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# Impact of hydraulic pressure on membrane deformation and trace organic contaminants rejection in pressure assisted osmosis (PAO)

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ABSTRACT

This study provides for the first time an extensive comparison of trace organic contaminants (TrOCs) rejection by commercial cellulose tri-acetate (CTA) and thin film composite (TFC) forward osmosis (FO) membranes from HTI and Porifera operated under pressure assisted osmosis (PAO) conditions. Commercial TFC membranes allowed for higher water permeabilities, higher selectivities and higher water fluxes in FO and PAO operation, compared to the HTI CTA benchmark. As for HTI CTA, TFC membranes suffered from deformation due to the hydraulic pressure applied in the PAO process. However, not only deformation by stretching of the active layer, but also compaction of the support layer was observed, reducing internal concentration polarisation (ICP) and allowing for flux enhancement. In FO operation, the TFC membranes demonstrated a high rejection (>80% for HTI TFC and >90% for Porifera) of the whole range of tested TrOCs due to steric hindrance. It was also noticed that, being more negatively charged, the TFC membranes allowed for very high rejection of negatively charged compounds, but lower rejection of positively charged molecules, as a consequence of electrostatic interactions. In PAO operation, a general decrease of TrOCs rejection was observed. This could possibly be a consequence of decreasing selectivity (due to membrane deformation), increased TrOCs external concentration polarisation and/or lower reverse salt diffusion (less hindrance of forward TrOCs diffusion).


## 1. Introduction

The increasing world population and its associated water demand and pollution are inevitably leading to water scarcity (United_Nations, 2009). To alleviate the stress on fresh water resources, alternative resources such as seawater desalination (Khawaji et al., 2008) or more recently waste water reuse and recycling (Gerrity et al., 2013) are gaining importance for potable water supply. Treatment schemes have been implemented thanks to membrane technology. Process such as

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reverse osmosis (RO) has proven its efficiency and the technology has been significantly improved over the past decades. However, RO still remains highly energy demanding, limiting its even wider implementation (Ghaffour et al., 2013). Alternative membrane technologies are currently under investigation for seawater desalination, such as membrane distillation (MD) (Kesieme et al., 2013), electrodialysis (ED) (Mohammadi and Kaviani, 2003) and forward osmosis (FO) (Elimelech and Phillip, 2011), mainly to evaluate whether it is possible to produce water at a lower cost than RO. FO has also been studied in the context of water reuse (Butler et al., 2013; Cath et al., 2006, 2009; Lutchmiah et al., 2011; Su et al., 2012). One interesting configuration using FO is the FO-RO hybrid process, in which FO is implemented as a pre-treatment step before RO. Here, the seawater to desalinate in the RO, is first prediluted in a controlled manner with impaired water in the FO step. Such FO-RO hybrid system has demonstrated to be a promising method to combine water reuse and desalination (Bamaga et al., 2011; Cath et al., 2009, 2010), lowering the specific RO desalination energy consumption and offering a double-barrier protection against contaminants from the impaired water (which could increase consumer confidence towards potable water reuse (Cath et al., 2010)).

However, one of the major upcoming concerns related to water reuse is the presence of contaminants such as endocrine-disrupting chemicals, pharmaceutically active compounds, pesticides and/or disinfection by-products in impaired water (Schwarzenbach et al., 2006; Siegrist and Joss, 2012). These compounds, generally called trace organic contaminants (TrOCs) due to their low concentrations (ng/L to $\mu g L^{-1}$ level) could represent a human and environmental threat, even at these trace concentrations (D'Haese et al., 2013). As such, recent research has been performed to evaluate the capability of FO to efficiently remove these TrOCs, especially in association with RO (FO-RO hybrid process) (Hancock et al., 2011) or with MD (FO-MD hydrid) (Xie et al., 2013a) so to provide an efficient double barrier protection (Valladares Linares et al., 2011). These studies demonstrated the efficiency of both hybrid systems to remove TrOCs, while practical challenges like TrOCs concentration build-up in closed-loop FO configuration have also been highlighted (D'Haese et al., 2013).

Most studies on TrOCs removal mechanisms by membranes have focused on dense, pressure-driven membrane processes, mainly nanofiltration (NF) and RO. These studies have now established that TrOCs rejection by NF/RO is driven by a complex interplay of several mechanisms such as size exclusion, electrostatic interactions, van der Waals and polar/apolar interactions and adsorption. As such, TrOCs rejection is dependent on TrOCs properties, membrane properties, feed water matrix and also membrane fouling (Hajibabania et al., 2011a,b; Verliefde et al., 2008a,b, 2010). TrOCs rejection in FO has been studied as well, and the rejection mechanisms involved are largely similar to those in NF/RO, as also stated in a recent review on the fate of TrOCs in FO (Coday et al., 2014). Throughout the 14 studies cited in this review, it was observed that the FO process provides a robust barrier to TrOCs. Most studies confirmed that TrOCs rejection by FO was generally high, owing to low solute permeability membranes with small pore sizes, and the associated size exclusion mechanism (Alturki et al., 2012). In addition to size exclusion, rejection of charged TrOCs could be further enhanced by electrostatic repulsion (Alturki et al., 2012). It has also been stated that reverse salt diffusion (RSD) appeared to increase TrOCs rejections, which was explained by the back-diffusion of salts hindering the forward diffusion of TrOCs (Xie et al., 2013b). Hydrophobic TrOCs were demonstrated to be better rejected by FO membranes as a consequence of adsorption onto the hydrophobic membrane. It however needs to be stressed that high rejections due to adsorption are typically only a temporarily effect, until membrane saturation occurs (Jin et al., 2012). After membrane saturation, TrOCs adsorbing readily onto high-pressure membranes, are generally transported to a higher extent due to their higher partition coefficient (Verliefde et al., 2013).

As stated before, most of the FO studies on TrOCs rejection by FO have been carried out using the commercial cellulose tri-acetate (CTA) membrane from Hydration Technology Innovation (HTI), which is a dense membrane that demonstrates low permeation flux. To fit to economic reality, FO requires higher permeation fluxes and new progress has been achieved in that aspect by novel generations of commercial membranes, especially of these novel commercial membranes, only the thin-film composite (TFC) membrane developed by Oasys Water (Boston, MA) has been recently evaluated with regards to TrOCs rejection (Coday et al., 2013; Xie et al., 2014). Interestingly, despite having higher permeability and pore size compared to HTI CTA membrane, the Oasys-TFC membrane demonstrated higher rejections of neutral TrOCs, which was attributed to a higher active layer structural factor and pore hydration induced by a more negative charge (Xie et al., 2014). As such, it demonstrated that new opportunities and rejection mechanisms could arise with those membranes, but did not clearly show how high water flux could directly impact TrOCs rejection. Moreover, the recent review on TrOCs insisted on the lack of standardised test conditions for rejection experiments and the need to test the rejection performance of newly developed membranes (Coday et al., 2014). Thus, further work is needed to better assess the fate of TrOCs and associated rejection mechanisms for novel FO membranes in similar operating conditions.

In parallel to new membrane development, another alternative to improve flux in FO is to implement hydraulic pressure on the feed solution to synergize osmotic and hydraulic pressure driving forces. Such process, called pressure assisted osmosis (PAO), has been validated recently and demonstrated water flux enhancement due to the additional driving force and membrane deformation (Blandin et al., 2013; Lutchmiah et al., 2015). Despite the fact that this membrane deformation led to lower membrane selectivity for salts (higher salt permeability B), the higher permeation fluxes outweighed this, leading to decreased RSD in PAO compared to FO. PAO thus has some clear advantages, but the effect on rejection of TrOCs yet remains to be investigated. Although PAO results in higher fluxes (which normally lead to higher rejections according to solution-diffusion theory), the lower membrane selectivity (due to deformation) and the lower RSD observed in PAO (which might sterically hinder TrOCs transport less, as stated above) might adversely impact TrOCs rejection. As such, a fundamental study on TrOCs rejection mechanisms in PAO is required.

This study therefore offers, for the first time, a critical evaluation of rejection of a wide range of TrOCs, for three commercially available FO membranes, in PAO operation, and compares this to rejection in FO operation. In addition, for all membranes, the impact of hydraulic pressure on membrane deformation and water and (reverse) salt permeability are assessed, and the impact of these parameters on TrOCs