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Atrazine removal from aqueous solutions by nanofiltration

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ABSTRACT

There is an increasing concern about the release of herbicides and other organic compounds to the environment as a result of agricultural activities, due to their high toxicity for living organisms and their difficult to be degraded. Triazines are widely used herbicides that are highly toxic and frequently appear in natural watercourses, atrazine being one of the most commonly detected herbicides in aquatic systems. The atrazine rejection coefficients and the permeate fluxes of different nanofiltration membranes (NF-99, NF-97, Desal-5-DL and Desal-5-DK) for the removal of atrazine from water solutions in different operating conditions (feed atrazine concentration, pressure and pH) are studied in this article. Atrazine rejection was greater with the NF 99 and NF 97 membranes (90–98%), while the DL and DK membranes show much lower rejections (40–50%). The highest permeate fluxes are obtained with NF-99 and DL membranes. Atrazine rejection and permeate flux show no dependence on the atrazine feed concentration, low dependence on pH and a high positive dependence on pressure (especially the permeate flux). The results are explained by taking into account different solute parameters and membrane properties that affect the nanofiltration process.

Keywords: Nanofiltration; Atrazine removal; Rejection; Permeate flux

1. Introduction

Water contamination is a worldwide problem due to urban, agricultural and industrial pollution. Among the different pollutants, herbicides such as s-triazines are priority pollutants as they are widely used throughout the world. Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine), the most common s-triazine, is used as pre- and post-emergence herbicide for the control of annual and perennial grass and annual broad-weeds [1]. It is the most widely used herbicide in agricultural and forestry applications, with 70,000–90,000 tons applied annually [2]. This herbicide belongs to the group of persistent organic pollutants because of its low biodegradability and long half-life in water (between 30 and 100 days). Moreover, it is slightly soluble in water and shows relatively low adsorption to soil; consequently, it migrates easily towards the underground waters, thus presenting a potential danger for public health [3]. Though the commercial use of atrazine has been banned in several countries, its presence, and that of its metabolites, in surface and ground water will continue for several years, and so atrazine is included in the priority list of 76 substances of the Water Framework Directive in Europe [4].

With this in mind, there is a need to develop efficient remediation treatments to eliminate atrazine from water sources. To this end, different techniques have been proposed, among them biological methods

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[5–7], adsorption on different types of sorbents [8–11], covalent bonding [12], advanced oxidation processes [13–15], pressure driven membrane processes [16–19] and hybrid processes [20–22].

Nanofiltration is a promising pressure-driven membrane process with a growing number of applications for the treatment of drinking water and wastewater. Its energy requirements are much lower than those of reverse osmosis because of the lower transmembrane pressures involved and because nanofiltration membranes are designed to selectively remove multivalent ions and organic contaminants.

Different parameters have been described as affecting retention and retention mechanisms in nanofiltration [23,24]. The key parameters affecting solute retention are molecular weight, molecular size (length and width), the acid dissociation constant, hydrophobicity/hydrophilicity (log K_{ow}) and polarity. Similarly, the key membrane properties affecting retention are membrane cut-off weigh, pore size, surface charge and hydrophobicity/hydrophilicity. Knowing the solute rejection coefficient and permeate flux of the nanofiltration membrane used is of great importance in order to elucidate the solute retention mechanisms in nanofiltration.

The solute rejection coefficient is defined as a percentage by the mathematical expression $R = (1 - C_p/C_f)\cdot 100$, where C_p and C_f are the solute concentrations in permeate and feed streams, respectively. The flow or permeation rate, J, is defined as the volume flowing through the membrane per unit area and time.

A study of the atrazine rejection coefficients and permeate fluxes of different nanofiltration membranes (NF-99, NF-97, Desal-5-DL and Desal-5-DK) in the removal of atrazine from water solutions in different operating conditions (pressure, feed atrazine concentration, and pH) is carried out in this article.

2. Experimental equipment and procedure

Experimental tests were performed in an INDEVEN flat membrane test module. The module comprises a unit, which provides data concerning the behaviour of the membranes in cross flow conditions with a reduced surface area, low feed rate and short times. The recycling of both concentrate and permeate was carried out in order to keep the feed concentration practically constant and so simulate a continuous process in a quasi-steady state. Fig. 1 shows a schematic flow diagram of the nanofiltration test unit.

Two polyamide membranes (NF-99, NF-97) and two polypiperazinamide membranes (Desal-5-DL and Desal-5-DK) were used. Those membranes are thin

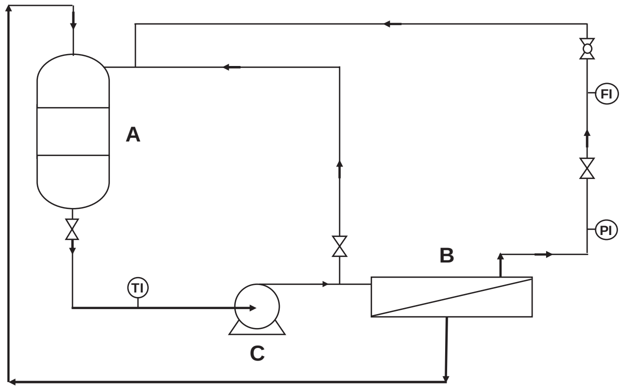

Fig. 1. Schematic flow diagram of nanofiltration test unit (flat membrane module): (A) feed tank, (B) membrane module, (C) pressure pump.

film composite membranes with a high selectivity towards divalent ions that can be used in a relatively wide range of temperatures, pressures and pH values. The main characteristics of the membranes, according to the manufacturer, are described in Table 1.

Atrazine main molecular parameters and general properties are given in Table 2.

To determine the influence of the feed atrazine concentration on atrazine rejection and on permeate flux, feed atrazine concentrations from 3.5×10^{-3} to 8.0×10^{-3} kg/m^3 were used at a pressure of 15×10^5 N/m^2 and a pH of 6.0.

To study the influence of pressure on atrazine rejection and on permeate flux, pressures varying from 5×10^5 to 20×10^5 N/m^2 were used, at a feed atrazine concentration of 6.5×10^{-3} kg/m^3 and a pH of 6.0.

The influence of pH on atrazine rejection and on permeate flux was studied, varying the pH of the feed atrazine solution from 2,0 to 10,0 at a pressure of 15×10^5 N/m^2 and a concentration of atrazine of 6.5×10^{-3} kg/m^3.

A feed rate of 4.17×10^{-5} m^3/s was used in all the cases.

Atrazine concentrations were determined spectrophotometrically at 230 nm.

3. Results and discussion

3.1. Influence of studied parameters on atrazine rejection

The variation of atrazine rejection with feed atrazine concentration, pressure and pH in the four studied membranes is shown in Fig. 2.

The nature of membranes leads to differences in the rejection coefficients. In all cases, NF-99 and NF-70 membranes provide rejection coefficients of higher than 90%, with very close values, while LK and DK

Table 1
Main characteristics of the membranes used in the experimental test module.

Characteristic	Membrane			
Product denomination	NF-99	NF-97	DESAL-5-DL	DESAL-5-DK
Manufacturer	Dow chemical		GE osmonic	
Type	Thin film composite membrane			
Composition	Polyamide		Polypiperazinamide	
Molecular weigh cut-off (MWCO) (Da)	≤200	≤200	340[a]	230[a]
Effective membrane surface area (m^2)	0.003	0.003	0.003	0.003
Maximum operating pressure (N/m^2)	$55.0 \cdot 10^5$	$55.0 \cdot 10^5$	$40.0 \cdot 10^5$	$34.5 \cdot 10^5$
Maximum temperature (°C)	50	50	90	50
Water permeability constant (h/m)	9.0	7.8	8.6	7.1
MgSO4 rejection (%)	≥98	≥97	≥96	≥97
pH range	3–10	3–10	1–11	2–11

[a] [25].

membranes provide rejections of lower than 50%, the DK membrane retention being higher.

Size exclusion factors can partially explain these results. The membranes with lower MWCO (NF-99 and NF-97) show higher rejection coefficients than the membranes with higher MWCO (DK and DL). In this way, the lowest rejection of DL membrane can be explained by its higher MWCO (340 Da).

Nevertheless, the difference in MWCO between DK membrane and NF-99 and NF-97 membranes is not great enough to explain the big differences observed in their rejection coefficients. Another important parameter that affects membrane rejection is the relation of hydrophobicity of the solute in relation to the membrane. The hydrophobic/hydrophilic character of a solute can be described by its log K_{ow}, with log $K_{ow} > 2$ meaning a hydrophobic character. So, atrazine with a log $K_{ow} = 2.61$ can be considered hydrophobic and tends to avoid hydrophilic membranes. The higher atrazine rejection coefficients of the NF-99 and NF-97 membranes compared with the DK membrane suggest the higher hydrophilic character of the latter, possibly due to the hydrophilic nature of the polypiperazine backbone compared with polyamide [27].

No significant effect of feed atrazine concentration on the rejection coefficient was observed (Fig. 2a), and similar results have been obtained by other researches [28,29].

An increase in operation pressure leads to a slight increase in atrazine rejection in polyamide membranes (NF-99 and NF-97), but to a more significant increase in atrazine rejection in polypiperazinamide membranes (DL and DK; Fig. 2b). This can be explained by assuming that an increase in pressure leads to both an increase in the water flux, the permeate becoming more dilute, and to an increase in the fouling layer on the membrane, which partially obstructs the permeation of atrazine and leads to higher *R* values [30].

A very slight, non-significant, increase in atrazine rejection was observed between pH 2 and pH 8, but a more significant decrease in atrazine rejection between pH 8 and pH 10 (Fig. 2c). The membranes tested in this study contain carboxyl groups in their polymeric structures which become negatively charged at approximately neutral pH [31]. This should not greatly affect atrazine permeation because atrazine molecule has no net charge in the pH range studied [32] and it is polar (3.44D). This means that in the permeation process, the dipole is directed to the membrane charge in such a way that the side of the dipole with the opposite charge is closer to the membrane, encouraging permeation. However, it has been suggested that the electrostatic repulsion between negative carboxylate groups within the membrane leads to an increase of the pore size of the membrane [33,34] and so to an atrazine rejection decrease.

Table 2
Main atrazine molecular parameters and general properties [17,18,26]

Chemical formula	Molecular weigh (g/mol)	Length (Å)	Width (Å)	Log K_{ow}	Dipole moment (D)
$C_8H_{14}ClN_5$	215.69	10.36	8.02	2.61 2.82	3.44

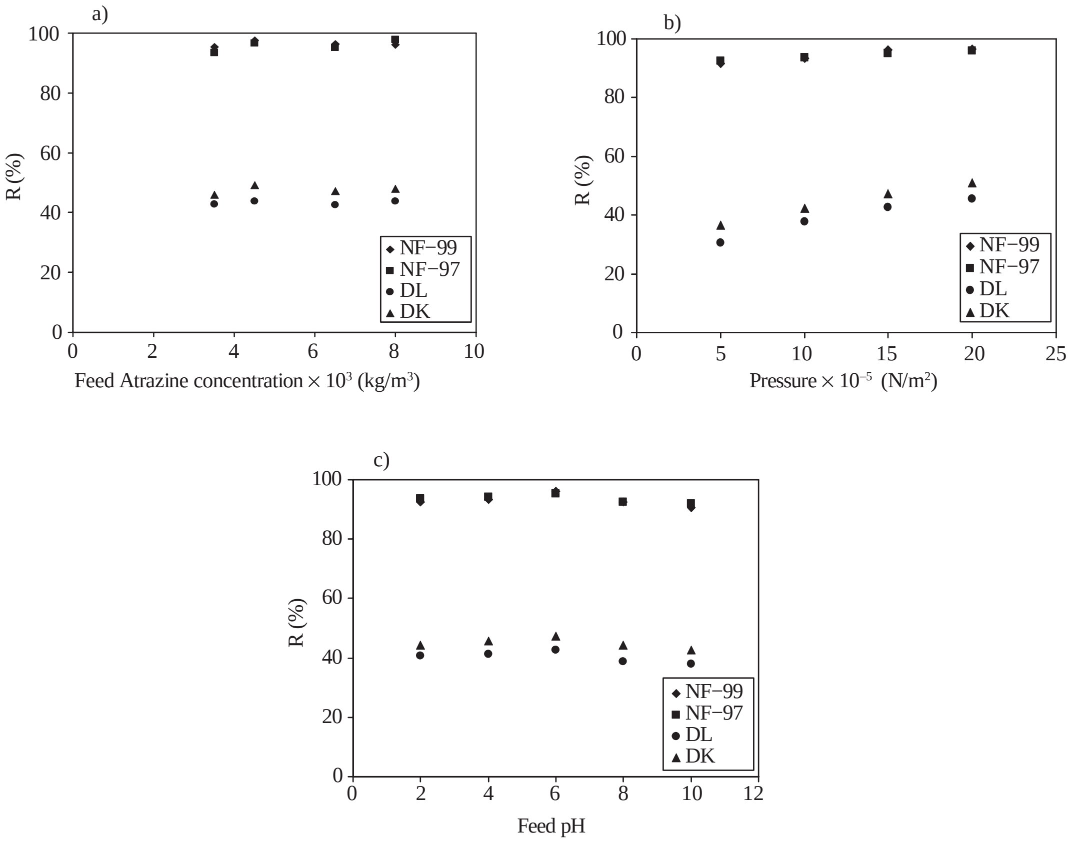

Fig. 2. Influence of feed atrazine concentration (a), pressure (b) and pH (c) on atrazine rejection.

3.1. Influence of studied parameters on permeate flux

Variations in permeate flux with feed atrazine concentration, pressure and pH is shown in Fig. 3.

Higher permeate fluxes are shown by NF-99 and DL membranes while permeate fluxes of NF-97 and DK membranes are lower. These results agree with the water permeabilities of the membranes (Table 1) and the atrazine rejections mentioned above.

Feed atrazine concentration had no significant effect on permeate flux (Fig.3a) and, as could be expected, the increase of pressure had a positive effect on the permeate flux in all the tested membranes, with an almost linear variation (Fig. 3b). It has been pointed out [35] that this linear relationship is a characteristic of less severe fouling phenomena occurring in membranes with a low molecular weigh cut-off, such as the nanofiltration membranes used in this study.

No significant influence of pH on permeate flux was observed between pH 2 and pH 8, but permeate flux increased slightly between pH 8 and 10 (Fig. 3c). As we said above, to explain the influence of pH on atrazine rejection, the electrostatic repulsion between negative carboxylate groups within the membrane can lead to an increase of the pore size of the membrane and so to an increase in permeate flux.

4. Conclusions

The atrazine rejection coefficients and permeate fluxes of different nanofiltration membranes (NF-99, NF-97, Desal-5-DL and Desal-5-DK) for the removal of atrazine from water solutions at different operating conditions (feed atrazine concentration, pressure and pH) have been studied. Higher atrazine rejections were obtained for NF 99 and NF 97 membranes (90-98%), while DL and DK membranes showed much lower rejections (40–50%). Higher permeate fluxes were obtained for NF-99 and DL membranes.

Atrazine rejection and permeate flux showed no dependence on feed atrazine concentration, a low dependence on pH, (only at basic pH), and a strong positive dependence on pressure. The results are explained by taking into account different solute parameters and membrane properties that affect the nanofiltration process.

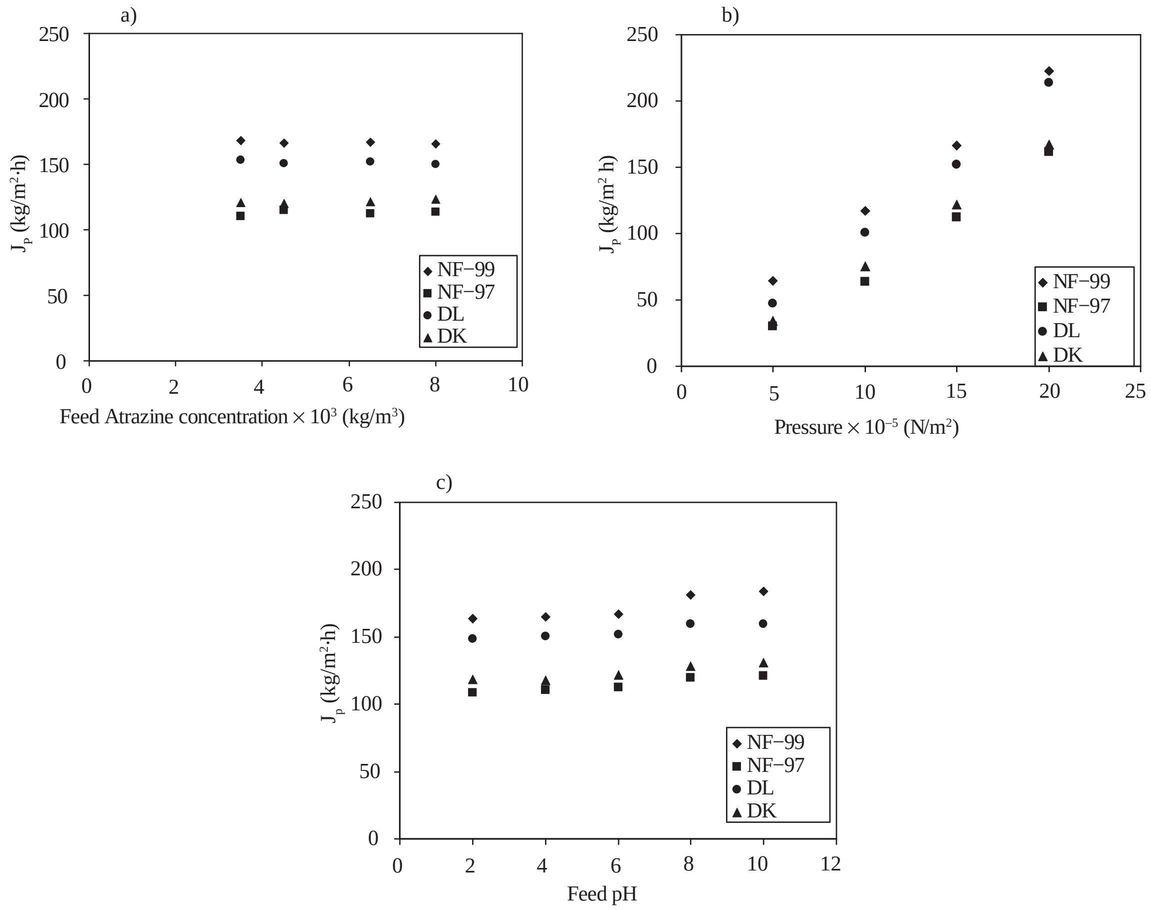

Fig. 3. Influence of feed atrazine concentration (a), pressure (b) and pH (c) on permeate flux.

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