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Comparative study of the removal of heavy metals by two nanofiltration membranes

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ABSTRACT

This study describes the rejection of heavy metal ions (Cu(II), Cd(II), and Zn(II)) using two commercial nanofiltration membranes (DL and DK). The effect of transmembrane pressure and metal concentration on the metal rejections and permeate flux was explored. The results showed that for DL membrane the maximum rejection was obtained at ΔP = 4 bar for all studied heavy metals. The rejections of Zn, Cu, and Cd were 93, 90, and 86%, respectively, when the concentration of each heavy metal was fixed to 10^{-5} mol/L and were 79, 76, and 78%, respectively, when the concentration of each heavy metal was fixed to 10^{-3} mol/L. The rejection sequence was identical for both membranes ($R_{Cu} < R_{Zn} < R_{Cd}$). However, the transmembrane pressure and the metal concentration had no great effect on rejection factors in the case of DK membrane. The variation of the permeate flux vs. the transmembrane pressure after treating different mixtures containing Cu(II), Cd(II), and Zn(II) metals by nanofiltration using DL and DK membranes was studied. A deviation from the straight line representing J_v vs. ΔP of different mixtures studied compared to pure water line was observed, but it was much more important in the case of DL membrane confirming a greater sensitivity to pores clogging.

Keywords: Nanofiltration; Heavy metals; Rejection; Membrane; Permeate flux

1. Introduction

Tunisia is characterized, in most regions, by a semi-arid to arid climate. The country suffers as much from inadequate rainfall as their uneven distribution in time and space. Climate constraints, population growth, and economic and social transformations lead to the increase in water demand. Meanwhile, the use of irrigation has become a necessity, given the importance of climate and water deficit intensification of agriculture. Now, faced with these demands, water resources are scarce and insufficient.

Thus, to satisfy all the needs of the country in order to reserve water and water quality in drinking water to ensure better public health and protect the environment, the need to promote domestic and industrial wastewater treatment is important. In this context, the use of treated wastewater has become a necessity and an integral part of the current strategy to mobilize all available resources [1–3]. Pollutant loads contained in wastewaters have various origins.

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The five main categories of polluters are industry, agriculture, households, transport, and urbanization [4]. Particularly, industrial wastewater containing heavy metals must be treated before being discharged into the natural environment or in sewage treatment plants. The presence, in the environment, of these toxic metals is an increasing danger to human health and to the balance of ecosystems [5–7]. The incorporation of membrane technology in the effluent treatment process loaded with metal ions has emerged. The membrane processes (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis) were then used for this purpose with various effectiveness and selectivity [8–11].

In this work, rejection of three metal solutions (Cu(II), Cd(II), and Zn(II)) was investigated using the DL and DK membranes. The effect of the following factors on each membrane separation was studied: pressure (3–7 bar) and initial feed concentration (10^{-6}–10^{-3} mol/L) of the solution. In this study, flux reduction with these metals was also studied and an industrial application using actual wastewater was performed.

2. Methods

2.1. Nanofiltration membranes characteristics

Two flat sheet membranes were used in this study: DL and DK provided by SEPA CF GE Osmonics, Florida, USA, with an effective surface area of 140 cm^2. These membranes were made of polyamide. Their support was made of polysulfone. The main characteristics of these membranes are shown in Table 1.

2.2. Membrane filtration experiments

A cross-flow stainless steel nanofiltration unit was used (Fig. 1). This nanofiltration unit was equipped with one membrane module with an effective membrane area of 140 cm^2 which can be operated in the pressure range of 3–7 bar. The nanofiltration unit consisted of a feed tank, a membrane module, a high-pressure pump, and two pressure gauges.

Table 1
Membranes characteristics [12]

Parameter	DL characteristics	DK characteristics
TOC rejection (%)	88.4	98.9
Roughness (RMS) (nm)	13.2	10.2
Contact angle (°)	50.9	58.3
Zeta potential (mV)	−9.4	−5.9

The pure water permeability coefficient (L_o) was determined by measuring the pure water flux (J_o) vs. transmembrane pressure (ΔP) for NF HL membrane. The Darcy law is used to fit the pure water permeability data defined by Eq. (1):

$$J_o = L_o \times \Delta P = \frac{\Delta P}{\eta_{\text{water}} \times R_{\text{m}}} \tag{1}$$

where R_{m} (m^{-1}) is the intrinsic resistance of the membrane and η_{water} (kg m^{-1} s^{-1}) represents the water dynamic viscosity.

2.3. Heavy metal rejection using nanofiltration membranes

In the experiments of heavy metal removal (Cu(II), Cd(II), and Zn(II)), an initial volume (500 mL) of the metal solution was pumped and circulated through the membrane module. Permeate was continuously collected until 25 mL of the permeate had been acquired, at which point the experiment was stopped.

Heavy metal retention can be represented by rejection factor (R) presented in Eq. (2):

$$R(\%) = 100 \times \left(1 - \frac{C_{\text{permeate}}}{C_{\text{feed}}}\right) \tag{2}$$

where C_{permeate} and C_{feed} represent the metal concentrations, respectively, in permeate and feed streams.

3. Results

3.1. Membrane permeability

Pure water flux measurements as a function of transmembrane pressure (ΔP) for NF membranes was carried out (Fig. 2). Using Eq. (1), the membrane permeability (L_0) was found to be 6.788 L/m^2 h bar for DL membrane and 3.162 L/m^2 h bar for DK membrane.

3.2. Effect of transmembrane pressure

Different mixtures of the three heavy metals (Cu(II), Cd(II), and Zn(II)) were prepared. The concentration of every metal in the mixture was varied from 10^{-5} to 10^{-3} mol/L and the transmembrane pressure was varied from 3 to 7 bar. Figs. 3 and 4 show the variation of the rejection factor (R) vs. the transmembrane pressure after treating two mixtures by nanofiltration using, respectively, DL and DK membranes.

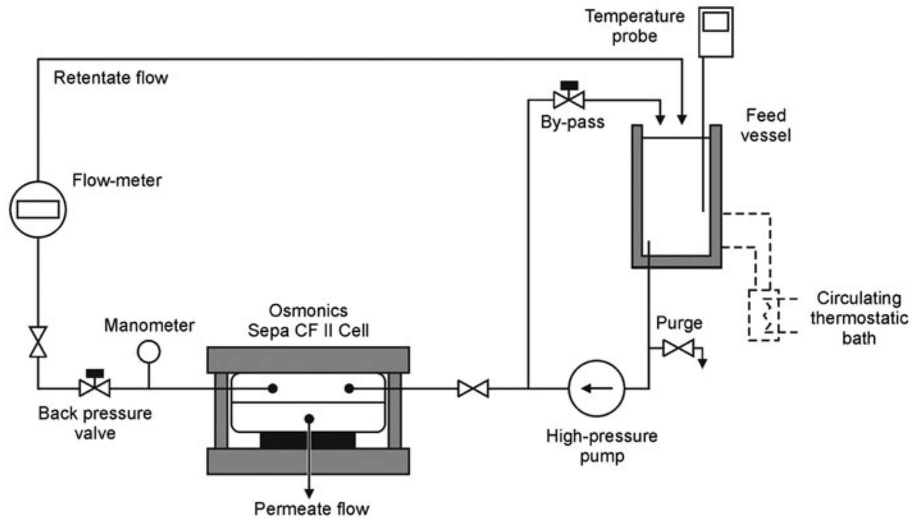

Fig. 1. Membrane filtration experimental set-up.

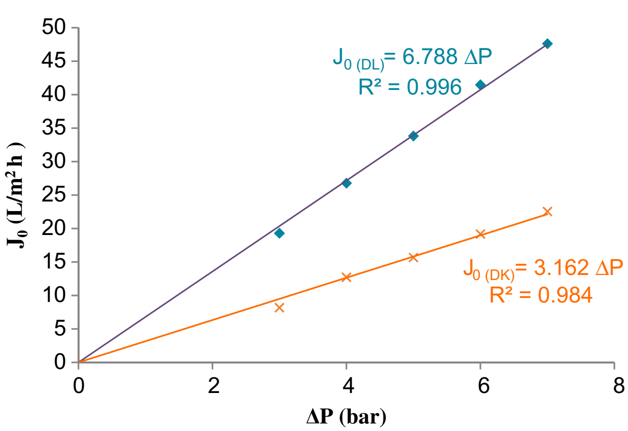

Fig. 2. DL and DK membrane permeabilities.

In the case of the DL membrane (Fig. 3), the maximum rejection was obtained at ΔP = 4 bar for all studied heavy metals. The rejections of Zn, Cu, and Cd were 93, 90, and 86%, respectively, when the concentration of each heavy metal was fixed to 10^{-5} mol/L and were 79, 76, and 78%, respectively, when the concentration of each heavy metal was fixed to 10^{-3} mol/L.

For the first mixture ([metal] = 10^{-5} mol/L, Fig. 3(a)), 84 < $R_{Cu} \approx R_{Zn}$ < 93% and 69 < R_{Cd} < 86%. The decrease in the Cd rejection factor could be attributed to its diffusion coefficient and its ionic radius which are greater that those of Cu and Zn. In fact, the diffusion coefficients of cations Cd^{2+}, Zn^{2+}, and Cu^{2+} in water at 25°C are 1.438 × 10^{-5}, 1.406 × 10^{-5}, and 1.428 × 10^{-5}, respectively [13]. The order of diffusion coefficients is inversely reflected in the rejection sequence. The ionic radius of cations Cd^{2+}, Zn^{2+}, and Cu^{2+} are 97, 74, and 72 pm [14], respectively. Tansel et al. [15] reported that ions with lower ionic radius tend to hold their hydration shell and are strongly attached to water molecules, and thus would be more removed by membrane.

For the second mixture ([metal] = 10^{-3} mol/L, Fig. 3(b)), a decrease in all rejection factors and a deviation between R_{Cu} and R_{Zn} were observed, especially at high transmembrane pressure (7 bar). For cadmium, copper, and zinc, at low concentration the rejection was higher and as the concentration of the metal solution increased the rejection decreased. DL membrane can reject 84% of Cu at 10^{-5} mol/L and only 34% at a concentration of 10^{-3} mol/L at 7 bar.

Using the DK membrane in the some conditions, different results were obtained comparing to DL membrane (Fig. 4). In fact, the transmembrane pressure and the metal concentration in the mixture had no great effect on the rejection factors of the studied heavy metals. In the case of the first mixture, 94 < R_{Cu} < 97%; 81 < R_{Cd} < 85%; and 80 < R_{Zn} < 90%. However, the rejection sequence was identical to its obtained with DL membrane ($R_{Cu} < R_{Zn} < R_{Cd}$).

Increasing metal concentration in the mixture from 10^{-5} to 10^{-3} mol/L has slightly improved the rejection factors (Fig. 4(b)), especially for Zn, which were between 83 and 96%. For the second mixture and using DK membrane, the rejection sequence was no longer observable.

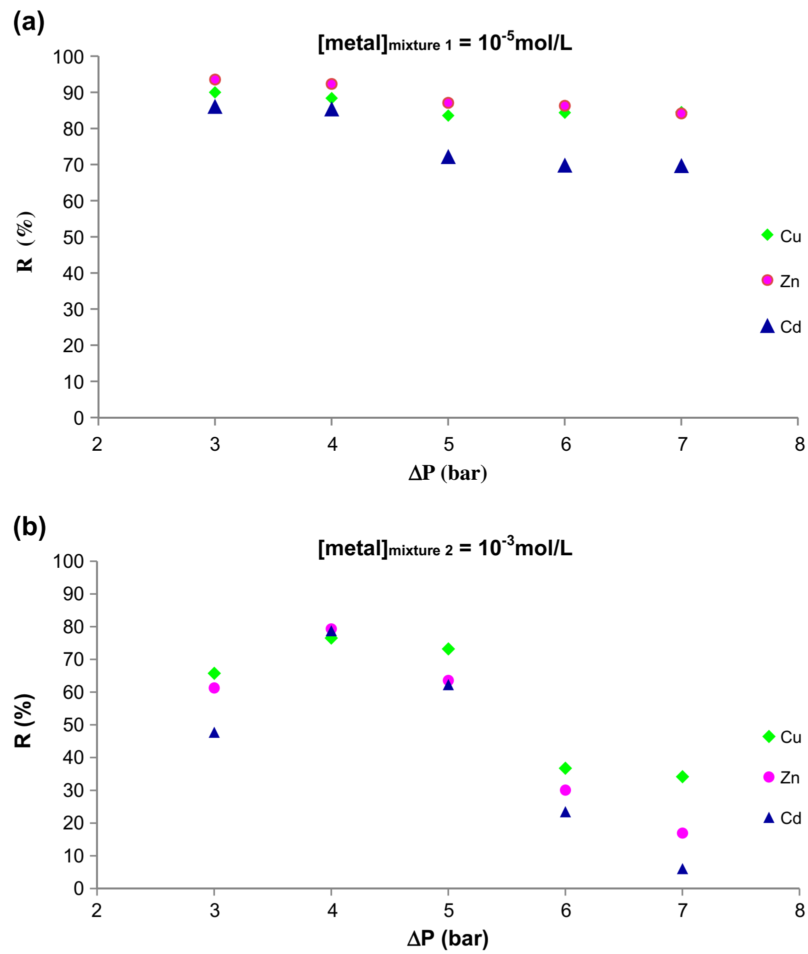

Fig. 3. Effect of ΔP on heavy metal ions rejection using the DL membrane (a) [metal] = 10^{-5} mol/L; (b) [metal] = 10^{-3} mol/L.

3.3. Effect of metal concentration

Figs. 5 and 6 illustrate the variation of the permeate flux (J_v) vs. the transmembrane pressure (ΔP) after treating different mixtures containing Cu(II), Cd(II), and Zn(II) metals by nanofiltration using, respectively, DL and DK membranes. The metal concentration in the mixture was varied from 10^{-5} to 10^{-3} mol/L and the transmembrane pressure was varied from 3 to 7 bar. For both membranes studied, the curves shown in Figs. 5 and 6 are line segments passing through the origin reflecting the negligible effect of the osmotic pressure and negligible concentration polarization. A deviation from the straight line representing J_v vs. ΔP of different mixtures studied compared to pure water line was observed, but it was much more important in the case DL membrane. This result shows that the DL membrane is much more sensitive to pores clogging than the DK membrane and confirms the best retention rates previously obtained by the latter membrane.

We also note that in the case of DL membrane increasing the concentration of heavy metals has the effect of reducing the permeate flux, as shown in Fig. 5. For cons, the opposite result was obtained using the DK membrane, as shown in Fig. 6. In this case, the membrane behaves, with the mixtures studied, almost like pure water (very slow deviation was observed).

3.4. Industrial application

In general, industrial effluents are complex mixtures of chemicals whose composition differs over time and depending on the installation. They may have high salinity, turbidity, and pH. Industrial wastewater for this study was taken from a Tunisian wiring

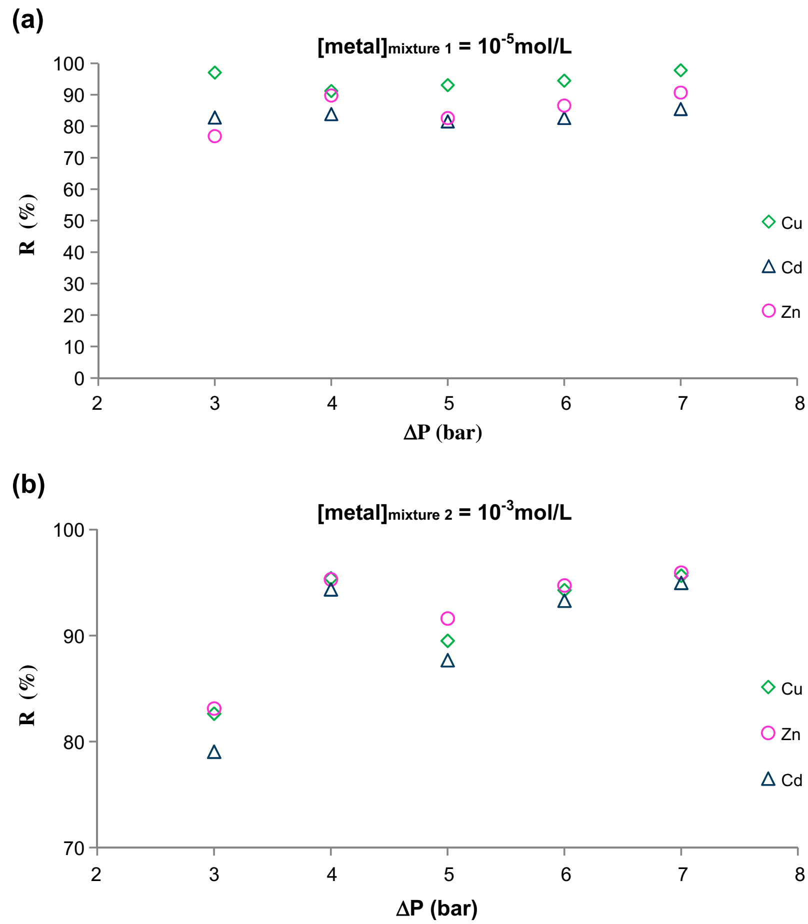

Fig. 4. Effect of ΔP on heavy metal ions rejection using the DK membrane (a) [metal] = 10^{-5} mol/L; (b) [metal] = 10^{-3} mol/L.

industry. Table 2 shows the results of the physico-chemical analysis of the industrial wastewater.

For the treatment of the industrial wastewater using nanofiltration process, an initial volume of 500 mL was circulated through the module containing the DK membrane at optimal transmembrane pressure (4 bar); then, 5 mL of permeate was collected every 10 min at the output of the module and then

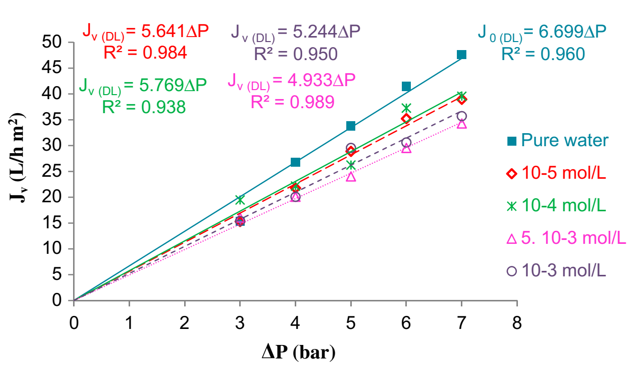

Fig. 5. Effect of metal concentration on permeate flux using DL membrane.

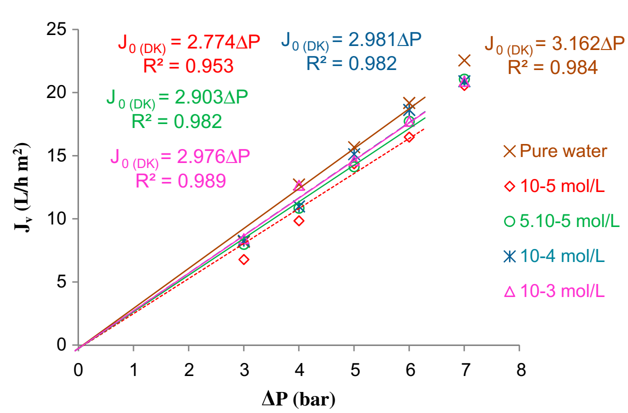

Fig. 6. Effect of metal concentration on permeate flux using DK membrane.

Table 2
Industrial wastewater characteristics

Parameter	Value
Turbidity (NTU)	2.78
Conductivity (μS/cm)	1987
Total dissolved salts (g/L)	1.183
pH	6.83
DCO (mgO_2/L)	930
DBO (mgO_2/L)	210
Cd (mg/L)	112.5
Cu (mg/L)	63.5
Zn (mg/L)	63.4
Cl^- (mg/L)	275.0
SO_4^{2-} (mg/L)	303.5
F^- (mg/L)	2.6

analyzed. The concentrations of Cu (II), Cd (II), and Zn (II) before and after the membrane treatment are shown in the following histogram (Fig. 7).

A considerable decrease in heavy metals concentration was obtained, as shown in Fig. 7, especially in the case of copper. In fact, 10 min of treatment was sufficient to reach 95, 76, and 62% of copper, zinc, and cadmium retention rates. But, this reduction is still insufficient to satisfy the Tunisian standard which requires a total elimination of these heavy metals. This result demonstrates that a single nanofiltration using DK membrane remains insufficient to eliminate efficiently the heavy metals contained in the industrial wastewater. So, we suggested to proceed with multi-stages membrane process or to add adequate polyelectrolytes in order to improve the nanofiltration performances.

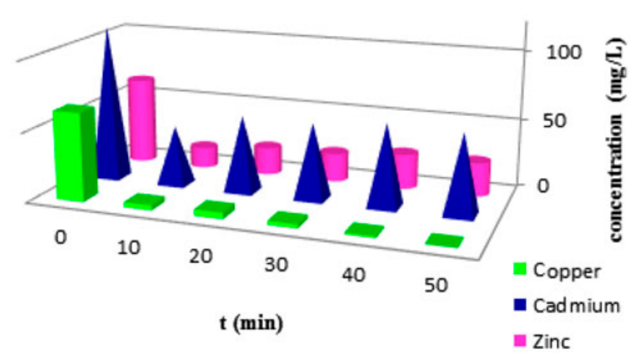

Fig. 7. Variation of metal concentration during NF process using DK membrane at 4 bar.

4. Conclusion

Taking into account the previous experimental results, a comparison between DL and DK membranes' performances may be suggested. Although both membranes showed good efficiency in the retention of heavy metals studied, the effect of transmembrane pressure on metal rejection was most notable in the case of DL membrane. In fact, for the first mixture ([metal] = 10^{-5} mol/L), 84 < R_{Cu}≈R_{Zn} < 93% and 69 < R_{Cd} < 86% were obtained using DL membrane and 94 < R_{Cu} < 97%; 81 < R_{Cd} < 85% and 80 < R_{Zn} < 90% were obtained using DK membrane. The best performance obtained by this membrane was observed at an optimum transmembrane pressure of ΔP = 4 bar.

The DL membrane performance was also limited by the increase in heavy metals' concentration, which significantly decreased the rejection factor, especially at high pressure (at 7 bar, 84% of Cu was obtained at a concentration of 10^{-5} mol/L and only 34% at 10^{-3} mol/L).

The study of J_v vs. ΔP for different heavy metal mixtures shows that the DL membrane is much more sensitive to pores clogging.

For the treatment of the industrial wastewater using DK membrane at optimum transmembrane pressure, 95, 76, and 62% of copper, zinc, and cadmium retention rates were obtained. This reduction is still insufficient to satisfy the Tunisian standard, which requires a total elimination of these heavy metals.

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