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Removal of 4-chloro-2-methylphenol from aqueous solutions by nanofiltration and reverse osmosis

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ABSTRACT

Chloromethylphenols are typical phenolic pollutants frequently found in wastewater treatment plants and industrial landfill leachates, while pressure-driven membrane processes have been demonstrated to be a practical and competitive alternative for their removal. The performance of two membranes (an NF99 nanofiltration membrane and an RO99 reverse osmosis membrane) for removing 4-chloro-2-methylphenol (4C2MP) from synthetic solutions at different pressures, feed concentrations and feed pH values is compared in this paper using permeate flux and rejection as representative parameters. Higher permeate fluxes were obtained with the NF99 membrane but higher rates of 4C2MP rejection were obtained with the RO99 membrane. There was a substantial increase in 4C2MP rejection as the pH was increased from 8 to 11 in the case of the NF99 membrane. The results are explained by the different chemical structures of the active layers of both membranes.

Keywords: 4-chloro-2-methylphenol; Membrane process; Nanofiltration; Reverse osmosis

1. Introduction

Chlorophenols and cresols constitute particular groups of toxic pollutants classified as first-degree toxic pollutants by the US Environmental Protection Agency [1] and EC Environmental Directive (2455/2001/EC) [2]. Most of them are toxic, poorly biodegradable and difficult to remove from the environment—their half-life in water has been estimated as 3.5 months in aerobic waters and several years in organic sediments [3].

They are used extensively as fungicides, herbicides, insecticides, pharmaceuticals, and as preservative for wood, glue, paint, vegetable fibres and leather; they are also intermediates in the manufacture of phenolic resins, herbicides, pesticides, dyes and plant growth regulators [4]. They can also be formed by the

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degradation of other chlorinated compounds, such as chlorophenoxyacetic acids, chlorobenzenes or chlorinated pesticides [5], by the reaction of chlorinated water supplies with phenol in the environment, during water chlorination and during the incineration of organic materials [6]. Furthermore, they are observed as by-products of chlorine bleaching in the pulp and paper industry, particularly when elemental chlorine is used [7].

Such compounds should obviously be removed from wastewater before discharge to the environment. Different techniques have been described for removing chlorophenols and cresols from wastewater, including adsorption [8,9], bioadsorption [10], ionic exchange [11], biological treatments [12], conventional and advanced oxidation processes [13–15], hydrodechlorination [16], sonochemical methods [17], membrane processes [18,19] and combined processes [20,21].

Pressure-driven membrane separation processes have been demonstrated to be a practical and competitive alternative for the removal and/or recovery of a variety of pollutants or valuable organic compounds [22]. Although these techniques are effective for the removal of large molecular mass organic substances, their effectiveness in removing smaller organics varies with the type of chemical species and the nature of the membrane [23]. In this respect, several authors have studied the applicability of reverse osmosis and nanofiltration polyamide membranes for the removal of low molecular weight organic compounds, including phenols [24–26].

Chloromethylphenols are representative phenolic pollutants frequently found in wastewater treatment plants and industrial landfill leachates [27]. The production of 4-chloro-2-methylphenol and its use as an intermediate in the synthesis of the herbicides 2-methyl-4-chlorophenoxyacetic acid (MCPA) and 2-methyl-4-chlorophenoxybutyric acid (MCPB) would result in its release to the environment through waste streams. Moreover, the degradation of these herbicides to 4-chloro-2-methylphenol is thought to be an additional important source of this chemical in the environment. The degradation of chloromethylphenols by Fenton's reagent or by electrochemical processes has been described [28–30], but their removal by nanofiltration or reverse osmosis has not been reported. The objective of this paper is to compare the behaviour of nanofiltration and reverse osmosis membranes and processes for the removal of 4-chloro-2-methyphenol from aqueous solutions by analysing the influence of applied pressure, feed pH and feed concentration on the efficiency of the removal process.

2. Materials and methods

2.1. Reagents and membranes

4-Chloro-2-methylphenol (97% purity) was purchased from Sigma Aldrich, and analytical grade NaOH and HCl 37% purity were obtained from Probus and Panreac, respectively. All chemicals were used without purification and aqueous solutions were prepared with doubly distilled water. Table 1 summarizes some relevant properties of 4C2MP.

Two polyamide thin-film composite membranes were used, NF99 and RO99, supplied by Alfa Laval and manufactured by Dow Chemical. The NF99 membrane is a thin-film composite nanofiltration membrane with an active layer of semi-aromatic/aliphatic polyamide (piperazine) [31,32], while the RO99 membrane is a thin-film reverse osmosis membrane with an active layer of fully aromatic polyamide [33]. The specifications of these membranes are shown in Table 2.

2.2. Experimental set-up and operation control

Tests were performed in an MMS Triple System Model F1 flat membrane test module. The experimental unit consisted of a thermostated stainless steel feed tank with a capacity of $0.8 \times 10^{-3}\,m^3$, a flat sheet membrane module that supports the membrane (specific area $4.66 \times 10^{-3}\,m^2$) and a pressure pump which drives the feed solution through the membrane module.

Aqueous 4-chloro-2-methylphenol solutions in distilled water (concentrations ranging between 0.025 and $0.10\,kg/m^3$) were treated in the test module at transmembrane pressures varying from 5 to 20 bar for the nanofiltration assays (NF99 membrane) and from 15 to 30 bar for the reverse osmosis assays (RO99 membrane), varying the pH from 8 to 11.

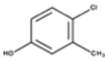
2.3. Analytical method and data processing

The 4-chloro-2-methylphenol concentration was determined using a colourimetric method based on the reaction of phenolic compounds with 4-aminoantipyrine in the presence of potassium ferricyanide reagent [35]. The reaction product absorbs light at 505 nm and concentrations were determined with a Shimadzu UV-160 spectrophotometer.

Membrane performance was measured in terms of membrane rejection (%R) and permeate flux (J_p).

For dilute aqueous mixtures consisting of water and a solute, the selectivity of a membrane is usually expressed in terms of the solute rejection coefficient [36], which is defined as a percentage by Eq. (1),

Table 1
Some physico-chemical properties of 4-chloro-2-methylphenol

Molecular formula	Structural formula	Molecular weight (g/mol)	Water solubility (g/L)	Log $K_{o/w}$	pK_a	Length* (Å)	Width* (Å)	Height* (Å)
C_7H_7ClO		142.59	2.3	3.09	9.71	6.33	5.92	1.77

*Values calculated from the structural representation from National Institute of Standards and Technology.

Table 2
Main characteristics of the membranes used in the experimental flat membrane test module

Provider	Alfa Laval	Alfa Laval
Manufacturer	Dow Chemical	Dow Chemical
Product denomination	NF99	RO99
Type	Thin-film composite (NF)	Thin-film composite (RO)
Composition	Semi-aromatic polyamide (polypiperazine)	Fully aromatic polyamide
Molecular weight cut-off (MWCO) (Da)	200*	–
Maximum pressure (bar)	55	55
pH range	3–10	3–10
Maximum temperature (°C)	50	50

*Ref. [34].

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

where C_p and C_f are the solute concentration in the permeate and feed streams, respectively.

The permeate flux was calculated according to the following Eq. (2),

$$J_p = \frac{Q_p}{S}\,(\text{m/s}) \tag{2}$$

where Q_p is the permeate flow (m^3/s) and S is the effective membrane area (m^2).

2.4. Membrane characterization

For an initial characterization of the membranes used in the study, the water permeability coefficients (A_w) and Cl_2Mg rejections of both membranes were obtained.

For the determination of A_w, distilled water was used as feed and fluxes were measured at pressures of 5 to 20 bar for the NF99 membrane and from 15 to 30 bar for the RO99 membrane. The water flux (J_w) depends on the hydraulic pressure applied across the membrane, ΔP, according to Eq. (3) [37].

$$J_W = A_W \times (\Delta P) \tag{3}$$

Rejections of 0.2 g/L Cl_2Mg aqueous solutions were determined at 15 bar for NF99 membrane and at 30 bar for RO99 membrane. The concentrations of salt in the feed and in the permeate were determined by a conductivity meter using previously obtained calibration curves.

3. Results and discussion

3.1. Membrane characterization

Similar Cl_2Mg rejections (99%) were obtained for both membranes. The water permeability coefficient of the NF99 membrane (1.02×10^{-8} m/s) was about four times higher than that of the RO99 membrane (2.32×10^{-9} m/s), which was probably related with the different chemical structures of the active layers of the membranes. The less dense and thinner polyamide layer of semi-aromatic/aliphatic polyamide (piperazine) of NF99, which is more prone to pinholes and local defects [38–41], was also partly responsible for the higher water permeability obtained with it than with the fully aromatic membrane, RO99.

3.2. Influence of pressure

Fig. 1(A) shows the effect of pressure on permeate flux. It can be observed that the NF99 membrane permits a higher permeate flux than the RO99 membrane. The higher permeability of the semi-aromatic

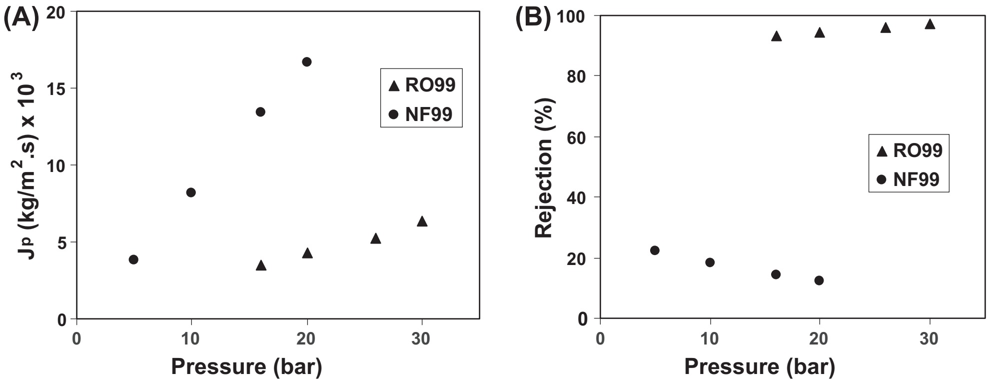


Fig. 1. Variation in permeate flux (A) and rejection coefficient (B) with pressure for: pH 7, 4C2MP concentration = 0.050 kg/m^3, pressure (5×10^5–20×10^5 N/m^2) nanofiltration membrane (•) and (15–30 bar) reverse osmosis membrane (♦).

membrane (NF99) can be attributed, as mentioned above, to its less dense and thinner polyamide layer and to the probable presence or more pinholes and local defects.

The permeate flux increases linearly with pressure for both membranes, which means that no important fouling or polarization effects are to be expected [42]. The greater increase in permeate flux in the case of the NF99 membrane may also be due to the less dense and thinner polyamide layer of this membrane.

Fig. 1(B) shows the effect of pressure on rejection. Higher 4-chloro-2-methylphenol rejections were obtained with the RO99 membrane (>90%) than for the NF99 membrane (~20%), as can be seen for the common pressure range used in nanofiltration and reverse osmosis conditions (15–20 bar).

Size exclusion and the Donnan effect are the two main mechanisms involved in rejection during nanofiltration and reverse osmosis [42,43]. For the uncharged molecules, such as 4C2MP at pH 8, size exclusion was the dominating factor influencing retention, while for the charged molecules, the Donnan effect resulting from the electrostatic interaction between membrane and charged solutes governed solute transport.

Although the higher rejections obtained for the RO99 membrane can obviously be explained by simply taking into consideration size exclusion effects derived from the denser and wider polyamide layer of this membrane, rejection is also influenced (when the solute molecular weight is below the MWCO of the membrane) by solute–membrane and solute–water interactions. Semi-aromatic piperazine membranes are more hydrophilic than fully aromatic-based membranes [40,41], probably due to their lower aromaticity [44,45]. Hydrophobic compounds have less interaction with the water phase (through which these compounds permeate more readily in the membrane phase [46,47]) than hydrophilic compounds. 4C2MP is extremely hydrophobic ($\log K_{o/w} = 3.09$), due to its aromatic ring, but the presence of the non-ionized polar –OH group increases its affinity for the more hydrophilic NF membrane and for water (via polarity and hydrogen bonding), and this facilitates its adsorption to the membrane surface and its passage through the membrane, resulting in a lower retention.

For the RO99 membrane, 4C2MP rejection slightly increases as pressure increases probably due to the increase in permeate flux, which leads to a decrease in the 4C2MP concentration in the permeate. In contrast, in the case of the NF99 membrane, 4C2MP rejection decreases with the increase in pressure, despite the great increase in permeate flux. This has also been observed by other authors in their studies with different organic compounds [48]. It may be assumed that the decrease in solute rejection with increased pressure is the result of the increase in the degree of mobility of the sorbed 4C2MP as pressure increases [48].

3.3. Influence of feed pH

Fig. 2(A) shows the effect of pH on permeate flux. It can be observed that no significant variations in permeate flux accompany the change in pH.

Fig. 2(B) shows the influence of pH on 4C2MP rejection. As can be observed, 4C2MP rejection increases strongly with the increase in pH for the NF99 membrane and only slightly increases in the case of the RO99 membrane.

As mentioned above, size exclusion and the Donnan effect are the two main mechanisms involved in the rejection process during NF and RO. The pK_a of 4C2MP is 9.71, which means that as pH increases from 8 to 11, ionization of the phenolic -OH group occurs,

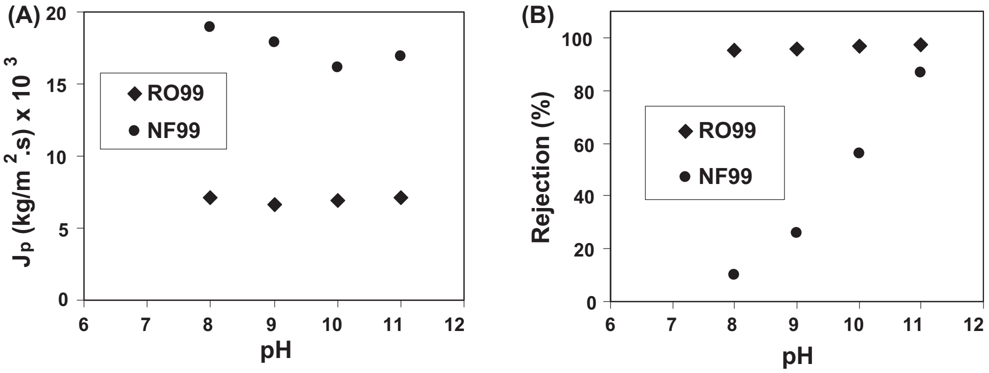


Fig. 2. Variation in permeate flux (A) and rejection coefficient (B) with pH for: 4C2MP concentration = 0.050 kg/m^3, pressure = 20 bar nanofiltration membrane (•) and pressure = 30 bar reverse osmosis membrane (♦).

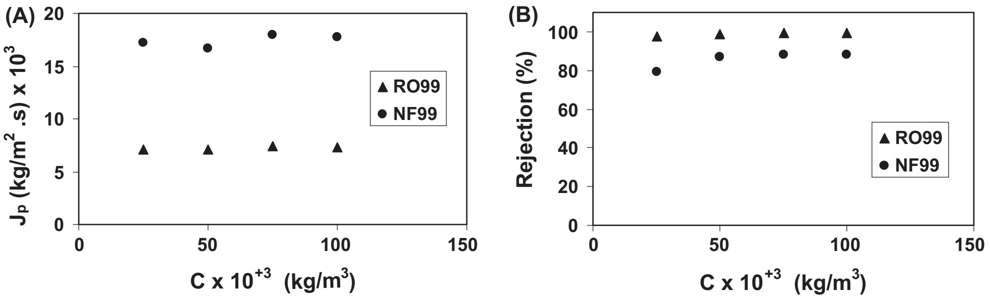


Fig. 3. Variation in permeate flux and rejection coefficient with 4-chloro-2-methylphenol concentration: pH 11, pressure = 20 bar nanofiltration membrane (•) and pressure = 30 bar reverse osmosis membrane (♦).

and so the negative charge of 4C2MP increases as the pH increases, at least in this range. This has two effects on solute permeation, one related with the Donnan effect and the other with size exclusion. On the one hand, as the surface of polyamide membranes is negatively charged in the pH range studied (8–11), due to the deprotonation of carboxylic groups, the increase of negative charge of 4C2MP leads to an increase in repulsion in the face of the negative charges of the membrane, resulting in an increase in rejection caused by the Donnan effect. Moreover, in nanofiltration membranes, there is an additional substantial increase in rejection due to the size exclusion effect resulting from the membrane pore constriction (shrinking membrane material) with the increase of pH [49].

3.4. Influence of feed concentration

Fig. 3(A) shows the effect of 4C2MP concentration on the permeate flux. As can be observed, there were no significant variations in permeate flux with increases in feed concentration, which can be explained by the sum of two contrary effects: the increase in solute flux due to the increase of feed concentration, and the decrease in water flux as a consequence of the increase of $\Delta\Pi$.

No significant effect of the 4C2MP concentration in the feed phase on rejection was observed (Fig. 3(B)). When the feed concentration increases, the permeate concentration also increases so that there is no significant change in 4C2MP rejection. Similar results have been obtained by researchers working with other organic compounds [50–52].

4. Conclusions

A study of 4-chloro-2-methylphenol removal by nanofiltration and by reverse osmosis using an NF99 nanofiltration membrane and an RO99 reverse osmosis membrane, respectively, at different pressures, feed concentrations and feed pH values was carried out, using permeate flux and rejection as representative parameters. A preliminary characterization of both membranes was carried out by obtaining their water permeability coefficients and their $MgCl_2$ rejection rates. The different chemical structures of the active layers of these membranes—semi-aromatic/aliphatic polyamide (piperazine) in NF99 membrane and fully aromatic polyamide in RO99 membrane—may explain the higher permeate fluxes obtained with the NF99 membrane and the greater 4C2MP rejections obtained with the RO99 membrane. The same explanation would apply to the substantial increase in 4C2MP rejection obtained with the NF99 membrane (but not with the RO99 membrane) as the pH increased from 8 to 11.

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