

Removal of pesticide residues in water using the nanofiltration process

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Abstract

A study on a nanofiltration pilot with synthetic waters was carried out in order to evaluate the performances of two nanofiltration membranes in the removal of some selected pesticides (triazines and urea herbicides). The influence of the presence of humic acid, sulfate and chloride ions on the removal of these pesticides was shown. The results show very different behaviours between the two membranes. With a Desal DK membrane, only diuron was affected negatively by the matrix change. But with an NF200 membrane, the effects were more perceptible and led to a better comprehension of the mechanisms which govern the removal of pesticides by nanofiltration.

Keywords: Nanofiltration; Pesticides; Triazines; Urea herbicides; Humic acid; Sulfates; Chlorides

1. Introduction

The intensive use of pesticides in agriculture has generated a contamination of groundwater and surface waters. Usually the removal of these organic pollutants in water production chains is performed through activated carbon (in powder or granular form) and through oxidation by ozone or ozone and hydrogen peroxide. But these two techniques have some disadvantages. The carbon filters are saturated rapidly and their efficiency to

eliminate pesticides decreases with a high presence of natural organic matter (NOM) due to a competitive adsorption [1]. Furthermore, the cost is enhanced by the frequent regeneration of the carbon. With the second technique, the formation of small molecules after the cut of pesticide molecules can cause bacterial regrowth in water distribution systems and also the formation of byproducts (peroxides, ozonides, organobromine and bromate) [1]. Over the last few years, membrane technology such as ultrafiltration (UF), reverse osmosis (RO) and nanofiltration

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tion (NF) has been introduced in the field of water treatment [2]. The increasing interest in NF from water producers is due to the fact that it is the most economical: this pressure-driven membrane process uses lower pressures than UF for comparable fluxes [3]. It can remove dissolved organic matter [4,5], colour [6], sulphate [7], heavy metal complexes [8] and some organic pollutants such as pesticides [9–13]. It can be particularly useful in softening [7].

The aim of this study is to test the efficiency of two NF membranes to remove some selected pesticides [atrazine and its metabolite desethyl-atrazine (DEA), simazine, cyanazine, isoproturon and diuron] and to investigate the influence of the organic matter (humic acid) and the inorganic matter (calcium sulfate and calcium chloride) on the quantities of pesticides removed and adsorbed by the membranes, in order to understand the phenomena which govern the NF technique.

2. Materials and methods

The NF pilot (Fig. 1) used in this study is composed of a feed tank in stainless steel, a separation module (Separation Technology, Inc.) and a pump (Hydra-Cell). The tested NF membranes were from Osmonics Autotrol, France (Desal DK) and Dow Filmtec Corporation (NF200). Their technical characteristics are listed in Table 1.

Table 1
Membrane characteristics (given by the manufacturers)

	Desal DK	NF200
Manufacturer	Osmonics Desal	Filmtec Dow Chemical
Chemical family	Polyamide	Polyamide
Membrane structure	Composite	Composite
Molecular weight cut-off, Dalton	150–300	300

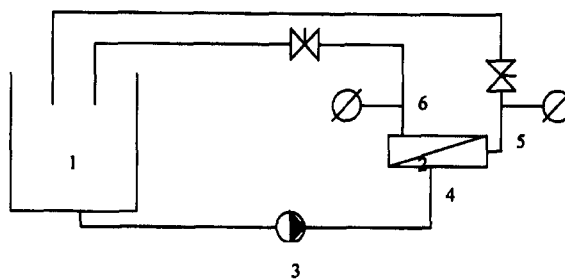


Fig. 1. Schematic representation of the nanofiltration pilot. 1 feed tank, 2 separation module, 3 pump, 4 feed, 5 retentate, 6 permeate.

The synthetic waters were prepared with distilled water produced in our laboratory on an Elix apparatus (Millipore). All pesticide standards (atrazine and its metabolite DEA, simazine, cyanazine, isoproturon and diuron) were obtained from Cluzeau. Individual standard solutions of 1 g/L of each pesticide were prepared in HPLC-grade methanol from SDS and a mixed working solution of 10 mg/L was prepared from them.

For the study of the influence of inorganic matter on the removal of pesticides, we have added to the distilled water 500 ppm of CaCl_2 (Prolabo) or 750 ppm of CaSO_4 (Prolabo) and 1 $\mu\text{g/L}$ of each pesticide. For the experiments on the effect of the humic acid, we prepared a solution containing 10 g/L of humic acid (Aldrich) and 10 mg/L of each pesticide. This solution was let to rest for 48 h in order to allow the contact between humic acid and the pesticides. After that we fortified distilled water by this mixture at a level of 1 $\mu\text{g/L}$ of each pesticide and 1 mg/L of humic acid. These synthetic waters were treated on the NF pilot for 96 h. We set the feed flow at 67.2 L/h and the permeate flow at 1 L/h. Five samples were taken after 4, 24, 48, 72 and 96 h, respectively, at the feed, permeate and the retentate. The samples were replaced by equivalent volumes of the original solution in the feed tank.

These different samples were analyzed with an on-line SPE/HPLC system composed of:

- An HPLC apparatus with three pin pumps, a column oven and diode-array detector (Hewlett Packard HP 1090 series II),
- Prospekt (Programmable On line Solid Phase ExtraKtion Technique), Spark Holland,
- SDU (solvent delivery unit), Spark Holland,
- PC (Hewlett Packard 486 DX2 66 MHz).

Pesticide extraction by the Prospekt was done on PLRP-S cartridges of 30 mg (Varian), firstly activated by acetonitrile HPLC-grade (Carlo Erba) and 5 ml of water HPLC-grade produced in our laboratory on Milli-Q apparatus (Millipore). A volume of 100 ml of the sample was passed through the cartridge. Concentrated analytes are eluted towards a Supelcosil LC-ABZ + column (Supelco) of 250 × 4.6 mm. The mobile phase was a mixture of acetonitrile HPLC-grade (Carlo Erba) and water HPLC-grade with elution gradient: 85/15 (water/acetonitrile) at 0 min, 63/37 at 32 min, 50/50 at 45 min during 3 min and 85/15 at 50 min. The flow of the mobile phase was set at 1.2 ml/min and the oven temperature at 40°C. The detection of triazines was made at 225 nm and of urea herbicides at 245 nm. Their identification was carried out according to their retention times and UV spectra.

3. Results and discussion

The efficiency of the membranes in removing the studied pesticides was determined as follows:

$$R = \left(1 - \frac{C_p}{C_f} \right) \cdot 100\% \quad (1)$$

where R represents the percentage of pesticides removed, and C_p and C_f the concentration of pesticides, respectively, in the permeate and the feed solution.

We have also calculated the percentage of pesticides adsorbed by the membrane materials in

order to be able to explain the mechanisms which govern the removal of these pollutants. This calculation has been possible from a material balance:

$$A = \left(1 - \frac{C_p \cdot Q_p - C_r \cdot Q_r}{C_f \cdot Q_f} \right) \cdot 100\% \quad (2)$$

where A represents the percentage of pesticide being adsorbed, C and Q , respectively, the concentration of pesticides in $\mu\text{g/L}$ and the flow rate in L/h, and r , p and f represent, respectively, the retentate, permeate and feed.

The obtained results are presented in Figs. 2–5. First, it can be seen the effect of the membrane material on the removal percentage of pesticides. The best results were obtained with the Desal DK membrane for all the molecules and matrices. This can be explained by its MWCO of 150–300 daltons. This physical characteristic justifies that the percentage removal of all the pesticides (except diuron) is close one to another for all the matrices. On the contrary, the NF200 membrane, which has a MWCO of 300 daltons, gives a pesticide the removal which is a function of the molecule characteristics (size and dipole moment), since cyanazine and atrazine are more removed than DEA, simazine and isoproturon. The second observation is the low percentage removal of diuron by both membranes compared to the other pesticides. This can be explained by its higher dipole moment and the linear form of this molecule [9].

As for the effect of the inorganic matter (CaCl_2 and CaSO_4) on the pesticide removal percentage, it appears to be different for the two membranes. A small effect is noted in the case of the Desal DK membrane, but for the NF200 membrane the removal of all pesticides has been improved compared to the reference distilled water. This is due to the retention of the divalent ions which block the membrane pores [9]. The results are better with the biggest ions

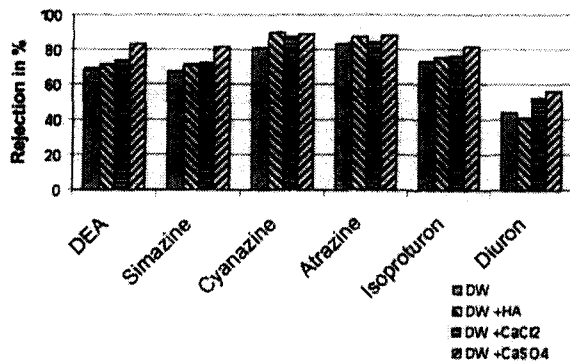


Fig. 2. Pesticide rejection by the NF200 membrane (DW, distilled water; HA, humic acid).

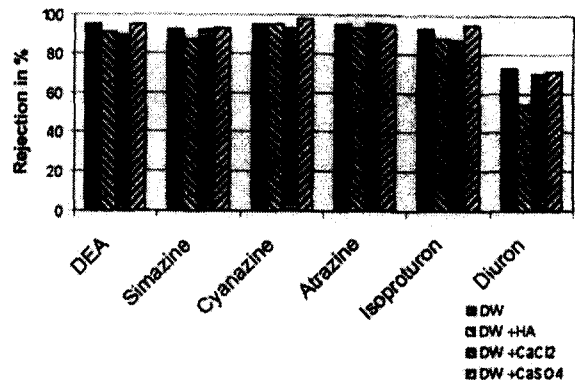


Fig. 3. Pesticide rejection by the Desal DK.

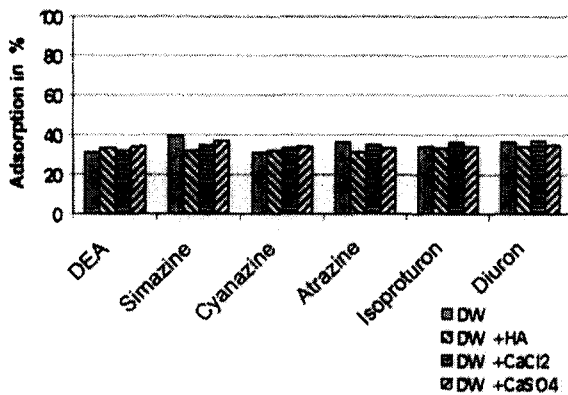


Fig. 4. Pesticide adsorption by the NF200 membrane.

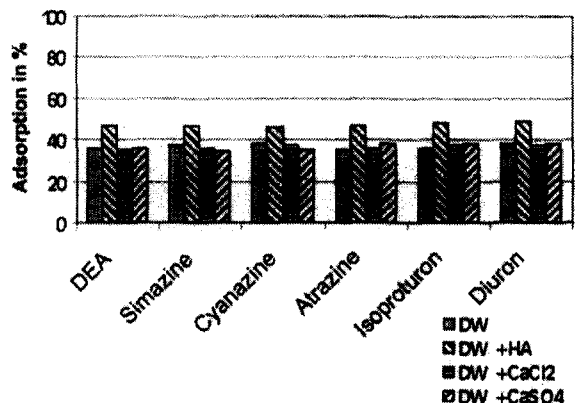


Fig. 5. Pesticide adsorption by the Desal DK membrane.

(sulphates). The percentage of the pesticides adsorbed on the two membranes did not change much because the Ca^{2+} ions have no effect on the net charge of the membrane [10].

On the other hand, the influence of humic acid on the removal of pesticides from water turned out to be higher than with inorganic matter. An increase of the percentage of pesticides adsorbed was observed on the Desal DK for all the molecules ($\approx 10\%$) which has greatly affected the removal of the diuron (-20%), slightly those of simazine and isoproturon (-5%) and with no effect on those of cyanazine and atrazine. With

the NF200 membrane, it can be seen that the percentage of pesticides adsorbed slightly decreased for simazine and atrazine (-5%) and has remained unchanged for the others. The consequence was an increase of the removal of all the pesticides (between 5% and 10%), except diuron, which remained the same.

All the pesticides were removed well by the Desal DK membrane ($R \geq 90\%$) except diuron ($R \leq 70\%$). This is essentially due to the MWCO of the membrane. Due to the form of its molecule, diuron diffuses easily through the membrane: this phenomenon was accentuated by the

presence of humic acid, which is very well adsorbed on the membrane and then charges it negatively [10,11]. Diuron, which has a high dipole moment, permeates through the membrane more easily than other non-polar molecules with the same size [9,12].

In the case of the NF200 membrane, the increase of the percentage removal is due to the phenomenon of the formation of macromolecules between humic acid and pesticides (except diuron [11], which accentuates the rejection by steric exclusion. At the same time, the decrease of the adsorption on the membrane of some pesticides reduces the diffusion through the membrane as reported in the literature [13]. There was no effect of humic acid on the removal and the adsorption of diuron: this is in good agreement with the nature of this molecule which has a small cross section and a high dipole moment [9].

4. Conclusions

The results clearly indicate that NF has a good capacity to remove some pesticides from water. The membrane material influences the percentage of pesticides removal.

The presence of organic matter (humic acid) and inorganic matter (sulfates and chlorides) improve the elimination of some pesticides (except diuron) either by forming macromolecules with them or by reducing the pore size of the membrane.

Diuron was the least removed pesticide, and the presence of organic matter accentuates its diffusion through the membrane.

The combination of the NF technique with a column of granular activated carbon (GAC) can assure the total removal of pesticides and other organic molecules and also decrease the regeneration frequency of GAC.

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