Dichloroaniline retention by nanofiltration membranes

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Abstract

This study evaluates the performance of two nanofiltration membranes in removing a herbicide: dichloroaniline. The membranes, one polyamide and one cellulose acetate, have a cut-off in the range 150–300 g/mol (manufacturers' data). The experiments were carried out with solutions of dichloroaniline in demineralized water, with concentrations from 1 to 10 ppb. For each membrane, the amount of herbicide retained and adsorbed by the membrane was determined as a function of feed concentration and transmembrane pressure. The two membranes, made of different materials but having the same nominal cut-off, retained dichloroaniline to very different extents and by different mechanisms.

Keywords: Nanofiltration; Membranes; Pesticide; Dichloroaniline; Retention mechanisms; Adsorption

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1. Introduction

Underground and surface water or sewage water are increasingly found to contain micro-pollutants such as pesticides or antibiotics. Membrane technology and in particular cross-flow filtration is potentially capable of solving such problems of micro-pollution, whether of biological or chemical origin. However, the problem of making absolute barriers to such contaminants is still unsolved. Moreover, faced with the constraints of the European directive that fixes low maximum concentrations for potable water ($0.1\,\mu g\,L^{-1}$ for each individual pesticide and $0.5\,\mu g\,L^{-1}$ for the sum of all pesticides and related products), improvements to conventional lines and research into new treatment technologies have become a major preoccupation in water treatment.

In this context, nanofiltration is a promising membrane technique that offers improvements to the traditional methods. The increasing interest from water producers in this process is due to the good rejections that can be obtained for micropollutants such as pesticides and herbicides. Numerous works have been published on the influences of molecular weight, molecular size, hydrophobicity, polarity and charge on the retention of organic molecules by nanofiltration. These works show that pesticide rejection does not always increase with pollutant molecular weight (Kiso et al., 2001). For some aromatic pesticides like atrazine or diuron the molecular length appears to be more significant than molecular width with respect to rejection (pesticide rejection increases as its molecular length increases, Chen et al., 2004). On the contrary, Kiso et al. (2001) conclude that molecular width is a useful descriptor for steric hindrance in the case of non-phenilic pesticides, alkyl phthalates, mono substituted benzenes, alcohols and saccharides. Van der Bruggen et al. (1999) showed that the correlation with retention is

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Nomenclature

C_p	solute concentration in the permeate ($\mathrm{kg\,m^{-3}}$)
C_r	solute concentration in the retentate ($\mathrm{kg\,m^{-3}}$)
$J_{\mathrm{stabilized}}$	permeation flux density in steady state conditions ($\mathrm{m^3\,m^{-2}\,s^{-1}}$)
r_{pore}	mean pore radius (m)
P	*n*-octanol/water partition coefficient
R_{obs}	observed retention coefficient (%)

generally only slightly improved by using size parameters with a physical meaning such as Stokes diameter, equivalent molar diameter or a calculated molecular size instead of molecular weight. Therefore, they conclude that the latter remains useful for the description of retention. Kiso et al. (2001) also show that for hydrophilic solutes, steric hindrance is the most important factor controlling rejection. In the case of hydrophobic compounds, they use a partition coefficient P as the measure of hydrophobicity (hydrophobic compounds are characterized by $\log P > 2$) and find that it is one of the most useful descriptors for the adsorption properties of organic compounds onto membrane materials. Finally, these authors show that the effects of steric hindrance remain remarkable in hydrophobic compound rejection. An effect of polarity on retention is observed: molecules with a high dipole moment have lower retentions compared to non-polar molecules (Van der Bruggen et al., 1999). Finally, the retention behavior of an organic molecule is also influenced by charge effects, specifically when the membrane pores are large as compared to solute size. The most important conclusion that can be drawn from this short survey on NF performance is that in some cases pollutants with molecular weights higher than the membrane molecular weight cut-off were still detected in the permeate, depending on the physico-chemical properties of the component. Determination of rejection by a membrane is all the more difficult if the compound is hydrophobic due to adsorption (Nghiem et al., 2002; Kimura et al., 2003). In that case, when low concentrations are used, breakthrough of components can be observed when the membrane becomes saturated. This demonstrates the need for a more fundamental understanding of micropollutant rejection by NF membranes.

Concerning transfer phenomena involved in pollutant retention mechanisms, most authors conclude that diffusion is the limiting one. Agbekodo et al. (1996) suggest that adsorption and diffusion through the nanofiltration membranes govern atrazine and simazine removal mechanisms. Chen et al. (2004) observed a higher percent rejection of aromatic pesticides at high flux and low recovery, which is in accordance with the diffusion-control theory.

The objective of the present work was to evaluate the retention of herbicides by nanofiltration membranes and to better understand the transfer mechanisms of these contaminants through the porous structure.

2. Solutions and procedures

2.1. Experimental set-up and procedure

Dead-end filtration was performed with a 7.5×10^{-2} m diameter stirred cell (Berghof) (Fig. 1). The trans-membrane pressure was set by air pressurization of the cell. The pressure on the filtrate side was approximately atmospheric under all conditions. The range of trans-membrane pressure used during experiments depends on the membrane tested: $5 \times 10^{+5}$–$20 \times 10^{+5}$ Pa for the polyamide membrane and $5 \times 10^{+5}$–$11 \times 10^{+5}$ Pa for the cellulose acetate membrane. These ranges have been chosen as a function of the maximum pressure acceptable by the membrane material according the manufacturer's specifications: $40 \times 10^{+5}$ Pa for the polyamide membrane and only $15 \times 10^{+5}$ Pa for the cellulose acetate membrane (see Table 1).

Table 1
Characteristics of tested nanofiltration membranes (provided by the manufacturer)

Membrane reference	Material	MWCO ($\mathrm{g\,mol^{-1}}$) on sucrose and glucose	r_{pore} (nm)	Max. pressure (Pa)	Surface energy ($\mathrm{J\,m^{-2}}$)	Surface charge (neutral pH)	Permeability[a] (m)
Desal 5 DK	Polyamide	150–300	0.47	$40 \times 10^{+5}$	33×10^{-3}	Negative	1.4×10^{-14}
CK	Cellulose acetate	200	0.40	$15 \times 10^{+5}$	39×10^{-3}	Negative	0.6×10^{-14}

[a] Our measurements.

The cell contained a nanofiltration membrane with an effective area of $3.52 \times 10^{-3}\,m^2$. Each experiment was conducted in four steps. At first the membrane was soaked in ultra pure water for 24 h. Secondly, Milli-Q water was filtered through the membrane at a transmembrane pressure of $20 \times 10^{+5}$ Pa for polyamide specimens and $11 \times 10^{+5}$ Pa for cellulose acetate specimens. This compaction was stopped once the flux had stabilized, after a filtration period of approximately 2 h. The membrane permeability was then determined. In the fourth step, the cell was emptied and filled with the herbicide feed solution.

During each filtration run, the maximum value for the volume reduction ratio in the cell was 2. The stirring rate was maintained constant over all the experiments. The filtrate flux $\boldsymbol{J}$ ($m^3\,m^{-2}\,s^{-1}$) was measured by timed collection using an electronic balance (Ohaus) with an accuracy of ±0.01 g. For each imposed pressure, retentate and filtrate samples were collected for subsequent analysis both during and at the end of the run in order to monitor the evolution of contaminant concentration. Each time the pressure was modified, the cell was emptied and refilled with 0.37 L of feed solution.

After each run, the membrane and the O-ring gasket were replaced by new ones. This was to avoid cross contamination between runs by adsorption–desorption of radio-labeled molecules.

All experiments were performed at room temperature ($20 \pm 2\,^{\circ}C$).

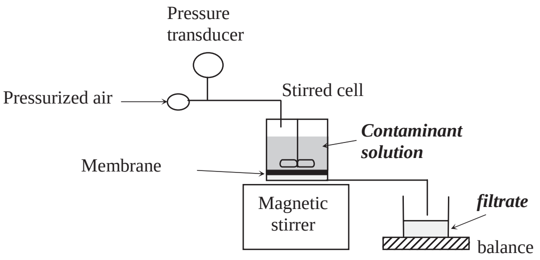


Fig. 1. Experimental set-up.

2.2. Membranes

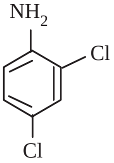
Two nanofiltration membranes provided by Osmonics were chosen, one of polyamide (Desal 5 DK) and the other of cellulose acetate (CK), in order to evaluate the effect of the material and the structure of the membrane on performance. Their technical characteristics are reported in Table 1. Polyamide membranes are the most often used in pesticide removal. Cellulose acetate was chosen in order to evaluate the effect of the membrane material and structure on performance. According to Hofman et al. (1997), it can be expected that the cellulose acetate membranes were less sensitive to fouling while the polyamide membranes were more productive as, in the same conditions of transmembrane pressure, the permeation fluxes through the polyamide membrane are higher than those measured with the cellulose acetate membrane.

2.3. Herbicide solutions and analytical method

The pollutant selected in this study was the 2,4-dichloroaniline that is primarily used as a dye intermediate, but may also be found as an intermediate of contact-type herbicides. 2,4-dichloroaniline present in soil, biodegrades relatively slowly. However, this contaminant does not adsorb onto soil particles very tightly and as a result may leach into the groundwater. It is particularly toxic to aquatic organisms, as it reduces the oxygen carrying capacity of the bloodstream. Similar effects can be expected for humans subjected to prolonged exposure to 2,4-dichloroaniline that could rapidly result in death. The removal of this pollutant from water is then crucial in drinking water production but also in the treatment of process waters from the textile industry. However, very few studies on the removal of this component from water can be found in the literature.

Table 2 provides general relevant data of 2,4-dichloroaniline (Aldrich). This substance is hydrophobic (Log $P > 2$). In order to use contaminant concentrations as low as the ones that are found in water (ranging from

Table 2
General characteristics of 2,4-dichloroaniline

Structure	Molecular formula	Molecular weight ($g\,mol^{-1}$)	Effective radius[a] (nm)	pKa	Log P
	$C_6H_5Cl_2N$	162	0.30	2.50	2.78

[a] Van der Bruggen and Vandecasteele, 2002.

1 to 10 ppb ($\mu g\,L^{-1}$)), molecules radio-labeled with ^{14}C were used in combination to the appropriate analytical technique. All the solutions were prepared from ultra pure water (Milli-Q).

At low concentrations, 1 ppb, two different solutions were used: the first one named I (impure) contained eighty percent (80%) of pure dichloroaniline, the 20% remainder are decomposition products. The second solution named P (pure) was obtained from the previous one by removal of the decomposition products and contained 98% pure dichloroaniline. The objective here was to evaluate the influence of the presence of intermediates, thought to be present in real water sources, on the membrane performances (adsorption and retention). Other concentrations (2, 5 and 10 ppb) were obtained from stock solution I.

The solutions were filtered at their natural pH ranging from 5 and 6 for which the molecules were negatively charged. The pH value did not change during experiments. In these conditions, the membranes also carried negative charges.

Scintillation liquid was added to the samples before analysis with a scintillation counter (1500 Tricares Packard, Simonnet and Oria, 1986). Scintillation liquid essentially contains aromatic organic molecules such as toluene. The scintillant molecule is excited due to the disintegration of a ^{14}C atom and emits photons that have been counted. The detection limit of the scintillation counter is 0.02 ppb.

The dichloroaniline concentrations were determined with an accuracy of ± 0.02 ppb.

3. Experimental results

Two parameters were monitored to evaluate membrane performance:

- The amount of 2,4-dichloroaniline adsorbed on the membrane expressed in $\mu g\,m^{-2}$ of membrane area ($\pm 0.007\,\mu g\,m^{-2}$), with an evaluation of the reversible and irreversible contributions, as explained below.
- The observed retention coefficient of 2,4-dichloroaniline $R_{obs} = (1 - C_p/C_r) \times 100\%$ ($\pm 1.5\%$) calculated from concentrations measured in the permeate C_p and the retentate C_r.

3.1. Adsorption

Static batch tests were performed in order to quantify adsorption of dichloroaniline only due to solute-membrane surface contact, without transmembrane pressure. In this case the cell was filled with the herbicide solution (1 ppb I) and left open to atmospheric pressure. Every 10 min, a sample was collected from the cell for analysis. The duration of the experiment was 90 min, an estimated sufficient amount of time for adsorption mechanisms to reach equilibrium. The results, reported in Table 3, show more adsorption by the polyamide membrane.

In a second step, filtration runs were performed at pressures increased step-wise. For each, pressure filtration was stopped once the flux had stabilized. These steady-state conditions are taken to correspond to equilibrium in terms of dichloroaniline adsorption by the membrane surface. The determination of the herbicide concentration in the permeate and retentate allowed the amount of 2,4-dichloroaniline adsorbed onto the membrane to be calculated from a mass balance. At the end of each run, the feed solution was replaced in the cell by demineralized water that was then filtered under the last applied pressure to evaluate the reversible and irreversible parts of the adsorption. Analysis of permeate samples allowed the amount of 2,4-dichloroaniline thus desorbed to be calculated (this quantity was considered as "reversible adsorption"), with the hold-up volumes of the experimental set-up taken into account (volumes of sintered stainless steel used as membrane support and permeate collector).

Table 3
Quantity of dichloroaniline adsorbed on tested nanofiltration membranes

Membrane	Concentration of dichloroaniline (ppb)	Quantity adsorbed without pressure ($\mu g/m^2$)	Total quantity adsorbed with pressure ($\mu g/m^2$)	Reversible part		Irreversible par	
				($\mu g/m^2$)	(%)	($\mu g/m^2$)	(%)
Desal 5 DK	1 (P)		96	3	3	93	97
	1 (I)	63	104	3	3	101	97
	2 (I)		73	4	5.5	69	94.5
	10 (I)		135	15	11	120	89
CK	1 (P)		43	22	51	21	49
	1 (I)	37	60	32	53	28	47
	5 (I)		78	42	54	36	46
	10 (I)		112	48	43	64	57

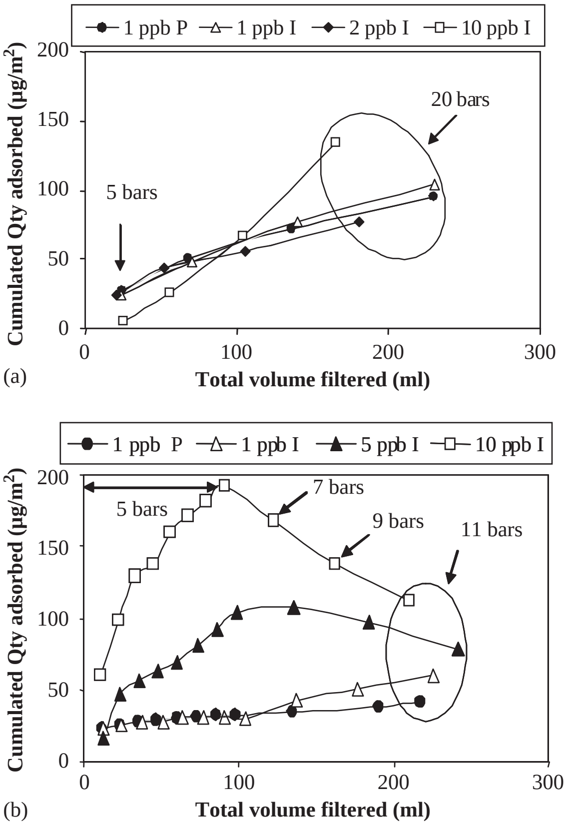


Fig. 2. Quantity of dichloroaniline adsorbed by the membrane versus total volume filtered: (a) polyamide membrane, (b) cellulose acetate membrane.

Fig. 2 reports the cumulated amounts of dichloroaniline adsorbed on the two membranes for various herbicide concentrations. With the polyamide membrane, the quantity adsorbed increased linearly versus the total volume filtered. Whereas this increase was independent of the solution purity and of the initial concentration for low concentrations, a change in slope was observed for 10 ppb.

For cellulose membrane, two behaviors were observed depending on the initial herbicide concentration. At 1 ppb, the quantity of dichloroaniline adsorbed on the membrane slowly increased versus filtered volume. For higher concentrations (5 and 10 ppb), a volume of 0.1 L under $5 \times 10^{+5}$ Pa (corresponding to a filtration run of 2 h) was not sufficient to reach equilibrium in terms of adsorption. Moreover, part of the adsorbed dichloroaniline was desorbed when the transmembrane pressure (i.e. the permeation flux) was increased. These results suggest competition between adsorption forces and hydrodynamic forces, which would be consistent only if the bonds between dichloroaniline and cellulose acetate were loose.

As can be seen in Fig. 2, for each initial concentration, the total volume filtered at the end of the filtration run was around 0.2 L. The total amounts of dichloroaniline adsorbed in these conditions are reported in Table 3. We can conclude that whatever the initial dichloroaniline concentration or solution purity, adsorption by the polyamide membrane was generally greater. This conclusion is in agreement with the results obtained in the static batch at 1 ppb I. The lower adsorption observed in this last case (see Table 3) as compared to the amount of dichloroaniline adsorbed by the two types of membrane in dynamic filtration suggests that 90 min are not sufficient in static conditions for adsorption mechanisms to reach equilibrium if pore adsorption takes place as the transfer inside the membrane structure in this case is pure diffusion.

Moreover, the reversible part of adsorption by the polyamide membrane was low (from 3% to 11%); we can thus assume that dichloroaniline–polyamide bonds are strong. With the herbicide–cellulose acetate system, the reversible part of adsorption was around 50% for all the herbicide concentrations studied, thus confirming loose bonds between the dichloroaniline and cellulose acetate.

Finally, Table 3 compares the quantity of dichloroaniline adsorbed from the solutions whether they contain decomposition products (1 ppb I) or not (1 ppb P). We can observe, on both types of membrane, greater adsorption for solution 1 ppb I. This result seems to show that the presence of decomposition products favors adsorption of dichloroaniline.

3.2. *Retention*

For each dichloroaniline solution filtered, the observed retention coefficient R_{obs} was determined at each pressure step once the flux had stabilized: after a filtration period of 20 min (the run time that allowed a stable R_{obs} value to be obtained, excepted for cellulose acetate at pressure 5 bars, experiment for which a filtration run of 2 h is necessary). Evolutions of R_{obs} versus $J_{\mathrm{stabilized}}$ are reported in Fig. 3 for the two types of membrane.

First, it can be seen that the initial concentration and purity of dichloroaniline in the feed solution have a negligible effect on the variation in herbicide retention at steady state, at least within the range investigated here.

The two membranes made of different materials, but having the same nominal cut-off, retained dichloroaniline to very different extents. The polyamide membrane was the more efficient in retaining dichloroaniline with R_{obs} ranging from 60% to 95%, as compared with 10% to 25% obtained with the cellulose acetate membrane. As a consequence, in all the filtrations performed with cellulose acetate membrane, sample analysis showed filtrate concentrations far above the legal limit, fixed at

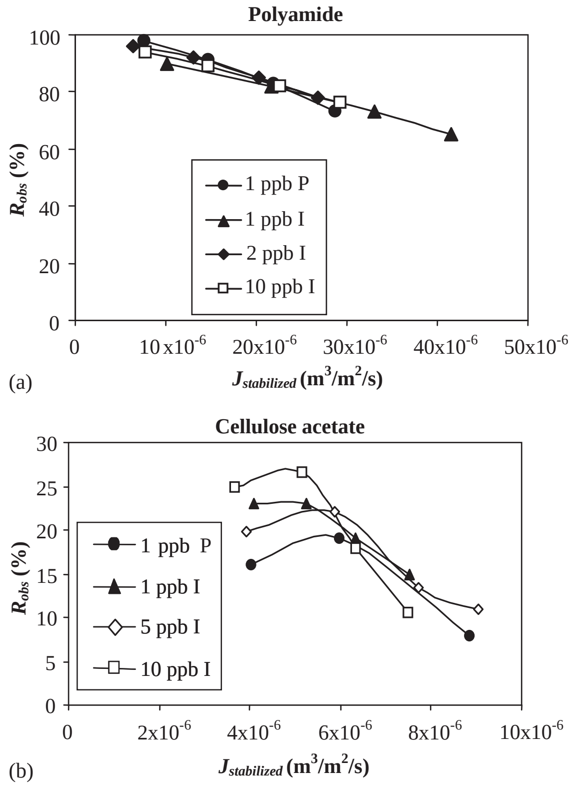


Fig. 3. Dichloroaniline observed retention versus stabilized permeation flux.

0.1 ppb. In this case, the use of two units in series could be considered in order to increase the overall rejection (Van der Bruggen et al., 2001). With the polyamide membrane, all filtrate concentrations measured were lower than the legal limit.

Morever, as expected, process productivity was also better with the polyamide membrane: permeation fluxes can be twice those measured with the cellulose acetate membrane in the same conditions of pressure (for example, with the solution 10 ppb I filtered under a pressure $10 \times 10^{+5}$ Pa: $J_{\text{stabilized,polyamide}} = 14.7 \times 10^{-6}\,\text{m}^3\,\text{m}^{-2}\,\text{s}^{-1}$ to be compared to $J_{\text{stabilized,cellulose}} = 7.5 \times 10^{-6}\,\text{m}^3\,\text{m}^{-2}\,\text{s}^{-1}$).

4. Discussion

The results show that the two types of membrane adsorbed dichloroaniline in very different amounts. In the case of the polyamide membrane, dichloroaniline seems tightly bound to the membrane. As a consequence, the higher the applied pressure (i.e. the higher the permeate flux) the more rapidly saturation was achieved, allowing the accurate evaluation of dichloroaniline retention by the membrane. In the case of cellulose acetate, adsorption is partly reversible (50%) whatever is the initial pesticide concentration. Moreover, for initial concentrations higher than 1 ppb, permeate flux has a significant effect on the degree of compound adsorption and thus on the apparent R_{obs}. An accurate evaluation of herbicide retention by cellulose membrane is then difficult to achieve.

The strongest affinity observed between dichloroaniline and polyamide membrane agrees with a more hydrophobic membrane material as compared with cellulose acetate (Table 1 surface energy).

As a first approximation, the removal efficiency of the two membranes does not vary greatly, regardless of the initial 2,4-dichloroaniline concentration. This conclusion has also been drawn by other authors (Van der Bruggen et al., 1998). According to Agbekodo et al. (1996), this result is in agreement with the transfer model based on solubilization–diffusion theory that assumes that, given the range of low micropollutant concentrations, solute removal efficiency by membranes is independent of the solute concentration in the feed water.

The results obtained in terms of adsorption (specifically the volume of bulk solution that has to be filtered to achieve membrane saturation), flux and retention seem to be consistent with a difference in pore structure for the two membranes: (i) For the polyamide membrane, we can assume that the adsorption essentially occurs on membrane skin, the structure of which is a priori dense (composite membrane). As a consequence, this surface adsorption is rapid. The skin structure of this membrane also leads, under steady state conditions, to good, although incomplete dichloroaniline retention. (ii) For the cellulose acetate membrane, the skin structure is probably more porous, this leading to an adsorption across the whole membrane thickness with slower kinetics but in larger amounts in low-flux conditions (more sites of adsorption accessible). In addition, the open skin structure of this membrane leads to a dichloroaniline observed retention that does not exceed 25% under our operating conditions.

For polyamide membrane, Fig. 3 exhibits a slow decrease in retention as flux increased, which is typical of the influence of concentration on solute transfer. For the cellulose acetate membrane we observe a maximum for R_{obs}, whatever the initial concentration. This behavior is characteristic of situations where concentration polarization still influences the solute transfer with, at the same time, a non-negligible contribution of diffusion in the pores. At low flux ($J_{\text{stabilized}} < 5 \times 10^{-6}\,\text{m}^3\,\text{m}^{-2}\,\text{s}^{-1}$), there is a negligible concentration polarization, but strong diffusion in the porous medium leads to dispersion and then to a poor observed retention.

The efficiency of membranes in removing small chemicals such as 2,4-dichloroaniline would have to be evaluated with natural water in order to quantify the effect of the matrix. In actual NF applications, membrane adsorption sites will be occupied not only by many types of hydrophobic micropollutants but also by bulk natural organic matter. Moreover, the presence of NOM enhances the size exclusion, hydrophobicity of NOM-pollutant complex and makes electrostatic repulsion appear during transport through the membrane (Zhang et al., 2004). In these conditions, it can be expected that efficiency increases as our filtration tests conducted with contaminant dissolved in demineralized water underestimate retention.

5. Conclusion

This study reveals two different types of behavior in nanofiltration membranes with respect to 2,4-dichloroaniline retention. The two membranes tested, despite having the same nominal cut-off, retained dichloroaniline to very different extents and by different mechanisms. Due to the dense structure of the skin of the polyamide membrane, adsorption was superficial and hence rapidly reached equilibrium. At the same time, the pure retention was high, ranging from 60% to 95%. On the other hand, a looser skin (cellulose acetate membrane) may lead to a slower kinetics of adsorption as it occurs across the whole structure of the membrane and lower dichloroaniline retention that did not exceed 25% under our operating conditions.

The characterization of nanofiltration membranes with regards to the efficiency at retaining small chemicals has to be carried out with very special attention, due to the very complex nature of the mechanisms involved and of the material structures commercially available.

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