Nanofiltration as tertiary treatment method for removing trace pharmaceutically active compounds in wastewater from wastewater treatment plants

Jorge Garcia-Ivars\textsuperscript{a, *}, Lucia Martella\textsuperscript{b}, Manuele Massella\textsuperscript{c}, Carlos Carbonell-Alcaina\textsuperscript{a}, Maria-Isabel Alcaina-Miranda\textsuperscript{a, d}, Maria-Isabel Iborra-Clara\textsuperscript{a, d}

\textsuperscript{a} Research Institute for Industrial, Radiophysical and Environmental Safety (ISIRYM), Universitat Politècnica de València, C/Camino de Vera s/n, 46022 Valencia, Spain
\textsuperscript{b} Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali (DICAM), Università di Bologna, Via Terracini, 28, 40131 Bologna, Italy
\textsuperscript{c} Dipartamento di Ingegneria Civile, Edile e Ambientale, Università Sapienza di Roma, Via Eudossiana 18, 00184 Rome, Italy
\textsuperscript{d} Department of Chemical and Nuclear Engineering, Universitat Politècnica de València, C/Camino de Vera s/n, 46022 Valencia, Spain

Keywords: Pharmaceutically active compounds; Nanofiltration; Rejection efficiency; Fouling mechanisms; Phenomenological model.

Abstract

The ever-increasing occurrence and persistence of pharmaceutically active compounds (PhACs) in soils, sediments, drinking water supplies and wastewater effluents are a matter of serious environmental concern for governments and researchers worldwide. Nanofiltration as tertiary treatment method can be a viable and practical tool to remove these pollutants from aquatic environments. However, organic matter present in water sources can foul the membrane surface during operation, thus being potentially able to affect the membrane performance. Therefore, fouling mechanisms could heavily influence on the removal efficiencies. The purpose of this study was to investigate the implementation of three nanofiltration membranes (TFC-SR2, NF-270 and MPS-34) and to study both the rejection of trace PhACs and the fouling mechanisms for each membrane as a function of feed solution pH. Fouling mechanisms were predicted by Hermia's model adapted to cross-flow configurations. Results demonstrated that higher
removals were obtained at slightly alkaline pH, especially for anionic trace PhACs. At
the same conditions, more severe fouling was observed, which resulted in strong flux
debacliues and an increase in hydrophobicity. This indicates that the attached organic
matter on the membrane surface acts as a secondary selective barrier for separation.

1. Introduction

An extremely increasing presence of emerging contaminants and in particular
pharmaceutically active compounds (PhACs) has been detected at trace concentration
(ranging from ng/L up to several mg/L) as free compounds and/or as metabolites in
many environmental matrices worldwide, including drinking water supplies, wastewater
effluents and soils and sediments (Heberer, 2002; Verlicchi et al., 2012; Wang and
Wang, 2016; Smith Jr., 2014). This growing occurrence and persistence in soils and
aquatic environments, together with their diversity, make them some of the most
targeted compounds to be removed. In the last decades, pharmaceuticals have been
extensively used in large quantities but they are incompletely absorbed and metabolised
by human and animal organism, thus resulting in non-absorbed and non-metabolised
portions which are disposed of in the environment through their excretions (urine and
faeces) (Picó and Barceló, 2015; Archer et al., 2017). The potential health risks
associated with the release of these pollutants into the environment and their completely
possible interactions with living organisms are a matter of serious environmental
concern for national/international scientific communities, governments and regulatory
agencies (Verlicchi and Zambello, 2015; Jung et al., 2015; Grandclément et al., 2017).

PhACs are synthetic organics designed with the objective of enhancing human
health standards. However, their continuous discharge to aquatic environment may
cause unwanted side effects on non-target living organisms. Some examples of such
side effects would be human and wildlife reproduction disorders and the development
and proliferation of antibiotic-resistant bacteria, mainly due to many of them are
recalcitrant to biodegradation and prone to bioaccumulation (Halling-Sørensen et al.,
1998; Schmidt et al., 2012; Petrie et al., 2015). Due to their ubiquitous and
nonbiodegradable character, pharmaceutical residues cannot be completely removed or
degraded in conventional wastewater treatment plants (WWTPs) and PhACs are
released into the environment, thus making the secondary effluents discharged from
WWTPs into a major source of pharmaceutical micropollutants (Chon et al., 2013; Grandclément et al., 2017). In some cases, their concentration has increased after passing through conventional wastewater treatment due to their transformation into conjugates (Vergili, 2013). This situation has led researchers to explore new treatment strategies as tertiary processes to efficiently remove PhACs from secondary effluents from WWTPs, such as activated carbon adsorption, advanced oxidation processes using ozone and hydroxyl radicals or membrane technology.

As a well-established sustainable technology for removing natural organic matter, macromolecules, colloids, pathogens and turbidity, membrane technology is increasingly applied in municipal and industrial wastewater treatment as an affordable alternative for sustainable water reclamation/reuse. Several studies employing ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) have been carried out to investigate the removal mechanisms and efficiencies of PhACs using membrane separation processes. In addition to the fouling phenomena and their detrimental effect on the lifespan and performance of membranes, which has been extensively reported by different researchers (Li and Elimelech, 2004; Van der Bruggen et al., 2008; Kochkodan and Hilal, 2015), the presence of natural organic matter (NOM) during membrane filtration can lead to a competition with PhACs and other micropollutants in the aquatic environment for the adsorption sites on the membrane surface, thus causing lowered adsorption rates of these low-molecular weight compounds (Jermann et al., 2009). This situation can also occur when activated carbon adsorption is used as alternative removal technique (Altmann et al., 2014). Previous studies demonstrated that the existing interactions between organic matter and PhACs can help remove them from aquatic environments, either as a part of the retentate stream or as a solute adsorbed on the membrane, especially due to the hydrophobic interactions between organic matter and PhACs and the adsorptive mechanism (Khansary et al., 2017; García-Ivars et al., 2017). Extensive studies demonstrated that nanofiltration have been efficiently implemented to remove PhACs and other micropollutants, but many of them were focused on its application in synthetic model waters where the target compounds were spiked (Nghiem and Hawkes, 2007; Comerton et al., 2009; Dolar et al., 2013; Lin et al., 2014) and very few of them were concentrated on its implementation in real wastewaters, rivers or drinking water production (Snyder et al., 2007; Bellona et al., 2010; Azaïs et al., 2016).
In this work, the role of feed solution and its constituents in the removal of PhACs with different physicochemical properties and the personal care product triclosan from real wastewater by using NF cross-flow membranes was studied. The performance of three different membranes from very loose to tight NF within the pH range from 6 to 8 was evaluated in terms of permeate flux and rejection indexes of each target compound. The present work includes the personal care product triclosan and eight selected PhACs which represented the most common PhACs found in WWTP secondary effluents at the Spanish Mediterranean area of Valencia, being found acetaminophen, ibuprofen and sulfamethoxazole in concentrations ranging from 20 ng/L to several mg/L (in the worst case scenario, up to 20-100 mg/L) and the rest of target compounds in lower concentration ranges from 1 to 2-4000 ng/L (Gracia-Lor et al., 2012; Pascual-Aguilar et al., 2015, Picó and Barceló, 2015). As a novelty, fouling mechanisms at each pH condition for each NF membrane were predicted by Hermia's model adapted to cross-flow configurations. The predominant fouling mechanisms at the studied conditions were related to the mechanism for which each target compound was rejected. The rejection indexes of the selected emerging contaminants were determined by the composition of both feed and permeate streams of the process via High-Performance Liquid Chromatography (HPLC).

2. Materials and methods

2.1. WWTP secondary effluent samples

Secondary effluent samples were obtained from a municipal WWTP located in the region of Valencia (Carraixet WWTP, Spain). Their characterisation was carried out according to the standard methods defined by the American Public Health Association to examine the characteristics of water and wastewater (APHA, 2012) and the results are summarised in Table 1. The samples of this secondary effluent have an alkaline pH with a high electrical conductivity, turbidity and moderate COD and BOD parameters in comparison with researchers who used secondary effluents (Katsoyiannis et al., 2017; Chon et al., 2017).
Table 1. Water quality parameters of the selected secondary effluents from a local waste-water treatment plant at 25°C.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average result ± standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.41 ± 0.10</td>
</tr>
<tr>
<td>m-Alkalinity (mg CaCO₃/L)</td>
<td>415.52 ± 19.34</td>
</tr>
<tr>
<td>Electrical conductivity (µS/cm)</td>
<td>1406.00 ± 71.06</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>363.73 ± 69.79</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>35.46 ± 3.41</td>
</tr>
<tr>
<td>COD (mg O₂/L)</td>
<td>94.77 ± 5.37</td>
</tr>
<tr>
<td>BOD (mg O₂/L)</td>
<td>11.71 ± 1.87</td>
</tr>
<tr>
<td>UV₅₅₄</td>
<td>0.283 ± 0.003</td>
</tr>
<tr>
<td>Ca²⁺ (mg/L)</td>
<td>76.61 ± 3.84</td>
</tr>
<tr>
<td>Mg²⁺ (mg/L)</td>
<td>25.17 ± 1.04</td>
</tr>
<tr>
<td>Cl⁻ (mg/L)</td>
<td>185.89 ± 0.64</td>
</tr>
<tr>
<td>Total Nitrogen (mg N/L)</td>
<td>73.30 ± 16.10</td>
</tr>
<tr>
<td>Proteins (mg/L)</td>
<td>65.25 ± 10.03</td>
</tr>
</tbody>
</table>

2.2. Chemicals

High purity standards (>99%) of acetaminophen, caffeine, diazepam, diclofenac, ibuprofen, naproxen, sulfamethoxazole, triclosan and trimethoprim were purchased from Sigma-Aldrich (Germany) and were used without further purification. The physicochemical properties of the selected PhACs are summarised in Table 2.

Table 2. Physicochemical properties of the nine PhACs employed in this study.
The logarithm of the octanol-water distribution coefficient (log \(K_{OW}\)) and acid dissociation constant (pKa) of each target compound were obtained from SciFinder Scholar database, whereas their volume of the solute (\(V_S, \text{cm}^3/\text{mol}\)) and dipole moment (\(M_{DIP}, \text{Debyes}\)) were determined using Chem3D Ultra 8.0 software. Additionally to these parameters, the hydrodynamic molecular radius or Stokes radius (\(r_S, \text{m}\)) of each compound was calculated using the Stokes-Einstein equation:

\[
r_S = \frac{T \cdot k_B}{6 \cdot \pi \cdot \eta \cdot D_s}
\]  

\(^a\) SciFinder Scholar, data calculated at 20 °C and 760 torr using Advanced Chemistry Development (ACD/Labs) Software V11.02 (©1994e2016 ACD/Labs).

\(^b\) Hydrophobic when log \(K_{OW}\) > 2.

\(^c\) Chem3D Ultra 8.0.
where $T$ is the absolute temperature (K), $k_B$ is the Boltzmann constant (kg·m$^2$/(K·s$^2$)), $h$ is the viscosity of solvent (kg/(m·s)), and $D_S$ is the diffusion coefficient of the organic compound in water (m$^2$/s). The diffusion coefficient of the target emerging contaminants ($D_s$) on aqueous solution can be approximated by the molecular weight ($M_W$, g/mol) of the solute in accordance with the empirical equation described by (Avdeef et al., 2004):

$$\log(D_s) = -4.113 - 0.4609 \log(M_W)$$

Solutions of 0.1 M HCl and 0.1 M NaOH were used to adjust the pH of feed solutions. Both chemicals were obtained of reagent grade from Panreac (Spain). Deionised water was used throughout the study.

### 2.3. Membranes

Three commercial spiral wound NF membranes were used in this investigation, namely TFC-SR2, NF270, and SelRO MPS-34 A2X (henceforth MPS-34). The TFC-SR2 and MPS-34 membranes with effective areas of 2.5 and 1.6 m$^2$ respectively were supplied by Koch Membrane Systems (USA), whereas NF270 membrane with an effective area of 2.6 m$^2$ was supplied by Dow FilmTec (USA). The selected membranes span a wide range of molecular weight cut-off (MWCO), from loose to tight NF membranes as follows: TFCSR2 > NF-270 > MPS-34. Both NF-270 and TFC-SR2 are considered as loose NF membranes with an estimated MWCO around 230-300 and 400 Da, respectively. Conversely, MPS-34 membrane can be defined as tight NF membrane with a MWCO of 200 Da. Their main characteristics are given in Table 3. As it can be observed, before the filtration experiments began, water permeability for each membrane was calculated at different transmembrane pressure ($\Delta P$, ranging from 2 to 10 bar), constant flow rate and operating temperature (500 L/h and 25 ºC, respectively).
Table 3. Properties of the selected NF membranes.

<table>
<thead>
<tr>
<th>Properties/Membrane</th>
<th>TFC-582</th>
<th>NF70B</th>
<th>SeRO MPS 54 AX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Koch Membrane Systems</td>
<td>Dow FILMTEC™ Membranes</td>
<td>Koch Membrane Systems</td>
</tr>
<tr>
<td>Material chemistry</td>
<td>Proprietary Polyamide TFC™ membrane</td>
<td>Polyamide Thin-Film Composite</td>
<td>Proprietary polyamide composite membrane</td>
</tr>
<tr>
<td>Geometry</td>
<td>Spiral wound</td>
<td>Spiral wound</td>
<td>Spiral wound</td>
</tr>
<tr>
<td>MWCO (Da)</td>
<td>&gt;300–400</td>
<td>250–300&lt;sup&gt;g,h&lt;/sup&gt;</td>
<td>200</td>
</tr>
<tr>
<td>Average pore radius (nm)</td>
<td>0.2–0.04&lt;sup&gt;f&lt;/sup&gt;</td>
<td>0.26–0.43&lt;sup&gt;b,h&lt;/sup&gt;</td>
<td>—</td>
</tr>
<tr>
<td>Water contact angle (°)</td>
<td>25–48&lt;sup&gt;c&lt;/sup&gt;</td>
<td>32–49&lt;sup&gt;b&lt;/sup&gt;</td>
<td>75–80&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Water permeability (L·h&lt;sup&gt;-1&lt;/sup&gt;·bar&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>17.7 ± 0.5</td>
<td>13.4 ± 0.2</td>
<td>11 ± 0.2</td>
</tr>
<tr>
<td>Maximum operating pressure (bar)</td>
<td>45</td>
<td>41</td>
<td>35</td>
</tr>
<tr>
<td>Allowable pH - continuous operation</td>
<td>4–6</td>
<td>2–11</td>
<td>0–14</td>
</tr>
<tr>
<td>Allowable pH - cleaning</td>
<td>2–11</td>
<td>1–12</td>
<td>0–14</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reported in (Nghiem and Hawkes, 2007); <sup>b</sup> Reported in (De Munari et al., 2013); <sup>c</sup> Reported in (Azaïs et al., 2014); <sup>d</sup> Reported in (Lopez-Munoz et al., 2009); <sup>e</sup> Reported in (Lin et al., 2016); <sup>f</sup> Reported in (Nghiem et al., 2006); <sup>g</sup> Reported in (Nghiem and Coleman, 2008); <sup>h</sup> Reported in (Chang et al., 2011); <sup>i</sup> Reported in (Ali Zazouli et al., 2009); <sup>j</sup> Reported in (Bellona et al., 2010); <sup>k</sup> Reported in (Drazevic et al., 2013); <sup>l</sup> Reported in (Owusu-Agyeman et al., 2017); <sup>m</sup> Reported in (Fernandez et al., 2010); <sup>n</sup> Deionised water flux was experimentally determined in this work at the following conditions: 2e10 bar, 25 °C, 500 L/h.

2.4. Experimental procedure

The filtration experiments were carried out in a laboratory scale cross-flow membrane filtration pilot plant equipped with a 2.5 inch AG 2540 spiral wound module. The feed solution was fed to the cross-flow system with a variable speed volumetric pump from a temperature-controlled feed tank with a capacity of 30 L. A pH meter was incorporated to the pump as well as two thermos immersion coolers (Haake® EK20, Thermo Electron Corporation, USA), which were used to control the operating temperature (25 ± 2 °C) and prevent an increase in water temperature resulting from using the pump. The transmembrane pressure was fixed at 5 bar using a stainless steel throttle valve on the retentate outlet and was monitored through two manometers located on the inlet and outlet of the membrane module. This low transmembrane pressure was selected mainly due to economic, energy and pressure vessel material savings. The use of such a transmembrane pressure (5 bar) to remove emerging contaminants (especially PhACs) from aquatic environments has been previously reported by other researchers (Yangali-Quintanilla et al., 2009; Yangali-Quintanilla et al., 2010; Miralles-Cuevas et al., 2017). Filtration experiments were performed at a constant flow of 500 ± 20 L/h, which was measured by a flow meter placed at the retentate outlet. The NF experiments operated in a total recirculation mode in which both concentrate and permeate streams were returned back to the feed tank to keep the feed concentration constant. Finally, a scale with an accuracy of ±0.01 g was employed to gravimetrically measure the permeate flux.
Prior to each experiment, membranes were first stabilised by filtering deionised water at 10 bar for at least 2 h until a stable water flux was reached. After that, filtration experiments consisted in filtration runs of 4 h with WWTP secondary effluents where target compounds were spiked (if necessary) to achieve the following initial concentrations: 1000 ng/L of acetaminophen, ibuprofen and sulfamethoxazole and 300 ng/L of caffeine, diazepam, diclofenac, naproxen, triclosan and trimethoprim. The experimental conditions were 500 ± 1 L/h, 5 bar and 25 ± 2 ºC. The influence of pH was tested at three pH levels from 6 to 8. The permeate flux (Jp, L/m²·h) was determined by measuring the volume of permeate (V, L) collected at regular time intervals (t, h) as follows:

\[
J_p = \frac{V}{A_m \cdot t}
\]  

(3)

where \( A_m \) (m²) is the effective area of the membrane.

The rejection index (R, %) was calculated based on the concentration of each PhAC in permeate (\( C_p \), ng/L) and feed (\( C_f \), ng/L) streams:

\[
R(\%) = \frac{C_f - C_p}{C_f} \times 100
\]  

(4)

In order to assess the fouling mechanism during the filtration of the WWTP secondary effluent samples, the Hermia’s model for constant pressure was selected. In this model, Hermia distinguished four models for each predominant fouling mechanism: gel layer formation, incomplete or intermediate blocking, standard blocking and complete blocking (Hermia, 1982). The adaptation of such a model to cross-flow configurations by incorporating the flux associated with the back transport mass transfer (evaluated at the steady state) was developed by several authors (Field et al., 1995; Vincent-Vela et al., 2009) and its general differential equation is the following expression:
where \( J_{\text{pss}} \) is steady-state permeate flux (same units as \( J_p \)), \( K \) is a phenomenological model constant with physical meaning and \( n \) is the model parameter, which depends on the fouling mechanism. Thus, when the value of \( n \) is 0 represents the formation of a gel layer by the accumulation of solute particles onto the membrane surface with a thickness proportional to the permeated volume. In this case, the pore blocking is neglected (Vincent-Vela et al., 2009). However, when \( n \) is 1, the fouling mechanism corresponds to the incomplete or intermediate blocking model in which the solute particles cannot penetrate completely inside the porous structure and then can settle on other particles deposited before, forming multilayers. The standard blocking model (with a value of \( n \) of 1.5) assumed that solute particles with a smaller size than the pores of the membranes can pass through the membrane pores and precipitate on inner pore walls, thus reducing the effective pore size. Finally, if \( n \) corresponds to 2, the complete blocking model is assumed. In this case, the size of the solute particles is similar to the pore size of the membrane, which results in that each solute particle participates in sealing the pore entrance without passing through the porous structure, thus forming a monomolecular layer on membrane surface (Corbatón-Báguena et al., 2016; Carbonell-Alcaina et al., 2016). The general representing equations for each fouling mechanism are the following expressions:

- Gel layer formation (\( n = 0 \)):

\[
\frac{dJ_p}{dt} = K \cdot (J_p - J_{\text{pss}}) \cdot J_p^{2-n}
\]

(5)

\[
t = \frac{1}{K_{GL} \cdot J_{\text{pss}}} \cdot \left[ \ln \left( \frac{J_p \cdot J_0 - J_{\text{pss}}}{J_0 \cdot J_p - J_{\text{pss}}} \right) - J \cdot \left( \frac{1}{J_p} - \frac{1}{J_0} \right) \right]
\]

(6)

- Incomplete or intermediate blocking (\( n = 1 \)):

\[
J_p = \frac{J_0 \cdot J_{\text{pss}} \cdot e^{K_B \cdot J_{\text{pss}} \cdot t}}{J_{\text{pss}} + J_0 \cdot \left( e^{K_B \cdot J_{\text{pss}} \cdot t} - 1 \right)}
\]

(7)
• Standard blocking ($n = 1.5$):

$$J_p = \frac{J_0}{\left(1 + J_0^{1/2} \cdot K_{SB} \cdot t\right)^2} \tag{8}$$

• Complete blocking ($n = 2$):

$$J_p = J_{ESS} + \left(J_0 - J_{ESS}\right) \cdot e^{-K_{CB} \cdot J_0 \cdot t} \tag{9}$$

2.5. Analytical methods

The extraction of the target compounds was based on solid-phase extraction (SPE) in accordance with (Vazquez-Roig et al., 2011). Analytes were isolated from water samples (250 mL, pH 7) using a polymeric Strata-X 33 mm Polymeric Reversed Phase cartridge (200 mg/6 mL, Phenomenex, France) preconditioned with 5 mL of methanol and 5 mL of Milli-Q water, and then eluted with methanol. The determination of the different concentrations was performed by a HPLC-MS/MS system, where the HPLC system (1260 Infinity Ultra, Agilent Technologies, USA) was coupled to an LC/MS spectrometer (6410 Triple Quadruple Mass Spectrometer, Agilent Technologies, USA) with an electrospray Turbo V ionisation source. Separation was achieved on a Kinetex C18 column (1.7 mm; 50 mm × 2.1 mm; Phenomenex, France) with the mixture of water/methanol 70:30 (v/v) as the mobile phase. The flow rate and injection volume were 0.2 mL/min and 20 mL, respectively. The mobile phase gradient started from a 30-95% of methanol in 12 min, which maintaining for 8 min. After that, the mobile phase returned to the initial conditions with an equilibrium time of 12 min (Carmona et al., 2014).

2.6. Method validation
Seven-point calibration curves using standard and matrix-matched solutions (from the limit of quantification, LOQ, to 3 mg/L) were obtained with a linear correlation coefficient $R^2 > 0.95$. These calibration standards were injected in triplicate. After the SPE method on water samples, the limits of detection (LODs) and LOQs were determined as the analyte concentration added to the water sample that produced in the extracted chromatogram of the transition used for quantification a peak signal of 3 and 10 times in the background noise, respectively. The results were displayed in a previous work (García-Ivars et al., 2017). The method LODs were between 0.3 and 5 ng/L, whereas LOQs were from 1.0 to 15 ng/L.

3. Results and discussion

3.1. Fouling mechanisms

Fig. 1 shows the decline of the permeate flux ($J_p$) for each nanofiltration membrane during the filtration of the WWTP secondary effluent at the studied pH range (from 6 to 8).

**Figure 1.** Evolution of the permeate flux $J_p$ over filtration time for each NF membrane at different pHs. Experimental conditions: 5 bar, 500 ± 20 L/h, and 25 ± 2 °C.
As expected, NF membranes with larger MWCO (loose NF membranes) showed higher permeate flux in the whole pH range than tighter membranes, thus indicating that the differences amongst NF membranes in terms of pore size and materials have a remarkable influence in the permeate flux. The TFC-SR2 membranes presented a more open porous structure (the highest MWCO of the selected membranes) and hence, showed the highest permeate flux (84.54, 75.49 and 74.00 L/m²·h for pH 6, 7 and 8 respectively) whereas MPS-34 membranes (a tight NF membrane) showed the lowest \( J_p \) value (4.78, 4.39 and 4.07 L/m²·h for the same pH values).

Two distinct stages can be distinguished in Fig. 1 and evidenced the membrane fouling: firstly, a rapid decrease of the permeate flux at low time scales in which the retained solute particles were accumulated and adsorbed onto the surface and inside the pore walls; and a subsequent and gradual flux decline at longer time periods, where the equilibrium between the attachment and detachment of solute particles on the membrane was reached, achieving an almost constant value of \( J_p \) (which will be considered as steady-state flux or \( J_{pss} \)). Based on the quality of the secondary effluent (see Table 1), the main cause of the observed flux decline is the adsorption and deposition of effluent organic matter (EfOM) onto the membrane surface, which is mainly evidenced by the values of COD, BOD, total nitrogen and proteins.

The effect of pH on fouling propensity can be clearly seen in Fig. 2, where the flux declines of each NF membrane at each pH condition (represented as normalised flux \( J_p/J_0 \)) as a function of time is displayed. All NF membranes were negatively charged at the investigated pH range due to the fact that their isoelectric point or zero-point of charge was 4 or lower, as was reported by several authors who characterised the selected membranes (Nghiem et al., 2006; Nghiem and Hawkes, 2007; López-Muñoz et al., 2009; Fernández et al., 2010; De Munari et al., 2013; Azaïs et al., 2014; Owusu-Agyeman et al., 2017). The pH had a significant influence on the permeate flux which decreased with increasing pH for each membrane. The charge variation of the membrane surface is a key factor to predict its behaviour and it strongly depends on the pH of the feed solution because the functional groups on the polymeric surface structure are pH dependent. In the case of polyamide NF membranes, the presence of carboxylic and amine functional groups on their active layer makes NF membranes susceptible to be ionised when pH changes. The ionisation of such groups is reflected in the variation...
of the zeta potential of the membrane surface with increasing and decreasing pH conditions (Nghiem and Hawkes, 2007; Chang et al., 2011; Al-Rashdi et al., 2013). The negative zeta potential of the polymeric NF membranes was higher with increasing pH (from 6 to 8), which resulted in more negatively charged membranes and promoted mightier electrostatic interactions between dissociated functional groups from the material surface. Such electrostatic interactions provoked the shrinking of the membrane material and then, a pore constriction. In parallel, the EfOM in the WWTP secondary effluent became deprotonated at the same circumstances, thus leading to an increase in the accumulation of organic matter on the negatively charged membrane surface and therefore, a higher propensity to be fouled. These results are in accordance with those obtained by other researchers in the same pH range (López-Muñoz et al., 2009; Chang et al., 2011).
Figure 2. Evolution of $J_p(t)/J_0$ over filtration time for each NF membrane at: a) pH 6, b) pH 7, and c) pH 8.

Experimental conditions: 5 bar, 500 ± 20 L/h, and 25 ± 2 °C.

Comparing the results of $J_p/J_0$ for each membrane, the decline of permeate flux was higher for NF membranes with lower pore size. However, these results should be analyzed carefully. The TFC-SR2 membrane showed the lowest flux decline at each pH value tested (88.02, 77.67 and 76.13% for pH values from 6 to 8, respectively). Despite being a very loose NF membrane, the TFC-SR2 membrane has a relatively high removal of EfOM and a great resistance to fouling phenomena, which is characteristic of the SR series (Ngïiem et al., 2006). Several authors reported that the unfouled TFC-SR2 membrane has a water contact angle of about 20-40°, which confirms its higher
antifouling character observed in this work (see Table 3). Thus, the higher flux decline of NF membrane with lower MWCO cannot be related to the difference of pore size amongst the selected NF membranes, because of their different surface material, and can be attributed to the adsorptive interactions between solute molecules in the WWTP secondary effluent and the polymeric membrane surface. The MPS-34 membrane (a tight NF membrane) showed the highest flux decline (43.51, 39.93 and 37.09% for pH 6, 7 and 8, respectively). This membrane is made up of polysulfone, which is a semi-hydrophobic material with low surface charge and water contact angles of about 70-80º, thus making this membrane more susceptible to be fouled (Fernández et al., 2010; Dickhout et al., 2017). Such hydrophobic interactions led to cause the sharpest decline of permeate flux. The NF-270 membrane showed a flux decline in between the two aforementioned NF membranes. Compared to MPS-34 membranes, the active layer of the NF-270 membrane is made of polyamide and presents a water contact angle of around 45º (see Table 3), which demonstrates that NF-270 membranes have a more hydrophilic character than MPS-34 membranes but less hydrophilic than TFCSR2 membranes.

The fouling mechanism for each NF membrane at the studied pH range was assessed using Hermia’s model adapted to cross-flow configurations. For the sake of simplicity, the fitting of the model was evaluated in terms of linear regression coefficient ($R^2$), standard deviation ($SD$) and fitted phenomenological constant parameter ($K$). Results of the goodness of data fitting are presented in Table 4.

**Table 4.** Fitting accuracy of the Hermia’s model in terms of $R^2$ and $SD$ for the selected NF membranes at 25 ºC, 5 bar and 500 ± 20 L/h.

<table>
<thead>
<tr>
<th>Fouling mechanisms</th>
<th>Gel layer formation</th>
<th>Incomplete blocking</th>
<th>Standard blocking</th>
<th>Complete blocking</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 6</td>
<td>$0.97 \pm 0.005$</td>
<td>$0.98 \pm 0.004$</td>
<td>$0.78 \pm 0.015$</td>
<td>$0.98 \pm 0.004$</td>
</tr>
<tr>
<td>pH 7</td>
<td>$0.98 \pm 0.028$</td>
<td>$0.93 \pm 0.017$</td>
<td>$0.82 \pm 0.120$</td>
<td>$0.88 \pm 0.040$</td>
</tr>
<tr>
<td>pH 8</td>
<td>$0.98 \pm 0.009$</td>
<td>$0.98 \pm 0.009$</td>
<td>$0.76 \pm 0.036$</td>
<td>$0.97 \pm 0.009$</td>
</tr>
</tbody>
</table>

Best results for each pH condition and membrane are highlighted in bold.

It can be observed that gel layer formation, intermediate blocking and complete blocking were fitted well to the experimental results in all the pH conditions, whereas
the standard blocking model showed the poorest fitting among the four fouling mechanisms and it only fitted well in some cases (e.g. $R^2$ value of 0.931 ± 0.020 for the NF-270 membrane at pH 6) but not enough to be considered as the main fouling mechanism. This indicates that the solute particles did not precipitate on the inner walls of membrane pores. In the light of the highest degree of model fitness ($R^2$), the dominant fouling mechanism was the complete blocking model for both loose TFC-SR2 and NF-270 membranes at pH 6, which means that solute particles completely blocked pore entrances without penetrating the porous structure. Thus, a monomolecular layer was formed on the polymeric surface and could act as a secondary barrier for separating the target emerging contaminants (Corbatón-Báguena et al., 2015a; García-Ivars et al., 2017). However, gel layer formation became the dominating mechanism at higher pH levels (see Table 4). In this case, solute particles were accumulated onto the polymeric surface forming a gel layer but without blocking the pores, which also led to a formation of a permeable layer on the membrane surface (Corbatón- Báguena et al., 2015a). As for tight MPS-34 membranes, gel layer formation played the major role in their fouling at all pH conditions. According to the fitted $K$ values displayed in Table 5 for each NF membrane and each fouling mechanism, the phenomenological constant $K$ increased at more alkaline pH values, which is consistent with the more severe flux decline of each membrane at such high pH levels (Fig. 2). Therefore, the predominant fouling mechanisms during the filtration experiments were the complete blocking model and the cake layer formation, which could be considered as external mechanisms that occur on the membrane surface and were more severe for membranes with smaller pore size (Brião and Tavares, 2012; Corbatón- Báguena et al., 2015b).

<table>
<thead>
<tr>
<th>Fouling mechanisms</th>
<th>Gel Layer formation</th>
<th>Incomplete blocking</th>
<th>Standard blocking</th>
<th>Complete blocking</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K = n$</td>
<td>$K = n-1$</td>
<td>$K = n-2$</td>
<td></td>
</tr>
<tr>
<td>TFC-SR2</td>
<td>$pH = 6$</td>
<td>0.01 $10^6$</td>
<td>0.24 $10^{-2}$</td>
<td>21.02</td>
</tr>
<tr>
<td>NF-270</td>
<td>$pH = 7$</td>
<td>0.40 $10^6$</td>
<td>0.63 $10^{-2}$</td>
<td>22.15</td>
</tr>
<tr>
<td>MPS-34</td>
<td>$pH = 8$</td>
<td>2.85 $10^5$</td>
<td>4.40 $10^{-2}$</td>
<td>356.29</td>
</tr>
<tr>
<td>TFC-SR2</td>
<td>$pH = 7$</td>
<td>1.19 $10^6$</td>
<td>0.54 $10^{-2}$</td>
<td>23.07</td>
</tr>
<tr>
<td>NF-270</td>
<td>$pH = 8$</td>
<td>2.47 $10^6$</td>
<td>0.76 $10^{-2}$</td>
<td>34.86</td>
</tr>
<tr>
<td>MPS-34</td>
<td>$pH = 9$</td>
<td>3.67 $10^5$</td>
<td>8.30 $10^{-2}$</td>
<td>457.86</td>
</tr>
<tr>
<td>TFC-SR2</td>
<td>$pH = 8$</td>
<td>1.58 $10^6$</td>
<td>0.61 $10^{-2}$</td>
<td>31.02</td>
</tr>
<tr>
<td>NF-270</td>
<td>$pH = 9$</td>
<td>3.04 $10^6$</td>
<td>0.80 $10^{-2}$</td>
<td>40.15</td>
</tr>
<tr>
<td>MPS-34</td>
<td>$pH = 10$</td>
<td>3.33 $10^5$</td>
<td>8.00 $10^{-2}$</td>
<td>254.72</td>
</tr>
</tbody>
</table>

3.2. Physicochemical properties of the selected PhACs
The organic compounds selected for this study have low molecular weight with values between 151.17 and 318.14 g/mol (of acetaminophen and diclofenac, respectively). Despite this similarity, these compounds have distinguishing properties that makes them interesting to be compared, including molar volumes, hydrophobicity, dissociation constants, dipole moments and molecular radii (see Table 2). Regarding the hydrophilic or hydrophobic character of PhACs and the personal care product triclosan, the octanol-water partition coefficient ($K_{OW}$) can be used as an indicator of the sorption properties of a pollutant, which indicates its hydrophobicity. The organic compounds with a value of log $K_{OW}$ higher than 2 could be considered as hydrophobic. This parameter is usually considered as pH independent and only reflects hydrophobic interactions, but unlike other properties of target compounds, hydrophobicity is strongly linked to electrostatic interactions, surface complexation or hydrogen bonding, which can significantly change with a variation of pH, especially around the dissociation constant (pKa). For this reason, a pH-corrected value of log $K_{OW}$, known as log $D_{OW}$, can be employed to predict the solute hydrophobicity and it can be defined as the ratio between the ionised and unionised form of the solute at a specific pH value (Wegst-Uhrich et al., 2014). Both parameters (log $K_{OW}$ and log $D_{OW}$) can be useful to describe the sorption potential of a compound in the aquatic environment and have the same value for non-ionisable compounds but substantially differ when the compound is ionisable. This occurs because of the acid-base transformation of the ionisable compounds, which also considerably affects both their solubility and electrostatic nature due to the presence of dissociable functional groups in the organic structures. The groups containing carboxyl or phenols may be deprotonated, thus becoming negatively charged, whereas groups containing amines may be protonated and thus, they gain a positive charge. Such changes in their speciation depend on the characteristic pKa value of each target compound (Nghiem and Fujioka, 2016). In general, when the pH of the solution is higher than the intrinsic pKa value of the target compound, this compound is deprotonated and presents a negative charge. Otherwise, the charge of the organic compound may be neutral or positive or a mixture of both (Ganiyu et al., 2015). A simple schematic diagram of the speciation of some target compound (ibuprofen, triclosan and sulfamethoxazole) is displayed in Fig. 3. Since the characteristic pKa values of some target compounds (such as diazepam, diclofenac, ibuprofen, naproxen and sulfamethoxazole) are below the investigated pH range (see Table 2), these compounds have a negative charge. Table 6 shows the values of log $D_{OW}$ for each
compound at the pH conditions, where caffeine and acetaminophen are hydrophilic (log $D_{OW} < 1$) throughout the studied pH range while diazepam, diclofenac and triclosan are highly hydrophobic (log $D_{OW} > 3$). At higher pH values, trimethoprim became more hydrophobic whereas ibuprofen, naproxen and sulfamethoxazole became more hydrophilic, being more soluble these compounds in their anionic form, which was confirmed by other researchers (Nghiem and Hawkes, 2007; Jin et al., 2012). For these reasons, it can be concluded that the pH of the feed solution has a crucial role in the application of membrane technology in order to remove emerging contaminants (and especially PhACs) from wastewater, because both membrane surface and emerging contaminants properties including solubility, speciation and hydrophobicity are pH dependent. This influence on the solute rejection will be analysed and discussed in the following sections.

![Figure 3. Speciation of ibuprofen (a), triclosan (b) and sulfamethoxazole (c).](image)

Table 6. Log DOW values obtained for the nine selected PhACs in the tested pH conditions.

<table>
<thead>
<tr>
<th>Pharmaceutical active compound</th>
<th>pKa</th>
<th>Calculated Log $D_{OW}$*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 6</td>
<td>pH 7</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>9.86</td>
<td>0.91</td>
</tr>
<tr>
<td>Caffeine</td>
<td>10.40</td>
<td>-0.55</td>
</tr>
<tr>
<td>Diazepam</td>
<td>3.40</td>
<td>3.08</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>4.08</td>
<td>4.28</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>4.40</td>
<td>2.67</td>
</tr>
<tr>
<td>Naproxen</td>
<td>4.15</td>
<td>1.18</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>5.70</td>
<td>0.60</td>
</tr>
<tr>
<td>Triclosan</td>
<td>7.80</td>
<td>4.97</td>
</tr>
<tr>
<td>Trimethoprim</td>
<td>7.10</td>
<td>0.27</td>
</tr>
</tbody>
</table>

* Software Calculator Plugins was used to calculate Log DOW at each pH.
3.3. Rejection of non-ionic target compounds in WWTP secondary effluent

After analysing the fouling mechanisms of each membrane depending on the operating conditions and the physicochemical properties of the selected organic compounds, the rejection of PhACs and the personal care product triclosan presented in WWTP secondary effluent will be studied, separating charged from uncharged PhACs. Rejection experiments were conducted at different pH values (from 6 to 8) with TFC-SR2, NF-270 and MPS-34 NF membranes. Fig. 4 illustrates the rejection indexes of non-ionic PhACs at the studied pH conditions during the filtration of WWTP wastewater samples for each NF membrane (TFC-SR2, NF-270 and MPS-34).
Previously to discuss these results, it must be remarked that triclosan has been included in this figure because this organic compound is uncharged within the pH range except at pH 8, when it becomes negatively charged. For TFC-SR2 membranes (Fig. 4a), acetaminophen and caffeine showed similar low removal efficiencies (around 30-40%) at the studied pH conditions, while triclosan presented higher rejection indexes with increasing pH, achieving rejections of more than 80% at pH 8. These differences are strongly related to their distinct molecular weight and hydrophobicity, where acetaminophen and caffeine are hydrophilic (log $K_{OW} < 1$) and have a lower molecular weight than the MWCO of the selected membranes, whereas triclosan is highly hydrophobic (log $K_{OW} > 4$) and nearly doubles the size of the molecule of acetaminophen. Comparing these results with those obtained for the NF-270 and MPS-34 membranes (Fig. 4b and c, respectively), rejection indexes of these non-ionic compounds increased with decreasing membrane pore size, classifying the results as follows (from loose to tight structure): $R_{TFC-SR2} < R_{NF-270} < R_{MPS-34}$. Thus, the highest removal efficiencies for non-ionic compounds were observed for the MPS-34 membranes which had the tightest structure.

However, the rejection results observed in Fig. 3 were not only related to the pore size of the membranes and could not consider sieving effect as the main separation mechanism. The impact of membrane fouling on the removal of trace emerging contaminants by using pressure-driven membrane separation processes cannot be neglected, especially for nanofiltration. Generally, the rejection of uncharged trace
solute by NF/RO membranes is considered to be predominantly caused by size exclusion, while the charged trace solutes are mainly rejected by electrostatic interactions with the charged membranes. However, when wastewater is used as feed solution, the existing interactions between non-ionic solutes and membranes may be influenced by EfOM and then, the separation mechanism of uncharged solutes could not be simply attributed to the sieving effect. In this case, hydrophobic interactions that take place between the fouled membrane surface and such solutes gain predominance (Ganiyu et al., 2015). For this reason, although the role of size exclusion in the rejection of triclosan is remarkably observed using NF-270 and MPS-34 membranes, the high removal efficiencies of triclosan can be related to the hydrophobic interactions between the highly hydrophobic triclosan (which has a very high affinity toward both organic matter and polymeric membranes) and the hydrophobic and negatively charged foulant layer formed on the membrane surface due to the adsorption and deposition of organic and inorganic compounds present in WWTP samples, which could act as a second barrier for separation. The formation of this foulant layer onto the membrane surface was demonstrated previously in Section 3.1, where the observed flux decline was attributed to fouling phenomena by EfOM and Hermia's model confirmed that both fouling mechanisms (complete blocking and cake layer formation) are external and occur onto the membrane surface. Moreover, Bellona and his group reported that both TFC-SR2 and NF-270 membranes became more hydrophobic, presenting higher contact angle values when different foulants were accumulated on the fouled membrane surface (Bellona et al., 2010). Therefore, the hydrophobic interactions between triclosan and the formed foulant layer entail a high sorption potential which led to hydrophobic triclosan molecules may be strongly adsorbed on the polymeric surface and also on the additional foulant layer formed onto that surface (Ngheim and Coleman, 2008; Narbaitz et al., 2013).

Comparing the rejection indexes at different pH conditions, there are some significant differences in the rejection of triclosan with increasing pH, resulting in almost complete rejection at higher pH values. This organic compound existed in both neutral and ionised form within the pH range according to its characteristic pKa value (see Table 2). Triclosan is mostly unionised at pH values lower than its pKa and its non-ionic molecules can be readily complexed with dissolved organic carbon and EfOM molecules (Rowett et al., 2016), while triclosan is mostly ionised at pH 8 (above the
pKa value of the compound), becoming a negative species. At these conditions, its rejection was also favoured by the appearance of electrostatic repulsion between compound and membrane. Concerning the behaviour of acetaminophen and caffeine at different pH values, these hydrophilic non-ionic compounds showed to be pH independent with similar values of rejection index at each pH, for a fixed NF membrane. Once the hydrophobic foulant layer is formed, these hydrophilic organic compounds have more affinity for water, thus allowing them to pass through the membrane. However, some molecules from these hydrophilic non-ionic compounds are rejected due to the solute-solute interactions between them and EfOM macromolecules. These solute-solute interactions took place in the effluent and were related to the association of emerging contaminants with EfOM macromolecules, thus forming EfOM-compound complexes as a result of hydrogen bonding and/or electrostatic attraction between the polar moieties of the organic molecules and the functional groups of the EfOM macromolecules, such as the phenolic or carboxylic groups of humic substances-like (Mahlangu et al., 2014; Azaïs et al., 2016). The adsorption of these compounds (humic-like substances) on membrane surfaces can also increase the hydrophobicity of the membrane, as was reported in literature (Nghiem and Coleman, 2008; Bellona et al., 2010). Martínez-Hernández and colleagues demonstrated in several sorption experiments with soils that acetaminophen and caffeine showed significant biodegradability in comparison with other PhACs tested (naproxen, carbamazepine and sulfamethoxazole) which resulted in high removal rates (Martínez-Hernández et al., 2016; Martínez-Hernández et al., 2017).

### 3.4. Rejection of ionic target compounds in WWTP secondary effluent

Fig. 5 shows the rejection indexes of charged PhACs during the filtration of the WWTP effluent for TFC-SR2, NF-270 and MPS-34 membranes. The lowest results were obtained for TFC-SR2 membranes (see Fig. 5a), where ionic compounds showed medium removal efficiencies at pH 6, achieving values between 45 and 65% (for trimethoprim and diazepam, respectively). This is because the MWCO of TFC-SR2 membranes are higher than the molecular weight of the ionic PhACs. These rejection indexes increased up to an average of 65% for almost all the ionic target compounds at pH 8, noting sulfamethoxazole rejection of around 80%. As occurred for non-ionic compounds, removal efficiencies of ionic compounds significantly increased for tighter
membranes, mainly due to size exclusion. The smaller pore size (or MWCO) was, the higher rejection index was obtained. Nevertheless, there is no significant difference between the results of the loose NF-270 membrane and the tight MPS-34 membrane, obtaining very high rejection indexes of ionic compounds with values greater than 90% in the studied pH range for both membranes (which are presented in Fig. 5b and c).

However, size exclusion was not the only separation mechanism in the removal of PhACs. These three membranes (TFC-SR2, NF-270 and MPS-34 membranes) were negatively charged under normal pH conditions due to acidic functional groups in the surface structure (as was explained above). In the same way, some PhACs such as diazepam, diclofenac, ibuprofen, naproxen and sulfamethoxazole were anionic compounds in aqueous solutions due to their pKa values are lower than the studied pH range (see Table 2), while trimethoprim varied its ionic state at such conditions, being positive at pH 6, neutral at pH 7 and negative at pH 8. Therefore, in addition to size exclusion, the separation mechanism would be governed by electrostatic interactions. It can be observed in Fig. 5a that diazepam showed similar rejection indexes at the studied pH range for TFC-SR2 membranes. Its negative charge (pKa$_{\text{diazepam}}$ < feed solution pH) indicated that electrostatic repulsion force with the negatively charged membrane surface (and with the formed foulant layer) will be the dominant separation mechanism. Furthermore, the hydrophobicity of diazepam (log D$_{\text{OW}}$: 3.08) could also favour its rejection because its molecules would be partially adsorbed by both the membrane and EfOM macromolecules, especially in proteins (Bojanić et al., 2011; López-Fernández et al., 2014). Similar behaviour was observed for diclofenac, which presented the highest molecular weight of all target compounds and was highly hydrophobic (log D$_{\text{OW}}$: 4.64) at the studied pH range. Thus, diclofenac possessed a high affinity for the hydrophobic surface and also for the EfOM macromolecules in the feed solution. As occurred with triclosan, the electrostatic repulsion between the deprotonated form of diclofenac and the anionic membrane surfaces together with its high sorption potential (log D$_{\text{OW}}$: 4.64) and high molecular weight, resulted in higher rejection indexes for all NF membranes. In regard to trimethoprim, the rejection indexes were higher when it was charged than when it existed as a non-ionic PhAC. At pH 6 (pKa$_{\text{trimethoprim}}$ < feed solution pH), the positively charged and highly hydrophilic molecules of trimethoprim was significantly rejected due to the electrostatic attraction between this cationic compound and the negatively charged membrane surface (and/or the negative foulant layer formed onto the
membrane surface). At the upper limit of the interval (pH 8), trimethoprim molecules with negative charge are less hydrophilic due to its growing log $D_{OW}$ with increasing alkaline pH values (see Table 6) and thus, charge repulsion became the main separation mechanism to reject this compound. However, because of its more hydrophobic character, the formation of trimethoprim-EfOM complexes cannot be avoided, thus increasing even more its rejection. The high rejection index observed when trimethoprim existed as a neutral species was predominantly caused by hydrophobic interactions due to the effect of fouling on the membrane. In these conditions, the electrostatic forces ceased to exist and nonionic trimethoprim molecules with low sorption potential (log $D_{OW} < 2$) were not easily adsorbed by both the hydrophobic membrane surface and the formed foulant layer (Hajibabania et al., 2011; Jewell et al., 2016). Ibuprofen, naproxen and sulfamethoxazole showed a more pH-dependent behaviour than the other studied PhACs, presenting higher rejection indexes with increasing pH, which was more visible for TFC-SR2 membranes (see Fig. 5a) than for both NF-270 and MPS-34 membranes (Fig. 5b and c, respectively). Despite their different hydrophobicity (ibuprofen and naproxen are hydrophobic while sulfamethoxazole is hydrophilic at neutral pH), these three anionic compounds became more soluble and hydrophilic with increasing pH, presenting log $D_{OW}$ values lower than 1 and hence, decreasing significantly their sorption potential and avoiding the hydrophobic interactions with the foulant layer and also with the NF membrane surface (Ngheim and Hawkes, 2007; García-Ivars et al., 2017). Furthermore, this rising rejection index could be also attributed to an increase in the negative surface charge of the polymeric NF membranes with increasing pH conditions until reaching the alkaline region, in which a stronger electrostatic repulsion occurred (López-Muñoz et al., 2009). This was also confirmed for both TFC-SR2 and NF-270 membranes by (Bellona et al., 2010), who reported that these fouled membranes slightly became more negatively charged at higher pH conditions. For this reason, it can be concluded that the electrostatic repulsion between these now hydrophilic anionic compounds and the highly negative surface of the polymeric NF membranes and between such compounds and the negative formed foulant layer which acted as a supplementary separation barrier.
Figure 5. Rejection indexes of charged PhACs at different pHs for each NF membrane: a) TFC-SR2, b) NF-270, and c) MPS-34. Experimental conditions: 5 bar, 500 ± 20 L/h, and 25 ± 2 °C.

4. Conclusions

The role of fouling on the nanofiltration performance at different pH conditions was elucidated. The flux and rejection of eight selected PhACs with different physicochemical properties and the personal care product Triclosan by using three spiral
wound nanofiltration membranes ranging from loose to tight nanofiltration (classified by size: TFC-SR2 > NF-270 > MPS-34) was studied. The Hermia’s model predicted with high accuracy the experimental permeate flux for these three membranes, confirming that the predominant fouling mechanisms were gel layer formation and complete blocking model (the latter was predominant only for TFC-SR2 and NF-270 membranes at pH 6). The impact of fouling caused by effluent organic matter on the membrane properties cannot be neglected. Effluent organic matter significantly fouled membranes and was found to be membrane dependent, being especially strong in those with more hydrophobic character. This was observed in both the severe flux decline and the high value of the phenomenological model constant obtained for MPS-34 membranes in comparison to those obtained for the other membranes tested (TFC-SR2 and NF-270) at the same operating conditions. Fouling heavily influenced the rejection of the nine target compounds due to the formation of a foulant layer onto the membrane surface, which acted as a secondary barrier for separation. This causes an improvement in the electrostatic repulsions between foulant layer/membrane surface and anionic compounds and in the adsorption of non-ionic compounds because of the complexation of emerging contaminants with organic macromolecules in effluent organic matter. At high pH conditions, the propensity for forming this secondary layer significantly improved the size exclusion or sieving mechanism of membranes, thus resulting in higher removal efficiency of some target compounds. The importance of size exclusion or sieving mechanism was observed in the increasing higher rejection indexes achieved with membranes with smaller pore sizes. Thus, the highest removal efficiencies for all the compounds were achieved with MPS-34 membrane which was the tightest nanofiltration membrane selected. The removal efficiencies of target compounds were shown to be mostly dependent on the pH conditions, especially the behaviour of charged target compounds. These ionic compounds presented high rejection indexes at pH, particularly when pH was higher than their characteristic pKa (becoming negative), at which conditions electrostatic repulsion (between the foulant layer and anionic target compounds) and size exclusion were the main separation mechanism. Other compounds such as triclosan and diclofenac showed a high sorption potential, being also rejected due to adsorptive mechanism. In contrast, hydrophilic non-ionic compounds showed a pH-independent behaviour within the studied pH range. For these reasons, it can be concluded that nanofiltration membranes can be a practical tertiary treatment technique to remove emerging contaminants from wastewater effluents, especially for anionic
compounds which were highly rejected for membranes with similar pore size to the molecular weights of such target compounds. However, it must take into consideration the generation of a waste stream with a high content of target compounds and inorganic and organic matter, which should be managed in a sustainable way.

Acknowledgements

The authors thank the financial support from the Spanish Ministry of Economy and Competitiveness through the project CTM2013-42342-P. Likewise, the authors also express their acknowledge to the personnel of the Carraixet WWTP for the kind supply of secondary effluent samples.

References


**List of symbols**

**Variables**

- $A_m$: Effective area of the membrane (m$^2$)
- $C_f$: Concentration of each pharmaceutically active compound in the feed stream (ng/L)
- $C_p$: Concentration of each pharmaceutically active compound in the permeate stream (ng/L)
- $D_{OW}$: pH-dependent octanol-water distribution coefficient (dimensionless)
- $D_S$: Diffusion coefficient of an organic compound in water (m$^2$/s)
- $J_0$: Initial permeate flux (L/m$^2$·h)
- $J_p$: Permeate flux (L/m$^2$·h)
- $J_{pss}$: Steady-state permeate flux (L/m$^2$·h)
- $K$: Phenomenological model constant (units depending on n)
- $k_B$: Boltzmann constant (kg·m$^2$/(K·s$^2$))
- $K_{OW}$: Octanol-water partition coefficient (dimensionless)
- $LOD$: Limit of detection (ng/L)
- $LOQ$: Limit of quantification (ng/L)
- $M_{DIP}$: Dipole moment (D or Debyes)
- $M_W$: Molecular weight of a compound (g/mol)
- $MWCO$: Molecular weight cut-off of a membrane (Da)
- $n$: Model parameter (dimensionless)
- $pK_a$: Dissociation constant (dimensionless)
- $R$: Solute rejection index (%)
- $R^2$: Linear regression coefficient (dimensionless)
- $r_S$: Molecular radius or Stokes radius (m)
- $SD$: Standard deviation (dimensionless)
- $t$: Filtration time (h)
- $T$: Temperature (K)
$V$: Total volume permeated during an experimental time interval (L)

$V_s$: Molar volume of a compound (cm$^3$/s)

$\Delta P$: Transmembrane pressure (bar)

$h$: Water viscosity (kg/(m·s))

### Abbreviations

COD: Chemical oxygen demand

EfOM: Effluent organic matter

HPLC: High-performance liquid chromatography

HPLC-MS/MS: High-performance liquid chromatography tandem-mass spectrometry

NF: Nanofiltration

NOM: Natural organic matter

PhAC: Pharmaceutically active compound

RO: Reverse osmosis

SPE: Solid-phase extraction

UF: Ultrafiltration

WWTP: Wastewater treatment plant