Removal of Cd(II) ions from aqueous solution and industrial effluent using reverse osmosis and nanofiltration membranes
Jamel Kheriji, Dorra Tabassi and Béchir Hamrouni

ABSTRACT
Industrial effluents loaded with cadmium have contributed to the pollution of the environment and health troubles for humans. Therefore, these effluents need treatment to reduce cadmium concentration before releasing them to public sewage. The purpose of the research is to study the major role of reverse osmosis (RO) and nanofiltration (NF) processes, which can contribute to the removal of cadmium ions from model water and wastewater from the battery industry. For this reason, two RO and two nanofiltration membranes have been used. The effects of feed pressure, concentration, ionic strength, nature of anion associated with cadmium and pH on the retention of Cd(II) were studied with model solutions. Thereafter, NF and RO membranes were used to reduce cadmium ions and total salinity of battery industry effluent. Among these membranes, there are only three which eliminate more than 95% of cadmium. This was found to depend on operating conditions. It is worth noting that the Spiegler–Kedem model was applied to fit the experimental results.

Key words | aqueous effluent, cadmium, NF/RO, Spiegler–Kedem model

INTRODUCTION
One of the priorities in the 21st century is the awareness of the negative impact of industrial effluents on the environment and human health. The treatment of such effluents is the worry of contemporary researchers who struggle to provide a clean environment for people of the world. The discharge of heavy metals is one of the major sources of environmental pollution, which is related to the toxicity of hydro-soluble metal ions. Indeed, water pollution caused by heavy metal industry poses one of the most serious environmental problems and the most difficult to solve (Keng et al. 2014). Among the most harmful metal ions in water is cadmium, which is present naturally in the earth’s crust. Owing to its physical characteristics (a good conductor of heat and electricity, possibility of alloys, etc.), cadmium is used for many industrial purposes such as industrial batteries, accumulators and electronic components. By using or recycling these products, cadmium could be easily overspread in the environment.

The valence II (Cd^{2+}) is probably the only valence of cadmium in water. The main cadmium compounds are cadmium chloride (CdCl_{2}), cadmium oxide (CdO), cadmium nitrate (Cd(NO_{3})_{2}, cadmium sulfate (CdSO_{4}) and cadmium sulfide (CdS). The physical and chemical properties of cadmium are similar to those of zinc and calcium and allow it to pass biological barriers and accumulate in the tissues (Menager et al. 2007). In addition, cadmium has a very high affinity for proteins, allowing its bio-accumulation in organisms (Menager et al. 2007). Consequently, cadmium has been identified as a highly toxic pollutant. According to the dose of exposure, the modes of contamination and considered organs, cadmium effects may be more or less important. The oral ingestion of a single dose of 10 mg of cadmium leads to intestinal and renal failure. If the dose ingested is greater, death can occur within 24 hours. The chronic cadmium exposure by inhalation or ingestion results in severe disorders of the kidneys, lungs and bone (osteoporosis and osteomalacia) (Nomiyama & Nomiyama 1998; Kazantzis 2004). Other consequences of chronic exposure to cadmium are hypertension (Nomiyama & Nomiyama 1998), disruption of the reproductive organs (Hew et al. 1993) and dysfunction of the liver (Nomiyama & Nomiyama 1998). In Tunisia, the legislation on wastewater discharges has become increasingly strict. Most chemical discharges exceed the thresholds tolerated and therefore require
disposal by special treatment systems. According to the Tunisian NT106.002 standard, the limit concentration of cadmium to release into sewer systems is fixed at 0.1 mg/L. Therefore, it is a great challenge to treat wastewater containing cadmium. Cadmium can be removed by several processes, including adsorption and biosorption, ion-exchange, chemical precipitation including electro-coagulation/flotation and membrane processes, such as reverse osmosis (RO) and nanofiltration (NF). Most of these methods have drawbacks, including high initial installation cost, deficiency of selectivity, low capacity, and regeneration or operation difficulty. RO and NF have become increasingly used for removing heavy metals (such as cadmium) from wastewater and improving water recovery rate due to their high efficiency and low cost (Feini et al. 2008).

The present study illustrates the experimental results related to the study of the retention of cadmium by two RO membranes (AG, SG) and two NF membranes (HL and NF-90). The influence of the operating parameters such as transmembrane pressure, the feed concentration, the nature and the concentration of the electrolyte and the pH was studied. This work was also extended to investigate the removal of cadmium from industrial effluent in order to meet the environmental local limits (<0.1 mg/L). The mathematical model Spiegler–Kedem was applied to determine the transfer parameters and to justify the experimental results.

**MATERIALS AND METHODS**

**Model applied**

The transport of solutes through a membrane can be described by using the principles of irreversible thermodynamics. For a two-component system, consisting of water and a solute, the irreversible thermodynamics approach leads to two basic equations:

\[
J_v = L_p \cdot (\Delta P - \sigma \Delta \pi) \tag{1}
\]

\[
J_s = P_s \cdot \Delta C_s + (1 - \sigma) \cdot C_{int} \cdot J_v \tag{2}
\]

where \(J_v\) and \(J_s\) are respectively the solvent flux and the solute flux, \(L_p\) is the pure water permeability, \(\Delta P\) and \(\Delta \pi\) define respectively the transmembrane pressure and the difference of osmotic pressure between each side of the membrane, \(\sigma\) is the reflection coefficient, \(P_s\) is the solute permeability, \(C_{int}\) is the solute concentration in the membrane and \(\Delta C_s = C_m - C_p\) with \(C_m\) and \(C_p\) the concentrations respectively at the surface of the membrane in the bulk side and in the permeate.

With constant fluxes and constant transport parameters, integration of Equation (2) on the membrane thickness, in terms of the real salt rejection, gives the following rejection expression:

\[
R = \frac{\sigma \cdot (1 - F)}{1 - \sigma F} \tag{3}
\]

with:

\[
F = \exp \left( -\frac{1 - \sigma}{P_s} J_v \right) \tag{4}
\]

According to the film theory, the relationship between the observed rejection rate and the true rejection \(R\) may be expressed as:

\[
\frac{R_{obs}}{1 - R_{obs}} = \frac{R}{1 - R} \cdot \exp \left( -\frac{J_v}{k} \right) \tag{5}
\]

where \(k\) is the mass transfer coefficient.

Substitution of Equation (3) into Equation (5) and rearranging results in the following equation:

\[
R_{obs} = \frac{1}{(1 - \sigma)/(\sigma \cdot (1 - \exp\{-((1 - \sigma)/P_s)J_v\})) \cdot \exp(J_v/k)} + 1 \tag{6}
\]

As can be seen in Equation (2), the total flux of solute appears as the sum of diffusion and convection terms. Thus, it is possible to write the following equation:

\[
J_{diff} + J_v C_{conv} = C_p J_v \tag{7}
\]

In this expression, \(J_{diff}\) is the solute flux due to diffusion and \(C_{conv}\) is the solute concentration due to convection. That is to say:

\[
C_p = \frac{J_{diff}}{J_v} + C_{conv} \tag{8}
\]

By following \(C_p\) versus the reverse of the permeate flux, it is possible to quantify separately both parts of the solutes mass transfer: convection and diffusion. From the \(C_{conv}\) values, it is possible to calculate the molecular weight cut-off (MWCO) of the membranes.
studied, from the Equation (9):

$$C_{\text{conv}} = C_0 \cdot \left[1 - \left(\frac{M}{\text{MWCO}}\right)^{1/3}\right]^2$$  \hspace{1cm} (9)

where $M$ is the molecular weight of a solute.

In this paper, the curves giving cadmium rejection depending on operating pressure or permeate flux were adjusted by the Spiegler–Kedem model. In the figures, experimental data used are marked as solid symbols, whereas dashed lines represent the Spiegler–Kedem model.

**RO/NF membranes**

The present work was carried out on a pilot plant equipped with commercial spiral-wound RO and NF membranes. Two RO membrane types, AG-2514 and SG-2514, and two NF membrane types, HL-2514 and NF90-2540, were employed. The main experimental condition and characteristics of these membranes are summarized in Table 1.

Before each experiment, the membranes were cleaned and rinsed with pure water ($<1 \mu S/cm$), for half an hour, at an operating pressure of 5.0 bar.

The pure water permeability ($L_p$) was determined by statistical linear regression of permeate flux $J_v$ versus transmembrane pressure $\Delta P$. This linear behavior is described by a slope corresponding to the pure water permeability. Table 2 summarizes values of the pure water permeability of these membranes.

The membrane charge was determined by the salts retention method. Three salt solutions of NaCl, CdCl$_2$ and Na$_2$SO$_4$ at a concentration $10^{-3}$ mol/L were prepared and filtered by the four membranes. The AG and NF-90 membranes show the following salt rejection sequence

$$R(\text{Na}_2\text{SO}_4) > R(\text{NaCl}) > R(\text{CdCl}_2)$$

while the other membranes (HL and SG) give the following retention sequence

$$R(\text{Na}_2\text{SO}_4) > R(\text{CdCl}_2) > R(\text{NaCl})$$. For the two first membranes ($R(\text{SO}_4^{2-}) > R(\text{Cl}^-)$ and $R(\text{Na}^+) > R(\text{Cd}^{2+})$), the model of Donnan exclusion plays an important role in retention, and the membrane is negatively charged. For the SG and HL membrane ($R(\text{SO}_4^{2-}) > R(\text{Cl}^-)$ and $R(\text{Cd}^{2+}) > R(\text{Na}^+)$), the retention is mainly caused by the difference in diffusion coefficients between three salts (Tabassi et al. 2014), even though the existence of negative charged groups at the surface of these membranes was confirmed by other researchers using the method of zeta potential measurements (Norberg et al. 2006; Tepus et al. 2009). Thus, the retention phenomenon is characterized by the involvement of the charge effect and the diffusion effect. Surface characteristics of these membranes were determined by some authors. Table 3 summarizes these various characteristics.

From the $C_{\text{conv}}$ values, it is possible, using the Equation (9), to calculate the MWCO of the membrane studied, using Na$_2$SO$_4$ electrolyte at a concentration of $10^{-3}$ mol/L. However, the most appropriate values are those obtained at low concentrations where the retention of Na$_2$SO$_4$ is higher than 90% (Tabassi et al. 2014). Table 4 summarizes the MWCO values obtained for the four membranes.

The performance of the tested membranes was measured in terms of flux ($J_v$) and rejection ($R$). Membrane rejection is calculated by Equation (10):

$$R(\%) = \frac{C_0 - C_p}{C_0} \cdot 100 = \left(1 - \frac{C_p}{C_0}\right) \cdot 100 \hspace{1cm} (10)$$

where $C_p$ and $C_0$ (mol/L) are permeate and feed concentrations, respectively.

<table>
<thead>
<tr>
<th><strong>Table 1</strong></th>
<th>Main characteristics and experimental conditions of the NF and RO membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>RO AG</strong></td>
<td><strong>RO SG</strong></td>
</tr>
<tr>
<td>Manufacture</td>
<td>Osmonics</td>
</tr>
<tr>
<td>Membrane type</td>
<td>TFC$^a$</td>
</tr>
<tr>
<td>Membrane area (m$^2$)</td>
<td>0.6</td>
</tr>
<tr>
<td>Percent salt rejection</td>
<td>99.5$^b$</td>
</tr>
<tr>
<td>Maximum operating pressure (bar)</td>
<td>30</td>
</tr>
<tr>
<td>Operating pH range</td>
<td>2–11.5</td>
</tr>
<tr>
<td>Maximum temperature (°C)</td>
<td>50</td>
</tr>
</tbody>
</table>

$^a$Polyamide thin-film composite.

$^b$NaCl 15.5 bar.

$^c$MgSO$_4$ 6.9 bar.
Permeate flux \( J_v \) \( (L/(h \, m^2)) \) was calculated as follows:

\[
J_v = \frac{V_p}{t \cdot S} = \frac{Q_p}{S}
\]  

(11)

where \( Q_p \) \( (L/h) \) is the permeate flux rate, \( V_p \) \( (L) \) is the volume of permeate collected in a given time interval \( t \) \( (h) \) and \( S \) \( (m^2) \) is the membrane surface area.

Chemicals and analytical methods

All chemicals and reagents were analytical grade and used without further purifications. Cadmium solutions were prepared by dissolving cadmium salts in distilled water. The influence of transmembrane pressure and cadmium feed concentration was determined using nitrate cadmium salt. For the first parameter, the metal ion solution was fixed to 1,000 mg/L whereas for the second it varied from 5 to 1,000 mg/L. Nitrate, chloride, and sulfate cadmium salts were used to determine the influence of pH, cadmium salt type and ionic strength. The pH was varied with HCl or NaOH solutions, while the ionic strength was adjusted using NaNO₃ solution. The real application of NF and RO processes was performed on a wastewater, containing Cd(II) ions, which was collected from a battery manufacturing plant in Tunisia. The characteristics of the wastewater after treatments by sand and micro-filtration are shown in Table 5.

The residual concentration of cadmium was determined using a potentiometer equipped with an ion selective electrode and a reference electrode. pH measures were made using a pH meter equipped with a combined electrode (model Metrohm No. 827). Chloride, nitrate, fluoride, and sulfate ions were analyzed by anion chromatography using a Metrohm 761 compact ion chromatograph with conductivity detector and chemical suppression, 4.6 \( \times \) 250 mm Metrosep A Supp 1 (6.1005.300), an eluent of 3 mmol/L sodium carbonate at 1 mL/min, an injection volume of 20 \( \mu L \) and a pressure from 80 to 90 bar.

RESULTS AND DISCUSSION

Effect of transmembrane pressure and membrane type

The effective pressure corresponds to the pressure that leads to the production of permeate. Generally, the operating pressure must be greater than the osmotic pressure. When this pressure is higher, the permeate flux becomes more important (Galambos et al. 2004; Lin & Yang 2004). Similarly, desalination experiments by NF and RO have shown that the salt retention increases when the pressure increases too (Sridhar et al. 2002; Lin & Yang 2004). To examine the influence of transmembrane pressure on the removal of cadmium, experiments were investigated with Cd(NO₃)₂ salt containing 1,000 mg/L of cadmium at 25°C and pH = 6.8; the results are justified by the Spiegel–Kedem model and shown in Figure 1.

It can be seen that cadmium rejection by AG, SG and NF-90 membranes was higher than 90% over the pressure range. The performance of AG membrane is slightly higher than the two other membranes. NF-90 membrane

### Table 2 | Pure water permeability of membranes at 25 °C

<table>
<thead>
<tr>
<th>Membrane</th>
<th>NF-90</th>
<th>HL</th>
<th>AG</th>
<th>SG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability ((L/(h , m^2 , bar)))</td>
<td>11.450</td>
<td>9.015</td>
<td>3.882</td>
<td>3.457</td>
</tr>
</tbody>
</table>

### Table 3 | Surface characteristics of RO/NF membranes (Norberg et al. 2006; Tepus et al. 2009)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Zeta potential ((mV))</th>
<th>Surface roughness ((nm))</th>
<th>Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG</td>
<td>-10.8</td>
<td>46.1</td>
<td>50.3</td>
</tr>
<tr>
<td>SG</td>
<td>-7.6</td>
<td>13.1</td>
<td>60.9</td>
</tr>
<tr>
<td>HL</td>
<td>-8</td>
<td>12.8</td>
<td>51.6</td>
</tr>
<tr>
<td>NF-90</td>
<td>-14.2</td>
<td>108.9</td>
<td>38.7</td>
</tr>
</tbody>
</table>

### Table 4 | Molecular weight cutoff of the studied membranes \((Na_2SO_4, 10^{-3} \text{mol/L})\)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>AG</th>
<th>SG</th>
<th>HL</th>
<th>NF-90</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCO ((\text{Da}))</td>
<td>144</td>
<td>160</td>
<td>247</td>
<td>167</td>
</tr>
</tbody>
</table>

### Table 5 | Battery effluent quality and comparison with Tunisian standards for liquid discharges into the National Office for Sanitation network (NT 106.002)

<table>
<thead>
<tr>
<th>Battery effluent</th>
<th>NT 106.002, 1989</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature ((\degree C))</td>
<td>24</td>
</tr>
<tr>
<td>pH</td>
<td>6.2</td>
</tr>
<tr>
<td>TDS* ((\text{mg/L}))</td>
<td>6160</td>
</tr>
<tr>
<td>Cd²⁺ ((\text{mg/L}))</td>
<td>7</td>
</tr>
<tr>
<td>Cl⁻ ((\text{mg/L}))</td>
<td>355</td>
</tr>
<tr>
<td>NO₃⁻ ((\text{mg/L}))</td>
<td>130</td>
</tr>
<tr>
<td>SO₄²⁻ ((\text{mg/L}))</td>
<td>1500</td>
</tr>
</tbody>
</table>

*TDS: total dissolved solids.
Frares et al. were found by Murthy & Chaudhari (2005) that the convective transport is becoming more important and the retention at low pressure. When increasing the pressure, the permeate will be less concentrated, i.e. the retention rate is decreased of permeate flux density. Therefore, an increase of solute concentration in the feed water will cause an increase of its concentration in permeate, so the retention rate remains constant (Alwazzan et al. 2003).

Figure 1 presents the effect of feed concentration on the operating pressure (Cd(NO₃)₂ salt, $[Cd^{2+}] = 1,000 \text{mg/L}$, pH = 6.8 and $T = 25^\circ\text{C}$).

Cadmium rejections increased with increasing operating pressure for HL membrane while it remains constant for the three membranes AG, SG and NF-90. Cadmium rejection by HL membrane increases to achieve 65% at 12 bar. This increase can be explained by the increase of solvent flux inversely to solute transport that remains constant. Therefore, the solute is divided into a larger volume of solvent and the permeate will be less concentrated, i.e. the retention rate is more important. A predominantly diffusive transport compared to convective transport is the reason for the low retention at low pressure. When increasing the pressure, the convective transport is becoming more important and the cadmium retention will also increase. Similar results were found by Murthy & Chaudhari (2008) and Ben Fraires et al. (2005) for metal cations removal. For AG, SG and NF-90 membranes, cadmium retention is independent of operating pressure. The opposite contribution of increased convective transport and the occurrence of the concentration polarization phenomenon thus result in constant cadmium retention in the pressure range of 3–15 bar for these membranes.

**Effect of feed concentration**

Generally, enhancing the feed concentration causes the decrease of permeate flux density (Bilstad 1995). On the one hand, the high concentration leads to the rise of the osmotic pressure, causing a decrease in the effective pressure. Without increase of transmembrane pressure, the flux decreases (Allègre et al. 2004). On the other hand, the increase of concentration may increase the clogging by gelation or precipitation of solutes. The retention can also decrease when increasing the solute concentration (Sridhar et al. 2002). Indeed, the reduction of the effective pressure and therefore of the permeate flux density, contribute to the rise of the permeate concentration. However, this trend is not systematic; solute rejection can be also independent of the feed concentration. In fact, an increase of solute concentration in the feed water will cause an increase of its concentration in permeate, so the retention rate remains constant (Alwazzan et al. 2003).

Figure 2 presents the effect of feed concentration on rejection of cadmium by RO and NF membranes at 25°C. This decrease is more visible for SG and HL membranes which are less negatively charged.

The decrease of cadmium retention as a function of the feed concentration has been obtained by other authors (Murthy & Chaudhari 2009). As indicated before, this result can be explained by the appearance of the clogging phenomenon when increasing the solute concentration. On the other side, increasing the feed concentration causes a formation of cation layer on the membrane surface. This layer neutralizes the negative charges of the membrane and causes a reduction of the total charge of the membrane. Consequently, the repulsion force between the membrane and the nitrate anions present in solution is reduced. These anions will easily pass through the membrane and, due to the electro-neutrality principle, the counter-ion ($\text{Cd}^{2+}$) will also be less rejected.

To check the experimental results of the effect of concentration on the cadmium removal, the Spiegler–Kedem model was applied. The transfer parameters $\sigma$ and $P_s$ were determined and are summarized in Table 6. This table shows that the calculated values of $\sigma$ decrease with the feed concentration, thus showing a decrease of cadmium rejection. The lowest values of $\sigma$ are obtained for a concentration of 1,000 mg/L, while the highest values correspond to a concentration of 5 mg/L. For the latter concentration, $\sigma$ values corresponding to the three membranes AG, SG and NF-90 are very close to 1, which translates into total rejection of cadmium. Concerning the $P_s$ parameter, it is clear that the values of this parameter increase with the concentration of the cadmium in the feed solution. This shows that the proportion of cadmium passing through the membrane increases by increasing the feed concentration.
Effect of the nature of associated anion

In reality, cadmium never exists in the elemental form in water but in the form of salts such as cadmium chloride, cadmium nitrate and cadmium sulfate. The influence of the co-ion on cadmium retention was carried out with three salts of Cd²⁺ (CdCl₂, Cd(NO₃)₂ and CdSO₄) at 1,000 mg/L of metal concentration. The experiments were performed at 25 °C and pH 6.8. The pressure varied from 3 to 15 bar. The results of cadmium retention as a function of the permeate flux are justified by the Spiegle–Kedem model and shown in Figure 3.

The sequence of cadmium salt retention by the four membranes is R(CdSO₄) > R(CdCl₂) > R(Cd(NO₃)₂). The cadmium associated with the divalent anion (SO₄²⁻) is more rejected than the cadmium associated with monovalent anions (Cl⁻ and NO₃⁻). The rise of cadmium retention depending on the anion valence is related to the electrostatic repulsion force exerted by the membrane on the more loaded anion. Comparing the retention of CdCl₂ and Cd(NO₃)₂, the retention order is related to the hydration energy (Eₕ) of chloride and nitrate anions (Table 7). The less hydrated ions penetrate more easily through the membrane surface, thus resulting in a lower retention of cadmium associated with nitrate anions. These results are in accordance with other cadmium removal results found by Garba et al. (2003), Ballet et al. (2004) and Murthy & Chaudhari (2009).

<table>
<thead>
<tr>
<th>Membrane</th>
<th>5 mg/L Cd²⁺</th>
<th>50 mg/L Cd²⁺</th>
<th>500 mg/L Cd²⁺</th>
<th>1,000 mg/L Cd²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>σ</td>
<td>Pₛ (L/h)</td>
<td>σ</td>
<td>Pₛ (L/h)</td>
</tr>
<tr>
<td>AG</td>
<td>0.999</td>
<td>0.059</td>
<td>0.999</td>
<td>0.109</td>
</tr>
<tr>
<td>SG</td>
<td>0.999</td>
<td>0.121</td>
<td>0.997</td>
<td>0.198</td>
</tr>
<tr>
<td>NF-90</td>
<td>0.999</td>
<td>0.832</td>
<td>0.999</td>
<td>0.851</td>
</tr>
<tr>
<td>HL</td>
<td>0.962</td>
<td>30.07</td>
<td>0.901</td>
<td>30.05</td>
</tr>
</tbody>
</table>

Table 6 | Cadmium transfer parameters (σ and Pₛ) for different membranes and feed concentrations
The transfers parameters ($\sigma$, $P_s$, $J_{\text{diff}}$ and $C_{\text{conv}}$) corresponding to CdSO$_4$, CdCl$_2$ and Cd(NO$_3$)$_2$ salts were determined and are summarized in Table 8.

According to Table 8, the calculated values of $\sigma$ and $P_s$ agree with the experimental removal results. They depend on the nature of the anion associated with cadmium. The highest values of $\sigma$ are observed for cadmium sulfate while lower values are obtained for the cadmium nitrate. Inversely, the lowest values of $P_s$ correspond to CdSO$_4$ salt and the highest values are those of the Cd(NO$_3$)$_2$ salt. For the four membranes, $J_{\text{diff}}$ is inversely proportional to the hydration energy of anions associated with cadmium. Sulfate is the most hydrated ion ($E_{\text{H}} = 1047$ kJ/mol), it presents the lowest $J_{\text{diff}}$ value, while nitrate is the least hydrated ion ($E_{\text{H}} = 310$ kJ/mol), it corresponds to the highest values of $J_{\text{diff}}$.

### Effect of pH

To investigate the pH effect on the cadmium retention, CdSO$_4$, CdCl$_2$, Cd(NO$_3$)$_2$ solutions containing 1,000 mg/L of cadmium were prepared for different pH from 3 to 8. The pH was adjusted by the addition of HCl or NaOH solutions. Figure 4 shows the variation of the retention rate of the three cadmium salts depending on pH for the four membranes.

A polymeric membrane acquires surface charge when brought into contact with an aqueous medium (Desmukh & Childress 2013; Bellona & Drewes 2005). Owing to this
charge, it may create electrostatic interactions between the membrane and the charged solutes. Membrane charge affects the ion distribution at the membrane–solution interface; co-ions are repelled from the membrane surface while counter-ions are attracted to it (Childress & Elimelech 1996). For most thin-film composite polyamide membranes, increasing feed water pH results in an increasingly negative surface charge due to the dissociation of carboxyl group (R–COOH), although decreasing feed water pH favors protonation of the amine groups (R–NH–R) and leads to a more positive membrane surface. On the other side, membrane charge changes sign at a particular pH called the isoelectric pH. The literature suggests that the isoelectric pH of the HL, SG, AG and NF90 membranes is between 4 and 5 (Hoang et al. 2013; Richards et al. 2013).

The higher cadmium retention is obtained at acid pH (pH = 3) or neutral or slightly alkaline pH (7–8). At pH = 3, the high rejection of cadmium is related to the repulsive force between the cations in solution and the positively charged membrane surface. At pH greater or equal to 7, the membrane is negatively charged, and the rejection of the cadmium is related to the exclusion of the associated anion which is expressed by the repulsive effect of the negatively charged membrane surface. At isoelectric pH, a minimum retention of cadmium was observed. This decrease is clear for SG and HL membranes. It can be explained by the absence of the repulsive forces between the uncharged membrane surface and the ions in solution. Some authors explain this decline by the increasing of the pore size due to the expansion of the membrane polymer at pH equal to the isoelectric pH (Qin et al. 2004).

Effect of ionic strength

The effect of ionic strength on the removal of cadmium was studied for a Cd(NO₃)₂ solution containing 500 mg/L of cadmium. NaNO₃ solutions (10⁻², 5 × 10⁻² and 10⁻¹ mol/L) were added. The rejection of cadmium for various electrolytes and concentrations is summarized in Figure 5.

The cadmium retention decreases when the NaNO₃ concentration increases. At a concentration of 0.1 mol/L, a decrease of 1–1.5% was observed for the AG, SG and NF-90 membranes and 17–19% for the HL membrane. This decrease can be attributed to the increase of sodium ions in solution, which neutralizes the negative charge of the membrane and reduces the rejection of the associated anion and thereafter the rejection of cadmium salt. Conversely, the membrane charge density depends strongly on the electrolyte concentration. Indeed, an increase in the concentration of NaNO₃ electrolyte leads to the adsorption...
of nitrate anion on the membrane surface leading to a more negative surface and an easier migration of Cd\(^{2+}\) cation at higher concentrations of electrolyte.

The Spiegler-Kedem model was applied to check the removal result at different concentrations of NaNO\(_3\). The transfer parameters \(P_s\) and \(\sigma\) were determined and are summarized in Table 9. It is clear that values of \(\sigma\) and \(P_s\) depend on the NaNO\(_3\) concentration; \(\sigma\) decreases and \(P_s\) increases with increasing NaNO\(_3\) concentration.

### Application on industrial effluents containing cadmium

A wastewater containing Cd(II) was used to evaluate the performance of NF and RO membranes. The Spiegler and Kedem model was applied to fit the experimental data and evaluate the parameters \(\sigma\) and \(P_s\). The experimental data for the permeate flux, with wastewater, as a function of the operating pressure are given in Figure 6 for the tested NF and RO membranes. The permeate fluxes obtained for the HL and NF-90 membrane were higher than those of the RO membranes. The wastewater permeabilities are:

\[
L_p (\text{HL}) = 4.132 \text{ L/(h m}^2\text{ bar), } L_p (\text{NF-90}) = 3.696 \text{ L/(h m}^2\text{ bar), } L_p (\text{SG}) = 1.533 \text{ L/(h m}^2\text{ bar) and } L_p (\text{AG}) = 1.257 \text{ L/h/m}^2\text{ bar. These values were lower than pure water permeabilities } L_p (\text{Table 2}).
\]

The tests of salinity retention are shown in Figure 7. The highest retentions are obtained for the AG, SG and NF-90 membranes (>80%) whereas salinity retention was between...
Concerning the first three membranes, the permeate salinity confirms the satisfactory performances of AG (400–200 mg/L), SG (480–230 mg/L) and NF-90 (1400–230 mg/L) for desalinating wastewater. To reduce the cadmium concentration present in the permeate and to possibly re-use the water, the studied membranes were employed. The results showed that only AG, SG and NF-90 membranes are suitable for removal of cadmium present in the effluent of the battery industry (Figure 7). The highest cadmium rejections are obtained for the AG (>99%), SG (98–99%) and NF90 (97–99%) whereas cadmium rejection between 40 and 75% for HL membrane. The permeate cadmium concentration reached 0.08 mg/L for AG, 0.09 mg/L for SG and 0.1 mg/L for NF-90 membrane.

As reported earlier, a maximum concentration of 0.1 mg/L of cadmium released into the sewer network of the National Sanitation Office (ONAS) was fixed by the Tunisian legislation. The treatment of this industrial effluent by one of the three membranes AG, SG and NF-90 allows the Tunisian standard for cadmium in the ONAS network to be met. Thus, the use of one of these membranes presents an effective solution for removal of cadmium from the effluent of the battery manufacturing plant.

The Spiegler–Kedem model was applied to fit the rejection of total salinity and cadmium ions. Table 10 gives the fitting parameters ($\sigma$ and $P_s$) for the four membranes. These parameter values depend on the type of the membrane. The AG, SG and NF-90 membranes present higher $\sigma$ values and lower salt permeability than the HL membrane. It seems that the retention behavior of NF 90 is comparative to that of the RO membranes. A good fit was obtained for the retention values of used membranes for solutions studied.

**CONCLUSION**

Cadmium removal from model water and battery industrial effluent was studied using four commercial membranes (AG, SG, NF90 and HL). For the used membranes, the removal efficiency for cadmium was influenced by operating conditions such as transmembrane pressure, feed water concentration, ionic strength, nature of anion associated with cadmium and pH. The ionic strength of feed solution causes the progressive neutralization of the negative charge of the membrane and leads to a reduction of the cadmium removal percentages. High retention rates were obtained for pH < 4 or pH > 6, with low concentration of cadmium in the feed solution or in case of cadmium sulfate salt. A greater effectiveness in cadmium retention is observed using the AG, SG and NF-90 membranes for both the model and real wastewaters. The NF90 behaves in a relatively similar way to the RO membrane. The treatment of this industrial effluent by one of the three membranes AG, SG and NF-90 allows to reach the Tunisian standard for cadmium in the ONAS network to be reached. Thus, the use of one of these membranes presents an effective solution for removal of cadmium from the effluent of the battery manufacturing plant. The Spiegler–Kedem model was used to obtain the convective and diffusive contributions, together
with the determination of solute parameters $\sigma$ and $P_s$ which allow the theoretical curves of the retention depending on the pressure or permeate flux to be obtained.

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