Atenolol removal by nanofiltration: a case-specific mass transfer correlation

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ABSTRACT

Concentration polarization is a phenomenon inherent to membrane separation operations and as a precursor of membrane fouling is frequently related to the decrease in the performance of these operations. In the present work, a case-specific mass transfer correlation was developed to assess the concentration polarization when nanofiltration, in different operating conditions, was applied to treat a pharmaceutical wastewater containing atenolol. NF runs with two membranes, two atenolol concentrations and three feed circulating velocities were conducted, and the corresponding experimental mass transfer coefficients were determined using film theory to describe the concentration polarization phenomenon. Higher velocities led to higher mass transfer coefficients and, consequently, lower concentration polarization. These mass transfer coefficients were correlated with the circulating velocity (Re), the solute diffusivity (Sc) and the membrane permeability (Lp) (the membrane is a permeable interface with effect on the concentration profiles developed from the interface towards the bulk feed), yielding the following correlation \( Sh = 1.98 \times 10^4 Re^{0.5} Sc^{0.33} L_p^{0.32} \). The good agreement between the calculated and the experimental results makes this correlation a valuable tool for water practitioners to predict and control the concentration polarization during atenolol-rich wastewater treatment by nanofiltration, thereby increasing its productivity and selectivity.

Key words | atenolol, concentration polarization, mass transfer, nanofiltration

INTRODUCTION

Pharmaceutical compounds are the class of contaminants of emerging concern with a major input into the environment, a fact that is associated with their high consumption (Collado et al. 2014). Among these, atenolol (ATN) is one of the pharmaceuticals most sold worldwide (Castro et al. 2006). It is the main beta-blocker, used in the treatment of hypertension, treatment of myocardial infarction and control of cardiac arrhythmias, recommended by the European Societies of Hypertension and of Cardiology (Sabídó et al. 2018). Consequently, this widespread use is associated with a severe environmental problem of the contamination of water bodies and soil. In fact, the occurrence of pharmaceuticals in the environment is usually attributed to the inefficiency of urban wastewater treatment plants (UWWTPs) (Papageorgiou et al. 2016). Recent research shows the presence of pharmaceuticals in UWWTPs of different countries, where they are found at an inlet concentration range from ng L\(^{-1}\) to μg L\(^{-1}\). Moreover, wastewaters from the pharmaceutical industry may contain higher pharmaceuticals concentration, generally in the range of mg L\(^{-1}\) (Larsson 2014). The presence of ATN in UWWTPs has been observed in different regions worldwide such as in Korea (Behera et al. 2011), Spain (Collado et al. 2014), Greece (Papageorgiou et al. 2016), the Czech Republic (Vymazal et al. 2017), India (Balakrishna et al. 2017), South Africa (Archer et al. 2017), Sweden (Kårelid et al. 2017), and Portugal (Rosa et al. 2018).

Membrane separation operations, like nanofiltration (NF) and reverse osmosis (RO), are promising technologies for the removal of pharmaceuticals from water and wastewaters, even when they are present at residual levels, since the majority of these compounds have a molar mass...
within the range of the molar cut-off of NF/RO membranes (Wang et al. 2015). Thus, NF and RO may increase the safety of the treatment system and reduce the environmental risks. Nevertheless, the overall performance of a membrane separation operation is related to the membrane and feed solution characteristics, as well as the transport phenomena occurring at the boundary layer adjacent to the membrane. These phenomena condition the membrane-solvent-solute interactions and the mode of action of the membrane operations in terms of the rejection to the solutes present in the feed solution, as well as having a great influence on the permeate fluxes. Therefore, the determination of mass transfer coefficients through experimental data is a recommended practice to predict and thus prevent the occurrence of undesirable phenomena like concentration polarization and fouling.

In the face of these considerations, the present study aims at the evaluation of the nanofiltration process in terms of membrane selection and operating conditions, transmembrane pressure (ΔP) and feed circulating velocity (u), leading to the quantification of concentration polarization in order to achieve minimal fouling. For this purpose of ATN removal by NF, a case-specific mass transfer correlation is developed, $Sh = Sh(Re, Sc, L_P)$, that relates the dimensionless mass transfer coefficient or the Sherwood number, $Sh$, with the Reynolds and Schmidt numbers and a dimensionless hydraulic permeability, $L_P$.

**THEORY**

The membrane selectivity to a given solute is conventionally measured by the apparent and intrinsic rejection coefficients, $f$ and $f'$, respectively, defined as:

$$f = \left(1 - \frac{C_P}{C_F}\right)$$  \hspace{1cm} (1)

and

$$f' = \left(1 - \frac{C_P}{C_m}\right)$$  \hspace{1cm} (2)

where $C_P$, $C_F$ and $C_m$ are the concentrations in the permeate, in the feed and at the membrane surface, respectively.

The difference between $f$ and $f'$ is associated with the development of a concentration profile in the laminar boundary layer adjacent to the membrane, that is, the concentration polarization. Film theory (Bird et al. 1960) in conjunction with the solution of the differential equation resulting from the differential mass balance in the boundary layer yields Equation (3):

$$\frac{C_m - C_P}{C_b - C_F} = \exp\left(\frac{f}{k}\right)$$  \hspace{1cm} (3)

where the left term is the concentration polarization modulus, $J_v$ is the permeate flux and $k$ is the mass transfer coefficient. Equations (1)–(3) yield Equation (4):

$$f = \frac{f'}{f' + (1 - f') \exp\left(\frac{k}{k}\right)}$$  \hspace{1cm} (4)

The prediction of the concentration polarization requires the determination of the mass transfer coefficient, $k$, that depends on the system geometry, feed hydrodynamic conditions, and feed physicochemical properties. The mass transfer coefficients are usually obtained from dimensionless correlations of the type

$$Sh = a \cdot Re^b \cdot Sc^c$$  \hspace{1cm} (5)

where $Sh = k \cdot d_h / D_{AW}$, $d_h$ is the hydraulic diameter, $D_{AW}$ is the diffusivity of solute A in water, $Re = \rho u d_h / \mu$ is the Reynolds number (dimensionless feed circulating velocity, $u$), $Sc = \mu / \rho D_{AW}$ is the Schmidt number (relative to the solute), $\mu$ and $\rho$ are the viscosity and density of the fluid, and $a$, $b$ and $c$ are empirical coefficients that depend on the system under study.

However, these are general correlations for impermeable interfaces as tubes and parallel plates and they do not take into consideration the fact that a membrane is a permeable interface with effect on the concentration profiles developed from the interface towards the bulk feed (Rosa 1995). In this sense, after a very extensive review of the mass transfer correlations used in ultrafiltration and nanofiltration, Rosa (1995) introduced a dimensionless hydraulic permeability, $L_P$, in the mass transfer correlations for permeable interfaces:

$$Sh = a \cdot Re^b \cdot Sc^c \cdot L_P^d$$  \hspace{1cm} (6)

where $L_P = \frac{L_P}{R_m}$, $R_m$ is the membrane radius (the tests were conducted in circular flat-cell units described previously.
LP is the membrane hydraulic permeability (expressed in length units) and d is an empirical coefficient.

The constants a, b, c and d of Equation (6) are system-specific. In the present study, the coefficients b and c were fixed at 0.5 and 0.33, respectively. This value of b = 0.5 is characteristic of a turbulent flow under development, and was previously obtained in studies carried out by Brites & de Pinho (1991) and Rosa (1995) using the same filtration cells. The coefficient c = 0.33 is a typical exponent for the Schmidt number reported in the literature of dimensionless mass transfer correlations for highly diluted solutions (Rosa 1995; Giacobbo et al. 2018).

Coefficients a and d were computed by fitting the model correlation to experimental mass transfer coefficients, the adjustment being performed by varying the constants and minimizing the sum of the squares of the deviations between the experimental, Sh\text{exp}, and calculated, Sh\text{calc}, Sherwood numbers.

For determining the experimental mass transfer coefficients, the velocity variation method (Jonsson & Boesen 1977) was used, assuming:

\[ k = C^* u^b \]  

and re-writing Equation (4) as:

\[ \ln \left( \frac{1 - f'}{f'} \right) = \ln \left( \frac{1 - f'}{f'} \right) + \frac{1}{C^* u^b} \]

In Equation (7), C* is a constant, u is the feed circulating (tangential) velocity and b is the empirical exponent of the Reynolds number, Re, in Equation (6), that is made equal to 0.5.

Thus, the linear regression of the experimental values of \( \ln \left( \frac{1 - f}{f} \right) \) vs \( \frac{f}{u_0^{0.5}} \) yields a straight line whose slope is \( \frac{1}{C^*} \), from which the experimental mass transfer coefficients, \( k_{\text{exp}} \), are computed for each velocity using Equation (7).

The intercept at the origin, \( \ln \left( \frac{1 - f'}{f'} \right) \), allows the determining of f', the intrinsic rejection of the target solute by the membrane used. A scheme of the algorithm to determine the experimental mass transfer coefficients and Sherwood numbers is displayed in Figure 1.

**MATERIALS AND METHODS**

The experiments were performed with two commercial nanofiltration membranes, NF 90 and NF 270, from Dow – Filmtec (Minneapolis, USA), in laboratory flat-cell units with a membrane surface area of 14.5 cm\(^2\), described in previous work (Giacobbo et al. 2015). Firstly, the membranes were thoroughly washed with NaOH solution at pH 9.0 and 30 °C for 30 min to remove residual chemicals. Then, they were compacted by the circulation of deionized water at 25 °C pressurized at 15 bar for 3 h, in order to avoid the effects of pressure on membrane structure in the subsequent experiments. They were characterized regarding their hydraulic permeability, as described in previous work (da Trindade et al. 2015), at ΔP from 6 to 15 bar, and in terms of salt rejection (sodium chloride, sodium sulfate, magnesium chloride and magnesium sulfate). The permeation runs of reference solutes were conducted at feed circulating velocity of 0.96 m s\(^{-1}\), 10 bar, 25 °C, and with 30 min of stabilization time.
Feed solutions with 8 and 16 mg L\(^{-1}\) of ATN, similar to concentrations found in wastewaters from the pharmaceutical industry, were prepared in deionized water (conductivity less than 5 μS cm\(^{-1}\) and pH 7.5). The ATN, with 99% purity, was purchased at a compounding pharmacy and has a molar mass of 266.34 g mol\(^{-1}\) and a diffusivity, \(D_{AW}\), of 5.1 × 10\(^{-10}\) m\(^2\) s\(^{-1}\) (Castro 2006), which corresponds to a Schmidt number of 1760.

The NF permeation runs were conducted in total recirculation mode, where the permeate and the retentate streams were recirculated to the feed tank to study the variation in the permeate fluxes and the solute rejection coefficients. In each run, the stabilization time was 30 min, after which permeate samples were collected for chemical analysis. The feed circulating velocity varied in the range of 0.24–0.96 m s\(^{-1}\) (i.e., \(Re = 5,750\)–23,000) and the transmembrane pressure from 6 to 12 bar, using 8 or 16 mg L\(^{-1}\) ATN solutions.

The ATN concentration was determined by a spectrophotometric method developed by Weich et al. (2007). The calibration curve, ATN (mg L\(^{-1}\)) = 23.167 absorbance (\(R^2 = 0.999\)), covering the range of concentrations investigated, was obtained by measuring the absorbance at 226 nm (wavelength of maximum absorbance), using a spectrophotometer T80+ UV-Vis (PG Instruments, UK).

**RESULTS AND DISCUSSION**

Table 1 presents the hydraulic permeabilities and the apparent rejection coefficients to salts for the NF 90 and NF 270 membranes, these results being in line with the ones achieved in previous work performed under the same conditions: reference solutes, membranes, operating parameters, and filtration cells (da Trindade et al. 2015; de Souza et al. 2018). NF 270 has about twice the hydraulic permeability of NF 90 and lower salt rejections, particularly for the monovalent salts.

Figure 2 shows the variation of permeate fluxes with the transmembrane pressure, \(\Delta P\), for the ATN solutions of 8 and 16 mg L\(^{-1}\) at different values of feed circulating velocities, for NF 90 and NF 270 membranes. Table 2 presents the intrinsic rejection coefficients, \(f\), and the experimental mass transfer coefficients, \(k_{exp}\), and Sherwood numbers, \(Sh_{exp}\), obtained using the algorithm in Figure 1.

For both membranes (Figure 2), the NF permeate fluxes of both ATN solutions vary linearly with \(\Delta P\) for all the feed velocities and the slopes of corresponding straight lines increase with the increase of the feed circulating velocity. Further, both presented similar behaviour when considering a particular feed concentration, 8 or 16 mg L\(^{-1}\). For the lowest feed concentration, 8 mg L\(^{-1}\), three distinct curves are observed with decreasing slopes as the feed circulating velocity decreases. On the other hand, for the highest feed concentration, 16 mg L\(^{-1}\), only two curves are displayed, one for the highest feed circulation velocity of 0.96 m s\(^{-1}\) and another for the low feed circulation velocities of 0.48 and 0.24 m s\(^{-1}\).

Summing up, the increase of the feed concentration leads to the decrease of the permeate fluxes and this can again be attributed to higher concentration polarization. One can also observe that this phenomenon becomes stronger under more adverse hydrodynamic conditions, i.e., at lower feed circulating velocities, and for the more permeable membrane. This is further confirmed in Figure 3, where the concentration polarization modulus, defined as \((C_m - C_p)/(C_b - C_p)\), also displays the same behaviour. To calculate it, \(C_b\) and \(C_p\) were determined by chemical analyses, while \(C_m\) was calculated using Equation (2) with the intrinsic rejection coefficients, \(f\), in Table 2.

Figure 3 displays the apparent rejections of ATN and the concentration polarization modulus at different feed circulating velocities, ATN feed concentrations and transmembrane pressures for the NF 90 and NF 270 membranes. One can observe a strong relation of the concentration polarization modulus with the apparent rejection coefficient. For all evaluated conditions, the concentration polarization modulus is inversely proportional to the rejection coefficient, that is, the higher the polarization modulus, the smaller the \(f\), this behaviour being more marked for the most permeable membrane, NF 270 (Figure 3). Therefore, higher concentration polarization resulted in higher solute fluxes across the membranes, thus reducing the apparent rejection coefficients. This behaviour had already been reported in a previous work (de Souza et al. 2018) using the same membranes, NF 90 and NF 270, however treating

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Membrane characterization</th>
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<tr>
<td>Membrane</td>
<td>(L_p) (kg h(^{-1}) m(^{-2}) bar(^{-1}))</td>
</tr>
<tr>
<td>NF 90</td>
<td>10.3</td>
</tr>
<tr>
<td>NF 270</td>
<td>19.7</td>
</tr>
</tbody>
</table>

*Multiplying \(L_p\) in (kg h\(^{-1}\) m\(^{-2}\) bar\(^{-1}\)) per \(\mu/(3.600 \times 10^5 \times \rho)\).
solutions containing another pharmaceutical compound, norfloxacin.

In fact, the apparent rejection coefficients for ATN varied with the operational conditions, mainly with the feed circulating velocity. For instance, for both membranes at the feed circulating velocity of 0.24 m s\(^{-1}\), as the concentration polarization modulus increases with \(\Delta P\), the apparent rejection coefficient decreases. On the other hand, at the highest feed circulating velocity, 0.96 m s\(^{-1}\), the apparent rejection coefficient slightly increases with \(\Delta P\), while the concentration polarization modulus decreases. Therefore, these results clearly show that the concentration polarization is governing both the productivity (Figure 2) and selectivity (Figure 3) of the nanofiltration operation, becoming more important as it reaches higher values.

The adverse hydrodynamic conditions of low feed circulating velocities lead to an increase of the concentration polarization modulus due to the decrease of the mass transfer coefficients, as shown in Table 2. This behaviour, as
expected, is more marked for the more permeable membrane, the NF 270. As a consequence, the NF 270 membrane shows a higher slope in Figure 3 as well as a more pronounced deviation between the two rejection coefficients, $f_0$ (82%, Table 2) and $f$ (65%–81%, depending on the feed circulating velocity, Figure 3), evidencing that it had a higher concentration polarization incidence than the NF 90 membrane.

In practice, this means that a higher circulating velocity is needed for similar concentration polarization control with the more permeable membrane. These results highlight the importance of including $L_P$ in the mass transfer correlation and point to a low $d$ constant.

Coefficients $a$ and $d$ were then computed by fitting Equation (6) to the experimental data ($L_P$ in Table 1; $Sc = 1,760$ for atenolol; $Re$ and $Sh_{exp}$ in Table 2; dimensionless numbers illustrated in Figure 1), considering $b$ and $c$ constants fixed at 0.5 and 0.33, respectively, and yielded:

$$Sh = 1.98 \times 10^4 Re^{0.5} Sc^{0.33} L_P^{0.32}$$

(9)

with root mean square (RMS) and mean relative deviation (MRD) values of 617 and 12.7%, respectively.

The $L_P$ exponent obtained is coherent with the ones obtained earlier for the same membrane cells but different membranes, solutes and operating conditions (Rosa 1995). Figure 4 shows the good agreement between the values of the experimental and calculated Sherwood numbers, demonstrating that the mass transfer correlation (Equation (9)) fits very well the experimental results obtained with the NF 90 and NF 270 membranes when applied to treat solutions containing atenolol. In addition, the proximity between the values of the experimental and calculated mass transfer coefficients for both membranes (Table 2; $k_{calc}$ obtained from the $Sh$ values computed using Equation (9)) also highlights the good quality of the mass transfer correlation of Equation (9). This correlation is valid for Reynolds numbers ranging from 5,750 to 23,000, an $L_P$ range of $1.20 \times 10^{-12}$–$2.29 \times 10^{-12}$ and an $Sc$ number of 1,760.

**CONCLUSIONS**

The mass transfer coefficients are crucial parameters in the modelling, forecasting, and scale-up of membrane operations, their determination being recommended from case-specific correlations validated by experimental values. The case-specific conditions pertain to the operating parameters of feed fluid dynamics and transmembrane pressure and to the membrane permeation characteristics.

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