



**HAL**  
open science

# Understanding and Predicting the Adsorption and Rejection of Pesticides and Metabolites by Hollow Fiber Nanofiltration Membranes

G. Dagher, G. Saab, A. Martin, G. Couturier, P. Candido, L. Moulin,  
Jean-Philippe Croué, B. Teychene

## ► To cite this version:

G. Dagher, G. Saab, A. Martin, G. Couturier, P. Candido, et al.. Understanding and Predicting the Adsorption and Rejection of Pesticides and Metabolites by Hollow Fiber Nanofiltration Membranes. Separation and Purification Technology, 2024, 330, pp.125323. 10.1016/j.seppur.2023.125323. hal-04245318

**HAL Id: hal-04245318**

**<https://hal.science/hal-04245318v1>**

Submitted on 17 Oct 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Understanding and Predicting the Adsorption and Rejection of Pesticides and Metabolites by Hollow Fiber Nanofiltration Membranes.

Authors: G. Dagher<sup>1</sup>, G. Saab<sup>1</sup>, A. Martin<sup>2</sup>, G. Couturier<sup>2</sup>, P. Candido<sup>2</sup>, L. Moulin<sup>2</sup>, JP. Croué<sup>1</sup>, B. Teychene<sup>1,\*</sup>

1. Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), Université de Poitiers, CNRS, E-BiCOM, F-86073 Poitiers, France.

2. Eau de Paris, DRDQE, R&D laboratory, 33 Avenue Jean Jaurès, 94200, Ivry-Sur-Seine, France

Keywords: Pesticides and metabolites, Hollow Fiber Nanofiltration, Random forest, Micropollutants Properties.

## Highlights

- The adsorption and rejection of 164 MP by HF-NF membranes is evaluated.
- The influence of 11 physicochemical properties is studied
- MP adsorption was primarily affected by log D values, followed by charge.
- MP rejection relied mainly on MP's size and charge.
- Random forest models were developed to predict MP's adsorption and rejection.

27 **Abstract**

28 Layer-by-layer Hollow fiber Nanofiltration (LbL HF-NF) membranes have shown great  
29 potential in the removal of micropollutants from water. Nonetheless, further research is required  
30 as the number of tested compounds remains limited. In this study, the adsorption and rejection  
31 of 164 micropollutants by two commercial HF-NF membranes with MWCO of 400 and 800 Da,  
32 were investigated. The investigation was conducted by evaluating the influence of 11  
33 physicochemical micropollutants' properties on the separation performances. Results showed  
34 that highly adsorbed compounds had average log D values above 3, while no or low adsorption  
35 was observed for compounds with negative log D values. Furthermore, adsorption was more  
36 frequently observed for neutral compounds compared to negatively charged ones.  
37 Micropollutants rejection results showed that steric exclusion plays the most important role in  
38 the rejection of micropollutants, and that the charge of micropollutants can also heavily  
39 influence their rejection. Likewise, negatively charged compounds were better rejected than  
40 neutral ones. Finally, the study demonstrated that adsorption and rejection of micropollutants  
41 can be predicted with good accuracy using the random forest algorithm. The prediction  
42 accuracy for adsorption was 80 % and 73 % for the 800 and 400 Da MWCO membranes,  
43 respectively. The RMSE for rejection predictions was 10.6 % and 6 % for the two membranes  
44 respectively.

45

46

47

48

49

50

51

52

## 53        **1. Introduction**

54    Climate change, droughts and pollution caused by human activities significantly impact the  
55    quality of freshwater resources. Increases in organic matter, microbial activity, algae blooms  
56    and micropollutants (MP) concentration have been widely documented in different parts of the  
57    world [1–3]. Particularly, the presence of MP in freshwater resources can be very problematic  
58    as they may have harmful effects on human health and the environment. Several technologies  
59    can be applied to remove MP from water sources like advanced oxidation processes [4],  
60    activated carbon [5], and membrane filtration [6]–[9]. Among these technologies, membrane  
61    filtration offers certain advantages like lower use of chemicals and high efficiency over a wide  
62    range of MP [6].

63    Nanofiltration (NF) and reverse osmosis (RO) are considered the most effective filtration  
64    methods for removing MP from water. Lipp et al. [10] studied the rejection of a selected number  
65    of compounds including pesticides, pharmaceuticals, antibiotics and perfluorinated chemicals  
66    by one RO membrane (molecular weight cut off (MWCO) of 100 Da) and three NF membranes  
67    (MWCO equal to 200, 290-360 and 200-300 Da respectively). Rejection values above 90%  
68    were found for most compounds with the four membranes. Interestingly, the rejection for NF  
69    membranes was only slightly lower than the RO membrane. Similarly, Yangali-Quintanilla et  
70    al. [11] worked on the filtration of organic contaminants and found that on average, tight NF  
71    membranes were able to effectively remove 82% of neutral contaminants and 97% of ionic  
72    contaminants. Whereas, RO membranes had an average removal rate of 85% for neutral  
73    contaminants and 99% for ionic contaminants. An analogous comparison was conducted by  
74    Jacob et al., 2012 where they examined the filtration of 30 compounds using RO and tight NF  
75    membranes and observed that 20 of the compounds exhibited similar rejections for both  
76    membranes.

77    As it requires less energy than RO, less post-treatment, and has a relatively good performance,  
78    the removal of MP by NF has become the focus of many studies and research. For that, the  
79    influence of MP physicochemical properties [8,13–17], organic matter [18], membrane fouling  
80    [19–21] and operating conditions [22] on MP rejection were extensively studied. In regards to  
81    the physicochemical properties specifically, several properties such as charge, molecular  
82    weight, molecular dimensions (length, width, and height), octanol-water partition coefficient  
83    ( $\log K_{ow}$  or  $\log P$ ), and dipole moment were assessed for their effect on rejection. The charge  
84    was found to have a significant impact on the rejection as negatively charged compounds were

85 effectively rejected by negatively charged membranes irrespective of their other properties.  
86 Molecular weight (MW) was found to be positively correlated with rejection, particularly for  
87 neutral compounds [13,14,16]. Likewise, polarity was observed to influence rejection, as  
88 molecules with high dipole moment exhibited lower rejections overall [15,16].

89 Furthermore, numerous works found that the adsorption of MP on the membrane material plays  
90 a crucial role in the filtration process. If not accounted for, this adsorption can lead to an  
91 overestimation of the rejection in the filtration process [23]. The adsorption was also found to  
92 be dependent on physicochemical properties [8,14,24], membrane properties [25] and operating  
93 conditions [20,22,26,27]. In brief, the hydrophobicity of MP, typically measured by log P (or  
94 log D, the distribution coefficient), was found to be the most important property. Moreover, the  
95 impact of pH on adsorption was also observed. This impact varies among different compounds  
96 and is dependent on the specific form of each compound at different pH values.

97 Given the large number of factors that can affect the adsorption and rejection of MP, some  
98 researchers have turned to advanced statistical techniques and artificial intelligence-based  
99 methods to gain a more comprehensive understanding and to make predictions about the MP  
100 rejection [28–33]. Yangali-Quintanilla et al. [28] used principle component analysis and  
101 multiple linear regression to understand the impact of 21 variables on the membrane rejection  
102 and emphasized that the MP size (length, depth and width) alongside the hydrophobicity and  
103 electrostatic repulsion of the membrane are the most affecting factors. However, given that the  
104 models were created using multiple linear regression, it was only possible to get linear relations  
105 between the variables and the rejection and therefore, non-linear relations and  
106 interdependencies between variables were not taken into consideration. Jeong et al [29] were  
107 able to overcome this limitation by using a machine learning method, based on a scalable  
108 decision tree model, to predict the MP rejection. This method considered variables such as zeta  
109 potential of the membrane, MWCO, log P, hydraulic pressure, and compound concentration.  
110 They obtained a mean absolute error of 10.17% and proved that the model's predictions were  
111 primarily based on the size exclusion and electrostatic interactions between the membrane and  
112 the MP. In a similar way, a recent study by Lee and Kim [33] used random forest (RF) model  
113 for predicting NF/RO membrane rejection of emerging organic contaminants using data  
114 collected from multiples studies. They demonstrated that RF model can reliably identify  
115 important features on MP rejection with less effort than using neural network model.

116 The findings of these studies provide valuable insights on the removal of MP and the  
117 mechanisms behind it. However, these studies have focused on flat-sheet polyamide NF

118 membranes. These membranes which are housed in spiral wound modules have limited  
119 hydraulic and chemical cleaning possibilities [34]. Consequently, extensive pre-treatment, like  
120 ultrafiltration (UF) or sand filtration, is necessary to mitigate fouling on the spacers and  
121 membrane surfaces. This pre-treatment incurs additional operational costs, making it desirable  
122 to explore alternatives [35]. Recent developments in membrane fabrication techniques have  
123 allowed the production of hollow-fiber nanofiltration (HF-NF) membranes through multiple  
124 methods, with the most promising one being the coating of HF-UF membranes by  
125 polyelectrolyte multilayers (PEMs) through a layer-by-layer (LbL) coating technique [36,37].  
126 These membranes, with their HF structure, offer a larger compacity and better cleaning  
127 capabilities than flat sheet ones, as well as high permeabilities and good selectivity. However,  
128 it is not straightforward to extrapolate results from previous research on polyamide NF  
129 membranes to HF-NF membranes. This is because they are constructed using different  
130 materials and operate at lower pressures. Moreover, the absence of a spacer in HF-NF  
131 membranes eliminates spacer-related fouling but leads to higher concentration polarization  
132 [38].

133 Recent studies have tested the efficiency of such membranes for MP rejection and showed  
134 promising results [39–42]. De Grooth et al. [41] synthesized NF membranes based on  
135 Polycation/Polyzwitterion/Polyanion multilayers and obtained high rejections from 50% to  
136 99% for charged compounds with varying performance for different compounds and  
137 membranes. Ilyas et al. [42] also developed PEMs based HF-NF membranes with rejections  
138 ranging between 60% and 80% even for neutral compounds. However, these two studies used  
139 high concentrations of MP in the range of mg/L which is considered as an unrealistic condition.  
140 For that, Abtahi et al. [39] evaluated the performance of the same membranes under more  
141 realistic conditions (concentrations in the  $\mu\text{g/L}$  range) and achieved similar rejections (44%-  
142 77%) for the four compounds studied. Moreover, they confirmed that the hydrophobicity of  
143 these four compounds is correlated to their adsorption on the membrane surface, and that the  
144 rejection is also correlated to their molecular size.

145 In this regard, the number of studies on this type of membrane is still relatively scarce,  
146 especially compared to polyamide flat sheet membranes. Additionally, the number of tested MP  
147 is limited. Therefore, further research is necessary to improve the understanding of the  
148 adsorption and rejection of MP by these HF-NF membranes. As a result, this study aims to  
149 investigate the behaviour of MP on HF-NF membranes. To achieve this, the adsorption and  
150 rejection of 164 MP on commercial lab-scale modules ( $500\text{ cm}^2$ ) were investigated. Notably,

151 the influence of MP physicochemical properties on their adsorption and rejection is highlighted  
152 and discussed. Finally, this study is concluded by an analysis based on random forest in which  
153 the adsorption and rejection of MP are predicted while highlighting the more important features.

## 154 **2. Materials and methods**

### 155 **2.1. Nanofiltration membranes**

156 Two commercial HF-NF lab-scale membrane modules (500 cm<sup>2</sup>) denoted dNF40 and dNF80  
157 were purchased from NX Filtration (Netherlands) and used in this study. According to the  
158 manufacturers, membranes of both modules are made from modified polyethersulfone (PES)  
159 and are negatively charged at pH=7. The modification of PES is performed through the LbL  
160 coating technique. Commercial modules operate in an inside-out crossflow filtration mode.  
161 They consist of 120 membrane fibers with an inside diameter of 0.7 mm and have an average  
162 surface area of 500 cm<sup>2</sup> (length = 30 cm). The dNF40 has a MWCO of 400 Da, a minimum  
163 MgSO<sub>4</sub> rejection of 91% and a measured permeability of  $7.9 \pm 0.1 \text{ L.m}^{-2}.\text{h}^{-1}.\text{bar}^{-1}$  (LMHB) at  
164 20°C. The dNF80 has a MWCO of 800 Da, a minimum MgSO<sub>4</sub> rejection of 76% and a  
165 measured permeability of  $11.6 \pm 0.1 \text{ LMHB}$  at 20°C.

### 166 **2.2. Raw water**

167 The experiments were carried out by adding the MP to a groundwater consisting of a mix of  
168 karst water from several permanent springs (Provins, France). The groundwater had a total  
169 organic carbon (TOC) content of  $0.46 \pm 0.06 \text{ mgC/L}$ , UV<sub>254nm</sub> absorbance equal to  $0.003 \pm$   
170  $0.001 \text{ cm}^{-1}$ , a turbidity of  $0.1 \pm 0.02 \text{ NTU}$ , a conductivity of  $584 \pm 87 \text{ }\mu\text{S/cm}$ , and a pH equal to  
171  $8.00 \pm 0.05$ .

### 172 **2.3. Micropollutants properties and spiking solution**

173 A mixture of 164 MP which including 144 pesticides and other plant protection products (PPP)  
174 and 20 metabolite (M) was used in this study. The MP mixture was dissolved in a methanol  
175 solution due to water solubility limitations and was diluted in the groundwater (by a factor of  
176 1000) to obtain MP concentrations around  $1 \text{ }\mu\text{g/L}$  per compound. Among these compounds,  
177 some of them were specifically chosen as metabolites of atrazine and dimethachlor,  
178 metazachlor, bentazone which are the most abundant compounds in France [43]. Information  
179 regarding the compounds present in this mixture along with their physicochemical properties  
180 are given in the supplementary data (Excel sheet).

181 As discussed above, the rejection and adsorption of MP by membranes are mostly influenced  
182 by size exclusion, hydrophobicity and electrostatic interactions. For that, the molar mass and  
183 molar volume were used to represent the size of these molecules. The molecular dimensions as  
184 well as the minimum projected area (MPA) were used to further understand the shape of each  
185 molecule. The three dimensions were denoted as  $L_1$ ,  $L_2$ , and  $L_3$ , with  $L_1$  being the longest side  
186 of the molecule's bounding box,  $L_3$  being the shortest, and  $L_2$  being the side with the median  
187 length. The octanol-water partition coefficient ( $\log K_{ow}$  or  $\log P$ ) and the corresponding  
188 dissociation coefficient ( $\log D$ ) are used as a measure of hydrophobicity. The polar surface area  
189 (PSA) is used as a descriptor that quantifies molecular polarity. It represents the ability of a  
190 molecule to form hydrogen bonds with other molecules and therefore is relevant in the context  
191 of contaminants and their interactions with organic matter and membrane surfaces [44]. The  
192 polarizability was used as it may correlate with contaminants rejection and adsorption for the  
193 same reasons as the PSA. Finally, the charge at pH=8 was calculated to reflect the electrostatic  
194 interactions taking place at the membrane surface. The monoisotopic mass, the molar volume,  
195  $\log P$ ,  $\log D$ , the polar surface area and the polarizability were based on the calculation of  
196 ACD/Labs. pKa values as well as the charge and the minimum projected area were determined  
197 using Chemicalize by Chemaxon. The molecular dimensions were calculated using jmol  
198 software. It's worth noting that the charge of the compounds was chosen as the determining  
199 factor, rather than pKa, as opposed to previous studies. This is because large organic  
200 compounds can have multiple pKa values, making it impossible to infer the charge from just  
201 one of these values.

#### 202 **2.4. Filtration protocol**

203 For all tests, cross-flow filtration with a transmembrane pressure (TMP) equal to 5 bars and a  
204 cross flow velocity of 0.3 m/s was performed using the Mexplorer<sup>TM</sup> test unit (NX Filtration,  
205 Netherlands). The protocol was divided into two steps: (i) The first step was performed to study  
206 the adsorption of contaminants on the membrane surface and remove its effects before studying  
207 the rejection. In this part, the filtration was conducted while recycling the permeate within the  
208 feed tank for 48 hours. During this step, 10 mL samples of the feed and the permeate were taken  
209 at multiple occasions ( $t=0h$ , 4h, 8h, 24h, 32h and 48h) and analysed to determine the  
210 concentrations of every contaminant. Additionally, 100 mL samples of both the feed and  
211 permeate were collected at  $t=0h$  and  $t=48h$  for various measurements, including TOC,  $UV_{254nm}$   
212 absorbance, turbidity, and pH. (ii) The second step focused on studying the rejection of MP at  
213 different recovery values. In this step, which starts at the end of the 48 hours, the permeate is



214 no longer recycled into the feed solution. The TMP remained at 5 bars and permeate samples  
215 were taken at recoveries of 25%, 50% and 75%. They are expressed in terms of the volume  
216 reduction factor (VRF) equal to the initial volume divided by the volume of the concentrate.  
217 The repeatability and stability of the filtration system were evaluated prior to these filtration  
218 tests on a smaller number of MP. The results indicated an average error notably smaller than  
219 the analytical error detailed in section 2.5, rendering it insignificant for consideration.

## 220 **2.5. Micropollutants analysis**

221 MP were analysed by direct injection of water samples with UHPLC-MS/MS by the laboratory  
222 of Eau de Paris accredited by the COFRAC (French Body of Accreditation). Ultra-high-  
223 performance liquid chromatography (UHPLC) was performed on a Shimadzu series Nexera  
224 X40 UHPLC system. Analytes were separated on an C18 BEH (1.7  $\mu\text{m}$  2.1 $\times$ 100 mm) column  
225 (Waters). Chromatographic separation of analytes was carried out with methanol and ultrapure  
226 water, both with formic acid 0.05% / ammonium acetate 5mM, in an analytical gradient from  
227 2% to 99% methanol lasting 14 min at 0.6 mL/min. The UHPLC system was coupled to a triple-  
228 quadrupole mass spectrometer (MS/MS) Shimadzu MS 8060 with electrospray ionization (ESI)  
229 set to positive or negative mode at 350°C depending on the compound. Identification and  
230 quantification were achieved by multi reaction monitoring with 18 deuterated compounds used  
231 as injection internal standard. Analytical uncertainties are expressed as a confidence interval  
232 ( $\alpha=0.05$ ,  $k=2$ ) with a mean value of 50% for the concentration between the limit of  
233 quantification (LOQ) and 5 $\times$ LOQ, 30% between 5 $\times$ LOQ and 50 $\times$ LOQ and 20% for values  
234 above 50 $\times$ LOQ.

## 235 **2.6. Decision trees and random forests**

236 A decision tree is a type of machine learning algorithm that is used for regression and  
237 classification tasks. The goal of decision trees is to learn the relationships between features and  
238 the target variable and use this information to make predictions. When applying decision trees  
239 to the filtration of MP, the features will consist of the MP physicochemical properties while the  
240 target variables are the adsorption and rejection values. Random forests are an ensemble  
241 machine learning algorithm that operates by aggregating the results of many decision trees. The  
242 concept behind random forests is to train numerous decision trees on random data subsets and  
243 then average their predictions, which results in more accurate predictions. The creation of  
244 random forests was done using RStudio and the R programming language using the “Caret”  
245 [45] and “randomForest” [46] packages. More information about decision trees and random  
246 forests and how to implement them in R can be found in James et al. [47].

## 247 **3. Results and discussion**

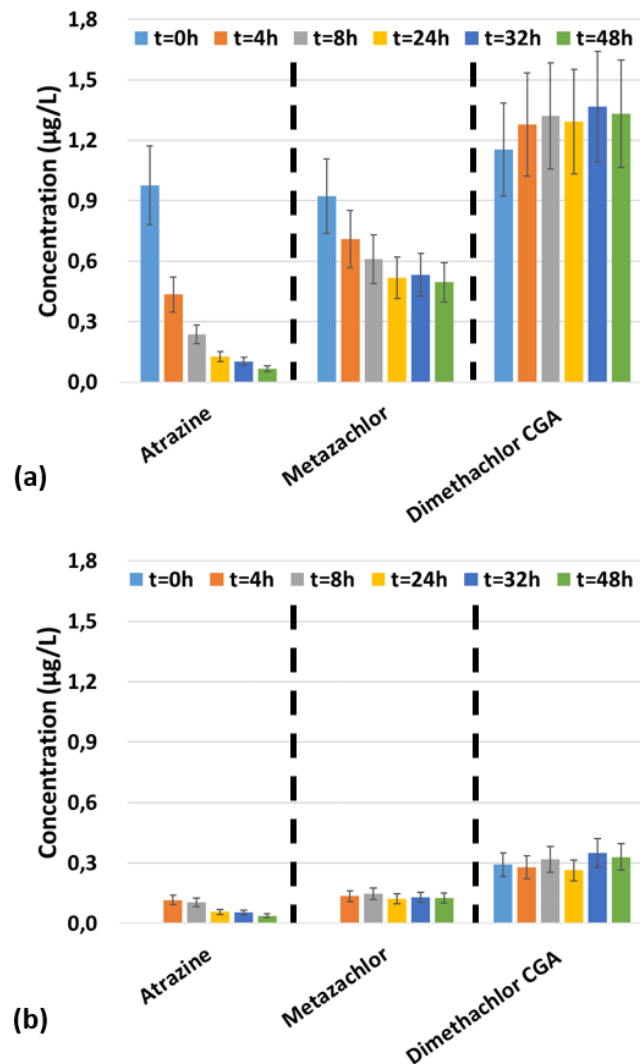
### 248 **3.1. Distribution and correlation of physicochemical properties**

249 Before studying the adsorption and rejection of the 164 MP, an assessment of the distribution  
250 of each property and the correlations between different properties was conducted to gain a better  
251 understanding of the data. The findings of both the distribution and correlations are depicted in  
252 figures 1S and 2S. To summarize, the monoisotopic mass ranged from 145 to 507 Da, while the  
253 molar volume varied from 81 to 339 cm<sup>3</sup>/mol. The log P values ranged from -1.38 to 8.19, and  
254 the log D values ranged from -3.34 to 5.28. Additionally, the polar surface area ranged from 30  
255 to 209 Å<sup>2</sup>, while the polarizability varied from 12.6 to 45.2 x10<sup>-24</sup> cm<sup>3</sup>. Among the MP assessed,  
256 31 were negatively charged, 131 were neutral, and 2 were positively charged (at pH=8). As  
257 shown in the two figures, several correlations were observed, with the most significant ones  
258 being between the monoisotopic mass, molar volume and polarizability, and as expected  
259 between log P and log D. Good correlations were also found between the minimum projected  
260 area (MPA) and the monoisotopic mass as well as the molecular dimensions. Finally, weaker  
261 correlations were found between the monoisotopic mass and the molecular dimensions.

### 262 **3.2. Adsorption of micropollutants and influence of physicochemical** 263 **properties**

264 As mentioned in section 2.4, in order to evaluate the adsorption of MP, the filtration was  
265 conducted for 48 hours while recycling the permeate and monitoring concentrations in both the  
266 feed and the permeate. By observing the variation in these concentrations, it becomes possible  
267 to understand the adsorption of MP and identify different behaviours among the tested  
268 molecules. Figure 1 illustrates this with three representative molecules, each representing a  
269 different behaviour. They are used as an example as all other compounds exhibited similar  
270 behaviour to one of these three. The first molecule, Atrazine, displayed a significant decrease  
271 in feed concentration (figure 1(a)) dropping from 0.975 µg/L to 0.04 µg/L and had very low  
272 concentration in the permeate as shown in figure 1(b). These variations in concentration suggest  
273 that Atrazine has been fully adsorbed onto the membrane surface. The second molecule,  
274 Metazachlor, exhibited a decrease in feed concentration from 0.92 µg/L to 0.49 µg/L while  
275 having an average rejection of around 75%. This decrease in concentration suggests that a  
276 fraction of Metazachlor was adsorbed on the membrane surface while the other portion  
277 remained in the feed solution. Notably, most of the decrease in concentration occurred within  
278 the first 24 hours, reaching 0.52 µg/L. This indicates that adsorption primarily occurs during

279 the initial 24 hours, and a steady state is approached between 24 and 48 hours. Finally, the third  
 280 molecule, Dimethachlor CGA, experienced an increase in its concentration in the feed from  
 281 1.15  $\mu\text{g/L}$  to 1.33  $\mu\text{g/L}$ , accompanied by an average rejection of 76%. Considering the  
 282 decreasing feed volume due to sample taking (260 mL of permeate) and the relatively  
 283 unchanged MP mass due to high rejection, an increase in feed concentrations is anticipated,  
 284 particularly if adsorption does not occur. Thus, the observed increase in feed concentration  
 285 leads to the conclusion that this molecule was not adsorbed onto the membrane surface.  
 286 Moreover, the major increase in concentration also occurred during the first 24 hours where the  
 287 concentration reached 1.29  $\mu\text{g/L}$  which confirms that a steady state is approached between 24  
 288 and 48 hours. It should be noted that Dimethachlor CGA, along with numerous other  
 289 compounds, displayed initial concentrations exceeding 1  $\mu\text{g/L}$ . This is attributed to the fact that  
 290 the raw water used already contained trace amounts of certain compounds.



291

292 *Figure 1: Variation of compounds concentration during the saturation phase in (a) the feed and (b) the permeate*  
 293 *for filtration tests performed on the dNF80 module (Error bars corresponding to 20% confidence intervals).*

294 Using the same approach as for these three molecules, all 164 MP compounds were classified  
 295 into three adsorption categories. The first category contains compounds that showed no or low  
 296 adsorption, the second category contains compounds that showed partial adsorption and the  
 297 third category contains compounds that showed high or complete adsorption. More precisely,  
 298 compounds that exhibited a reduction in concentration greater than 75% over the course of 48  
 299 hours were categorized as highly or completely adsorbed. Compounds that demonstrated a  
 300 constant or increased concentration were assigned to the no/low adsorption class, while all other  
 301 compounds were classified as partially adsorbed. The classification results are shown in the  
 302 supplementary data (Excel Sheet) and summarized in table 1, which shows the number of  
 303 compounds in each category. Two important points should be highlighted. First, for both  
 304 membranes, the adsorption of a few compounds could not be evaluated as their initial  
 305 concentrations in the feed were very low, leading to their classification as unknown (N=7 and  
 306 N=5 for dNF80 and dNF40, respectively). This low concentration might be attributed to matrix  
 307 effects, which can occur when numerous compounds are analysed using LC-MS, resulting in a  
 308 loss or increase in response [48]. Secondly, a mass balance calculation was performed, but due  
 309 to the low pollutant concentration used, the resulting values fell within the error margins.  
 310 Consequently, a qualitative approach to adsorption analysis was favoured.

311 *Table 1: Number of compounds per adsorption category*

<b>Adsorption class</b>	<b>dNF80</b>	<b>dNF40</b>
<b>No/Low adsorption</b>	16 (including 7 metabolites)	32 (including 10 metabolites)
<b>Partial adsorption</b>	39 (including 5 metabolites)	59 (including 6 metabolites)
<b>High/Complete adsorption</b>	102 (including 7 metabolites)	68 (including 4 metabolites)

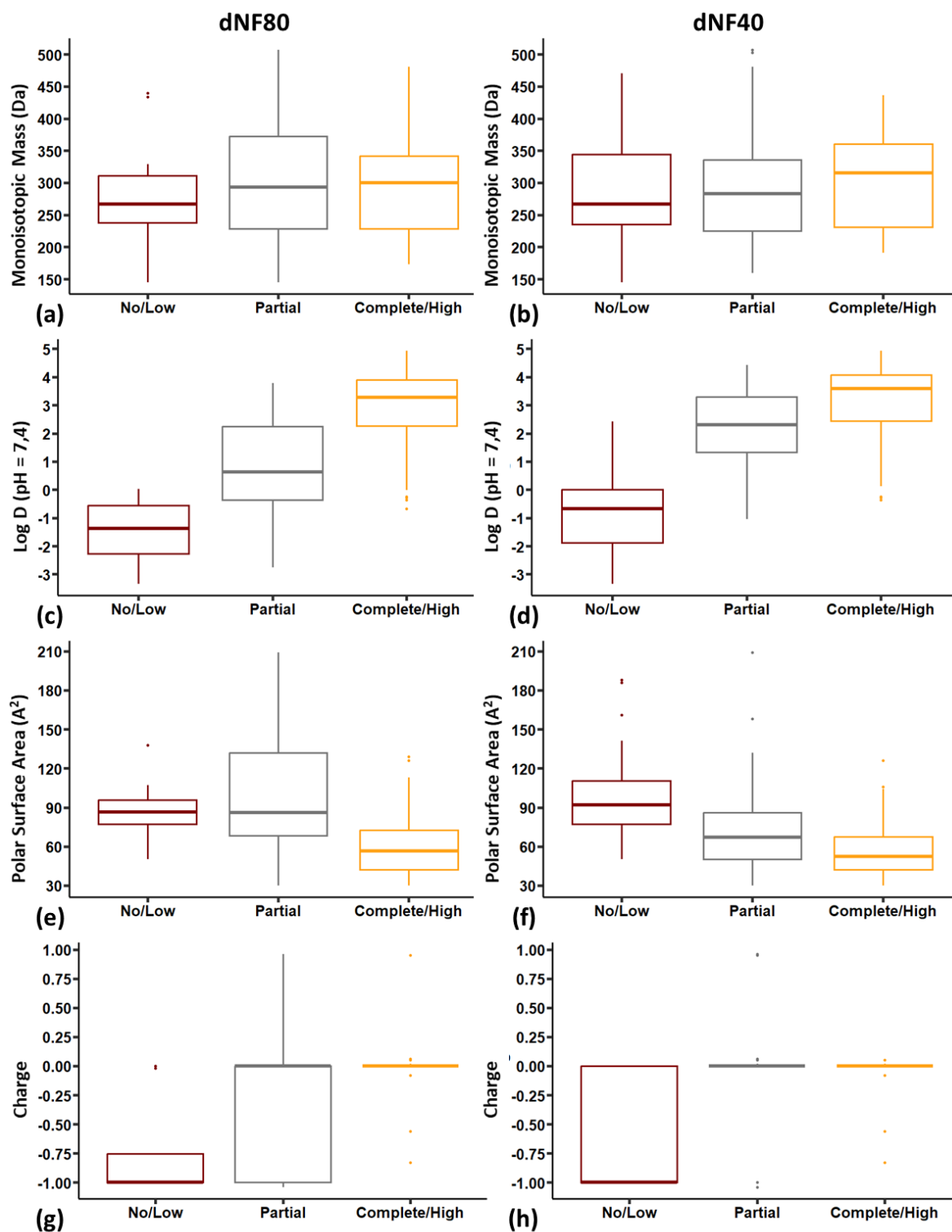
312  
 313 Upon comparing the adsorption of MP on the two membranes, it becomes evident that a  
 314 significant proportion of compounds tend to adsorb more on the dNF80 membrane as compared  
 315 to the dNF40 membrane. This observation can potentially be explained by the fact that, in the  
 316 case of LbL coated membranes, MP adsorption is believed to occur mainly on the polymeric  
 317 PES support membrane rather than on the coated layers, which is attributed to the higher  
 318 hydrophobicity of PES compared to the PEMs [39, 49]. This could account for the difference  
 319 in adsorption between the two membranes. In fact, as it will be discussed later, the rejection of

320 MP is higher for the dNF40 membrane, which might lead to fewer molecules reaching the PES  
321 support, resulting in less adsorption.

322 Concerning the influence of physicochemical properties, figures 2 and 3S plot the distribution  
323 of MP's physicochemical properties based on each class. The monoisotopic mass (Figures 2(a)  
324 and 2(b)) and molar volume (Figures 3S (a) and (b)) appear weakly related to adsorption as the  
325 three categories of compounds show similar distributions. However, log P (Figures 3S (c) and  
326 (d)) and log D (Figures 2(c) and (d)) exhibit significant differences between each category,  
327 indicating a strong relationship with adsorption. No adsorption was observed for compounds  
328 having negative log D values for both membranes, partial adsorption was seen for log D values  
329 around 1 for the dNF80 and around 2 for the dNF40 and high adsorption was seen for both  
330 membranes when log D values over 3. These observations are in agreement with numerous  
331 published works [14,23,25,39,49,50].

332 Figures 2(e) and (f) demonstrate that adsorption is related to the polar surface area, with highly  
333 adsorbed compounds having a lower polar surface area than non-adsorbed compounds for both  
334 membranes. For the dNF80 membrane, the highly adsorbed compounds had a median value  
335 equals to  $56.5 \text{ \AA}^2$  while the non-adsorbed compounds had a median value of  $86.5 \text{ \AA}^2$ . For the  
336 dNF40 membranes, these values were  $52.5 \text{ \AA}^2$  and  $92 \text{ \AA}^2$  respectively. The relationship between  
337 polar surface area and adsorption is likely due to hydrophilicity. In fact, figure 1S shows that  
338 compounds with a log D value above 1 and that are partially or highly adsorbed have lower  
339 polar surface areas compared to compounds with log D values lower than 1. The polarizability  
340 (Figures 3S (e) and (f)) has a small effect on adsorption, with highly adsorbed compounds  
341 showing slightly higher values than non-adsorbed compounds for both membranes, but the  
342 difference is relatively insignificant. The charge (Figures 2(g) and (h)) also appears to have an  
343 effect on adsorption, with negatively charged compounds exhibiting low adsorption, whereas  
344 neutral compounds display partial and high adsorption, which can be attributed to the repulsion  
345 of negatively charged compounds by the membrane.

346



347

348 *Figure 2: Boxplots showing the distribution of (a)-(b) monoisotopic mass, (c)-(d) log D, (e)-(f) polar surface*  
 349 *area and (g)-(h) charge of MP in each adsorption category for dNF80 and dNF40 membranes*

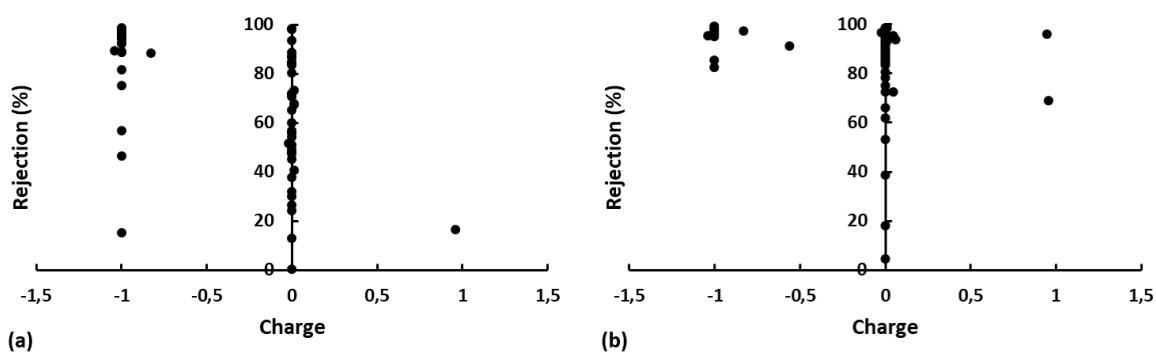
### 3.3. Influence of membrane MWCO, concentration and physicochemical properties on micropollutants rejection

In this part of the experiment, the rejection of MP was calculated for both membranes for a VRF of 1 and 4 (data shown in the excel sheet in supplementary data). For VRF=1, rejection was determined based on the feed and permeate concentrations measured at t=48h, while for VRF=4, the concentrations at the end of the experiment (recovery = 75%) were utilized for calculation. The calculations were made only for those compounds that were not fully adsorbed onto the membrane after 48 hours of saturation. For that, the rejection of 66 compounds for the dNF80 membrane and 101 compounds for the dNF40 membrane was determined.

Comparison of the rejection rates of the 66 common compounds demonstrates the significant impact of membrane MWCO on MP removal. The dNF40 membrane shows higher rejection values, indicating the importance of size exclusion. Ioxynil, in particular, exhibited a significant difference in rejection, with a rate of 15.3% for the dNF80 membrane compared to 85.3% for the dNF40 membrane. However, some compounds such as Clethodim, Metolachlor ESA, and Metolachlor OXA, which were highly rejected by the dNF80 membrane (>95%), showed either no change or only a small change in rejection when compared to the dNF40 membrane.

The impact of VRF on rejection was not very clear for both membranes. Most MP showed an increase in rejection at VRF = 4 (Excel Sheet), however, despite the improvement in rejection, the concentrations of MP in the permeate at VRF = 4 (75% recovery) were consistently higher than the initial concentrations (VRF = 1). This suggests that while rejections are improving, the water quality is slightly worsening.

The correlation between rejection and various physicochemical properties was also examined as shown in Figures 3, 4 and 4S. To begin, the influence of the charge was assessed for both membranes (shown in figure 3). In the case of the dNF80 membrane (figure 3(a)), it is evident that negatively charged compounds tend to be well rejected, with most compounds exhibiting a rejection rate of over 80%, while the rejection rate of neutral compounds varied from 0.47% to 99% depending on the compound. For the dNF40 membrane (figure 3(b)), the rejection rate was relatively high for all compounds regardless of their charge, with only a few exceptions for certain neutral compounds. The number of positively charged compounds is too low to draw any conclusions, so they will be disregarded for the remainder of the study.



380

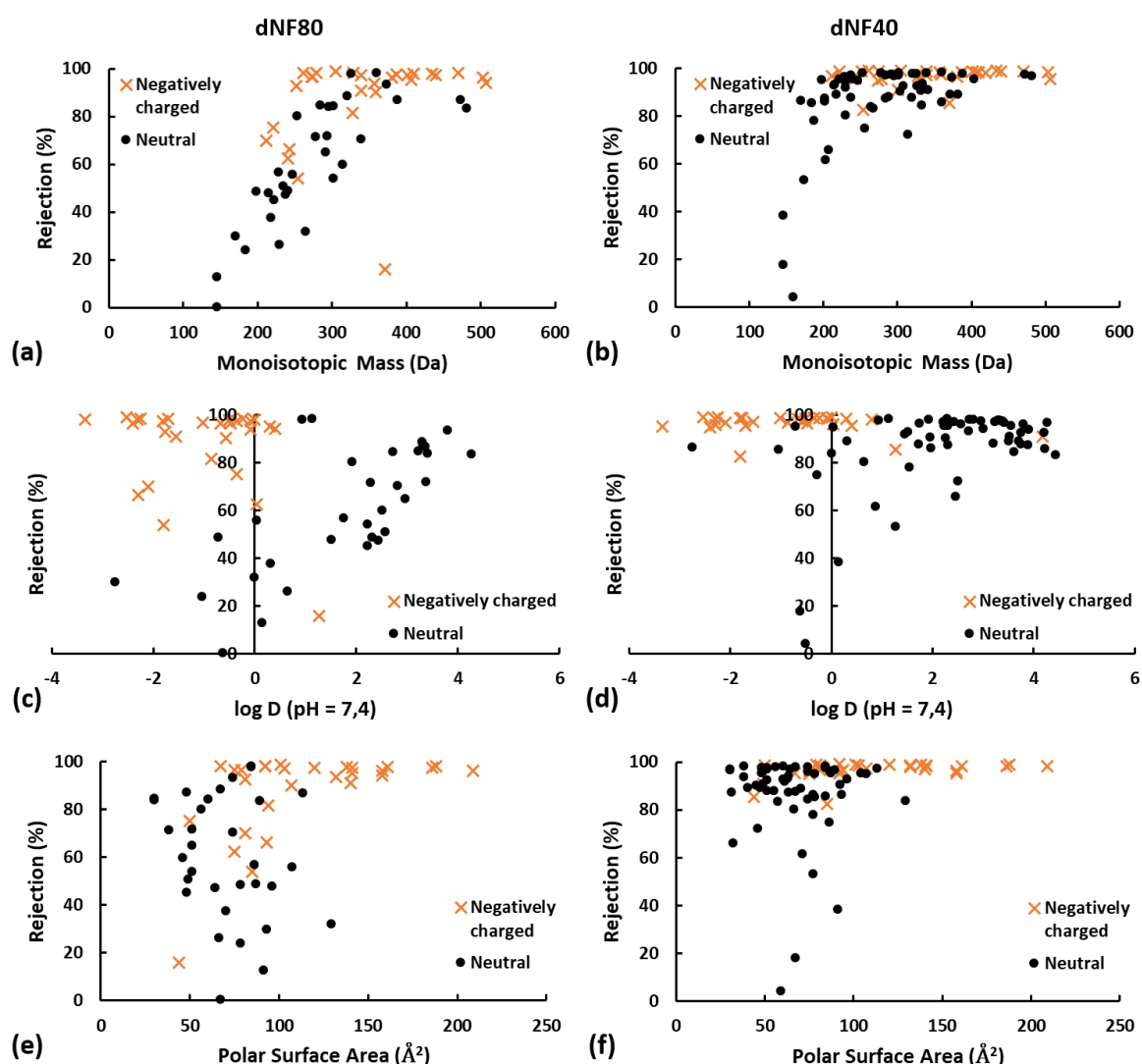
381 *Figure 3: Rejection of MP (VRF=1) function of the charge for the (a) dNF80 membrane and (b) dNF40*  
 382 *membrane*

383 When comparing the rejection in terms of the monoisotopic mass (figures 4(a) and 4(b)), results  
 384 show that negatively charged compounds are effectively rejected by the dNF80 membrane at a  
 385 monoisotopic mass of 250 Da, while the dNF40 membrane effectively rejects all negatively  
 386 charged compounds with a mass as low as 210 Da. One molecule, Ioxynil, stands out as it does  
 387 not follow the trend of negatively charged compounds on the dNF80 membrane and has low  
 388 rejection. However, this could be due to the fact that Ioxynil is a small 2-dimensional molecule  
 389 (Molar volume = 136.7 cm<sup>3</sup>/mol, L<sub>3</sub> = 0 Å) with a large monoisotopic mass resulting from the  
 390 presence of two iodine atoms. Neutral compounds are better rejected by the dNF80 membrane  
 391 as their monoisotopic mass increases from 145 Da to 380 Da, with rejection rates increasing  
 392 from less than 1% to over 90%. The dNF40 membrane effectively rejects neutral compounds  
 393 starting at a mass of 200 Da, which is consistent with previous research [51]. Moreover, there  
 394 is a notable threshold between 150 and 200 Da, where rejection rates increase rapidly from  
 395 approximately 4% to over 80%. Similar conclusions could be drawn regarding the effect of the  
 396 molar volume (figure 4S (a) and (b)), which is well-correlated with monoisotopic mass (figure  
 397 1S).

398 Figures 4 (c) and (d) indicate that the relationship between membrane rejection and log D is not  
 399 well-established (as well as Log P given the correlation between log P and log D, as shown in  
 400 figure 4S (c) and (d)). Negatively charged compounds, which have typically a negative log D,  
 401 are effectively rejected by both membranes. For neutral compounds, hydrophobic compounds  
 402 with higher log D values seem to be better rejected than hydrophilic ones, but it is uncertain  
 403 whether log D is the only factor influencing the rejection, or if other properties also play a role.  
 404 For example, Spirotetramat has a log D of 3.79 and a rejection rate of 93.5% (dNF80, VRF=1),  
 405 but exhibits also a monoisotopic mass of 373.2 Da much higher than the membrane MWCO.  
 406 Additionally, many compounds with log D > 2 for dNF80 and log D > 3 for dNF40 were



407 completely adsorbed on the membrane surface, so their rejection rates could not be calculated.  
 408 Therefore, the influence of log D and hydrophobicity cannot be confirmed, despite the presence  
 409 of some trends.



410  
 411 *Figure 4: Rejection of MP (VRF=1) function of (a)-(b) the monoisotopic mass, (c)-(d) log D and (e)-(f) the polar*  
 412 *surface for the dNF80 and dNF40 membranes*

413 Concerning the polar surface area, the rejection of negatively charged compounds by the dNF80  
 414 membrane (figure 4(e)) was higher for compounds having a polar surface area higher than 100  
 415 Å<sup>2</sup>. Apart from that, no effect of polar surface area on rejection was observed for the neutral  
 416 compounds on the same membrane. Additionally, like mentioned before, the rejection of most  
 417 compounds by the dNF40 membrane (figure 4(f)) was high which made it difficult to notice  
 418 any trend in case it existed. For the polarizability (figure 4S (e) and (f)), given that it was highly  
 419 correlated with the monoisotopic mass and the molar volume as presented early on, similar  
 420 variations were observed.

421 The relationship between rejection and molecular dimensions was also examined as displayed  
422 in figure 5S. In contrast to previous studies [31,52,53], no clear association was found between  
423 rejection and any of the dimensions. Nonetheless, on the dNF80 membrane, a moderate  
424 correlation was observed between rejection of neutral compounds and  $L_1$  ( $R^2 = 0.52$ ) as well as  
425  $L_3$  ( $R^2 = 0.67$ ), with rejection rates increasing as  $L_1$  and  $L_3$  increased. Additionally, while  
426 previous research has reported a strong correlation between rejection and MPA [39, 52], present  
427 results did not reveal any correlation between MPA and rejection for the two membranes, as  
428 shown in Figure 6S (a) and (b).

429 In summary, the analysis of MP rejection by HF-NF membranes in relation to their  
430 physicochemical properties and membrane MWCO yielded several observations. Steric  
431 exclusion was a crucial factor in rejection, evidenced by higher rejection rates with the dNF40  
432 membrane and the correlation between monoisotopic mass and rejection of neutral compounds  
433 by the dNF80 membrane. MP electrostatic charge also played a significant role, with negatively  
434 charged compounds being generally better rejected than neutral ones. Additionally, some  
435 properties like log D and polar surface area may affect rejection, but further investigation is  
436 needed. Finally, contrary to previous findings, only moderate and weak correlations were found  
437 between rejection and molecular dimensions and no correlation was found with MPA. In the  
438 following, a random forest model was developed to confirm these main features and investigate  
439 the rejection mechanisms of HF-NF membranes.

#### 440 **3.4. Application of random forest on the filtration of micropollutants**

441 Based on the results in sections 3.2 and 3.3, it is possible to say that the adsorption and rejection  
442 of MP are the result of the interplay between various properties related to the MP and the  
443 membrane. For that, given the complexity of these subjects and the impossibility of creating  
444 straightforward guidelines for the adsorption and rejection of MP by HF-NF membranes, the  
445 use of artificial intelligence has become crucial to estimate MP's adsorption and rejection. In  
446 the following, an attempt to predict the adsorption and rejection of the 164 MP was tested. First,  
447 available data was randomly divided into training and testing data, with the former containing  
448 80% of the total data. Then, random forests were applied on training data and used to predict  
449 the adsorption and rejection of the testing data.

450 Among the properties studied in this work, four properties were selected to predict the  
451 adsorption and rejection of MP. These properties are the monoisotopic mass, the charge, log D  
452 and the polar surface area. The choice was based on the correlation matrix presented in figures

453 1S and 2S and on the observed impact of each property. Specifically, when two properties were  
 454 found to be correlated, such as the monoisotopic mass and molar volume, only one was selected.  
 455 Conversely, properties that showed no or weak relation to adsorption or rejection, like  
 456 molecular dimensions, were disregarded.

457 The classification of MP into the three adsorption categories by random forests was tested on  
 458 the testing data set. A model was created for each membrane (dNF40 or dNF80) and results are  
 459 presented in the form of confusion matrices in tables 2 and 3. Table 2 shows the results of the  
 460 prediction of the adsorption of 30 compounds on the dNF80 membrane. In this table, 3  
 461 compounds correspond to the “No/low” adsorption category, 7 to the “Partial” adsorption  
 462 category and 20 to the “Complete/High” category. Out of these compounds 24 were correctly  
 463 classified (represented by the grey squares) and thus an 80% accuracy was obtained. Likewise,  
 464 for the adsorption on the dNF40 membrane (table 3), 22 compounds out of 30 were correctly  
 465 classified resulting in a 73% accuracy. Furthermore, when applying random forests to predict a  
 466 certain response it is possible to determine the degree of importance of the variables used to  
 467 make the predictions. For the adsorption of MP, log D was found to be the most important  
 468 property for both membranes followed by the charge, then the polar surface area and finally the  
 469 monoisotopic mass (figure 5). This corresponds well to the conclusions that were deduced in  
 470 the previous paragraph (section 3.2).

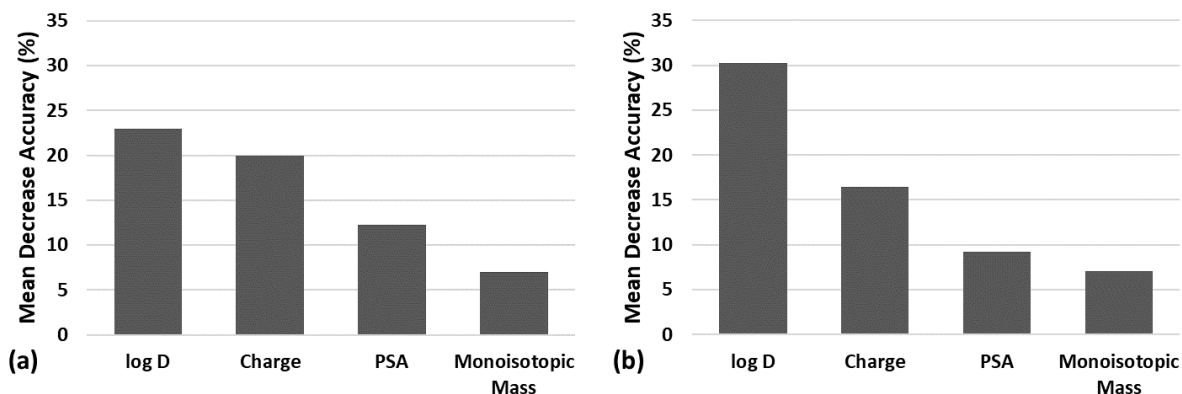
471 *Table 2: Confusion matrix comparing between the predicted and the observed adsorption behaviour on the*  
 472 *dNF80 membrane*

dNF80		Observed		
		No/Low	Partial	Complete/High
Predicted	No/Low	2	1	0
	Partial	0	4	2
	Complete/High	1	2	18

473

474 *Table 3: Confusion matrix comparing between the predicted and the observed adsorption behaviour on the*  
 475 *dNF40 membrane*

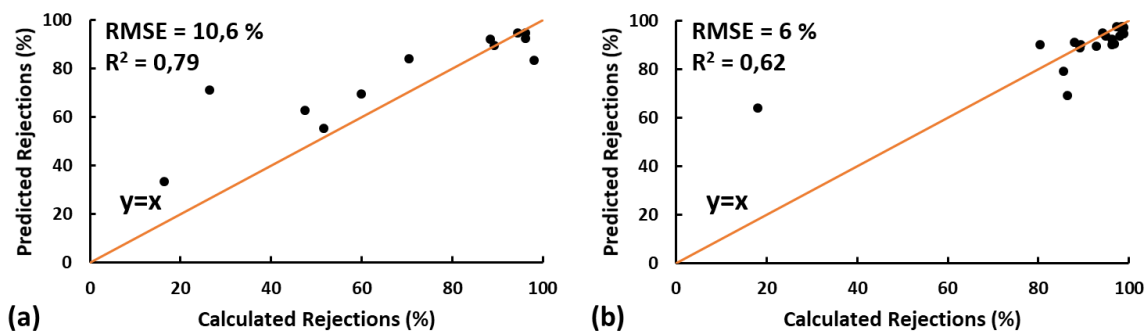
dNF40		Observed		
		No/Low	Partial	Complete/High
Predicted	No/Low	4	2	0
	Partial	2	7	2
	Complete/High	0	2	11



476

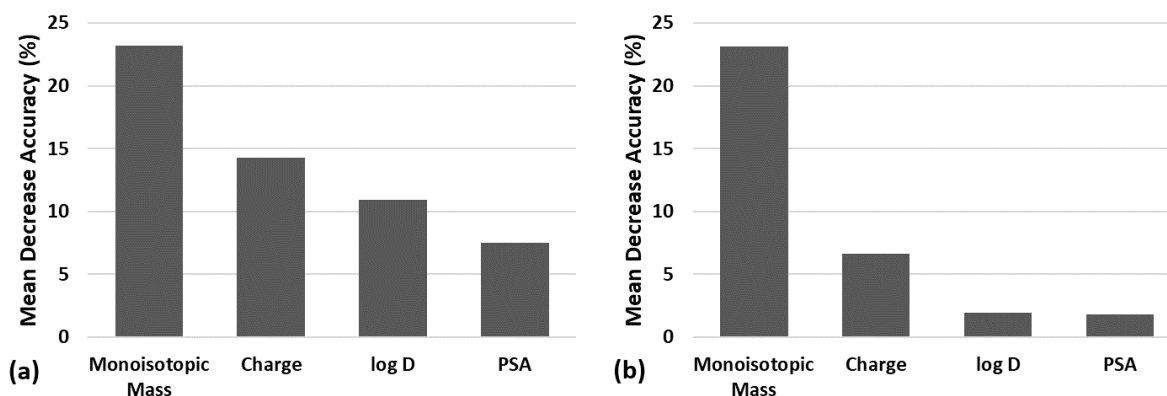
477 *Figure 5: Feature importance for adsorption prediction on (a) the dNF80 membrane and (b) the dNF40*  
 478 *membrane*

479 Regarding the rejection of MP, a comparison between the predicted and calculated values is  
 480 presented in figure 6. For the dNF80 membrane (figure 6(a)), the rejection was predicted with  
 481 a residual mean squared error (RMSE) of 10.6%. Similarly, for the dNF40 membrane (Figure  
 482 6(b)), an RMSE of 6% was obtained. In terms of physicochemical properties importance (figure  
 483 7), the monoisotopic mass was deemed the most significant property for rejection on both  
 484 membranes followed by the charge, log D and the polar surface area respectively. It is worth  
 485 mentioning that Ioxynil, despite showing an outlier rejection on the dNF80 membrane, was  
 486 included in the training data for the random forest model. This decision was made because the  
 487 presence or absence of Ioxynil did not have a significant impact on the results.



488

489 *Figure 6: Comparison between the predicted and calculated rejection by (a) the dNF80 membrane and (b) the*  
 490 *dNF40 membrane*



491

492 *Figure 7: Feature importance for rejection prediction on the (a) dNF80 membrane and (b) dNF40 membrane*

493 These results demonstrate that the adsorption and rejection of MP can be predicted with a  
 494 relatively high degree of accuracy no matter their nature (metabolites or PPP). Nonetheless, it  
 495 is essential to recognize that each model is constrained by the specific operating conditions  
 496 under which the data is collected. If any parameter is altered, resulting in different rejection and  
 497 adsorption outcomes, the random forest model cannot accurately predict these new values, as it  
 498 was trained on different data. For instance, variations in pH can lead to changes in some log D  
 499 values, affecting the hydrophobicity of the compounds and thereby altering their adsorption  
 500 behaviour. The same principle applies to any other influencing factor. To achieve reliable  
 501 predictions, it is crucial to either build a new model when the operating conditions change or  
 502 incorporate these conditions into the model, whenever possible. Once the model had been  
 503 established, it can then be used to predict the behaviour of new compounds with similar  
 504 properties.

## 505 4. Conclusion

506 This study investigated the influence of MP physicochemical properties on their adsorption and  
 507 rejection by HF LbL coated NF membranes. Two membranes with MWCOs of 400 Da and 800  
 508 Da were tested. The experimental procedure involved a two-step filtration test using a mixture  
 509 of 164 compounds. The first step evaluated adsorption during a 48-hour saturation period, while  
 510 the second step determined rejection at different recoveries.

511 Based on behaviour during the saturation period, compounds were classified into three  
 512 categories, with hydrophobicity (log D) and charge being crucial for adsorption. Compounds  
 513 with negative log D values showed little to no adsorption, while highly adsorbed ones had log  
 514  $D > 3$  for both membranes. Moreover, negatively charged compounds were less adsorbed  
 515 compared to neutral compounds. Regarding MP rejection, steric exclusion and electrostatic

516 repulsion played major roles. The 400 Da MWCO membrane had higher rejection rates for all  
517 compounds than the 800 Da MWCO membrane. Also, negatively charged compounds were  
518 better rejected, while neutral compounds showed varying rejection rates. Additionally, log D  
519 and polar surface area were observed to potentially impact rejection, although additional  
520 research is necessary. In contrast to prior research, rejection showed only moderate and weak  
521 correlations with molecular dimensions, and no correlation was observed with MPA.

522 Finally, the study demonstrated that artificial intelligence, specifically random forests, could  
523 predict MP adsorption and rejection with relatively good accuracy. The adsorption prediction  
524 accuracy was 80% and 73%, and the rejection prediction RMSE values were 10.6% and 6% for  
525 the dNF80 and dNF40 membranes, respectively.

526 To further advance the study, future research should aim to investigate the adsorption and  
527 rejection behaviour of the membranes on larger scale modules. The saturation period should be  
528 extended with continuous addition of MP to the feed to better understand the behaviour of  
529 adsorbed compounds during and after saturation. It is possible that some rejection results might  
530 be overestimated if the 48-hour saturation period is not sufficient, hence warranting a more  
531 extended saturation period. Additionally, it is interesting to investigate the individual behaviour  
532 of MP and compare it to their behaviour within mixtures. While testing each of the 164  
533 compounds individually might not be practical, it can be performed on selected molecules.  
534 Besides that, the inclusion of more positively charged compounds can aid in evaluating their  
535 behaviour during the filtration process. And last, it is recommended to explore the effects of  
536 achieving higher recovery values and the influence of operating conditions like the  
537 transmembrane pressure and crossflow velocity.

### 538 **Acknowledgments:**

539 The authors acknowledge financial support from the European Union (ERDF) and Région  
540 Nouvelle Aquitaine. This work pertains to the French government program "Investissements  
541 d'Avenir" (EUR INTREE, reference ANR-18-EURE-0010). The authors would also like to  
542 thank NX filtration for providing the membranes.

### 543 **Author Contribution**

544 **G. Dagher:** Methodology, Analysis, Writing. **G. Saab:** Experimentation. **A. Martin:**  
545 Methodology, Review and Editing. **G. Couturier and P. Candido:** UHPLC-MS/MS analysis.

546 **L. Moulin and JP. Croué:** Review and Editing. **B. Teychene:** Conceptualization, Resources,  
547 Methodology, Supervision, Review and Editing.

## 548 **5. References**

- 549 [1] P. Beaudou, M. Pascal, D. Mouly, C. Galey, and O. Thomas, Health risks associated with  
550 drinking water in a context of climate change in France: a review of surveillance  
551 requirements, *J. Water Clim. Change*. 2 (2011) 230–246. doi: 10.2166/wcc.2011.010.
- 552 [2] A. Mishra, A. Alnahit, and B. Campbell, Impact of land uses, drought, flood, wildfire, and  
553 cascading events on water quality and microbial communities: A review and analysis, *J.*  
554 *Hydrol.* 596 (2021) doi: 10.1016/j.jhydrol.2020.125707.
- 555 [3] L. M. Mosley, Drought impacts on the water quality of freshwater systems; review and  
556 integration, *Earth-Sci. Rev.* 140 (2015) 203–214. doi: 10.1016/j.earscirev.2014.11.010.
- 557 [4] R. Yin and C. Shang, Removal of micropollutants in drinking water using UV-  
558 LED/chlorine advanced oxidation process followed by activated carbon adsorption, *Water*  
559 *Res.* 185 (2020). doi: 10.1016/j.watres.2020.116297.
- 560 [5] M. Boehler, B. Zwickelpflug, J. Hollender, T. Ternes, A. Joss, and H. Siegrist, Removal  
561 of micropollutants in municipal wastewater treatment plants by powder-activated carbon,  
562 *Water Sci. Technol.* 66 (2012). doi: 10.2166/wst.2012.353.
- 563 [6] N. K. Khanzada *et al.*, Removal of organic micropollutants using advanced membrane-  
564 based water and wastewater treatment: A review, *J. Membr. Sci.* 598 (2020). doi:  
565 10.1016/j.memsci.2019.117672.
- 566 [7] Y. S. Khoo *et al.*, Removal of emerging organic micropollutants via modified-reverse  
567 osmosis/nanofiltration membranes: A review, *Chemosphere.* 305 (2022). doi:  
568 10.1016/j.chemosphere.2022.135151.
- 569 [8] P. Xu *et al.*, Rejection of Emerging Organic Micropollutants in Nanofiltration–Reverse  
570 Osmosis Membrane Applications, *Water Environ. Res.* 77 (2005) doi:  
571 10.2175/106143005X41609.
- 572 [9] S. Kim *et al.*, Removal of contaminants of emerging concern by membranes in water and  
573 wastewater: A review, *Chem. Eng. J.* 335 (2018). doi: 10.1016/j.cej.2017.11.044.
- 574 [10] P. Lipp, F. Sacher, and G. Baldauf, Removal of organic micro-pollutants during drinking  
575 water treatment by nanofiltration and reverse osmosis, *Desalination Water Treat.* 13  
576 (2010). doi: 10.5004/dwt.2010.1063.

- 577 [11] V. Yangali-Quintanilla, S. K. Maeng, T. Fujioka, M. Kennedy, and G. Amy, Proposing  
578 nanofiltration as acceptable barrier for organic contaminants in water reuse, *J. Membr.*  
579 *Sci.* 362 (2010). doi: 10.1016/j.memsci.2010.06.058.
- 580 [12] M. Jacob, C. Li, C. Guigui, C. Cabassud, G. Lavison, and L. Moulin, Performance of  
581 NF/RO process for indirect potable reuse: interactions between micropollutants, micro-  
582 organisms and real MBR permeate, *Desalination Water Treat.* 46 (2012) doi:  
583 10.1080/19443994.2012.677507.
- 584 [13] P. Berg, G. Hagemeyer, and R. Gimbel, Removal of pesticides and other micropollutants  
585 by nanofiltration, *Desalination.* 113 (1997) doi: 10.1016/S0011-9164(97)00130-6.
- 586 [14] K. Kimura, G. Amy, J. E. Drewes, T. Heberer, T.-U. Kim, and Y. Watanabe, Rejection of  
587 organic micropollutants (disinfection by-products, endocrine disrupting compounds, and  
588 pharmaceutically active compounds) by NF/RO membranes, *J. Membr. Sci.* 227 (2003).  
589 doi: 10.1016/j.memsci.2003.09.005.
- 590 [15] B. Van der Bruggen, J. Schaep, W. Maes, D. Wilms, and C. Vandecasteele, Nanofiltration  
591 as a treatment method for the removal of pesticides from ground waters, *Desalination.* 117  
592 (1998). doi: 10.1016/S0011-9164(98)00081-2.
- 593 [16] B. Van der Bruggen, J. Schaep, D. Wilms, and C. Vandecasteele, Influence of molecular  
594 size, polarity and charge on the retention of organic molecules by nanofiltration, *J. Membr.*  
595 *Sci.* 156 (1999). doi: 10.1016/S0376-7388(98)00326-3.
- 596 [17] A. Verliefde, E. Cornelissen, G. Amy, B. Van der Bruggen, and H. van Dijk, Priority  
597 organic micropollutants in water sources in Flanders and the Netherlands and assessment  
598 of removal possibilities with nanofiltration, *Environ. Pollut.* 146 (2007). doi:  
599 10.1016/j.envpol.2006.01.051.
- 600 [18] A. De Munari, A. J. C. Semiao, and B. Antizar-Ladislao, Retention of pesticide  
601 Endosulfan by nanofiltration: Influence of organic matter–pesticide complexation and  
602 solute–membrane interactions, *Water Res.* 47 (2013). doi: 10.1016/j.watres.2013.03.055.
- 603 [19] K. O. Agenson and T. Urase, Change in membrane performance due to organic fouling in  
604 nanofiltration (NF)/reverse osmosis (RO) applications, *Sep. Purif. Technol.* 55 (2007) doi:  
605 10.1016/j.seppur.2006.11.010.
- 606 [20] Y.-L. Lin, Effects of organic, biological and colloidal fouling on the removal of  
607 pharmaceuticals and personal care products by nanofiltration and reverse osmosis  
608 membranes, *J. Membr. Sci.* 542 (2017). doi: 10.1016/j.memsci.2017.08.023.



- 609 [21] L. D. Nghiem, P. J. Coleman, and C. Espendiller, Mechanisms underlying the effects of  
610 membrane fouling on the nanofiltration of trace organic contaminants, *Desalination*, 250  
611 (2010).doi: 10.1016/j.desal.2009.03.025.
- 612 [22] A. Imbrogno and A. I. Schäfer, Micropollutants breakthrough curve phenomena in  
613 nanofiltration: Impact of operational parameters, *Sep. Purif. Technol.* 267 (2021). doi:  
614 10.1016/j.seppur.2021.118406.
- 615 [23] K. Kimura, G. Amy, J. Drewes, and Y. Watanabe, Adsorption of hydrophobic compounds  
616 onto NF/RO membranes: an artifact leading to overestimation of rejection, *J. Membr. Sci.*  
617 221 (2003). doi: 10.1016/S0376-7388(03)00248-5.
- 618 [24] B. Van der Bruggen *et al.*, Assessment of a semi-quantitative method for estimation of the  
619 rejection of organic compounds in aqueous solution in nanofiltration, *J. Chem. Technol.*  
620 *Biotechnol.* 81 (2006). doi: 10.1002/jctb.1489.
- 621 [25] A. J. C. Semião and A. I. Schäfer, Removal of adsorbing estrogenic micropollutants by  
622 nanofiltration membranes. Part A—Experimental evidence, *J. Membr. Sci.* 431 (2013).  
623 doi: 10.1016/j.memsci.2012.11.080.
- 624 [26] J. L. Acero, F. J. Benitez, F. Teva, and A. I. Leal, Retention of emerging micropollutants  
625 from UP water and a municipal secondary effluent by ultrafiltration and nanofiltration,  
626 *Chem. Eng. J.* 163 (2010). doi: 10.1016/j.cej.2010.07.060.
- 627 [27] A. J. C. Semião and A. I. Schäfer, Estrogenic micropollutant adsorption dynamics onto  
628 nanofiltration membranes, *J. Membr. Sci.* 381 (2011). doi:  
629 10.1016/j.memsci.2011.07.031.
- 630 [28] V. Yangali-Quintanilla, A. Sadmani, M. McConville, M. Kennedy, and G. Amy, A QSAR  
631 model for predicting rejection of emerging contaminants (pharmaceuticals, endocrine  
632 disruptors) by nanofiltration membranes, *Water Res.* 44 (2010). doi:  
633 10.1016/j.watres.2009.06.054.
- 634 [29] N. Jeong, T. Chung, and T. Tong, Predicting Micropollutant Removal by Reverse Osmosis  
635 and Nanofiltration Membranes: Is Machine Learning Viable?, *Environ. Sci. Technol.* 55  
636 (2021). doi: 10.1021/acs.est.1c04041.
- 637 [30] B. Teychene *et al.*, Investigation of polar mobile organic compounds (PMOC) removal by  
638 reverse osmosis and nanofiltration: rejection mechanism modelling using decision tree,  
639 *Water Supply* 20 (2020). doi: 10.2166/ws.2020.020.
- 640 [31] S. Sanches, C. F. Galinha, M. T. Barreto Crespo, V. J. Pereira, and J. G. Crespo,  
641 Assessment of phenomena underlying the removal of micropollutants during water

- 642 treatment by nanofiltration using multivariate statistical analysis, *Sep. Purif. Technol.* 118  
643 (2013). doi: 10.1016/j.seppur.2013.07.020.
- 644 [32] A. Shahmansouri and C. Bellona, Application of quantitative structure–property  
645 relationships (QSPRs) to predict the rejection of organic solutes by nanofiltration, *Sep.*  
646 *Purif. Technol.* 118 (2013). doi: 10.1016/j.seppur.2013.07.050.
- 647 [33] S. Lee and J. Kim, Prediction of Nanofiltration and Reverse-Osmosis-Membrane  
648 Rejection of Organic Compounds Using Random Forest Model, *J. Environ. Eng.* 146  
649 (2020). doi: 10.1061/(ASCE)EE.1943-7870.0001806.
- 650 [34] A. Al-Amoudi and R. W. Lovitt, Fouling strategies and the cleaning system of NF  
651 membranes and factors affecting cleaning efficiency, *J. Membr. Sci.* 303 (2007). doi:  
652 10.1016/j.memsci.2007.06.002.
- 653 [35] F. Vince, E. Aoustin, P. Bréant, and F. Marechal, LCA tool for the environmental  
654 evaluation of potable water production, *Desalination.* 220 (2008). doi:  
655 10.1016/j.desal.2007.01.021.
- 656 [36] A. Toutianoush, W. Jin, H. Deligöz, and B. Tieke, Polyelectrolyte multilayer membranes  
657 for desalination of aqueous salt solutions and seawater under reverse osmosis conditions,  
658 *Appl. Surf. Sci.* 246 (2005) doi: 10.1016/j.apsusc.2004.11.068.
- 659 [37] N. Joseph, P. Ahmadiannamini, R. Hoogenboom, and I. F. J. Vankelecom, Layer-by-layer  
660 preparation of polyelectrolyte multilayer membranes for separation, *Polym. Chem.* 5  
661 (2014). doi: 10.1039/C3PY01262J.
- 662 [38] W. A. Jonkers, E. R. Cornelissen, and W. M. de Vos, Hollow fiber nanofiltration: From  
663 lab-scale research to full-scale applications, *J. Membr. Sci.* 669 (2023) doi:  
664 10.1016/j.memsci.2022.121234.
- 665 [39] S. M. Abtahi, S. Ilyas, C. Joannis Cassan, C. Albasi, and W. M. de Vos, Micropollutants  
666 removal from secondary-treated municipal wastewater using weak polyelectrolyte  
667 multilayer based nanofiltration membranes, *J. Membr. Sci.* 548 (2018). doi:  
668 10.1016/j.memsci.2017.10.045.
- 669 [40] S. M. Abtahi *et al.*, Micropollutant rejection of annealed polyelectrolyte multilayer based  
670 nanofiltration membranes for treatment of conventionally-treated municipal wastewater,  
671 *Sep. Purif. Technol.* 209 (2019). doi: 10.1016/j.seppur.2018.07.071.
- 672 [41] J. De Grooth, D. M. Reurink, J. Ploegmakers, W. M. de Vos, and K. Nijmeijer, Charged  
673 Micropollutant Removal With Hollow Fiber Nanofiltration Membranes Based On  
674 Polycation/Polyzwitterion/Polyanion Multilayers, *ACS Appl. Mater. Interfaces*, 6 (2014).  
675 doi: 10.1021/am504630a.

- 676 [42] S. Ilyas, S. M. Abtahi, N. Akkilic, H. D. W. Roesink, and W. M. de Vos, Weak  
677 polyelectrolyte multilayers as tunable separation layers for micro-pollutant removal by  
678 hollow fiber nanofiltration membranes, *J. Membr. Sci.*, 537 (2017). doi:  
679 10.1016/j.memsci.2017.05.027.
- 680 [43] N. Baran, A. E. Rosenbom, R. Kozel, and D. Lapworth, Pesticides and their metabolites  
681 in European groundwater: Comparing regulations and approaches to monitoring in France,  
682 Denmark, England and Switzerland, *Sci. Total Environ.*, 842 (2022). doi:  
683 10.1016/j.scitotenv.2022.156696.
- 684 [44] G. Caron and G. Ermondi, Molecular descriptors for polarity: the need for going beyond  
685 polar surface area, <http://dx.doi.org/10.4155/fmc-2016-0165>, (2016).
- 686 [45] K. Max, Building Predictive Models in R Using the caret Package, *J. Stat. Softw.*, 28  
687 (2008). doi: 10.18637/jss.v028.i05.
- 688 [46] A. Liaw and M. Wiener, Classification and Regression by RandomForest, *Forest*, 23  
689 (2001)
- 690 [47] G. James, D. Witten, T. Hastie, and R. Tibshirani, *An Introduction to Statistical Learning:  
691 with Applications in R*. New York, NY: Springer US, 2021. doi: 10.1007/978-1-0716-  
692 1418-1.
- 693 [48] W. Zhou, S. Yang, and P. G. Wang, Matrix effects and application of matrix effect factor,  
694 *Bioanalysis*, 9 (2017). doi: 10.4155/bio-2017-0214.
- 695 [49] A. R. D. Verliefde *et al.*, Influence of Solute–Membrane Affinity on Rejection of  
696 Uncharged Organic Solutes by Nanofiltration Membranes, *Environ. Sci. Technol.*, 43  
697 (2009). doi: 10.1021/es803146r.
- 698 [50] H. Xu *et al.*, A Simple Method to Identify the Dominant Fouling Mechanisms during  
699 Membrane Filtration Based on Piecewise Multiple Linear Regression, *Membranes*, 10  
700 (2020). doi: 10.3390/membranes10080171.
- 701 [51] S. van der Poel, Parting ways – removal of salts and organic micropollutants by direct  
702 nanofiltration: Pretreatment of surface water for the production of dune infiltration water,  
703 2020, Accessed: Feb. 23, 2023. [Online]. Available:  
704 [https://repository.tudelft.nl/islandora/object/uuid%3A6774b91c-6850-4c82-b3c0-  
705 a3110f0c40b9](https://repository.tudelft.nl/islandora/object/uuid%3A6774b91c-6850-4c82-b3c0-a3110f0c40b9)
- 706 [52] T. Fujioka, S. J. Khan, J. A. McDonald, and L. D. Nghiem, Nanofiltration of trace organic  
707 chemicals: A comparison between ceramic and polymeric membranes, *Sep. Purif.  
708 Technol.*, 136 (2014). doi: 10.1016/j.seppur.2014.08.039.

709 [53] Y. Kiso *et al.*, Effect of molecular shape on rejection of uncharged organic compounds by  
710 nanofiltration membranes and on calculated pore radii, *J. Membr. Sci.*, 358 (2010). doi:  
711 10.1016/j.memsci.2010.04.034.