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Water purification from pesticides by spiral wound nanofiltration membrane

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Abstract. A spiral wound nanofiltration (NF) membrane (GE Osmonics, DK 4040F) was used to remove pesticides from water. Several solutions of single pesticides and their mixtures were prepared. The pesticides initial concentration ranged from ca. 50 ng/L (single pesticide) to ca. 700 ng/L (as sum of 14 pesticides) and progressively increased with time since the NF experiments were carried out in a concentration mode up to a Volume Concentration Ratio, VCR = 10. Permeate flux and pesticides retention were evaluated as a function of the Volume Concentration Ratio. The permeate flux did not practically change by varying VCR. Pesticide retention was found to be around 97-98% both in the cases of single pesticide solutions and different mixtures of pollutants, and was not affected by the VCR. Pesticides concentration in permeate samples was found to be lower than the maximum concentration level fixed in European directive.

Keywords: membrane; nanofiltration; pesticide removal.

1. Introduction

Pesticides are used in significant quantities all over the world to improve agricultural production. Some pesticides (aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex and toxaphene) are considered like persistent organic pollutants (POPs) (UNEP-Chemicals 2004, Wong *et al.* 2005).

One of the main problems generated by the use of pesticides is the risk of contamination of groundwater and surface waters, which are drinking water supplies. Usually the removal of these organic pollutants is performed through activated carbon or through oxidation by ozone or ozone and hydrogen peroxide. However these techniques present some disadvantages. The carbon filters need frequent regeneration since they are rapidly saturated. In addition their efficiency is affected by the presence of natural organic matter due to a competitive adsorption (van der Bruggen *et al.* 1998). Oxidation treatment can lead to the formation of small molecules that can cause bacterial growth and formation of byproducts (peroxides, ozonides, organobromine and bromate) in water distribution systems (Pelekani and Snoeyink 1999). Every country has to maintain the concentration of pesticides in potable water under the limit established by the European directive 1998/83/EC: 100 ng/L for each individual pesticide and 500 ng/L for the sum of all pesticides and related products (European Commission Directive 1998). Nanofiltration (NF) membrane process is widely used in

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the field of wastewater treatment. (Schafer 2001, Schafer *et al*. 2005, Lau and Ismail 2010, Nghiem 2010, Cavaco Morao *et al*. 2010) and has shown to be a more promising and alternative technology for removing hazardous organic pollutants with respect to the traditional methods above mentioned (Ahmad *et al*. 2008, Bhattacharya 2006, Kosutic *et al*. 2005, Sarkar *et al*. 2007a, Sarkar *et al*. 2007b, Shaalan *et al*. 2007, Tepus *et al*. 2009, Thuy *et al*. 2008).

Pesticide retention is largely governed by different pollutant characteristics. Van der Bruggen *et al.* (1999) carried out NF experiments to correlate the retention of a wide range of organic molecules to their molecular size. A good correlation was found between retention and size parameters as molecular weight, Stokes diameter, equivalent molar diameter and calculated molecular diameter. Since the only molecular weight does not represent the geometry of the molecule, the author suggested replacing the molecular weight cut-off by (MWCO) an appropriate model, describing the retention curve as a function of size parameters. More recently the same research group provided a semi-quantitative assessment of the pesticide retention in NF based on threshold values of above mentioned parameters as well as some pesticide properties such as the dissociation constant (pKa), the logarithm of n-octanol/water partition coefficient (LogKow), which is connected to the hydrophobic character of the pesticide and membrane charge (Van der Bruggen *et al.* 2006). Caus A. *et al.* (2009) studied the retention of pesticides and NaCl by cascades of nanofiltration membranes and confirmed that a nearly complete retention of pesticides is possible, depending on specific properties of the solutes such as molecular size and chemical structure (*e.g.*, hydrophobicity). Specifically referring to pesticide removal, Kiso *et al.* (2001) examined aromatic pesticide retention with different NF membranes, and concluded that the permeability was controlled by both sorption properties on the membrane and pesticides molecular weight and shape. Chen *et al.* (2004) underlined that pesticides retention by NF membranes was not only dependent on molecular weight, length and width, but also on operational flux and recovery. Nghiem *et al.* (2002) and Kimura *et al.* (2003) observed that the saturated adsorption of membrane with solutes can lead to the breakthrough of molecules, independently of the chemical nature of both the membranes and the rejected components.

The most important conclusion that can be deduced from these studies is that in some cases pollutants with molecular weight higher than the molecular weight cut-off of the membrane can pass in the permeate, depending on the physical-chemical properties of the component and that also operational parameters and membrane characteristics are important for pesticide removal.

It is worth remembering that the majority of these studies have been mainly focused on the treatment of solutions containing a limited number of pesticides. Recognizing that and with the aim to better understand how the performance of a NF membrane can be affected by the number and concentration of pesticides contained in the feed solution we carried out several tests with a NF plant fed with different solutions either obtained by dissolving a single component, or mixtures of them (3, 8, and 14 pesticides). Although the use of some of these micro-pollutants is nowadays forbidden, they were studied in the present work since they can be still found in supply water.

NF tests were carried out in concentration mode. Permeate flux and pesticide retention were evaluated as a function of the Volume Concentration Ratio (VCR). An initial concentration of 50 ng/L was used since some investigated pesticides, *e.g.*, triazines, are frequently found in both surface and ground waters of many European countries at levels below 100 ng/L (Biziuk *et al.* 1996, Gerecke *et al.* 2002, Garmouma *et al.* 1998, Rodriguez-Mozaz *et al.* 2004, Neal *et al.* 2000, Ollers *et al.* 2001, Quintana *et al.* 2001, van der Hoff and van Zoonen 1999). However in the period of field application the pesticide concentration can exceed this value, and as far as surface water is

concerned, peak levels around 2000 ng/L can be reached (Rodriguez-Mozaz *et al.* 2004). For this reason NF tests were performed at progressively increasing VCRs to verify the removal efficiency of the membrane at high pesticide concentration level.

2. Experimental

2.1 Materials

The main characteristics of the NF membrane, taken from the manufacturer catalogue, are listed in Table 1.

The pesticides, supplied by SUPELCO, are listed in Table 2 along with some relevant properties such as the dissociation constant (pKa), the logarithm of n-octanol/water partition coefficient (LogKow), and, for a limited number of pesticides, the molecular size.

Aqueous solutions of pesticides, used as NF feed, were prepared by adding a standard solution (1 mg/mL) of pesticide in Acetone (HPLC-grade from Sigma-Aldrich) to pure water (milliQ grade). The pH of the solution was 6,8 independently on the type of pesticide (pKa) and its concentration (owing to low solute concentration in the feed solution).

The different feed solutions are listed in Table 3. The concentration of each pesticide in the initial feed solution was around 50 ng/L as can it be seen from Tables 4-7, (VCR = 1).

2.2 Analytical method

Pesticides concentration in feed and permeate samples was determined by using a GC/MS instrumentation, consisting of a GC (Varian, model 3600) connected to a MS (Varian, model Saturn 2000). The samples were collected by means of an auto-sampler (Varian, model 8200). Volumes of 2 μL were injected and analysed in ramp mode (10°C/min), first for 1 minute at 50°C, and then for 10 minutes at 280°C. Helium was used as carrier gas at 10 psi through a column MDN 5S (length 30 m, inner diameter 0.25 mm, film thickness 0.25 μm) obtained from SUPELCO. The injector temperature was set at 250°C. The concentration of pesticides in the samples was determined by means of the MS operating at a trap temperature of 200°C, a transferline temperature of 220°C, a mass range of 45-500 m/z, and a filament delay of 5 min.

Table 1 Characteristics of GE osmonics NF membrane

Manufacturer	GE osmonics
Model	DK4040F
Dimensions	length 40" - diameter 4"
Membrane material	polyamide
Membrane structure	composite
MWCO (Da)	150-300
pH range	2.0-11.0
Active surface (m^2)	8.36
$MgSO_4$ Retention (%)	98.0

Table 2 Properties of the pesticide used for NF tests

Pesticide	Molecular weight (Da)	Formula	Lenght (nm)	Width (nm)	logKow	pKa
Desisopropylatrazine	175	$C_5H_8ClN_5$			1,15[a]	1,58[b,c]
Molinate	187	$C_9H_{17}NOS$		0,376[d]	2,88[d] 3,21[a,e]	-
Desethylatrazine	187	$C_6H_{10}ClN_5$			1,51[a] 1,53[a]	1,65[b]
Simazine	201	$C_7H_{12}ClN_5$	1,034[f]	0,329[d,g] 0,749[f]	2,18[d,g] 2,26[k] 2,34[h]	1,65[b,i] 1,67[j] 1,8[b]
Atrazine	215	$C_8H_{14}ClN_5$	1,036[f]	0,444[d,g] 0,802[f]	2,48[e] 2,61[d,g,k,m] 2,82[j,l]	1,68[b,e,i] 1,7[c,j,l,k] 1,85[b]
Ametryn	227	$C_9H_{17}N_5S$			2,6[h] 2,82[h] 3,07[m]	4,1[b,m]
Propazine	229	$C_9H_{16}ClN_5$			2,91[e] 3,24[l]	1,5[b] 1,7[j] 1,85[e,i]
Terbuthylazine	229	$C_9H_{16}ClN_5$			3,04[m] 3,27[j]	1,94[b,i] 2,0[j,m]
Cyanazine	240	$C_9H_{13}ClN_6$	1,038[f]	0,833[f]	1,7[m] 2,25[h]	1,0[m]
Prometryn	241	$C_{10}H_{19}N_5S$			3,4[m]	4,1[m]
Terbutryn	241	$C_{10}H_{19}N_5S$			3,47[a,o] 3,65[o] 3,74[a]	4,32[p] 4,4[b]
Linuron	248	$C_9H_{10}Cl_2N_2O_2$			2,72 [q] 2,76[a]	
Metolachlor	283	$C_{15}H_{22}ClNO_2$		0,474[g]	3,02[e] 3,28[a]	
Trifluralin	335	$C_{13}H_{16}F_3N_3O_4$			3,97[a] 5,07[n] 5,34[r]	5,3[s]

[a]Noble A. (1993); [b]Schmitt Ph. *et al.*; [c]Vermeulen N.M.J *et al.* (1982); [d]Kiso Y. *et al*. (2002); [e]Konstantinou I.K. *et al.* (2000); [f]Chen S-S *et al.* (2004); [g]Kiso Y. *et al.* (2002); [h]Finizio A. *et al.* (1991); [i]Pacáková V. *et al.* (1988); [j]Van der Bruggen B. *et al.* (2006); [k]Zhang Y. *et al.* (2004); [l]Caus A. *et al.*(2009); [m]Dauwe C. *et al.* (1996); [n]Turgut C. (2005); [o]Azejjel H. *et al.* (2009); [p]Neumann W. *et al.* (1987); [q]Hu J. Y. *et al.* (1997); [r]Asperger A. *et al.* (2001); [s]Chelme-Ayala P. *et al.* (2010).

2.3 NF plant and experiments

As can be seen from Fig. 1, the plant used to carry out NF tests is composed by a feed tank (about 200 litres of capacity), a piston pump, a membrane module, and devices to control feed pressure (P = 20 bar) and flow rate (Q = 1500 L/h). The feed tank, the suction line of the piston pump and the low pressure line after the glove valve are made of PVC, while the high pressure line between the

Table 3 Pesticide solutions used for NF tests

Feed solution	Pesticide
A (single pesticide)	Desethylatrazine
B (single pesticide)	Simazine
C (single pesticide)	Atrazine
D (single pesticide)	Cyanazine
E (single pesticide)	Linuron
F (single pesticide)	Metolachlor
G (3 pesticides)	Simazine, Atrazine, Metolachlor
H (3 pesticides)	Desethylatrazine, Cyanazine, Metolachlor
I (3 pesticides)	Molinate, Atrazine, Linuron
J (8 pesticides)	Desethylatrazine, Molinate, Simazine, Atrazine, Cyanazine, Prometryn, Linuron, Metolachlor
K (14 pesticides)	Desisopropylatrazine, Molinate, Desethylatrazine, Simazine, Atrazine, Ametryn, Propazine, Terbuthylazine, Cyanazine, Prometryn, Terbutryn, Linuron, Metolachlor Trifluralin

Table 4 Results of NF tests carried out with solutions of single pesticide

Feed solution	Pesticide	Feed or Retentate (ng/L)			Permeate (ng/L)			ΔW (%)		Retention (%)		
		VCR 1	VCR 2	VCR 10	VCR 1	VCR 2	VCR 10	VCR 2	VCR 10	VCR 1	VCR 2	VCR 10
A	Desethylatrazine	49,2	97,0	390,8	1,5	2,5	10,1	-1,1	2,1	97,0	97,4	97,4
B	Simazine	48,0	90,0	428,0	1,3	2,1	9,8	4,1	-7,5	97,3	97,7	97,7
C	Atrazine	45,0	92,0	385,0	1,1	2,0	8,2	-4,4	-2,0	97,6	97,8	97,9
D	Cyanazine	51,5	91,0	463,0	1,2	3,3	10,9	8,4	-9,0	97,7	96,4	97,6
E	Linuron	48,5	94,0	424,5	1,3	2,1	11,3	0,9	-8,5	97,3	97,8	97,3
F	Metolachlor	50,0	89,0	457,0	1,5	3,3	9,5	7,7	-8,5	97,0	96,3	97,9

Table 5 Results of NF tests carried out with solutions of 3 pesticides

Feed solution	Pesticide	Feed (ng/L)			Permeate (ng/L)	ΔW (%)	Retention (%)
		VCR 1	VCR 2	VCR 10	VCR 10	VCR 10	VCR 10
G	Simazine	48,0	90,0	428,0	9,7	-7,4	97,7
	Atrazine	50,5	97,0	463,0	9,5	-8,6	97,9
	Metolachlor	49,5	94,0	449,0	9,7	-8,3	97,8
H	Desethylatrazine	47,2	92,0	382,9	9,9	0,0	97,4
	Cyanazine	45,9	90,0	395,0	9,8	-5,3	97,5
	Metolachlor	48,7	96,0	399,7	9,9	-0,3	97,5
I	Molinate	48,6	95,0	430,0	10	-3,8	97,7
	Atrazine	47,2	93,0	399,3	9,9	-3,4	97,5
	Linuron	45,1	89,0	361,5	10	0,0	97,2

Table 6 Results of NF tests carried out with a solution of 8 pesticides

Feed solution	Pesticide	Feed (ng/L)			Permeate (ng/L)	ΔW (%)	Retention (%)
		VCR 1	VCR 2	VCR 10	VCR 10	VCR 10	VCR 10
J	Desethylatrazine	44,6	93,0	339,5	9,9	3,9	97,1
	Molinate	48,4	95,0	390,5	10,1	0,5	97,4
	Simazine	45,8	90,0	385,0	10,2	-4,0	97,4
	Atrazine	49,6	92,0	434,6	9,8	-5,3	97,7
	Cyanazine	46,1	90,0	353,2	9,9	4,0	97,2
	Prometryn	49,7	93,0	445,9	9,8	-7,4	97,8
	Linuron	47,9	92,0	421,1	10,1	-6,9	97,6
	Metolachlor	45,4	89,0	355,8	10,0	1,7	97,2

Table 7 Results of NF tests carried out with a solution of 14 pesticides

Feed solution	Pesticide	Feed (ng/L)			Permeate (ng/L)			ΔW (%)		Retention (%)		
		VCR 1	VCR 2	VCR 10	VCR 1	VCR 2	VCR 10	VCR 2	VCR 10	VCR 1	VCR 2	VCR 10
K	Desisopropylatrazine	53,9	101,0	490,9	1,1	2,1	9,6	4,3	-7,2	98,0	97,9	98,0
	Molinate	49,2	96,0	418,7	1,2	2,3	10,0	0,2	-3,3	97,6	97,6	97,6
	Desethylatrazine	48,5	87,0	424,6	1,2	2,4	9,6	7,8	-5,4	97,5	97,2	97,7
	Simazine	53,8	99,0	473,2	1,3	2,3	9,9	5,8	-4,5	97,6	97,7	97,9
	Atrazine	53,7	98,0	490,1	1,2	2,3	9,9	6,6	-7,9	97,8	97,7	98,0
	Ametryn	51,5	99,0	409,0	1,4	2,8	10,2	1,1	2,7	97,3	97,2	97,5
	Propazine	48,9	97,0	435,0	1,3	2,6	10,1	-1,8	-7,5	97,3	97,3	97,7
	Terbuthylazine	47,5	95,0	422,1	1,3	2,4	9,2	-2,5	-6,3	97,3	97,5	97,8
	Cyanazine	52,0	93,0	465,9	1,3	2,3	9,8	8,4	-6,6	97,5	97,5	97,9
	Prometryn	48,7	95,0	387,5	1,3	2,9	9,8	-0,6	2,2	97,3	96,9	97,5
	Terbutryn	47,7	93,0	378,2	1,4	2,1	10,0	0,2	1,8	97,1	97,7	97,4
	Linuron	48,0	89,0	425,2	1,2	2,5	9,9	4,6	-7,2	97,5	97,2	97,7
	Metolachlor	51,9	95,0	489,8	1,1	2,1	9,6	6,5	-11,0	97,9	97,8	98,0
	Trifluralin	52,6	95,0	483,6	1,1	2,1	9,5	7,6	-8,3	97,9	97,8	98,0

discharge connection of the pump and the globe valve (it included) is made of AISI 316 stainless steel.

Temperature is kept at T = 18°C by means of a cooling device located into the feed tank. The membrane separates the feed into two streams, the retentate and the permeate. The former is recycled to the feed tank, while the latter is continuously withdrawn, until to reach a proper volume concentration ratio, VCR, defined as follows

$$VCR = V_0/V_F = V_0/(V_0 - V_P) \quad (1)$$

where: V_0 = initial feed volume, V_F = retentate volume, V_P = permeate volume

Samples of feed, permeate and retentate were taken during (VRC = 2) and at the end (VCR = 10)

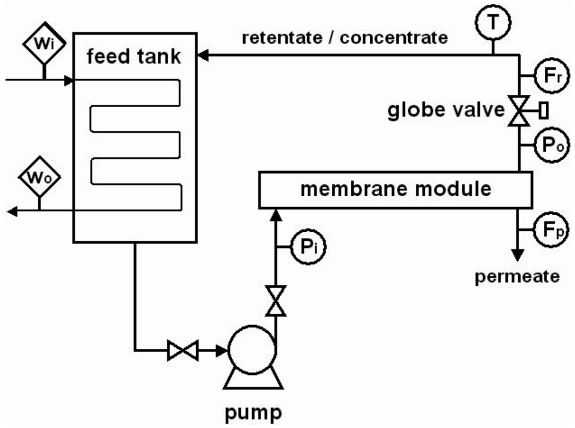

Fig. 1 Schematic representation of the plant: Wi cooling water inlet, Wo cooling water outlet, Fr-Fp flowmeters, Po-Pi manometers, T thermometer

of the NF tests, in order to evaluate the concentration of pesticides and calculate membrane retention as follows

$$R\ (\%) = (1 - C_P/C_F) \times 100 \tag{2}$$

where: C_P = pesticide concentration in the permeate, C_F = pesticide concentration in the feed (or retentate).

The initial and final volume was 200 L and 20 L, respectively. At the end of each concentration run (duration about 25 min) the concentrate solution was simply displaced by the plant with pure water. Then the plant was completely emptied prior to be fed with a new pesticide solution for the successive NF test.

Material balance on pesticides was determined for VCR = 2 and VCR = 10, through the equation

$$W_0 = W_F + W_P \tag{3a}$$

where: W_0 = amount of pesticide in the initial feed, W_F = amount of pesticide in the retentate, W_P = amount of pesticide in the permeate.

The material balance presented in terms of concentration and volumes becomes

$$C_0 \times V_0 = C_F \times V_F + C_P \times V_P \tag{3b}$$

where C_0 is the pesticide concentration at VCR = 1.

3. Results and discussion

Table 4 shows the concentration of pesticides in the feed (or retentate) and permeate, as a function of VCR, during NF tests of 6 solutions, each of which containing a single pesticide chosen among the standards. Being the pesticides largely rejected by the membrane, their concentration increases

with increasing VCR. As shown in Table 4 at VCR = n (n = 2 or n = 10) the concentration of each pesticide is not n times higher than that at VCR = 1. This is because pesticides are not completely retained by the membrane. The retention is always around 97-98% and does not substantially depend on the pesticides properties listed in Table 2.

As reported in the introduction section, proper correlations between retention and these properties have been found by various authors. However the NF membranes used were different from that employed in the present paper. To the best of our knowledge the only detailed investigation on pesticide removal by using a GE Osmonics (Desal) DK membrane was carried out by Boussahel *et al*. (2000). Six pesticides (desethylatrazine, simazine, atrazine, cyanazine, isoproturon, diuron) were chosen and, as far as the first four pesticides (*i.e*., the same pesticides employed in the this paper) is concerned, no practical difference in the retention was observed, while by using a different type of NF membrane (NF 200, Dow Filmtec) with a higher MWCO (300 Da) a good agreement between removal efficiency and molecular size of the pesticides was found.

By verifying the material balance of the NF process at VCR = 2 and VCR = 10 it was observed a difference between the amount ($W_{in} = W_0$) of pesticides in the initial feed (200 L) and that ($W_{out} = W_F + W_P$) in the final products (permeate = 100 L and retentate = 100 L at VCR = 2; permeate = 180 L and retentate = 20 L at VCR = 10).

The percentage difference (ΔW) calculated through the equation

$$\Delta W\ (\%) = (1 - W_{out}/W_{in}) \times 100 \tag{4}$$

and reported in Table 4 for VCR = 2 and VCR = 10, appears reasonable taking into account measurements errors due to the precise evaluation of the collected permeate and retentate volumes as well as to the dilution and preconcentration analytical procedure involved for GC/MS measurements of retentate and permeate samples.

Table 5 reports the results of NF tests carried out with 3 solutions containing 3 different pesticides, while in Tables 6 and 7 it is possible to observe the results obtained from the solutions containing 8 and 14 pesticides, respectively. Even in this latter case (Table 7) the material balance error falls within a reasonable range.

The comparison of Tables 4-7 shows that the removal efficiency of a single pesticide does not

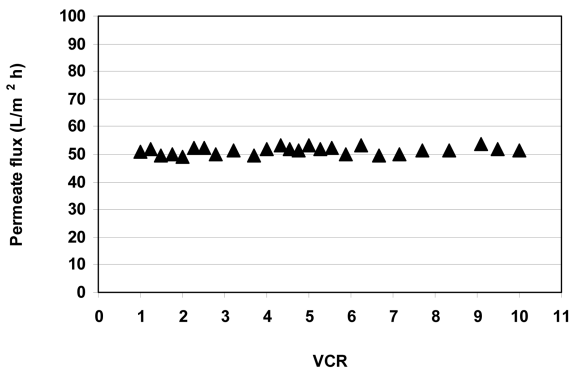

Fig. 2 Behaviour of the permeate flux vs. VCR during nanofiltration of K pesticide solution (see Table 3 for solution composition and Table 7 for pesticide retention)

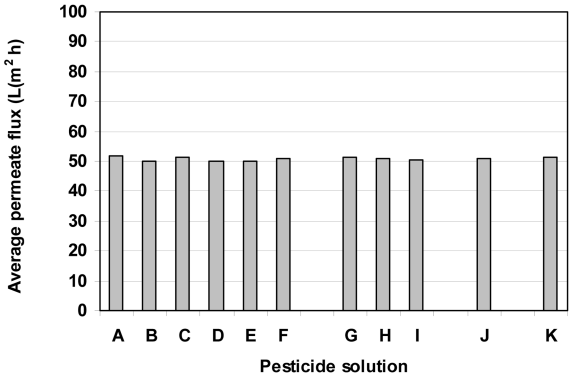

Fig. 3 Average permeate flux during nanofiltration NF tests of various pesticide solution (see Table 3 for solution composition and Tables 4-7 for pesticide retention)

depend on the particular composition of the feed. This finding which is due to the fact that pesticides in the mixture do not interfere each other in the transport through the small membrane pores of the NF membrane indicates that pesticides can be successfully removed from water whatever possible combination may result.

It is also worth noticing that permeate flux was found to be substantially independent on the VCR as well as on the feed composition. This is demonstrated as an example, in Figs. 2 and 3. The former figure refers to the behaviour of the permeate flux as a function of VCR during the concentration run of the K solution (14 pesticides) while the latter shows the average flux during concentration (VCR = 10) of the various pesticide solutions listed in Table 3.

Also this finding represents a further advantage for a successful application of NF in the water purification from pesticides.

However further work should be necessary to examine the behaviour of the membrane performance over a more long period, especially in order to avoid the risk of retention overestimation that occurs if saturation conditions are not reached (Kimura *et al.* 2003, Verliefde *et al.* 2009).

4. Conclusions

Experimental data highlighted that the NF membrane DK 4040F was successful in the removal of pesticides in a wide range of concentrations, which is close to the real situations that can be found in ground and surface water.

Permeate flux and pesticide retention were found to be around 50 L/m^2 h and 97-98%, respectively both in the cases of single pesticide solutions and different mixtures of pollutants, and were not affected by the volume concentration ratio.

The membrane was then able to turn the polluted water potable, even when the concentration of micro-pollutants was higher than that imposed by the European directive, thus confirming that this kind of membrane can be successfully employed to remove pesticides from water.

However accurate investigation of long-term performance of the membrane is necessary for industrial application.

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