

# Retention of nine micropollutants covering a wide range of physical-chemical properties by negatively charged hollow fiber nanofiltration membranes

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## INTRODUCTION

The increasing amount of micropollutants (MPs) released into aquatic environment due to anthropic activities is a great worldwide concern (Khanzada, Farid, et al., 2020). This concern is deepened by the global warming effects on water scarcity and water quality. Thence, the European Union is expected to impose stringent regulations on MPs discharges which emphasizes the great urgency to reach high quality water in a sustainable way. This objective goes through the control of MPs sources and their removal in wastewater treatment plants (WWTPs).

Today, technologies employed in WWTPs have a low removal efficiency in most of the micropollutants and their energy consumption tends to increase. In this context, redefining technologies employed in WWTPs appears critical. Since 2021, the project named SAVE (<https://filiere-save.com/>), worked on the design and the performances evaluation of a new process including biological reactors and membrane separation processes. Recently, the proportion of studies and application of membrane technologies for wastewater treatments increased specially regarding reverse osmosis (RO) and nanofiltration (NF) operations due to their high efficiency to remove MPs (Silva, Moreira, et al., 2017). NF technologies seems to be the most promising due to its rate of MPs retention very near to those obtained with RO and in the same time its higher hydraulic performances, and lower cost (Yangali-Quintanilla, Maeng, et al., 2010; Cartagena, El Kaddouri, et al., 2013). Amongst the membrane geometries available on the market, hollow fiber membranes are especially attractive for wastewater treatment due to their ability to process high foulant loaded stream and to maintain good hydraulic performances.

Unfortunately, conventional NF membranes retain both MPs and salts, which lead to unoptimized conditions for further MPs degradation in biological reactors. Low salt recovery can be achieved using modified membrane's structure. Polyelectrolyte multilayer (PEM) obtained by the layer-by-layer assembly of weak polyelectrolyte of opposite charge proved to be an effective option for high MPs retention and high salt passage (Abtahi, Ilyas, et al., 2018).

Retention of solutes by NF membranes is governed by three mechanisms: size exclusion, electrostatic interaction, and hydrophobic interaction. Thence, physical-chemical properties of solutes, membranes properties and matrix composition are well-known to be key parameters for the retention of MPs (Bellona, Drewes, et al., 2004). However, PEM membranes being very new-found technology there is a huge lack of data concerning most of the MPs rejection with this option. In addition, retention of MPs is also impacted by the fouling layer formed at the NF membrane surface by the adsorption of organic and/or inorganic contaminants. However, the inconsistency of results highlights the necessity of further investigation.

In this study the retentions of nine contaminants using nanofiltration hollow fiber with PEM were

investigated. Retentions have been evaluating at various volume reduction ratio (VRR), molecular weight cut-off of the membrane and fouling potential of the matrix. The compounds selected are: atenolol (ATL), paracetamol (PCT), trimethoprim (TMP), ciprofloxacin (CFX), dibenzylamine (DBZ), sulfamethoxazole (SFZ), diuron (DRN), diclofenac (DCL) and D-gluconic acid (ADG). They are either pharmaceuticals active compounds (anti-inflammatory, beta-blocker, analgesic, or antibiotic) or pollutants from agriculture or chemical industries and have been selected according to their molecular weight, hydrophilicity and charge at environmental pH.

## MATERIAL AND METHODS

### Chemicals

DCL was obtained from Cayman chemical company. CFX, TMP, DRN, ATL, DBZ, PCT and ADG were purchased from Sigma-Aldrich. SFZ was obtained from Fluka. All components had a minimum purity of 98 %.

The HPLC grade methanol and acetonitrile were obtained from Sigma-Aldrich. The potassium phosphate monobasic used for HPLC solution was purchased from Fisher.

Individual contaminant stock solutions were prepared at 1 g.L<sup>-1</sup> in HPLC grade methanol (ATL, PCT, TMP, CFX, DBZ, SFZ, DRN, DCL) or ultrapure water (ADG).

Stock solution of synthetic wastewater was prepared according to the “OECD Guideline for the Testing of Chemicals, Part 303B-Biofilms” (OECD, 2001; Alcántara, Muñoz, et al., 2015) than diluted in tap water to achieve 50 mg.L<sup>-1</sup> of COD.

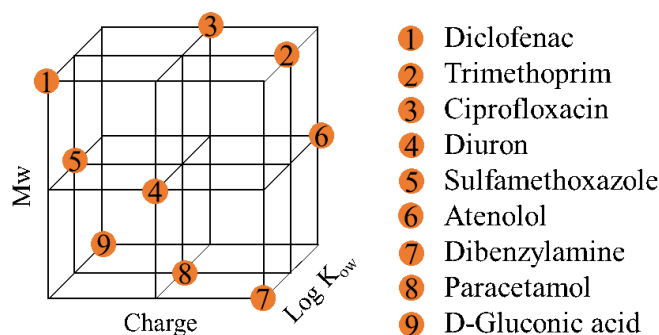
### Experimental design

To determine the impact of each physical-chemical property of MPs on their retention by NF membranes, an experimental design was achieved. Three factors were considered: charge at neutral pH, hydrophilicity (log K<sub>ow</sub>) and size (molecular weight, Mw) of contaminants. For each factor, three levels were established and are summarized in Table 1.

**Table 1:** Definition of the factor levels employed for determination of micropollutants of the study

	Charge	Hydrophilicity	Size
-	Negative	Log K <sub>ow</sub> > 2	Mw < 210 g.mol <sup>-1</sup>
0	Neutral	0.5 < Log K <sub>ow</sub> < 2	230 < Mw < 280 g.mol <sup>-1</sup>
+	Positive	Log K <sub>ow</sub> < 0.5	Mw > 300 g.mol <sup>-1</sup>

The number of contaminants to study was reduced using the Square Latin method (Figure 1).

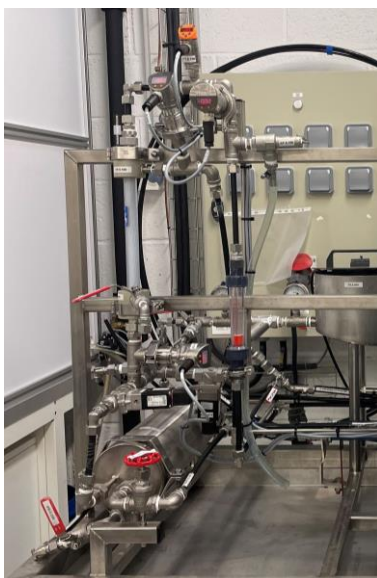


**Figure 1:** Pattern of the Square Latin design and list of micropollutants identified for the study

### NF set up and experimental protocol

Pilot-scale 400Da- or 800Da-NF was carried out using hollow fiber membranes (dNF40 or dNF80, modified PES, 0.7 mm fiber inner diameter, total membrane area of 0.05 m<sup>2</sup>, NX Filtration). Membranes were negatively charged at neutral pH.

NF was carried out in batch mode at 20 °C with a VRR of 1, 3 or 6, a crossflow velocity of 1 m.s<sup>-1</sup>, and a transmembrane pressure (TMP) of 3 bar. Temperature, VRR and TMP were remained constant using automation system (Figure 2). Process performances was studied by recording permeate flux (J<sub>p</sub>). NF system was feed with ultrapure water, synthetic wastewater at 50 mg.L<sup>-1</sup>-COD or real wastewater or mixture of MPs (10 mg.L<sup>-1</sup> each) in ultra-pure water, synthetic or real wastewater. Feed solution, retentate and permeate samples were collected after stabilization time comprise between 2 and 24 h of filtration.



**Figure 2:** picture of NF-pilot for micropollutants removal (France membrane)

### **Analysis**

Ions contents including ADG, sodium, ammonium, sulphate, and phosphate were determined by ionic chromatography with conductimetry detection (Dionex, Thermo instruments).

To quantify MPs content in feed, permeate and retentate fractions, a new analytical method has been developed using reversed-phase liquid chromatography with UV detection (RP-HPLC-UV). Separations of MPs were performed on a C18 column (Hypersil GOLD, 4.6 x 250 mm, 5 µm particles size, Thermo Fisher Scientific) at 30 °C. Several gradient elution based on acetonitrile and 20 mM-phosphate buffer (pH4.7) were investigated. Linearity of the method was studied between 1 and 50 mg.L<sup>-1</sup> of each contaminant. To determine optimal wavelength for UV detection, UV spectrum of individual MP solutions at 5 mg.L<sup>-1</sup> were realized between 200 and 400 nm in ultrapure water. Potential interactions between contaminants and matrix effect were evaluated by comparing individual or mixed MP solutions in ultrapure water or synthetic water.

### **RESULTS**

The RP-HPLC-UV method developed for the quantification of ATL, PCT, TMP, CFX, DBZ, SFZ, DRN and DCL showed recovery between 81 and 114 % with an average at 103 %.

No effect of interactions between contaminants was observed on the recovery of each MP. On the contrary, water matrix impacts the UV detection of TMP, CFX, DBZ and ATL for contents inferiors at 5 mg.L<sup>-1</sup>. To avoid matrix effect, quantification of TMP, CFX, DBZ and ATL will be carried out using the standard addition method.

NF trials and data analysis will be realized between December 2021 and March 2022, the results are expected to be validated, analyzed and synthetized in the last days of May 2022.

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