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Remediation of Pesticide-Polluted Waters Through Membranes

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Remediation of Pesticide-Polluted Waters Through Membranes

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Abstract: Pesticides are the man-made creation to protect the crops and household items. Too often running water can become insidiously polluted by pesticides. In this review, the possible paths in which water can be contaminated by pesticides are exposed. There are several techniques for water remediation. Membrane separation technique has its potentiality and is an advantageous technique amongst all. The performances of some commercial membranes in pesticides separation from water are enlisted. Factors such as the nature of membranes, nature of pesticides, presence of organic and inorganic matters, temperature and/or pH influence the pesticide separation are discussed.

Keywords: Pesticides, nanofiltration membrane, pores, Stokes radius, hydrophobicity, membrane charge

INTRODUCTION

Pesticides are chemicals designed to destroy pests, defined as unwanted living animal and/or vegetal organisms. Thus the term "pesticides" includes insecticides, herbicides, nematicides, acaracides, rodenticides, fungicides and so on. In the modern age, science is inseparably mixed up with life. So, scientists invented the pesticides, a chemical weapon to destroy the unwanted pests. The expected benefits of the use of pesticides are an enhanced productivity of crops and/or vegetables and the preservation of valuable household items.

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The goal was reached since today the human beings are totally dependent on pesticide use in agriculture as well as in the saving of vital household items. The most commonly used pesticides are synthetic organic compounds designed to interact with the various chemical processes in the pest's living body chemistry. Unfortunately, doing this, all pesticides may interact with the metabolism of non-targeted living organisms. With no exception, all pesticides bear some level of toxicity. Toxicity is the capability of the chemicals to poison. The alphabetic list of pesticide types includes:

- Algaecides: used to control algae in lakes, canals, swimming pools etc.
- Antimicrobials: to inhibit the growth of microorganisms (germs, microbes, bacteria and possibly viruses).
- Disinfectants/sanitizers: to kill or inactivate disease-producing microorganisms on inanimate surfaces.
- Fungicides: to destroy fungi (including blights, mildews, molds and rusts).
- Fumigants: they produce gas/vapor intended to destroy difficult to reach pests in building or soil.
- Herbicides: to control unwanted plants (weeds). Herbicides may be combined with other materials such as weeds and feed products.
- Insecticides: to kill insects and other anthropoids.
- Nematicides: to exterminate nematodes (non-segmented round worms) that infect roots of certain trees or crops.
- Pheromones: biochemicals used to disrupt the mating behavior of insects.
- Repellents: used to repel pests, including insects (such as mosquitoes) and birds.
- Rodenticides: to control mice, rats and other rodents.

The adverse effects of pesticides depend on their chemical characteristics and, especially, on the way there are used. The early chemicals used as pesticides were inorganic compounds based on arsenic, mercury, copper or lead. They were highly toxic. But, they were also not easily leached from the soil and therefore, they rarely appeared in groundwater. The use of synthetic chemicals as pesticides started in a large scale during the Second World War. The hydrophobic pesticides, which strongly bind with soil, are rarely found in water. The more polar compounds, which are significantly soluble in water and weakly adsorbed to soil, have a greater probability to percolate the natural bed and to reach natural groundwater reservoirs used by man.

Pesticides can be adsorbed through the skin and lungs as well as internally when present in drinking water. Adverse health effects are not expected from consuming water with pesticides at concentrations well below the health advisory levels. Potential health effects may and will be observed in people consuming water containing pesticide concentrations above the health advisory levels. The effects are highly variable depending on the kind and amount of pesticides, on how long the person will consume such polluted water, and on the person's overall health. Acute pesticide poisoning symptoms include headaches, dizziness, stomach and intestinal upset, spasms, convulsions and damage to nervous and reproductive systems. Long-term effects may result in cancer, kidney disorder, and heart problems (1, 2).

POSSIBLE REASONS OF PESTICIDE OCCURRENCE IN WATER

The possible modes by which pesticides could have occurred in groundwater or surface water include:

1. The nature of the pesticides: Pesticides, which have a significant polarity and a poor attachment with the soil, can seep into the natural filtration bed during recharge of groundwater and get into aquifers.
2. Uncertainty in climate: Unexpected rain on a treated area before the pesticide binds or degrades may carry the pesticide to surface water sources.
3. Direct addition: Pesticides are sometimes applied directly to lakes or wetlands to control aquatic weeds, insects or fish.
4. Improper application site or mode: Some pesticides can move in air from the application site (sprayed) to surface waters used in a drinking water system.
5. Ignorance factor: Pesticides are too often poorly handled as well as applied above the required level due to the ignorance factor. Excess of pesticides are washed out by rains and can easily percolate through soils to groundwater. When a pesticide is spilled, dumped or misused, the chance of it reaching aquifers is greatly increased. Pesticides can also get into drinking water when homeowners illegally dump unused pesticides down the drain. In water treatment plants, disinfectant pesticides are intentionally added to drinking water to help protect humans from disease causing organisms such as bacteria and viruses.

SEPARATION MECHANISMS

Three techniques are mainly used for pesticides: (1) Activated Carbon filtration, (2) Ozone/UV/H_2O_2 treatment and (3) Membrane Separation technique. The basic mechanisms of the techniques and their potentialities are rapidly described next.

Activated Carbon Filtration

This is primarily a physical process "adsorption" in which dissolved contaminants adheres to the porous surface of the carbon particles. The active carbon is prepared by subjecting it to steam and high temperature (1200°C) without oxygen (3). At this temperature, parts of carbon are oxidized in CO_2 by water vapor and hydrogen is formed. The gases are evacuated and microfractures and pores are generated in the carbon structure. It dramatically increases the carbon surface area making a useful material for the removal of contaminants. The contaminants are attracted to and held (adsorbed) onto the surface of the carbon particles. The efficiency of the adsorption process depends upon the characteristics of the carbon (particle and pore size, surface area, density and hardness) and of the contaminant (concentration, hydrophobicity, polarity and solubility of the contaminant and contaminant attraction to the carbon surface). The starting material for an activated carbon filter is typically petroleum coke, bituminous coal, lignite, wood products, coconut/peanut shells, which are all sources of carbon. In some cases the active carbon may be processed by an acid wash or coated with a compound dedicated to enhance the removal of some specific contaminants.

The active carbon is always crushed to produce a granular or pulverized black product. This creates small particles with more outside surface area available for compounds to enter the active carbon, yielding better results in contaminant removal. The origin of the carbon and the activation method used to prepare the final product determine the effectiveness of removal for specific contaminants. The duration of the contact time between the treated water and the carbon powder, determined by the water flow rate, also affects contaminant adsorption. The amount of carbon powder put in the filter obviously affects the contaminant removal yield. The amount of carbon also can affect how quickly the carbon becomes saturated and inefficient. Activated carbon filtration is an effective method of reducing pesticides as well as certain organic compounds and chlorine from water. It can also have the capability to reduce the quantity of lead, dissolved radon and harmless taste and odor-causing compounds (4, 5).

Ozone, UV and H_2O_2

Ozone, O_3, is an unstable form of oxygen. The tri-atomic form of oxygen is very unstable, wanting to lose the third oxygen atom and combine with whatever atom possible (oxidation). This property makes it the most active oxidizer known (excepting the very hazardous fluorine gas, F_2).

The first use of ozone as an oxidizing agent to disinfect water was tried in 1906 in France. In 1976, the combination of ozone, UV and hydrogen peroxide was started to create a technology running in flawless applications. It uses UV radiation and chemical oxidation to destroy the wide range of contaminants.

The very high oxidation potential of the ozone + peroxide association enables spontaneous reaction with most of the toxic organics. Ozone reacts with organic molecules i.e., pesticides in many ways: inserting oxygen into a benzene ring, breaking double bonds to form aldehydes and ketones, reacting with alcohol to form organic acids (6). UV radiation is powerful enough to break many covalent bonds. Apart from its own degradation ability, UV radiation can enhance the chemical oxidative property of other compounds. An UV/ozone/peroxide system is a destructive process, and the final products are only carbon dioxide and water.

Membrane Separation Techniques

Membrane separation is the most advanced filtration technology utilized to clarify, concentrate and separate continuously molecular or ionic compounds from their solution state. This process is potentially interesting for water processing, in particular in the treatment or recycling of water polluted by micron, submicron and/or ionic species. There are a number of membrane-based separation techniques, varying in the driving forces employed. These forces include concentration gradient, applied pressure and electrical potential. This review concentrates on the pressure-driven membrane separation technique only because it is the most useful for pesticide-polluted water remediation. The target is to separate solids from solid–liquid mixture. The features of pressure driven filtration techniques are described next.

Pressure-driven membrane processes are used widely today in different applications (7). There are basically four different processes to separate solids from solid–liquid mixture viz. microfiltration, ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (8). The separation ranges of various techniques have been illustrated in Figure 1. Microfiltration and ultrafiltration will not be commented since they are not used for pesticide removal.

FEATURES

Separation Mechanism Based on Size Exclusion

Nanofiltration (NF)

The naming of the method is linked to its capability: NF separates nano-ranged solute particles. In the membrane classification, NF-membranes are to be positioned between RO and UF membranes (9). NF needs relatively tight skin membranes with very small pores ($\sim$0.2 μm). Organic compounds in the 200 to 2000 molecular wt. ranges can be separated. The selective ability to separate multi-charge ions with moderate rejection of monovalent ions from water is the main characteristic of these membranes. Pressure in the order of magnitude of 7–15 kg/cm^2 (10–200 psi) is typically required. NF is also known as the “membrane softening process” (10).

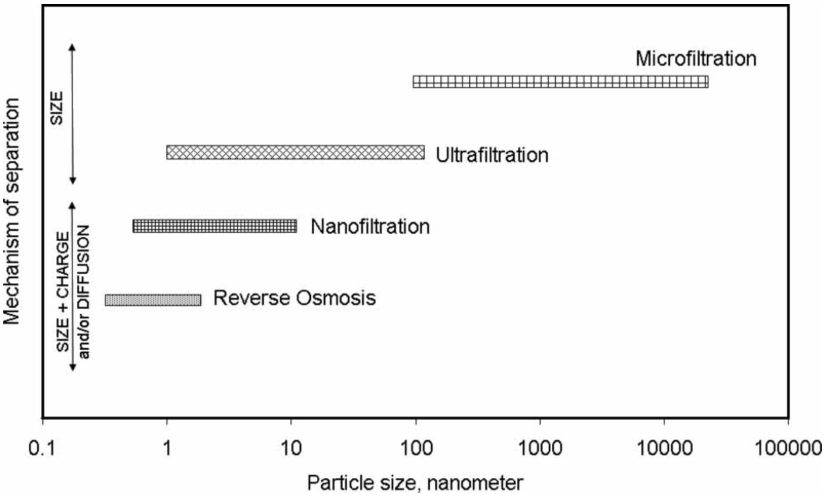


Figure 1. Comparison of mechanism and performance of pressure driven membrane processes.

Separation mechanism based on:

- Size exclusion for uncharged organic molecules,
- Electrostatic interactions between the membrane and the ions or mutual interaction between ions,
- Diffusivity and solubility of solute in the active layer of the membrane.

Reverse Osmosis (RO)

It employs the tightest skin membranes associated to the smallest pore size; 90 to 99% of all ions are rejected, like more than 99.9% of viruses. Bacteria and pyrogens are removed and virtually all organic compounds are eliminated. A high pressure, in the order of magnitude of 15 to 100 kg/cm^2 (200 to 1,200 psi), is normally required. The RO applications range from brackish water purification to seawater desalination. RO is also known as the "hyperfiltration" process.

Separation Mechanism Based on Charge Effect

Charge effect for charged low molecular weight solutes and size exclusion for low molecular weight organic solutes. The removal of the pesticides as well as organic pollutants by the usual methods such as adsorption by activated carbon (in powdered or granular form) or oxidation by ozone has some disadvantages. The limitation of carbon filters is that the filter saturates rapidly. That is why the cost is high due to the frequent change and/or regeneration of the carbon filter. Moreover, the method is not suitable for inorganic salt separation.

There are few limitations and dangers involved with the UV/ozone/peroxide treatment technology.

Ozone is also expensive, because it must be generated and immediately applied on site (6). It is explosive, toxic and an irritant to the skin, eyes, respiratory tract and mucous membrane (11). Hydrogen peroxide is an irritant that can even cause chemical burns, and it has explosive hazard property (12). Ultraviolet light can burn unprotected skin and especially eyes. The mercury in UV lamps can leak and damage the central nervous system, along with inflaming the nose and throat area (13). Ozone is also a significant air pollutant. Its concentration should always be monitored to ensure that ozone levels are never exceeding regulatory concentrations (6).

Recently the removal of organic pollutants by membrane retention (reverse osmosis, ultrafiltration and nanofiltration) has become increasingly popular. Due to its low cost, nanofiltration and low pressure reverse osmosis have both become interesting options. Apart from the pesticides, RO and NF can remove dissolved organic matter, color, sulfate, heavy metal complexes and some organic pollutants from water.

BASIC EXPRESSION

The rejection rate R (%) is calculated by the following expression (14–16):

$$R = (1 - C_p/C_r) \times 100$$

where C_p and C_r are the pesticide concentrations in the permeate and the retentate (avoiding the concentration polarization term). This equation is the only one needed to evaluate the capabilities of a particular membrane.

FACTORS INFLUENCING PESTICIDES REMOVAL

The removal of pesticides through the membrane process depends upon several factors, described next.

Physical Characteristics of the Membrane

Pores/Porosity of the Membrane

The rejection of pesticides is prevalently governed by the sieving mechanism based on the pore sizes of the membranes. The separation ability of the membrane is controlled by the size and number of pores defined as the polymer material-free void space through which fluid transport can take place under a driving force. Irregular packing of almost randomly kinked stiff-chain molecules causes it. The pores can be circular and cylindrical in shape or irregular (17). They can be open or closed, and may or may not form a continuous and interconnecting network. The pore size of the NF/RO membrane for the separation of pesticide molecules will be best suited. The pores/porosity of a membrane can be generally measured by different physical techniques (e.g., thermoporometry, gas adsorption/desorption (BET method), electron and/or atomic force microscopy, bubble press/ solvent permeability etc.) (18–23) as well as indirect methods based on the surface pore flow model (24) developed by Kastelan-Kunst et al. (25, 26).

The membrane pores are indirectly related to molecular weight cut off (MWCO), a well-acquainted term to characterize a membrane. MWCO is expressed as the molecular weight of a compound that is 90% rejected. There are many uncharged organic markers (e.g., alcohols, ketones etc.) used to characterize a membrane. Membranes, which have a MWCO lower than 400 Da are best fitted for the rejection of pesticides that are mostly molecules with a general molecular weight between 200 and 400 Da (16). The rejection threshold of membranes having a smaller molecular weight cut off (e.g., UTC 20, UTC 60) is significantly higher. However, in special cases involving small molecules such as diuron, membrane with small MWCO will be needed (e.g., Desal DK in that case). More examples will be described later.

Charge of the Membrane

The charge of the RO and NF membrane arises due to a special treatment (e.g. sulfonation, ion implantation, adsorption of surfactants, polyelectrolytes and charged macromolecules) on the base polymer (27). The negative charge of cellulose acetate is created after a post treatment with acetic anhydride or dissociation of dicarboxylic organic acid. The charge of the thin film composite (cross-linked polyamide) membrane is due to the presence of residual –COOH group in the polyamide structure. Typically polyamide membranes contain a net negative charge, but positive charge-carrying membranes do exist. The rejection of non-ionic solutes also depends upon the membrane charge if the molecules are somewhat polar (dipole moment $> 3D$). The charge of the membrane influences the orientation of the pesticide molecule and it will pass through the membrane. As it also depends upon the nature of the pesticide molecules, the details will be given later.

Salt Separation Ability

Kiso et al. tried to correlate the membrane rejection rate with its desalting property (14). They showed that the decrease in desalting property was correlated with the decreasing rejection ability of pesticides. They found that the different membrane materials were responsible for the poor correlation. When the solution fluxes are different (one was double compared to another) and the membranes are made of same material (NTR-729HF/NTR-7250 or NTR-7450/NTR-7410) (Table 1), the rejection of the pesticides basically depends on the ratio flux over pore size. However, in the case of hydrophobic petrochemical pollutants, a lower rejection rate was observed with the highest salt rejection membrane. The order of the rejection degrees of the pesticides is NTR-729HF > NTR-7250 > NTR-7450 > NTR-7410 as listed in the Table 1. The performance in salt rejection is listed in Table 2. However, chloropyrifos is the exception of the lot. It is rejected at a very high degree (>99.3%) by all membranes.

Nature of Pesticides

Apart from the nature of the membranes, rejection of the pesticides also depends on its own physicochemical properties, size, charge, polarity as discussed next.

Size of the Pesticides

The main rejection mechanism depends on size exclusion, so the first and foremost condition to reject pesticides by the membrane is their size. Though membrane molecular weight cutoff (MWCO) apparently signifies the size of the pesticides that will be rejected, it is better to consider the pesticide volume, which is proportional to its diameter. The pesticide's Stokes diameter and its equivalent molar diameter are the proper terms to be considered.

The Stokes radius, r_d, is determined by the following equation (28, 29):

$$r_d = kT/(6\pi\eta D_w),$$

where k is the Boltzmann constant, T is the absolute temperature, η is the viscosity of water and D_w is the pesticide diffusion co-efficient.

However, there are some limitations in calculating Stokes radiuses for the pesticides molecules. In the calculation process, the molecule is considered as spherical, but it may not actually be. Moreover, diffusion coefficient data is not readily available for many pesticides (30). Considering molecules that are not spherical in shape, different parameters (e.g., STERIMOL, molecular mean size, MMS) are reported to estimate the molecular size of the pesticides (29, 30). It was found that for the filtration membranes with MWCO > 500 Da, molecular width and molecular mean size are slightly better than molecular weight. For nanomembranes with MWCO < 250 Da, the molecular width parameter has a better correlation with the rejection rate than MMS and molecular weight in the case of alcohols and saccharides. The molecular weight and molecular width data

Table 1. Performance of pesticides removal for some commercial membranes

Membrane type	Specifications	Pesticides	Performance (%)	Ref.
Desal DK	Osmonics Desal Polyamide MWCO 150–300	Atrazine	>90%	(46)
		DEA	>90%	
		Simazine	>90%	
		Cyanazine	>90%	
		Isoproturon diuron	>70%	
NF200	Filmtec Dow Chem. Polyamide MWCO 300	Atrazine	>80%	(46)
		DEA	∼75%	
		Simazine	∼75%	
		Cyanazine	∼80%	
		Isoproturon	∼75%	
		diuron	45%	
NTR-729 HF	Nitto Denko Poly(vinyl alcohol)/polyamide	Imidacloprid	97.6	(14)
		Dichlorvos	86.7	
		Simazine	96.7	
		Simetryn	98.6	
		Atrazine	97.5	
		Thiram	97.7	
		Malathion	99.64	
		Molinate	98.5	
		Isoprothiolane	99.76	
		Diazinon	99.52	
		Chloropyrifos	>99.95	
		Anilazine	99.3	
		Pyridine	18.5	
		2,3,5-trichloro pyridine	96.8	
NTR-7250	Nitto Denko Poly(vinylalcohol)/polyamide	Imidacloprid	54.6	(14)
		Dichlorvos	46.2	
		Simazine	59.8	
		Simetryn	57.6	
		Atrazine	68.4	
		Thiram	56.4	
		Malathion	88.1	
		Molinate	60.7	
		Isoprothiolane	93.7	
		Diazinon	95.1	
		Chloropyrifos	>99.95	
		Anilazine	72.8	
		Pyridine	5.52	
		2,3,5-trichloro pyridine	88.9	

(*continued*)

Table 1. Continued

Membrane type	Specifications	Pesticides	Performance (%)	Ref.
NTR-7450	Nitto Denko Sulfonated polyethersulfone	Imidacloprid	3.7	(14)
		Dichlorvos	13.0	
		Simazine	9.15	
		Simetryn	6.95	
		Atrazine	14.9	
		Thiram	18.7	
		Malathion	42.0	
		Molinate	20.4	
		Isoprothiolane	36.3	
		Diazinon	44.8	
		Chloropyrifos	99.32	
		Anilazine	29.3	
		Pyridine	96.5	
		2,3,5-trichloro pyridine		
NTR-7410	Nitto Denko Sulfonated polyethersulfone	Imidacloprid	2.92	(14)
		Dichlorvos	4.28	
		Simazine	6.4	
		Simetryn	6.69	
		Atrazine	10.9	
		Thiram	8.42	
		Malathion	41.4	
		Molinate	20.6	
		Isoprothiolane	28.1	
		Diazinon	44.6	
		Chloropyrifos	99.51	
		Anilazine	21.8	
		Pyridine	95.6	
		2,3,5-trichloro pyridine		
NF70	Dow/Film Tec.	Simazine	96.4	(15)
		Atrazine	96.8	
		Diuron	91.6	
		Isoproturon	95.7	
NF45	Dow/Film Tec. MWCO 200	Simazine	82.6	(15)
		Atrazine	92.4	
		Diuron	50.6	
		Isoproturon	76.5	
UTC20	Toray Inc. MWCO 180	Simazine	78.0	(15)
		Atrazine	87.5	

(*continued*)

Table 1. Continued

Membrane type	Specifications	Pesticides	Performance (%)	Ref.
		Diuron	47.9	
		Isoproturon	71.1	
NTR-7450	Nitto-Denko-7450	Simazine	17.4	(15)
		Atrazine	26.2	
	MWCO	Diuron	6.4	
	600–800	Isoproturon	23.1	
HR		Atrazine	99	(38)
		MCPA	93.6	
		Triadimefon	82.9	
		Propham	96.8	
ULP		Atrazine	89.6	(38)
		MCPA	89.4	
		Triadimefon	78.5	
		Propham	89.8	
CPA2		Atrazine	88.9	(38)
		MCPA	82.3	
		Triadimefon	80.7	
		Propham		
TS80		Atrazine	81.2	(38)
		MCPA	91.2	
		Triadimefon	58.1	
		Propham	84.3	
Desal 5	Osmonics	Simazine	70	(43)
1HL	MWCO	Atrazine	71	
	150–300			
Desal	Osmonics	Simazine	45	(43)
5DL	MWCO	Atrazine	55	
	150–300			
UTC20	Toray Inc.	Simazine	80	(43)
	MWCO 180	Atrazine	95	
UTC60	Toray Inc.	Simazine	75	(43)
	MWCO 150	Atrazine	86	
4040 Spiral	Film Tec	Atrazine	86.1	(66)
wound	MWCO 200	Bentazone	100	*Reco
Polyamid		Cyanazine	92.2	very
eNF		Diuron	50.1	50%
membrane		DNOC	60.8	Flux
		Mecoprop	93	10gfd
		Metamitron	87.5	

(*continued*)

Table 1. Continued

Membrane type	Specifications	Pesticides	Performance (%)	Ref.
		Metribuzin	100	
		Pirimicarb	71.6	
		Simazine		
HNF1	Hollow fiber composite membrane	Atrazine	61.4	(34)
		Pirimicarb	89.9	
		Simazine	42.2	
		Aldicarb	43.2	
	Skin layer:Polyamide	Alachloro	88.7	
		Metolachlor	93.9	
		Methoxychlor	99.2	
		Thiobencarb	88.7	
NF70	Film Tec/Dow Chem. Co	Atrazine	93.48	(42)
		Simazine	90.13	
		Diuron	92	
		Isoproturon	90	
NF45	Film Tec/Dow Chem. Co	Atrazine	86.98	(42)
		Simazine	64.49	
		Diuron	51	
		Isoproturon	75	
UTC20	Toray Ind. Inc	Atrazine	84.19	(42)
		Simazine	71.4	
		Diuron	50	
		Isoproturon	73	
UTC60	Toray Ind. Inc	Atrazine	83.25	(42)
		Simazine	71.40	
		Diuron	49.76	
		Isoproturon		
NF45	Filmtec, Dow Chem. Co	Atrazine (280 μg/L)	31	49 *Raw water
NF200	Filmtec, Dow Chem. Co	Atrazine (280 μg/L)	38	49 *Raw water
YC05	Amicon MWCO 100 Da	Atrazine (280 μg/L)	10	49 *Raw water

of some pesticides are listed in Table 3. The molecular structure of pesticides is also determined using the computer programme Hyperchem (31). The energy of a given molecule can be minimized by adjusting the configuration of the molecules with this program (32).

Table 2. Performance of salt rejection of membranes

Membrane	NTR-729HF	NTR-7250	NTR-7450	NTR-7410
NaCl rejection (%)	92	60	51	15

Although the molecular weight is not a direct measure of the dimensions of a molecule, it still reflects the molecular size and it is a readily accessible parameter, whereas complicated calculations are necessary to obtain the effective diameter. Vanderbruggen et al. (33) proposed an empirical relationship between the effective diameter, D_d, and molecular weight, MW, of a pesticide. Their equation is simply $D_d = A(MW)^B$ where $A = 0.065$ and $B = 0.438$. This correlation is valid for the molecular weight range up to 600 Da.

The rejection rate is positively correlated with molecular weight, as well as molecular width (34). This substantiates that the rejection mechanism is primarily controlled by size exclusion. The rejection mechanism of the pesticides could be sketched by Figures 2 and 3.

In the study of Kiso et al. (14, 35), the relatively high rejection rate for the pesticide malathion, compared to the other studied pesticides and using the same membranes NTR-7450 and NTR-7410 (Table 1) could be explained by the relatively high molecular width of malathion. Diazinon has a rejection rate nearly comparable to that of malathion. It is noted that both pesticides have very similar molecular width.

Hydrophobic Nature of the Pesticides

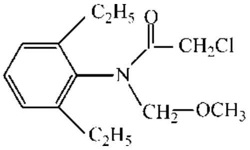
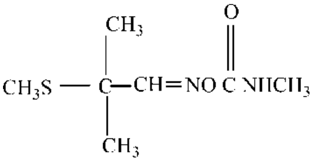
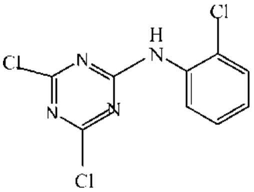
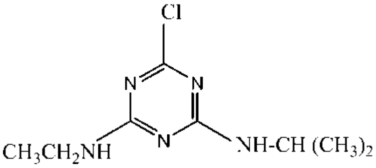
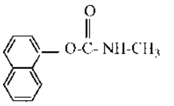
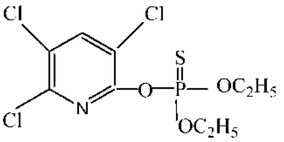
The rejection rate of the pesticides is also influenced by the polarity or hydrophobic nature of the solutes. Molecular hydrophobicity is usually estimated using the octanol/water partition coefficient of the molecule in the form log P (14). The log P values of the studied pesticides are listed in Table 3. Log P is simply defined by:

$$\log P = \log(C_0/C_w)$$

where C_0 and C_w are, respectively, the pesticide concentrations in the n-octanol and water liquid phases.

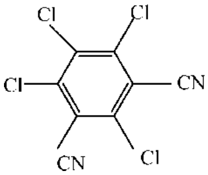
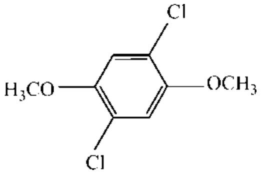
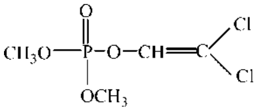
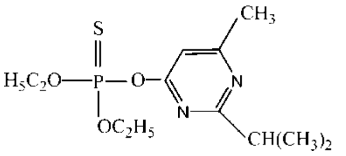
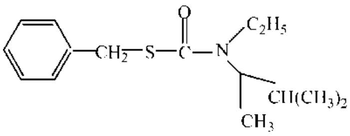
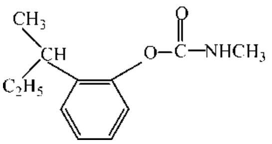
The rejection rate is positively correlated with log P (36) for aromatic as well as non-phenyl containing pesticides as shown by Kiso et al. (37) (Figure 4). In the other study of Kiso et al. (14), the high rejection of chloropyrifos could not be explained by the molecular weight/molecular width factors. Hydrophobic effects involving the log P values were significantly correlated. Indeed the largest log P value of the studied pesticides belonged to chloropyrifos (Table 3). However, hydrophobic effects alone cannot explain all observed differences. In a study, the log P of the pesticides could not

Table 3. Structure, molecular weight and log *P* values for most common pesticides

Name of pesticides	Molecular mass	Molecular width, nm	log *P*	Ref.
Alachlor 		0.508	3.42	(34)
Aldicarb  $CH_3S-C(CH_3)_2-CH{=}NOC(O)NHCH_3$	190.3	0.38	1.11	(34)
Anilazine 	275.5	0.358	3.00	(14)
Atrazine 	215.7	0.444	2.61	(14)
Carbaryl(NAC) 	201.2	0.377	2.36	(35)
Chloropyrifos 	350.6	0.485	5.27	(14)

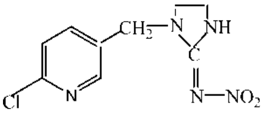
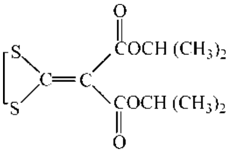
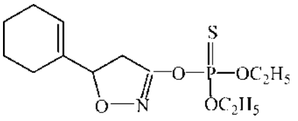
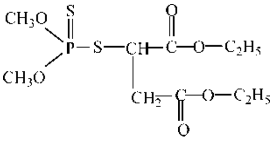
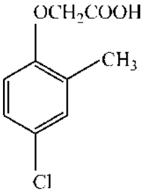
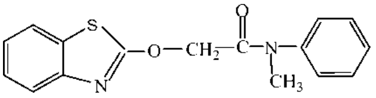
(*continued*)

Table 3. Continued

Name of pesticides	Molecular mass	Molecular width, nm	log P	Ref.
Chlorothalonil (TPN) 	265.9	0.320	2.90	(35)
Chloroneb 	207.1	0.365	3.09	(35)
Dichlorovos 	221.0	0.410	1.43	(14)
Diazinon 	304.4	0.547	3.81	(14)
Esprocarb 	265.4	0.446	4.52	(35)
Fenobucarb (BPMC) 	207.3	1.201	2.78	(35)

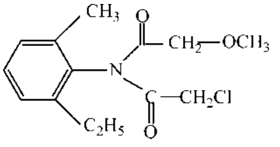
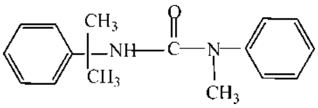
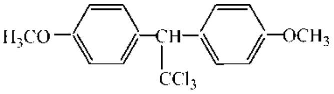
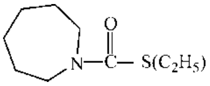
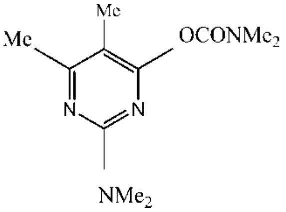
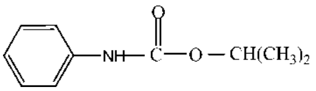
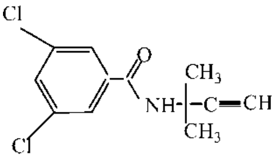
(*continued*)

Table 3. Continued

Name of pesticides	Molecular mass	Molecular width, nm	log P	Ref.
Imidacloprid 	255.7	0.407	0.57	(14)
Isoprothiolane 	290.4	0.437	3.32	(34)
Isoxathion 	313.3	0.459	4.77	(35)
Malathion 	330.4	0.510	2.36	(14)
MCPA 	200.6	0.632	2.8	(38)
Mefenacet 	298.4	0.354	3.23	(35)

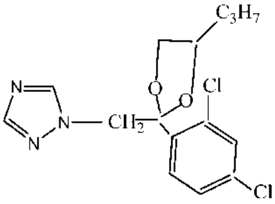
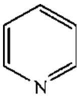
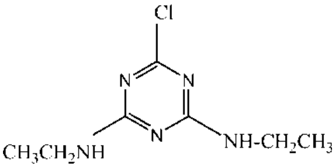
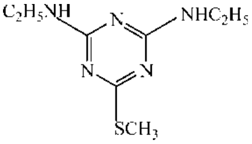
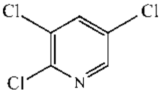
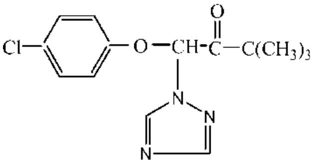
(*continued*)

Table 3. Continued

Name of pesticides	Molecular mass	Molecular width, nm	log *P*	Ref.
Metolachlor 	283.8	0.474	3.02	(34)
Methyl dymron 	268.4	0.406	2.56	(35)
Methoxychlor 	345.7	0.467	4.43	(34)
Molinate 	187.3	0.376	2.88	(14)
Pirimicarb 	238.3	0.404	1.71	(34)
Propham 	179.2	0.627	2.60	(38)
Propyzamide 	256.1	0.437	3.17	(35)

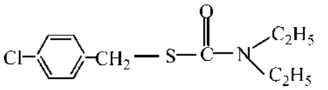
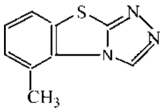
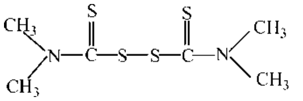
(*continued*)

Table 3. Continued

Name of pesticides	Molecular mass	Molecular width, nm	log *P*	Ref.
Propiconazole 	342.2	0.481	4.58	(35)
Pyridine 	79.1	0.267	0.65	(14)
Simazine 	201.7	0.329	2.18	(34)
Simetryn 	213.3	0.35	2.54	(14)
2,3,5-Trichloropyridine 	182.4	0.299	3.11	(14)
Triadimefon 	293.8	0.743	2.77	(38)

(*continued*)

Table 3. Continued

Name of pesticides	Molecular mass	Molecular width, nm	log *P*	Ref.
Triobencarb 	257.8	0.404	4.14	(34)
Tricyclazole 	189.2	0.331	1.70	(35)
Thiram 	240.4	0.344	1.62	(14)

explain the important rejection differences (38). A similar case occurring with alkyl phthalate was reported (30).

Electrical Interaction with Polarizable Pesticides

Kosutie et al. (38) showed that the ionic charge built in some membranes will certainly influence the rejection of ionized solute molecules (39). However, for

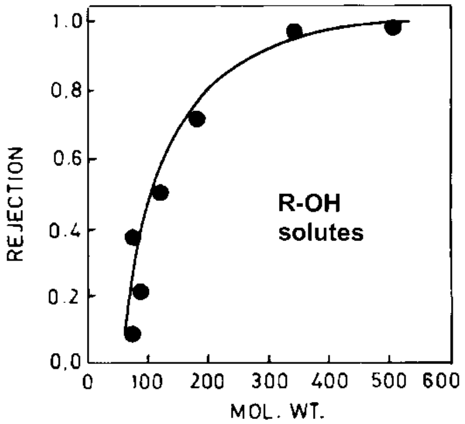


Figure 2. Variation of rejection rate with molecular weight. (adapted from Ref. 34). Membrane: hollow fiber NF; solutes: n-butanol, t-butanol, glycerol, trimethylolethane, glucose, lactose, raffinose.

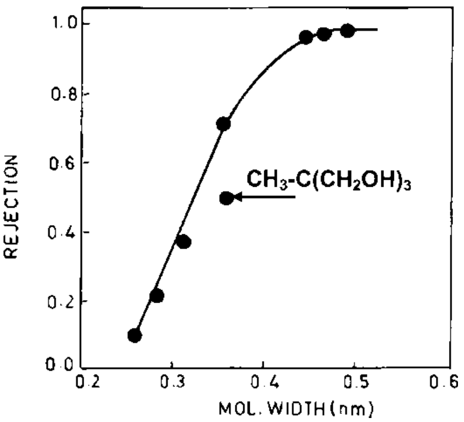


Figure 3. Variation of rejection with molecular width. (adapted from Ref. 34) Membrane: hollow fiber NF; solutes: n-butanol, t-butanol, glycerol, trimethylolethane, glucose, sucrose, lactose, raffinose

the rejection of non-ionic solutes (40), the dipolar character of the solute molecule in the membrane material/solvent/non-ionic solute system should be considered. It has been indicated that a high dipole moment of a molecule (with value above 3 Debye) might decrease the solute rejection by NF membranes (15). A plausible explanation for such effect is that, by electrostatic attraction, the dipolar molecule is oriented and directed towards the membrane charge in such a way that the side of the dipole with the opposite charge is closer to the membrane. This direction is not static, but must be seen as a statistical tendency of the fast-moving molecules to have this preferential orientation (41). The dipole is thus directed towards the pores and enters

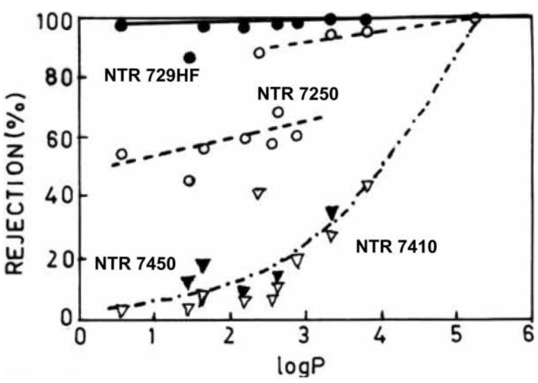


Figure 4. Relationship between rejection degree and log P, ● NTR 729HF, ○ NTR 7250, ▼ NTR 7450 and ▽ NTR 7410 (adapted from Ref. 14).

more easily into the membrane structure. Because entry into the membrane structure is facilitated, a higher fraction of polarizable molecule permeates through the membrane, compared to non-polarizable molecules with the same size. This explains the lower rejection rate observed with electrically charged membranes for polarizable molecules (Figure 5).

In a study by Van der Bruggen et al. (42) two polarizable pesticides (diuron and isoproturon) with a high dipole moment were less efficiently removed because the dipoles were directed perpendicularly to the membrane, rendering the pesticide permeation more difficult. The molecular dipole moment is important for membranes with an average pore size that is larger than the components to be retained such as the UTC-20 membrane (pore diameter 1.08 nm). The rejection rate for diuron was the lowest because it has the largest dipole moment among the pesticides studied. The rejection of simazine is lower because this pesticide has a smaller molecule. As the dipole moment of isopoturon is higher, its rejection is lower than the rejection of atrazine even though the isoproturon molecule is larger. It means that the membrane charge effect is more important and controls the rejection rate rather than the size effect.

The electrostatic repulsions by the charged TS 80 NF membrane are the cause of the high rejection of MCPA (Table 1). The rejections of the non-ionized pesticide molecules by the same RO membrane either HR or ULP can be due to physicochemical factors (viz. dipole moment). The highest rejection of atrazine followed by the slightly lower propham rejection and the remarkably lowest rejection values of triadimefon are all explained by the dipole moment of the pesticide molecules. It is apparent that molecules with a carbonyl group have higher dipole moments and are less rejected by charged membranes (15). In this study it has been shown that the triadimefon

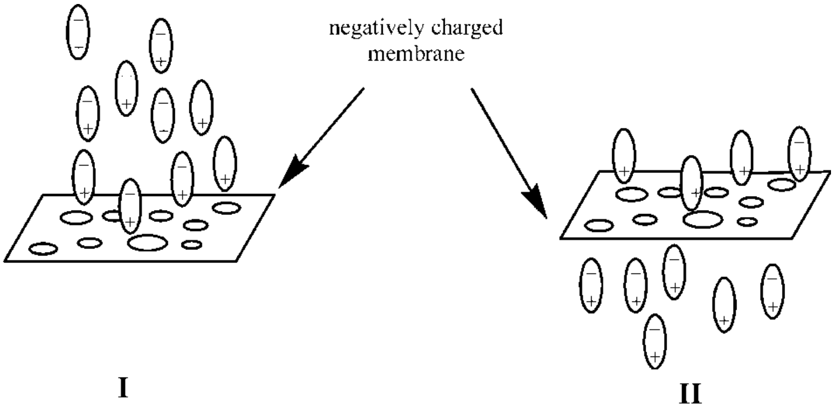


Figure 5. A sketch view of the permeation of polar compounds through a negatively charged membrane. I. Direction of polar pesticides to the membrane. II. Permeation through the charged membrane.

molecule had the highest dipole moment and its rejection rate by all the membranes was the lowest compared to other pesticides including atrazine. However, the polarizability effect cannot explain the rejection rate obtained with propham, which is polarizable since it also contains a carbonyl group in its molecule and cannot permeate as easily as other pesticides (38).

Chemical Structure of the Pesticides

Apart from the above factors, the rejection of pesticides also depends on their chemical structure. Zhang et al. (43) has observed rejection rate differences between atrazine and simazine, in agreement with a previous work by Van der Bruggen et al. (42). The structure of the atrazine is different from that of simazine (Table 3). The higher rejection rate of atrazine (~10%) is probably due to the larger steric hindrance caused by the branched methyl group (15). Berg et al. (44) explained better rejection of terbutyl azine (having three methyl groups) than atrazine and simazine in a similar manner. Here also simazine shows the lowest rejection among the three pesticides studied.

Kiso et al. have studied the higher rejection rate of phenyl containing pesticides compared to pesticides without any aromatic ring in their structure. They used a hollow fiber NF membrane (HNF-1) (34), and considered the sorption property of the membrane. The membrane can adsorb the pesticides when they are submerged in the pesticide solutions. The support layer as well as skin layer of the membrane may contribute to the sorption of the pesticides and these effects are very difficult to distinguish. Sorption property is evaluated by the partition coefficient expressed by the equation

$$K = Q/C_b$$

where Q is the sorption amount per unit area (in $\mu g/cm^2$), C_b is the concentration in bulk solution (in mg/L) and the unit of K is $[\mu g\, cm^{-2}]/[mg\, L^{-1}]$. The variations of log K vs log P is shown in Figure 6. It shows that the sorption is controlled by the hydrophobicity of the pesticide. Moreover, phenyl containing pesticides are entrapped more effectively than non-phenylic pesticides, although no linear relationship is observed for all the pesticides studied. This suggests that, in addition to hydrophobicity, other factors influence the pesticide sorption.

Although the Kiso research group has shown that the presence of phenyl groups in pesticide molecules could have an effective influence on the rejection rate, later, in another study with other membranes (14), they also showed that pesticides with phenyl group (i.e., anilazine) showed only slightly higher rejection rate than others without. It can be concluded that the effects of phenyl groups are not critical.

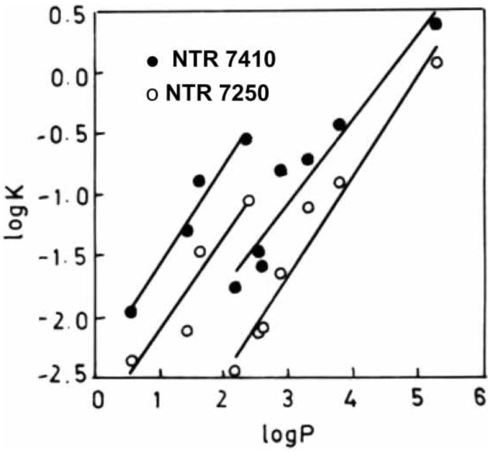


Figure 6. Relationship between log P and log K. K: the partition coefficient of pesticide between membrane and bulk solution in $(\mu g/cm^2)/(mg/L)$. (adapted from Ref. 14).

Nature of the Water Matrix

Influence of Inorganic/Organic Matters Present in Water

The removal of pesticides not only depends on the nature of the membrane and pesticide molecule; it also depends on the presence of compounds (inorganic or organic) present with the pesticides in the aqueous matrix. In presence of inorganic ions, the difference in rejection of pesticides can be caused by interactions between ions and the membrane. It has been evidenced that ion adsorption might play a significant role in nanofiltration (39, 45). Such adsorption may narrow the membrane pores and lead to higher rejections. Boussahel et al. (46) have studied the removal of pesticides in presence of Ca^{2+} cations. They have shown that the removal efficiency of the NF 200 membrane is improved with 5% of $CaCl_2$ and 10% of $CaSO_4$ for the pesticides listed in Table 1. This is probably due to the blocking of pores by ions at high concentrations (16, 47). At higher ionic concentration, a reduction in the electrostatic forces of intra-membraneous repulsion is reflected by a reduction effect in the actual sizes of the pores and a lower permeability of the membrane. Consequently, a better elimination of the pesticides is observed (48). The blocking effect of pesticides is accentuated by the retention of divalent anions (sulfates) in the membrane matrix (14). However, in case of the desal DK membrane, the removal efficiency is not following the same trend and a slight decrease in the removal efficiency of desethylatrazine and simazine was observed upon addition of $CaCl_2$.

The presence of dissolved organic macromolecules (humic acids) also influenced the rejection of pesticides. The general feature is that, with the formation of pesticide-macromolecule associations, the sizes of the pseudo-complexes are large and they are rejected primarily by size exclusion as studied by Devitt et al. (49). Weak interactions by H-bonding as well as mechanical trapping of atrazine by association with tannic/humic acids can occur. Macromolecular conformation may change with the increase in ionic strength (50, 51). Ionic coverage can alter the interaction sites for atrazine, making atrazine macromolecular association with organic material more reversible. Moreover, it has also been observed that the addition of calcium or sodium salts tended to increase the retention of tannic acids while decreasing atrazine rejection. Increasing ionic strength results in charge shielding and neutralization of the organic matter charged functional groups and can shrink the natural organic matter matrix.

Apart from the improvement in the removal of pesticides in presence of organic matter (humic acids) decrement also can happen. Boussahel et al. have observed that the remediation efficiency is increased by the presence of organic matter with the NF 200 membrane compared to distilled water solution (except for the removal of diuron) (46). The opposed result was observed with the DESAL DK membrane that is less effective when organic material is found in solution. With this membrane, a slight decrease in the removal of desethyl, atrazine, simazine, isoproturon, and a substantial drop for diuron (20%) has been observed with no change for cyanazine and atrazine. This can be explained by the nature of the membrane on which adsorption can take place through physisorption as well as chemisorption.

The steric congestion and density of the pseudo-complexes (pesticide-organic matter) are high, which facilitates the elimination of certain pesticides with the (wide pore) NF 200 membrane by accentuating the effects of steric exclusion, electrostatic repulsion and thus decreasing adsorption. The increased adsorption of the pesticides on the DESAL DK membrane generates a negative influence on the removal of some pesticides. As diuron has no ability to bind to humic acids, its removal rate is not changed when a wide pore (NF 200) membrane is used. However, a greater adsorption of organic matter by the narrower-pore such as the Desal DK membrane favored diuron adsorption and, consequently, its diffusion into permeate.

In the above part, the interaction of pesticides with the matter present in water was treated. Now, it will be focused on the pesticide removal performance related to membrane deterioration due to the presence of matter in the feed water. Many micro-organisms as well as humic acids and micro-pollutants cause membrane fouling. The consequences of the fouling are membrane performance as well as lifetime deteriorations.

Running waters contain natural organic matter (e.g., humic acids) that interacts with membranes affecting their performance in pesticide removal. Generally, humic acids have a molecular structure containing numerous carboxylic, hydroxyl and phenol groups. The nature of humic acids depends upon the solution chemistry (viz. pH). At neutral to high pH, humic acids bear negative charges due to the dissociation of the –COOH and phenolic –OH groups. At low pH, these functional groups are mostly protonated that makes humic acid less negatively charged and reduces intermolecular electrical repulsion (52, 53). Also a pH increase in the presence of humic acids makes the zeta potential (ζ) of the membrane is more negative (Fig. 10) and increase the rejection rate of polarizable pesticides. Of course, the zeta potential depends upon the nature of the membrane. Apart from the explanation given above, i.e. formation of macromolecules between NOM and pesticides (16, 43, 49), repulsive forces and pore-blocking mechanism are enhanced by the fouling. In hard waters, the bivalent metal cations (e.g., Ca^{2+}) somewhat decrease the negative membrane zeta potential. This effect associated with the presence of humic acids explained the observed decrement in atrazine rejection (49, 54, 55). Fouling appears with the other solutes mixed with water. A concentration polarization and accumulation of humic acids or other solutes due to solvent convection can hinder the membrane permeability. It produces a reduced permeate flux seen either in the form of an increased osmotic pressure on the feed side (thus reducing the effective trans-membrane pressure) or seen as a build up of a region of higher viscosity in the boundary layer (and thus creating an additional resistance to filtration). The concentration of pesticides in permeate is not governed by the concentration of the desired solute (pesticides) in the bulk of the feed solution, but by the concentration near the membrane surface. As this later concentration is decreased by the accumulation of junk matter on the membrane surface, the pesticide concentration in permeate is also decreased (7). As a result, concentration polarization exerts unfavorable effect on the performance of the membrane. If concentration polarization effects are strong, the solute in the boundary layer can reach its solubility limit and cause irreversible fouling.

Devitt et al. (49) have studied the performances of NF45 membranes and the atrazine rejection rate through them during batch filtration. In the absence of organic matter, the atrazine concentration in the permeate exactly follows that in the concentrate, continually rising as filtration proceeds (Figure 7). This suggests that atrazine is rejected in this case due to mass transport limitations across the membrane, which depends on the transmembrane concentration. Atrazine is able to enter the membrane, but is transported to a lesser extent than water.

Influence of pH and Concentration

The membrane performance depends on the pH of the feed solution. The polymeric membrane acquires a surface charge when it is brought into contact with an aqueous solution of different pHs. pH of the feed solution imparts surface charge in different manner viz. by varying the inbuilt functional group on the membrane and through ion adsorption (56).

For polyamide thin film composite membranes, the third acyl group of the trimesoyl chloride hydrolyses to a carboxylic acid (Figure 8). Generally at low

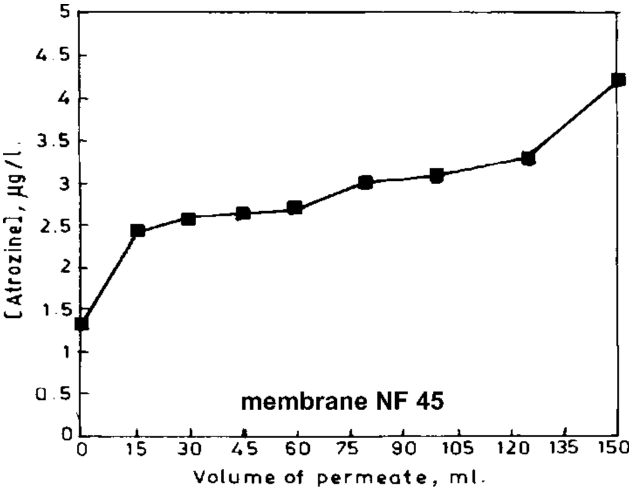


Figure 7. Concentration of atrazine in NF 45 permeates during the filtration of the first 150 mL of a 200 mL sample (adapted from Ref. 49).

pH, the carboxyl groups are protonated and neutral. At elevated pH, the carboxyl groups are ionized bearing a negative charge. Other ionizable chemical functionalities (viz. sulfonates, amines) also have the ability to influence the charge of the membrane. The unreacted pendant amino groups exist on the membrane surface and acquire a positive charge at low pH. These "pendant" groups include terminal groups on the edges of the polyamide structure as well as groups within the structure. Unlike the composite membranes, however, the behavior of cellulose acetate cannot be explained by dissociation of polymer functional groups. The acetyl and hydroxyl groups at the polymeric structure of the cellulose acetate

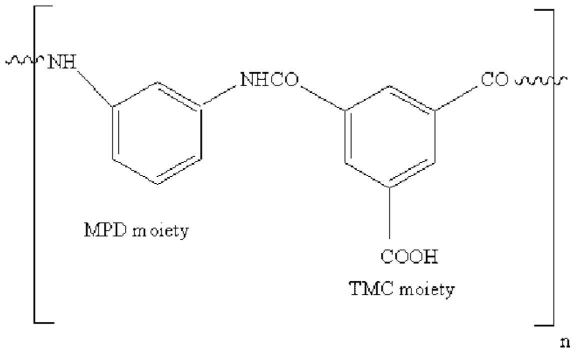


Figure 8. Structure of polyamide, interfacially formed between Trimesoyl chloride and m-phenylene diamine.

membrane do not dissociate in normal working conditions. The positive charge imparted on the cellulose acetate membrane surface at low pH is due to a divalent cation post-treatment.

Polymeric membrane surface can also acquire a surface charge through the adsorption of anions from solution. Preferential adsorption of anions has been suggested as a source of surface charge on non-ionogenic surfaces (i.e., surfaces with no ionizable functional groups) and hydrophobic polystyrene latex colloids (57–59). It has been postulated that anions can approach more closely to non-polar or hydrophobic surfaces because they are less hydrated than cations.

The charge on the membrane influences the distribution of ions at the membrane-solution interface. The distribution of ions at the solid–liquid interface can be described by several models (60–62).

The vital feature of the electric double layer is that the surface charge is balanced by counterions, some of which are located very close to the surface in the so-called Stern layer; the remainder ions are distributed away from the surface in the diffuse layer (Figure 9). An important parameter of the electric double layer is the Stern potential, i.e., the potential at the boundary between the Stern and diffuse layers. The Stern potential cannot, however, be measured directly; so the electrokinetic zeta potential is often considered an adequate substitute. The zeta potential is the potential at the plane of shear between the surface and solution where relative motion occurs between them. Several techniques can be used to determine the zeta potential of the surfaces. Among these techniques, the streaming potential technique is most suitable for membrane surfaces (63, 64). Many researchers have estimated the zeta potential value varying the pH of the feed solution. Some of the results of such experiments are presented here.

In Figure 10, the zeta potential is plotted versus the variation of pH in the presence of 0.01 M NaCl. The pattern of the two NF membranes (TFCS and

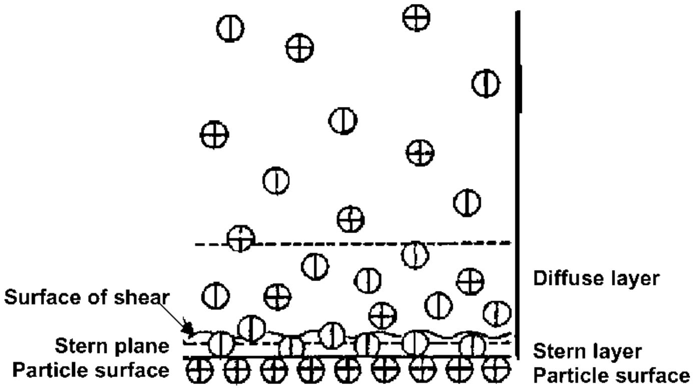


Figure 9. Electrical Double layer according to Stern's model (adapted from Ref. 60).

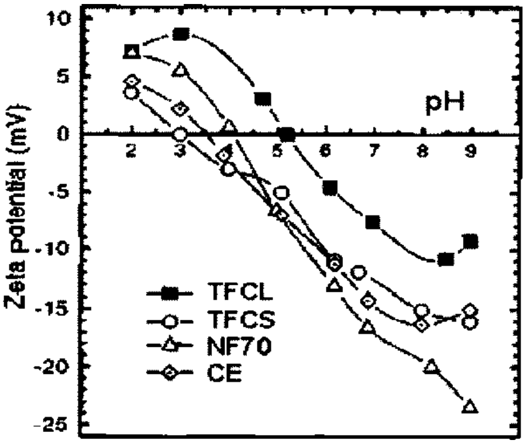


Figure 10. Comparison of zeta potential of four different membranes over the pH range 2–9. Experiments were carried out with a background electrolyte 0.01 M NaCl (adapted from Ref. 65).

NF 70) is similar. The behavior of the RO membrane (TFCL) is different (65). NF membranes are more negatively charged than the RO membrane. The two NF membranes have a low iso-electric point (pH 3 for TFCS and pH 4 for NF 70) when the TFCL membrane has a pH 5.2 iso-electric point. The two NF membranes acquire more negative charges corresponding to negative zeta potentials (-16 and -23 mV, respectively) at high pHs. The RO membrane (TFCL) is more positively charged as it exhibits the highest positive zeta potential ($\sim$9 mV). In general, for all the membranes, featured in Figure 10, the surface charge is positive in the lower acid pH range and negative in the higher basic pH range.

The effect of humic acid (from Suwannee River) on the surface charge of the TFCL membrane is presented in Figure 11. As it was shown in Figure 10, the membrane surface charge becomes negative with the increase in pH value. In the presence of Ca^{2+}, the negative surface charges will be reduced, as Ca^{2+} is attracted by the negative charges and cancels them over the membrane.

The influence of pH on pesticide rejection is shown in Figure 12. It has been observed for Desal 51 HL and UTC-20 (43) that the simazine rejection rate was the highest at pH 8, and much lower at pH 4 and 11.

At higher pH, the OH^- ions' adsorption increases the negative membrane charge. Pesticides have a lower rejection when the negative membrane charge increases. Many pesticide molecules have a dipole moment with a preferential orientation towards the negatively charged membrane. The pesticide molecule orientate in the sense that the positive side of the dipole, opposite to the negative membrane charge is very close to the membrane. In this situation, the preferential orientation produces an increased attraction, an increased

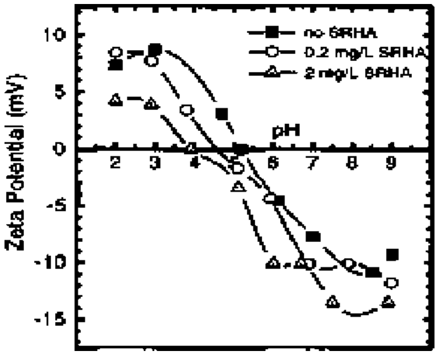


Figure 11. Zeta potential of the TFCL membrane as a function of pH in the presence of Suwannee river humic acid (SRHA) and co-occurring divalent cations (Ca^{2+}). Experiments were carried out with a background electrolyte of 0.01 M NaCl. (adapted from Ref. 65).

permeation and thus a lower rejection rate. At lower pH, the same effect might occur with H^+. Additionally, lower or higher pH could cause the dissociation of NOM pesticide complex for water containing natural organic matter. The dissociation results in an increase of free pesticide molecules able to pass through the membrane. However, Berg et al. (45) explained the lower rejection of pesticides by pore diameter changes induced by ion adsorption or functional group ionization. Pore enlargement could be caused by stronger electrostatic repulsions between the dissociated functional groups of the membrane material.

Zhang et al. (43) also studied the influence of the pesticide concentrations on rejection rates of pesticides. It appears that there is no clear or significant effect, although in some cases (simazine rejection with DESAL 5DL and atrazine rejection with UTC 20 and UTC 60) a higher rejection is found at higher concentrations. This is possibly due to the adsorption effects of pesticides on the membrane.

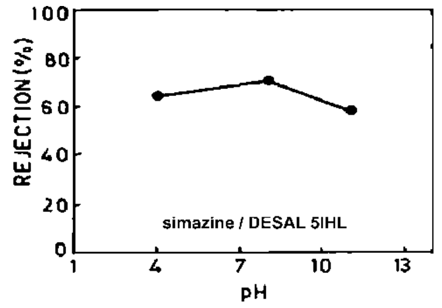


Figure 12. Rejection of Simazine by DESAL 5IHL at different pH for distilled water. (adapted from Ref. 43).

Techniques Involved

In addition to the above factors influencing pesticide rejection, i.e., nature of the membrane and the pesticides, Kiso et al. (14) observed that the rejection depends also on the experimental protocole. For example, the rejection of malathion is lower when the polluted water is pressurized after stirring than when it is immediately pressurized after cell filling. The rejection difference may be due to pesticide adsorption on the membrane and/or a relatively slow adsorption rate.

Rejection of pesticides depends on some time variables (43, 49). With DESAL 51HL membranes, Zhang et al. (43) observed that the initial rejection of all pesticides was always lower that the constant rejection rate reached after some time (Figure 13). This can be explained by the slower transport of dissolved molecules through nanofiltration membranes compared to the transport of water (due to sterical hindrance and slower diffusion). The effect is observed only in the initial stage of the experiment, because a steady state is reached after some time. This effect is found for all three water matrices (viz. distilled water, raw water and tap water).

The rejection depends upon the flux and recovery. Table 4 presents the functions of different fluxes for the same recovery as well as same fluxes for different recovery (66). It shows that for the same recovery, the higher percent rejection is obtained for higher fluxes. But, for the same flux, rejection is higher in the case of low recovery. The difference in rejection for different fluxes is not identical for all the pesticides listed in Table 4. It follows their respective solute mass transfer coefficient. However, for DNOC membranes, the data of 50% recovery does not follow the trend.

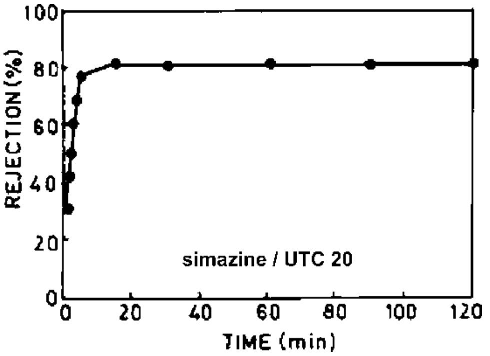


Figure 13. Rejection of Simazine as a function of time for UTC-20 for distilled water (adapted from Ref. 43).

Table 4. Dependence of rejection on flux and recovery

Name of pesticides	Recovery 50%		Recovery 15%	
	Flux 10gfd	Flux 15gfd	Flux 10gfd	Flux 15gfd
Atrazine	86.1	92.4	93.5	94.7
Cyanazine	92.2	95.8	93.6	96.8
Diuron	50.1	60.2	71.4	85.1
DNOC	60.8	56.8	87.2	89.2
Metamitron	NA[a]	46.5	53.4	81
Metribuzin	87.5	94.1	93.7	97.4
Simazine	71.6	84.5	86.4	92.6

[a] 'NA' not available: the sample was broken during transportation for Metamitron.

Compatibility of Membranes

Pesticides are organic molecules containing a variety of functionalities that could create membrane compatibility problems. Pesticides can cause swelling of membranes with subsequent changes in both permeability and solute retention characteristics. However, these possible interactions are still speculative and no report has come yet on this topic. Here, in a review, this compatibility problem is evoked.

Compatibility of polymeric membranes with organic solvent is a major performance factor. The use of nanofiltration membranes in non-aqueous media has been much less investigated than the application in aqueous media (67–71). The performance of nanofiltration membrane in an organic solvent instead of water is complicated. The activity of the permeating molecule inside the polymer can be expressed according to the Flory-Huggins theory as follows (72, 73):

$$lna_i = ln\phi_i + (1 - V_m/V_p)\phi_i + \chi\phi_i^2$$

where a_i is the activity of the penetrant molecule, ϕ_i is the volume fraction of the species and V_m and Vp are the molar volume of the solvent and solute. The χ parameter gives a qualitative estimate of the type of interactions possible between the polymer and solvent.

If χ is higher than 2, it is considered as large and in this case the interactions are small between the chosen pair polymer/solvent. If the χ values are between 0.5 and 2, the interactions are high between the polymer and the solvent and high permeabilities exist. However, when χ is below 0.5, the interactions are so large that the polymer becomes likely soluble in the solvent: the membrane is destroyed.

Apart from the pore size of the membranes, solute-solvent affinity and interaction between the membrane and the solvent also have a role in solute rejection. It is quite common that the pore size of the membranes blocks the solute by steric hindrances.

With the increase in pore size, the resistance against permeation is lowered and the solute rejection decreases. The high affinity of solute-solvent results in solute salvation. The association of solvent molecules with the solute leads to an apparent increase of the effective size of the solvated solute. Of course, this results in high rejection rate. Finally, interaction between the membrane and solvent may lead to solvation of the pore wall (swelling), causing a decrease in the effective pore diameter also increasing solute rejection (74–76). Depending upon the mobility of polymeric chains in particular solvents, pore enlargement as well as shrinkage can occur. As a result, increases as well as decreases in solute rejection were observed (74, 76).

CONCLUSIONS

The pesticide-water pollution is an environmental problem occurring due to the uncertainty in climatic change and people ignorance. Different potential techniques are mentioned here to purify pesticide-polluted waters. Of them, membrane separation techniques made a major breakthrough in the remediation of pesticide polluted waters. The use of membranes has clear advantages over more conventional methods. It is economical, it needs less energy and thus makes the environment less polluted. However, recent reports proposed to combine various conventional processes with the membrane nanofiltration technique (77). To increase efficiency and throughput, capillary nanofiltration can also be employed to treat raw water in a single step (78).

The two main mechanisms that govern the membrane process of pesticide elimination are repulsion (steric and electrostatic) and adsorption on the membrane. Separation of the uncharged pesticides is mainly sterically controlled. The electrostatic charge on the membrane also influences the rejection of pesticides having a dipole moment. The origin of the membrane charge is discussed. The chemical structures of rejecting layer, pH, and matters present in the water matrix, as well as ion adsorption are the causes to impart the charge on the membrane. The formation of an electrostatic double layer is discussed. The fouling and concentration polarization on the membrane has a significant effect its performance. The performances of some commercial membranes are tabulated listing their chemical structure, and log *P* value (octanol/water partition coefficient). This is helpful to get an idea of the hydrophobicity of the pesticides. Hydrophobicity of the pesticides is indeed a critical factor influencing rejection. The rejection rate depends on the flux and recovery. Considering membrane applications in non-aqueous solution, the compatibility of the membranes with pesticides is also discussed. The adsorption on the membrane reduces the elimination of pesticides by fostering their transition in the direction of permeates. The sorption and accumulation of pesticides on membranes in long-term operations in water treatment are the major limiting factors for a widespread use of the technique. Surface modification of the membranes by proper functionality can take the challenges.

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REFERENCES

1. Gohil, J.M., Ray, P., and Bhattacharya, A. (2005) Pesticides in water-alarm and encountering. *Science and Culture*, 71 (9–10): 348–350.
2. Available on world wide web (http://www.epa.gov/safewater/mcl.html). List of Contaminants and their Maximum Contaminant Level (MCLs).
3. Available on world wide web (http://ianpubs.unl.edu/water/g1489.htm). Drinking Water Treatment: Activated Carbon Filtration.
4. Martin-Gullon, I. and Font, R. (2001) Dynamic pesticide removal with activated carbon fibers. *Water Res.*, 35 (2): 516–522.
5. Heijman, S.G.J. and Hopman, R. (1990) Activated carbon filtration in drinking water production: Model prediction and new concepts. *Colloids and Surf A: Phys. and Eng. Aspects*, 151 (1–2): 303–310.
6. LaGrega, M., Buckingham, P., and Evans (1994) *J. Hazardous Waste Management*; McGraw-Hill Inc.: New York.
7. Matsuura, T. (1994) *Synthetic Membranes and Membrane Separation Processes*; CRC Press Inc.: Boca Raton, FL.
8. Bhattacharya, A. and Misra, B.N. (2004) Grafting: A versatile means of polymer modification techniques, factors and applications. *Prog. Polym. Sci.*, 29 (8): 767–814.
9. Bhattacharya, A. and Ghosh, P. (2004) Nanofiltration and reverse osmosis membrane: Theory and application in separation of electrolytes. *Review in Chem. Eng.*, 20 (1–2): 111–180.
10. Vander Bruggen, B. and Vandecasteele, C. (2003) Removal of pollutants from surface water and groundwater by nanofiltration: overview of possible applications in the drinking water industry. *Env. Poll.*, 122: 435–445.
11. The New Encyclopedia Britannica. (1998) 15th edition. Vol. 2. Chicago, IL: Encyclopedia Britannica, Inc.
12. O'Brien & Gere Engineers, Inc. (1995) *Innovative Engineering Technologies for Hazardous Waste Remediation*; Van Nostrand Reinhold: New York.
13. Available on world wide web (http://www.frtr.gov/matrix2/section4/456.html). Ultraviolet (UV) Oxidation.
14. Kiso, Y., Nishimura, Y., Kitao, T., and Nishimura, K. (2000) Rejection properties of non-phenylic pesticides with nanofiltration membranes. *J. Membr. Sci.*, 171: 229–237.
15. Vander Bruggen, B., Schaep, J., Maes, W., Wilms, D., and Vandecasteele, C. (1998) Nanofiltration as a treatment method for the removal of pesticides from groundwaters. *Desalination*, 117: 139–147.

16. Boussahel, R., Bouland, S., Moussaoui, K.M., and Montiel, A. (2000) Removal of pesticide residues in water using the nanofiltration process. *Desalination*, 132: 205–209.
17. Kamide, K. and Iijima, H. (1994) Recent advances in cellulose membranes. In *Polymers, Blends and Composites*; Gilbert, R.D. (ed.), Carl Hanser Verlag: Munich, 189–207.
18. Ho, C.C. and Zydney, A.L. (2000) Measurement of membrane pore interconnectivity. *J. Membr. Sci.*, 170: 101–112.
19. Masselin, I., Chasseray, X., Chevalier, M.-R., Laine, J.-M., and Lemordant, D. (2000) Determination of the porosity to thickness ratio Ak/Λx for UF and MF membranes by diffusion experiments. *J. Membr. Sci.*, 172: 125–133.
20. Serrano, D.A. and Wio, H.S. (2002) Separation factor of membranes used for isotopic separation by gaseous diffusion: Pore morphology influence and effect of cracks. *J. Membr. Sci.*, 204: 5–25.
21. Fritzsche, A.K., Arevalo, A.R., Connolly, A.F., Moore, M.D., Elings, V., and Wu, C.M. (1992) The structure and morphology of the skin polyethersulfone ultrafiltration membranes: A comparative atomic force microscope and scanning electron microscope study. *J. Appl. Polym. Sci.*, 45: 1945–1950.
22. Matsuura, T. (2001) Progress in membrane science and technology for seawater desalination-a review. *Desalination*, 134: 47–54.
23. Bowen, W.R. and Doneva, T.A. (2000) Atomic force microscopy studies of nanofiltration membranes: Surface morphology, pore size distribution and adhesion. *Desalination*, 129 (2): 163–172.
24. Matsuura, T. and Sourirajan, S. (1981) Reverse osmosis transport through capillary pores under the influence of surface forces. *Ind. Eng. Chem. Process Des. Dev.*, 20: 273–282.
25. Kastelan-Kunst, L., Dananic, V., Kunst, B., and Kosutie, K. (1996) Preparation and porosity of Cellulose triacetate reverse osmosis membranes. *J. Membr. Sci.*, 109: 223–230.
26. Kosutie, K., Kastelam-Kunst, L., and Kunst, B. (2000) Porosity of some commercial reverse osmosis and nanofiltration polyamide thin-film composite membranes. *J. Membr. Sci.*, 168: 101–108.
27. Peterson, R.J. (1993) Composite reverse osmosis and nanofiltration membranes. *J. Membr. Sci.*, 83: 81–150.
28. Bellona, C., Drewes, J.F., Xu, P., and Amy, G. (2004) Factors affecting the rejection of organic solutes during NF/RO treatment—A literature review. *Water Res.*, 38: 2795–2809.
29. Kiso, Y., Kitao, T., Kiyokatsu, J., and Miyagi, M. (1992) The effects of molecular width on permeation of organic solute through cellulose acetate reverse osmosis membrane. *J. Membr. Sci.*, 74 (1–2): 95–103.
30. Kiso, Y., Ton, K., Kitao, T., and Nishimura, K. (2001) Rejection properties of alkyl phthalates with nanofiltration membranes. *J. Membr. Sci.*, 182: 205–214.
31. Hyperchem. (1994) *Release 3 for Windows, Molecular Modeling System*; Hyperchem Inc. and Autodesk, Inc.: Waterloo, Ontario.
32. Taylor, J.S., Chen, S.-S., Mulford, L.A., and Norris, C.D. (2000) Flat sheet, bench and pilot testing for pesticide removal using reverse osmosis. AWWA Research Foundation Report: Denver, Co.
33. Van Derbruggen, B. and Vandecasteele, C. (2002) Modelling of the retention of uncharged molecules with nanofiltration. *Water Res.*, 36: 1360–1368.

34. Kiso, Y., Mizuno, A., Othman, R.A.A., Jung, Y.J., Kumano, A., and Ariji, A. (2002) Rejection properties of pesticides with a hollow fiber NF membrane (HNF-1). *Desalination*, 143: 147–157.
35. Kiso, Y., Sugiura, Y., Kitao, T., and Nishimura, K. (2001) Effects of hydrophobicity and molecular size on rejection of aromatic pesticides with nanofiltration membranes. *J. Membr. Sci.*, 192: 1–10.
36. Kiso, Y. (2001) Factors affecting adsorption of organic solutes on cellulose in an aqueous system. *Chromatography*, 22 (1): 55–58.
37. Kiso, Y. (1986) Factors affecting adsorption of organic compounds on cellulose acetate in an aqueous solution system. *Chromatographia*, 22: 55–60.
38. Kosutic, K. and Kunst, B. (2002) Removal of organics from aqueous solutions by commercial RO and NF membranes of characterized porosities. *Desalination*, 142: 47–56.
39. Schaep, J., Vander Bruggen, B., Van Decasteele, C., and Wilms, D. (1998) Influence of ion size and charge in a nanofiltration. *Sep. Purif. Tech.*, 14: 155–162.
40. Sourirajan, S. and Matsura, T. (1985) *Reverse Osmosis/Ultrafiltration Process Principles*; National Research Council Canada: Ottawa, Chapters 1, 2, 5.
41. Vander Bruggen, B., Schaep, J., Wilms, D., and Vandecasteele, C. (1999) Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration. *J. Membr. Sci.*, 156: 29–41.
42. Vander Bruggen, B., Everaert, K., Wilms, D., and Vandecasteele, C. (2001) Application of nanofiltration for removal of pesticides, nitrate and hardness from ground water: Rejection properties and economic evaluation. *J. Membr. Sci.*, 193: 239–248.
43. Zhang, Y., Vander Bruggen, B., Chen, G.X., Braeken, L., and Vandecasteele, C. (2004) Removal of pesticides by nanofiltraion: Effect of the water matrix. *Sep. Purif. Tech.*, 38 (2): 163–172.
44. Berg, P., Hagmeyer, G., and Gimbel, R. (1997) Removal of pesticides and other micropollutants by nanofiltration. *Desalination*, 113: 205–208.
45. Thanuttamavong, M., Yamammuto, K., Oh, J.L., and Choo, K.H. (2002) Rejection characteristics of organic and inorganic pollutants by ultralow-pressure nanofiltration of surface water for drinking water treatment. *Desalination*, 145: 257–264.
46. Boussahel, R., Montiel, A., and Baudu, M. (2002) Effects of organic and inorganic matter on pesticide rejection by nanofiltration. *Desalination*, 145: 109–114.
47. Hofman, J.A.M., Noij, T.N.M., and Schrippers, J.C. (1993) Removal of pesticides and other organic micropollutants with membrane filtration. *Water Supply*, 11: 101–111.
48. Yoon, S.H., Lee, C.H., Kim, K.J., and Fand, A.G. (1998) Effect of calcium ion on the fouling of nanofilter by humic acid in drinking water production. *Water Res.*, 32 (7): 2180–2186.
49. Devitt, E.C., Ducellier, F., Cote, P., and Wiesner, M.R. (1998) Effects of natural organic matter and the raw water matrix on the rejection of atrazine by pressure driven membranes. *Water Res.*, 32 (9): 2563–2568.
50. Rajalakshmi, N., Sivarajan, S.R., and Vold, R.D. (1959) The viscosity of sodium humate solutions from coal. *J. Colloid Sci.*, 14: 419–429.
51. Ghosh, K. and Schnitzer, M. (1980) Macromolecular structures of humic substances. *Soil Sci.*, 129: 266–276.
52. Wang, Y., Combe, C., and Clark, M.M. (2001) The effects of pH and calcium on the diffusion coefficient of humic acid. *J. Membr. Sci.*, 183: 49–60.

53. Majeswska-Nowak, K. and Winnicki, T. (1999) Analysis of membrane fouling in the treatment water solutions containing humic acids and mineral salts. *Desalination*, 126: 179–185.
54. Hong, S. and Elimlech, M. (1997) Chemical and physical aspects of natural matter (NOM) fouling of nanofiltration membrane. *J. Membr. Sci.*, 132: 159–181.
55. Manttari, M., Puro, L., Jokinen, J.N., and Nystrom, M. (2000) Fouling effects of polysaccharides and humic acid in nanofiltration. *J. Membr. Sci.*, 165: 1–17.
56. Elimlech, M., Chen, W.H., and Wayapa, J.J. (1994) Measuring the zeta (electrokinetic) potential of reverse osmosis membranes by a streaming potential analyzer. *Desalination*, 95: 269–286.
57. Jordan, D.O. and Taylor, A.J. (1952) Electrophoretic mobilities of hydrocarbon droplets in water and dilute solution of EtOH. *Trans. Faraday Soc.*, 48: 346–351.
58. Voegtli, L.P. and Zukoski, C.F. (1991) Adsortion of ionic species to the surfaces of polystyrene latexes. *J. Coll. Inter. Sci.*, 141: 92–96.
59. Elimelech, M. and O'Melia, C.R. (1990) Effect of particle size on collision efficiency in the deposition of Brownian particles with electrostatic energy barriers. *Coll. Surf.*, 44: 165–170.
60. Shaw, D.J. (1969) *Electrophoresis*; Academic Press: London.
61. Westall, J. and Hohl, H.A. (1980) Comparison of electrostatic models for the oxide solution interfaces. *Adv. Coll. Inter. Sci.*, 12: 265–294.
62. Elimlech, M. and O'Melia, C.R. (1990) Effect of electrolyte type on the electrophoretic mobility of Polystyrene latex colloids. *Coll. Surf.*, 44: 165–178.
63. Fievet, P., Sbai, M., Szymezyk, A., and Vidonne, A. (2003) Determining the ζ-potential of plane membranes from tangential streaming potential measurements: Effect of membrane body conductance. *J. Membr. Sci.*, 226: 227–236.
64. Mockel, D., Staude, E., Cin, M.D., Darcovich, K., and Guiver, M. (1998) Tangential flow streaming potential measurements: Hydrodynamic cell characterization and zeta potentials of caroxylated polysulfone membranes. *J. Membr. Sci.*, 145: 211–222.
65. Childress, A.E. and Elimlech, M. (1996) Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes. *J. Membr. Sci.*, 119: 253–268.
66. Chen, S.S., Taylor, J.S., Mulford, L.A., and Norris, C.D. (2004) Influences of molecular weight, molecular size, flux and recovery for aromatic pesticide removal by nanofiltration membranes. *Desalination*, 160: 103–111.
67. Vander Bruggen, B., Geens, J., and Vandecasteele, C. (2002) Influence of organic solvents on the performance of polymeric nanofiltration membranes. *Sep. Sci. Technol.*, 37 (4): 783–797.
68. Machado, D.R., Hasson, D., and Semiat, R. (1999) Effect of solvent properties on permeate flow through nanofiltration membranes. Part I. Investigation of parameters affecting solvent flux. *J. Membr. Sci.*, 163: 93–102.
69. Yang, X.J., Livingston, A.G., and Freitas dos Santos, L. (2001) Experimental observations of nanofiltration with organic solvents. *J. Membr. Sci.*, 190: 45–55.
70. Geens, J., Vander Bruggen, B., and Vandecasteele, C. (2004) Characterisation of the solvent stability of polymeric nanofiltration membranes by measurement of contact angles and swelling. *Chem. Eng. Sci.*, 59 (5): 1161–1164.
71. Tarleton, E.S., Robinson, J.P., Millington, C.R., and Nijmeije, A. (2005) Non-aqueous nanofiltration: Solute rejection in low polarity binary systems. *J. Membr. Sci.*, 252: 123–131.
72. Mulder, M. (1997) *Basic Principles of Membrane Technology*, 2nd ed.; Kluwer Academic Publishers: Dordrecht.

73. Bhanushali, D., Kloos, S., Kurth, C., and Bhattacharyya, D. (2001) Performance of solvent-resistant membranes for non-aqueous systems: Solvent permeation results and modeling. *J. Membr. Sci.*, 189: 1–21.
74. Geens, J., Peeters, K., Vander Bruggen, B., and Vandecasteele, C. (2005) Polymeric nanofiltration of binary water-alcohol mixtures: Influence of feed composition and membrane properties on permeability and rejection. *J. Membr. Sci.*, 255: 255–264.
75. White, L.S. (2002) Transport properties of a polyimide solvent resistant nanofiltration membrane. *J. Membr. Sci.*, 205: 191–202.
76. Vander Bruggen, B., Geens, J., and Vandecasteele, C. (2002) Fluxes and rejections for nanofiltration with solvent stable polymeric membranes in water, ethanol and n-hexane. *Chem. Eng. Sci.*, 57: 2511–2518.
77. Bonne, P.A.C., Beerendonk, E.F., Vander Hoek, J.P., and Hofman, J.A.M.H. (2000) Retention of herbicides and pesticides in relation to aging of RO membranes. *Desalination*, 132: 189–193.
78. Futselaar, H., Schonewille, H., and Vander Meer, W. (2002) Direct capillary nanofiltration—A new high grade purification concept. *Desalination*, 145: 75–80.