crossflow)	Atrazine Diuron Isoproturon Simazine	91.6-91.8 59.4 81.0 84.8-85.9	Van der Bruggen et al., 1998
		Lab scale (crossflow)	Atrazine Diuron Isoproturon Simazine	87.0 51.0 75.0 64.5	Van der Bruggen et al., 2001
NF70	Dow Filmtec MWCO 200-300Da	Pilot and industrial scale	Atrazine Simazine	50-90 50-100 (Dissolved organic carbon present: 0.4-3.6 mg/L)	Agbekodo et al., 1996
		Lab scale (dead-end)	Atrazine	~65	Devitt et al., 1998a
		Lab scale (crossflow)	Atrazine Diuron Isoproturon Simazine	89.9-92.0 85.9 90.3 88.5-89.2	Van der Bruggen et al., 1998
		Lab scale (crossflow)	Atrazine Diuron Isoproturon Simazine	93.5 92.0 90.0 90.1	Van der Bruggen et al., 2001

Table A. Rejection characteristics of pesticides by commercially available NF/RO membranes (alphabetical listing of membrane manufacturers).

Membrane	Specifications	Remarks	Pesticides	Retention (%)	Reference
NF70	Dow Filmtec MWCO 200-300Da	Pilot scale (retention for two different water recoveries: 50 and 15%)	Atrazine Bentazone Cyanazine Diuron DNOC Mecoprop Metamitron Metribuzin Pirimicarb Simazine Vinclozolin	86.1/93.5 100/100 92.2/93.6 50.1/71.4 60.8/87.2 93.0/100 -/53.4 87.5/93.7 100/100 71.6/86.4 100/100	Chen et al., 2004
NF90	Dow Filmtec MWCO 200Da	Lab scale (dead-end)	Atrazine Prometryn Isoproturon	86.2-99.3 96.3-99.8 91.8-95.1 in single or multi-solute solutions	Plakas et al., 2008
		Lab scale (dead-end)	Atrazine Dimethoate	>95 ~90	Ahmad et al., 2008a
NF200	Dow Filmtec MWCO 300Da	Lab scale (dead-end)	Atrazine	~39	Devitt et al., 1998a
		Industrial scale	Atrazine Chlorotoluron Simazine	<<0.1μg/L permeate concentration	Wittmann et al., 1998
		Pilot scale	Atrazine Cyanazine DEA Diuron Isoproturon Simazine	~82 ~81 ~70 ~45 ~75 ~70	Boussahel et al., 2000, 2002
		Lab scale (dead-end)	Atrazine Prometryn Isoproturon	83.3 97.0 82.0	Plakas et al., 2006
		Lab scale (dead-end)	Atrazine Dimethoate	75-78 ~55	Ahmad et al., 2008
NF270	Dow Filmtec MWCO 200-400Da	Lab scale (crossflow)	Atrazine Diazinon Dichlorvos Triadimefon	81-85 90-93 ~40 >99.0	Košutić et al., 2005
		Lab scale (dead-end)	Atrazine Prometryn Isoproturon	73.2-86.1 82.7-90.8 63.8-85.0 in single or multi-solute solutions	Plakas et al., 2008

Table A. Continued

Membrane	Specifications	Remarks	Pesticides	Retention (%)	Reference
NF270	Dow Filmtec MWCO 200-400Da	Lab scale (dead-end)	Atrazine Dimethoate	65-70 25-35	Ahmad et al., 2008
		Lab scale (crossflow)	Alachlor Atraton DEET Metolachlor	13.4±11.0 11.6±1.8 11.5±2.2 21.7±11.3	Comerton et al., 2008
TFC-8821ULP	Fluid Systems Co.	Lab scale (crossflow)	Atrazine MCPA Propham Triazimefon	89.6 89.4 89.8 78.5	Košutić et al., 2002
BQ-01	GE Water Technol. (Osmonics)	Lab and pilot scale	Atrazine Diuron Melazachlorine Simazine Terbutylazine	~50 ~68 ~35 ~20 ~45	Berg et al., 1997
CK	GE Water Technol. MWCO 200Da	Lab scale (crossflow)	Dichloroaniline	<25	Causseran d et al., 2005
Desal 5 DK	GE Water Technol. MWCO 150-300Da	Lab and pilot scale	Atrazine Diuron Melazachlorine Simazine Terbutylazine	~47 <10 ~73 ~35 ~53	Berg et al., 1997
		Pilot scale	Atrazine Cyanazine DEA Diuron Isoproturon Simazine	>95 >95 >95 ~75 ~95 ~95	Boussahel et al., 2000, 2002
		Lab scale (dead-end)	Dichloroaniline	60-95	Causseran d et al., 2005
		Lab scale (dead-end)	Atrazine Dimethoate	75-82 62-75	Ahmad et al., 2008
Desal 5 DL	GE Water Technol. MWCO 150-300Da	Lab scale (crossflow)	Atrazine Simazine	~58 ~45	Zhang et al., 2004
Desal 51HL	GE Water Technol. MWCO 150-300Da	Lab scale (crossflow)	Atrazine Simazine	~71 ~70	Zhang et al., 2004

Table A. Continued

Membrane	Specifications	Remarks	Pesticides	Retention (%)	Reference
NF-CA 50	Hoechst	Lab and pilot scale	Atrazine	<10	Berg et al., 1997
			Diuron	<10	
			Melazachlorine	~20	
			Simazine	<10	
			Terbutylazine	~15	
CPA2	Hydranautics	Lab scale (crossflow)	Atrazine	95.9	Košutić et al., 2005
			Dichlorvos	94.7	
			Triadimefon	78.3	
		Lab scale (crossflow)	Atrazine	88.9	Košutić et al., 2002
			MCPA	82.3	
			Propham	80.7	
PVD1	Hydranautics	Lab and pilot scale	Atrazine	~89	Berg et al., 1997
			Diuron	~83	
			Melazachlorine	>95	
			Simazine	>90	
			Terbutylazine	>95	
NTR-7250	Nitto Denko	Lab and pilot scale	Atrazine	>95	Berg et al., 1997
			Diuron	~67	
			Melazachlorine	>95	
			Simazine	>90	
			Terbutylazine	>95	
		Lab scale (dead-end)	Anilazine	72.8	Kiso et al., 2000
			Atrazine	68.4	
			Chlorpyrifos	>99.95	
			Diazinon	95.1	
			Dichlorvos	46.2	
			Imidacloprid	54.6	
			Isoprothiolane	93.7	
			Malathion	88.1	
			Molinate	60.7	
			Pyridine	5.52	
			Simazine	59.8	
			Simetryn	57.6	
			Thiram	56.4	
			2,3,5-Trichloropyridine	88.9	

Table A. Continued

Membrane	Specifications	Remarks	Pesticides	Retention (%)	Reference
		Lab scale (dead-end)	Carbaryl (NAC)	40.3	Kiso et al., 2001a
			Chloroneb	53.3	
			Chlorothalonil (TPN)	70.5	
			Esprocarb	99.6	
			Fenobucarb (BPMC)	79.4	
			Isoxathion	99.8	
			Mefenacet	94.9	
			Methyldymron	95.9	
			Propiconazole	97.6	
			Propyzamide	81.8	
			Tricyclazole	26.5	
NTR-7450	Nitto Denko MWCO 600-800Da	Lab scale (crossflow)	Atrazine	19.2-19.8	Van der Bruggen et al., 1998
			Diuron	2.8	
			Isoproturon	15.5	
			Simazine	14.6-15.5	
		Lab scale (dead-end)	Anilazine	29.3	Kiso et al., 2000
			Atrazine	14.9	
			Chlorpyrifos	99.32	
			Diazinon	44.8	
			Dichlorvos (DDVP)	13.0	
			Imidacloprid	3.70	
			Isoprothiolane	36.3	
			Malathion	42.0	
			Molinate	20.4	
			Simazine	9.15	
			Simetryn	6.95	
			Thiram	18.7	
			2,3,5-Trichloropyridine	96.5	
		Lab scale (dead-end)	Carbaryl (NAC)	23.2	Kiso et al., 2001a
			Chloroneb	98.6	
			Chlorothalonil (TPN)	69.7	
			Esprocarb	98.7	
			Fenobucarb (BPMC)	14.6	
			Isoxathion	99.6	
			Mefenacet	90.0	
			Methyldymron	32.9	
			Propiconazole	72.4	
			Propyzamide	16.9	
			Tricyclazole	1.7	

Table A. Continued

Membrane	Specifications	Remarks	Pesticides	Retention (%)	Reference
		Lab and pilot scale	Atrazine	~53	Berg et al., 1997
			Diuron	~25	
			Melazachlorine	~73	
			Simazine	~45	
			Terbutylazine	~58	
CE 100	Spectrum MWCO 100Da	Lab scale (dead-end)	Atrazine	~48	Devitt et al., 1998a
CE 500	Spectrum MWCO 500Da	Lab scale (dead-end)	Atrazine	~13	Devitt et al., 1998a
NTC-60	Toray	Lab and pilot scale	Atrazine	~90	Berg et al., 1997
			Diuron	~58	
			Melazachlorine	~90	
			Simazine	~85	
			Terbutylazine	~93	
NTR-729 HF	Nitto Denko	Lab scale (dead-end)	Carbaryl (NAC)	92.4	Kiso et al., 2001a
			Chloroneb	93.9	
			Chlorothalonil(TPN)	96.1	
			Esprocarb	99.94	
			Fenobucarb (BPMC)	94.8	
			Isoxathion	99.84	
			Mefenacet	99.1	
NTR-729 HF	Nitto Denko	Lab scale (dead-end)	Methyldymron	98.4	Kiso et al., 2001a
			Propiconazole	96.9	
			Propyzamide	98.6	
			Tricyclazole	79.6	
NTR-729 HF	Nitto Denko	Lab scale (dead-end)	Carbaryl (NAC)	92.4	Kiso et al., 2001a
			Chloroneb	93.9	
			Chlorothalonil (TPN)	96.1	
			Esprocarb	99.94	
			Fenobucarb (BPMC)	94.8	
			Isoxathion	99.84	
			Mefenacet	99.1	
			Methyldymron	98.4	
			Propiconazole	96.9	
			Propyzamide	98.6	
			Tricyclazole	79.6	

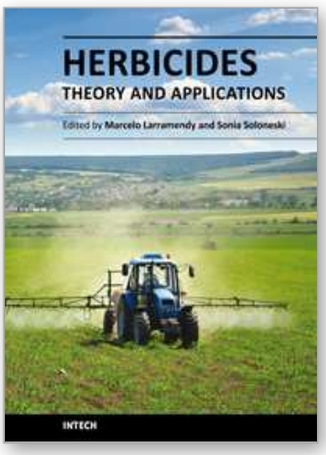
Table A. Continued

Membrane	Specifications	Remarks	Pesticides	Retention (%)	Reference
		Lab scale (dead-end)	Anilazine	99.3	Kiso et al., 2000
			Atrazine	97.5	
			Chlorpyrifos	>99.95	
			Diazinon	99.52	
			Dichlorvos (DDVP)	86.7	
			Imidacloprid	97.6	
			Isoprothiolane	99.76	
			Malathion	99.64	
			Molinate	98.5	
			Pyridine	18.5	
			Simazine	96.7	
			Simetryn	98.6	
			Thiram	97.7	
			2,3,5-Trichloropyridine	96.8	
NTR-7410	Nitto Denko	Lab scale (dead-end)	Anilazine	21.8	Kiso et al., 2000
			Atrazine	10.9	
			Chlorpyrifos	99.51	
			Diazinon	44.6	
			Dichlorvos (DDVP)	4.28	
			Imidacloprid	2.92	
			Isoprothiolane	28.1	
			Malathion	41.4	
			Molinate	20.0	
			Simazine	6.40	
			Simetryn	6.69	
			Thiram	8.42	
			2,3,5-Trichloropyridine	95.6	
		Lab scale (dead-end)	Carbaryl (NAC)	24.7	Kiso et al., 2001a
			Chloroneb	98.6	
			Chlorothalonil (TPN)	61.6	
			Esprocarb	94.6	
			Fenobucarb (BPMC)	17.8	
NTR-7410	Nitto Denko	Lab scale (dead-end)	Isoxathion	99.5	Kiso et al., 2001a
			Mefenacet	72.5	
			Methyldymron	22.6	
			Propiconazole	77.0	
			Propyzamide	22.4	
			Tricyclazole	1.8	

Table A. Continued

Membrane	Specifications	Remarks	Pesticides	Retention (%)	Reference
UTC-20	Toray MWCO 180Da	Lab scale (crossflow)	Atrazine Diuron Isoproturon Simazine	74.3-80.4 39.7 72.3 67.2-89.2	Van der Bruggen et al., 1998
		Lab scale (crossflow)	Atrazine Diuron Isoproturon Simazine	84.2 50.0 73.0 71.4	Berg et al., 1997
		Lab scale (crossflow)	Atrazine Simazine	~95 ~80	Zhang et al., 2004
UTC-60	Toray MWCO 150Da	Lab scale (crossflow)	Atrazine Diuron Isoproturon Simazine	83.2 49.0 79.0 71.4	Van der Bruggen et al., 2001
		Lab scale (crossflow)	Atrazine Simazine	~85 ~75	Zhang et al., 2004
TS80	TriSep Co. MWCO <200Da	Lab scale (crossflow)	Atrazine MCPA Propham Triazimefon	81.2 91.2 84.3 58.1	Košutić et al., 2002
		Lab scale (crossflow)	Alachlor Atraton DEET Metolachlor	41.8±2.8 21.7±9.4 18.1±6.2 50.5±7.9	Comerton et al., 2008
X20	TriSep Co. MWCO <200Da	Lab scale (crossflow)	Alachlor Atraton DEET Metolachlor	97.3±1.4 96.9±2.7 96.1±0.9 97.2±0.6	Comerton et al., 2008
HNF-1	Hollow fiber composite membrane	Lab scale (crossflow)	Alachlor Aldicarb Atrazine Methoxychlor Metolachlor Pirimicarb Simazine Thiobencarb	88.7 43.2 61.4 99.2 93.9 89.9 42.2 88.7	Kiso et al., 2002

Table A. Continued



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The content selected in Herbicides, Theory and Applications is intended to provide researchers, producers and consumers of herbicides an overview of the latest scientific achievements. Although we are dealing with many diverse and different topics, we have tried to compile this "raw material" into three major sections in search of clarity and order - Weed Control and Crop Management, Analytical Techniques of Herbicide Detection and Herbicide Toxicity and Further Applications. The editors hope that this book will continue to meet the expectations and needs of all interested in the methodology of use of herbicides, weed control as well as problems related to its use, abuse and misuse.

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