CHARACTERIZATION OF NANOFILTRATION MEMBRANES:
PORE RADIUS ESTIMATION USING TWO MODELS
Ibrahim Musbah¹, Delphine Cicéron², Abdellah Saboni³, Silvia Alexandrova⁴

¹Department of Engineering, University of Sirte, PO Box 674, Sirte, Libya
²Laboratoire LSPC-IUT, UCBN, Boul. Maréchal Juin, 14 032 Caen cedex, France
³Laboratoire SIAME-IUT, UPPA, Avenue de l’Université, 64 000 Pau, France
⁴Laboratoire LaTEP-ENSGTI, UPPA, rue Jules Ferry, BP 7511, 64 075 Pau cedex, France
E-mail: silvia.alexandrova@univ-pau.fr

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ABSTRACT

The pore sizes of two nanofiltration membranes (NF and OPMN-K) are calculated using MWCO and Spiegler-Kedem methods. The results are compared with rejections of usual pesticides and hydrated ions with similar Stokes radii (r_s). It is found that Stokes radius is not the only parameter affecting the rejection of the dissolved component: the molecular size (length and width) appears to be also a very important parameter for pesticide retention like the ionic strength for salt’s rejection.

Keywords: nanofiltration, pesticides, sugars, pore characterization, MWCO, Spiegler-Kedem.

INTRODUCTION

Nanofiltration is a relatively new, pressure driven membrane process. The very high selectivity of charged nanofiltration membranes is due both to the steric effect and to the charge effect.

Transport of the uncharged solutes, like sugars or pesticides, through membrane takes place by diffusion and in this case membrane pore size is the most important membrane property. The Donnan exclusion mechanism is often used to describe the charged solutes transport [1, 2].

The characterization of the pore size is an important step in understanding the transport mechanisms and membrane performances. Methods used classically for pore diameter determination can be divided into two groups: physical (mercury porosimetry, gas bubble, etc.) and based on molecular solute rejection (based on mass-transfer mechanisms). Among the most used methods of the second group, the MWCO and Spiegler-Kedem models [3] can be cited.

The subject of this study is the characterization of two nanofiltration membranes (NF and OPMN-K) using three molecular solutes (glycol, saccharose and glucose) in order to determine the pore radius of membranes by two methods: MWCO and Spiegler-Kedem equation.

Experiments were carried out with transmembrane pressure (Ptm) varying from 10 to 25 bars and the obtained results were compared between them and with those obtained with three pesticides (atrazine, diuron, simazine) and three usual hydrated ions (Na⁺, Ca²⁺, K⁺) with Stokes radii close to those of sugars.
EXPERIMENTAL

Solutes and membranes

For experiments, six molecular solutes are used: glucose, saccharose, glycerol and three pesticides (atrazine, simazine, diuron). Their properties are presented in Table 1. Simazine and atrazine are herbicides of the triazine class. Diuron is considered like a persistent herbicide (one month to one year). Salts used are NaNO₃, Ca(NO₃)₂.2H₂O and KNO₃ of pure analytical grade.

The solute concentration in the feed is in the range of 0.013 M to 0.23 M for glucose, saccharose and glycerol, from 5 to 100 µg l⁻¹ for pesticides and 20 ppm for nitrate salts. All solutions are prepared with deionised water (conductivity less than 2 µS cm⁻¹).

NF (FilmTec) and OPMN-K (Vladipor) flat sheet organic membranes are used in this study. Both membranes are negatively charged and their characteristics are summarized in Table 2.

Analytical methods

Glucose and saccharose concentrations were determined by polarimetry (Polartronic I de Schmidt & Haensch), glycerol concentration was measured by refractometry (Abbe RF 480 refractometer) and pesticides were analysed using solid-phase extraction (SPE) coupled to high performance liquid chromatography (HPLC). The samples pre-concentration by SPE was carried out with BondElut C18 cartridges [4]. The Na⁺, Ca²⁺ and K⁺ concentrations were determined by atomic absorption using a SpectrAA 2220 (Varian).

Experimental setting

In order to reduce swelling and compaction effects during the experiments and to get a reference state before each experiment, membranes were immersed during 48 hours in deionised water. After the swelling step, membranes were compacted with deionised water at 25 bars during 12 hours.

All experiments were carried out at constant temperature T = 20 ± 1°C in batch mode: permeate and retentate solutions were reintroduced to the feed tank. The experimental set-up was described in details in our previous works [4, 5]. The flat membrane cell used has an effective area of 86 × 10⁻⁴ m² and the circulation velocity in the cell is fixed to 0.45 m.s⁻¹ (Re = 3300).

Observed solute rejection is calculated using the following equation:

\[ R_{obs} = \left(1 - \frac{C_p}{C_0}\right) \times 100 \]  

where \( C_0 \), ppm, is the feed concentration and \( C_p \), ppm, is the permeate concentration.

RESULTS AND DISCUSSION

Water permeability

Firstly, the membranes were characterized with pure water in order to calculate the membrane permeability. Experiments were carried out at four transmembrane pressures (Ptm): 10, 15, 20 and 25 bars.

The pure water permeability (\( K_w \)) should ideally be independent of temperature and pressure. Consequently,

Table 1. Molecular mass and diffusivity of solutes.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Molecular formula</th>
<th>Molecular mass [Da]</th>
<th>Diffusivity x10^10 [m².s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>C₆H₁₂O₆</td>
<td>180.15</td>
<td>6.9</td>
</tr>
<tr>
<td>Saccharose</td>
<td>C₁₂H₂₂O₁₁</td>
<td>342.3</td>
<td>5.2</td>
</tr>
<tr>
<td>Glycerol</td>
<td>C₃H₈O₃</td>
<td>92.1</td>
<td>9.5</td>
</tr>
<tr>
<td>Atrazine</td>
<td>C₄H₁₄ClN₅</td>
<td>215.7</td>
<td>5.53</td>
</tr>
<tr>
<td>Diuron</td>
<td>C₉H₁₀Cl₂N₂O</td>
<td>233.1</td>
<td>5.34</td>
</tr>
<tr>
<td>Simazine</td>
<td>C₇H₁₂ClN₅</td>
<td>201.7</td>
<td>5.71</td>
</tr>
</tbody>
</table>

Table 2. Nanofiltration membranes used.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Pressure (bar)</th>
<th>NaCl rejection</th>
<th>Water flux (L.m⁻².h⁻¹)</th>
<th>pH range</th>
<th>Surface charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF</td>
<td>16</td>
<td>-</td>
<td>-</td>
<td>3-10</td>
<td>Negative</td>
</tr>
<tr>
<td>OPMN-K</td>
<td>55</td>
<td>-</td>
<td>100</td>
<td>2-12</td>
<td>Negative</td>
</tr>
</tbody>
</table>
the plot of $J_v$ versus transmembrane pressure ($P_{tm}$) is expected to be linear with a slope equal to $K_w$. This linear evolution is obtained for both membranes (Fig. 1).

For both membranes, the results show a flow proportional to the applied pressure according to Darcy’s law. The obtained water permeabilities are respectively $K_{w,NF} = 0.0045\text{ m h}^{-1}\text{bar}^{-1}$ and $K_{w,OPMN-K} = 0.0079\text{ m h}^{-1}\text{bar}^{-1}$. There are no literature data available for NF membrane, but obtained results for OPMN-K membrane are close to results of Boughenou [6].

**Membranes characterization using uncharged model solutes**

Three organic molecular solutes (saccharose, glucose and glycerol) are used to get average pore sizes of nanofiltration membranes. According to literature data, the solute retention is independent from the feed concentration for concentrations less than 0.1 M [7]. For NF membrane characterization, the chosen concentrations were $C_{\text{glucose}} = 0.02\text{ M}$, $C_{\text{saccharose}} = 0.053\text{ M}$ and $C_{\text{glycerol}} = 0.23\text{ M}$, respectively, and for OPMN-K membrane: $C_{\text{saccharose}} = 0.013\text{ M}$ and $C_{\text{glucose}} = 0.025\text{ M}$. Experiments were carried out at four transmembrane pressures: 10, 15, 20 and 25 bars.

Stokes radius of solutes [8] is calculated using the following expression:

$$\log r_s = -1.4854 + 0.461 \times \log M$$

(2)

where $r_s[\text{nm}]$ is the Stokes radius and $M[\text{g mol}^{-1}]$ is the molecular mass of the solute.

The retention performances of both membranes at different pressures are presented in Figs. 2 and 3.

For NF membrane, glucose and saccharose retentions are independent from the applied pressure (Fig. 2). This behaviour is described in the literature by many authors [5, 9]. In the contrary, glycerol rejection is strongly influenced: rejection increases with the applied pressure. The lower retention values for glycerol can be explained by its lower molecular mass [10, 11].

OPMN-K membrane shows a lower rejection performance, especially for the case of glucose: the saccharose retention varies between 95 % and 99 %, while for the glucose it varies between 81 % and 85 % (Fig. 3). On the contrary to the results obtained for the NF membrane, the solute rejection rate does not remain constant when the pressure rises. From the results shown in Fig. 3, it can be concluded that the retention increases when the value of the flux is low (about 17.5 $\mu\text{m s}^{-1}$), then it stabilizes and begins to decrease when the flux becomes more important (about 41 $\mu\text{m s}^{-1}$). Similar results are found.
in the literature [12, 13].

Figs. 4 and 5 show the influence of the applied transmembrane pressure on the permeate rate. From these results, it is obvious that the pressure has an important effect on the permeate flux for both membranes and for all solutes.

These results also show, that the permeate flux increases linearly with transmembrane pressure. For NF membrane, the permeate flux in the case of glucose solution (10 to 25 µm s⁻¹), is slightly higher than the permeate flux in the case of saccharose solution (10 to 23 µm s⁻¹). Concerning the glycerol, permeate flux also increases with pressure, but the values are slightly lower (7 to 19 µm s⁻¹). For OPMN-K membrane, the permeate fluxes are more important: Jᵥ increases from 17 µm s⁻¹ to 42 µm s⁻¹ for OPMN-K membrane while for the NF membrane, Jᵥ rises from 10 µm s⁻¹ to 25 µm s⁻¹.

The obtained results can also be used for the concentration polarization estimation. Indeed, if the ratio β = Kᵥ/Kₚ (solution permeability/water permeability) is near to 1, the phenomenon is negligible, if the ratio is lower, the concentration polarization exists and it cannot be neglected. Results obtained for NF membrane are: βᵥ(glucose) = 0.83, βᵥ(saccharose) = 0.76 and βᵥ(glycerol) = 0.60. The highest initial concentration of the glycerol can explain its highest concentration polarization. For OPMN-K membrane, solution fluxes are confounded therefore βᵥ(glucose) = βᵥ(saccharose) = 0.79. So, it can be concluded that the polarization concentration is not negligible for all cases presented in this study.

**Pore size estimation**

**MWCO method**

The molecular mass cut-off (MWCO) shows the effects of the molecular weight on the solute retention. The rejection is defined by Eq. (1) and the MWCO as corresponding to Rₒₐₜ = 95 %. The values obtained for NF and OPMN-K membranes are respectively MWCO = 170 Da and MWCO = 330 Da. Finally, using equation (2) pore radius may be estimated: r_p,NF = 0.35 nm and r_p,OPMN-K = 0.47 nm.

**Spiegler-Kedem model**

The second method of pore size determination used in this study, is the model based on the thermodynamics of irreversible processes. The equation proposed by Spiegler and Kedem [3] takes into account both diffusive and convective transport and solute rejection can be expressed as a function of pure water flux and solute permeability as follows:

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

(3)

with σ (-) is reflection coefficient, Jᵥ, m s⁻¹ - water flux and Pₛ, m s⁻¹ - solute permeability.

The solute retention increases with increasing of water flux and attains a limit value of σ when Jᵥ → ∞. When \(\lim R = 0\), Jᵥ → 0 and for \(\lim R = σ\), R→100%, Jᵥ → ∞. This means that at low pressure, the rejection coefficient is zero and at high pressure, it is equal to σ max. σ = 100 % indicates that the convective transport is hindered and σ < 100 % indicates that solute transport through membrane exists.
For uncharged solutes, the transport across the membrane is due only to the size of used solute and membrane pore. In this case, considering that only the ratio (solute radius) / (pore radius) determines the reflection coefficient, the steric hindrance pore model can be used [14]:

$$\sigma = 1 - \left[ 1 + \frac{16}{9} \left( \frac{r_s}{r_p} \right)^2 \times \left( 1 - \frac{r_s}{r_p} \right)^2 \times \left( 2 - \frac{r_s}{r_p} \right)^2 \right]$$ (4)

where $r_s$, nm, is the solute radius and $r_p$, nm, is the pore radius.

From eq. 4 one can see that the steric effect increases with ratio $r_s/r_p$ and for $r_s = r_p$, the reflection coefficient $\sigma$ reaches 100 %.

The experimental results presented above are used to estimate the pore radius using this second way. Solute radii are calculated using eq. 2 and solute rejections are calculated using eq. 3. Obtained values for pore radii are respectively $r_{p,NF} = 0.37 \pm 0.02$ nm and $r_{p,OPMN-K} = 0.48 \pm 0.04$ nm that is in good agreement with values obtained by the MWCO method.

The obtained rejections of neutral solutes (glucose, saccharose and glycerol) are also compared with those of some other organic molecules like pesticides (atrazine, simazine, diuron) or some hydrated ions (Na+, Ca2+, K+), with radii near to those of sugars.

In Table 3 are summarized the experimentally obtained solute rejections at 25 bars for NF and OPMN-K membranes. It can be seen that the solutes chosen have radii close to sugar radii and it can be expected that for all the solutes the steric effect will be important. For NF membrane ($r_{p,NF} = 0.37$ nm), the ratio $r_s/r_p$ for all solutes is close to 1 ($r_s/r_p = 0.9$ to 1.1) but the rejections of hydrated ions and pesticides are lower than those of sugars. For OPMN-K membrane, the same conclusion is valid, even if the ratio $r_s/r_p$ is lower ($r_s/r_p = 0.7$ to 0.8).

Concerning ion rejection, it is evident that the ion size is not the only parameter that determines the exclusion and it is essential to take into account the electrostatic interaction between the charged membrane sites and the solutes. For example, Stokes radii of glucose and Na+ are equal ($r_s = 0.36$ nm), but their rejections are very different: differences vary from 20 to 38 %. Comparing monovalent and divalent ions retention, one can see that the Stokes radius of Ca2+ is the same that this of K+ (0.33 nm), but the retention difference obtained with OPMN-K membrane is very significant - about 40 %. At low concentrations, chosen for this study, the co-ions (NO3-) are repelled outside the membrane by electrostatic interactions with membrane charges in order to assure the permeate electro neutrality, the counter-ions are also retained. The most important rejections are obtained for NF membrane. For this one, the membrane pores are smaller and consequently the retention is higher due to coupled screening and size effect [16].

From obtained results it is easy to conclude that the Stokes radius is not the best parameter for molecular retention estimation also in the case of pesticides rejection, the molecular shape and dipole moment may also affect solute rejection. For example, diuron presents the lowest rejection compared to the other pesticides despite its largest molecular mass. Diuron rejection at 25 bars is equal to 24 % for OPMN-K membrane and to 74 % for NF membrane. Similar results are reported by several authors for other nanofiltration membranes [17, 18]. This unexpected result can be explained by its higher dipole moment, higher than for simazine and atrazine, due to the large contribution of the carbonyl group and to their linear form.

For estimation of solute radius, eq. 2 takes into account only the molecular mass and does not take into account the molecular shape and size (length and width). Recently, some authors demonstrated that the molecule length and the width also have an important role in pesticide retention [4, 19].

In Table 4 are given values of length (L) and width (W) obtained using «Hyperchem», Stokes radii and re-

### Table 3. Observed solute rejections at 25 bars.

<table>
<thead>
<tr>
<th>Solute</th>
<th>$r_s$ (nm)</th>
<th>NF</th>
<th>OPMN-K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>0.39(1)</td>
<td>0.96</td>
<td>0.55</td>
</tr>
<tr>
<td>Simazine</td>
<td>0.38(1)</td>
<td>0.90</td>
<td>0.37</td>
</tr>
<tr>
<td>Diuron</td>
<td>0.40(1)</td>
<td>0.74</td>
<td>0.24</td>
</tr>
<tr>
<td>Glucose</td>
<td>0.36(1)</td>
<td>1.00</td>
<td>0.81</td>
</tr>
<tr>
<td>Saccharose</td>
<td>0.48(1)</td>
<td>0.99</td>
<td>0.95</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.26(1)</td>
<td>0.67</td>
<td>-</td>
</tr>
<tr>
<td>Na+</td>
<td>0.36(2)</td>
<td>0.79</td>
<td>0.45</td>
</tr>
<tr>
<td>Na+</td>
<td>0.36(2)</td>
<td>-</td>
<td>0.50</td>
</tr>
<tr>
<td>Ca2+</td>
<td>0.33(2)</td>
<td>0.66</td>
<td>0.28</td>
</tr>
</tbody>
</table>

(1) - data obtained using equation (2); (2) - data from Volkov et al. [15].
tentions obtained in this study. The molecular length (L) is defined as the distance between the two most distant atoms and the molecular width \( W = 0.5 \times S^{1/2} \), where \( S \) is the surface of projection of the molecule on the plane perpendicular to L-axis [19].

From these results it is evident that the retention increases when the molecule length and the width increase for both membranes. The pesticide length has a more important influence (slope of linear function for both membranes is equal to 0.18), than the width (slope of linear function for both membranes is equal to 0.07). Obtained results confirm conclusions of Chen et al. [20] that the influence of molecular length is more significant than that of the width. Our results coincide also with these of Kiso et al. [19] that the retention depends on mass and length but the width is also significant.

**CONCLUSIONS**

Organic, molecular solutes (saccharose, glucose and glycerol) have been used to define the average pore sizes for different membranes. The values obtained for NF and OPMN-K membranes, respectively, are MWCO = 170 Da and MWCO = 330 Da and corresponding pore radius was calculated: \( r_{p,NF} = 0.35 \) nm and \( r_{p,OPMN-K} = 0.47 \) nm. A second way, Spiegler-Kedem model is also used to calculate pore radii: \( r_{p,NF} = 0.37\pm0.02 \) nm; \( r_{p,OPMN-K} = 0.48\pm0.04 \) nm. A good agreement between the results obtained by these two methods was found.

Observed rejections for sugars are compared with rejections obtained for usual pesticides and hydrated ions with Stokes radii (\( r_s \)) close to those of sugars. It is found that \( r_s \) is not the only parameter influencing the rejection: a molecular size (length and width) seems to be a very important parameter for pesticide retention and ionic strength concerning salts rejection.

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