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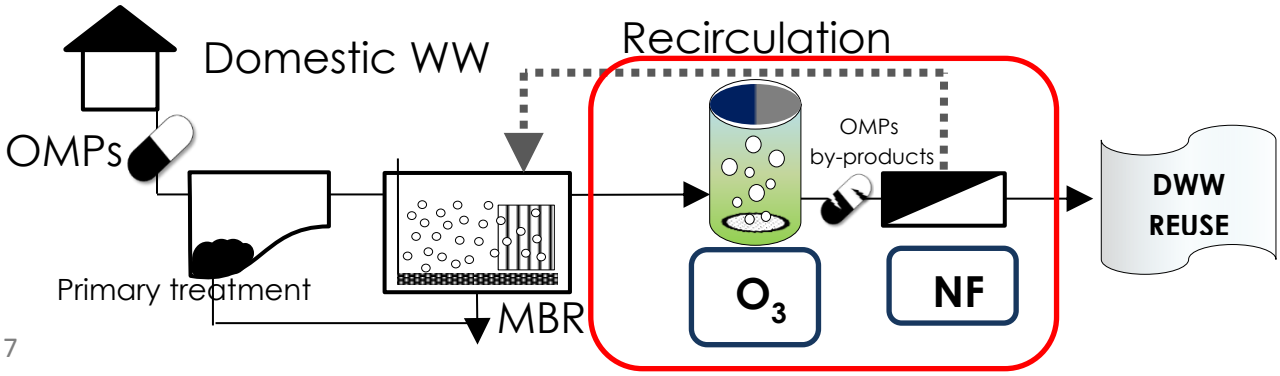
Graphical abstract



Abstract

The objective of this study was to develop an innovative and advanced integrated "membrane and oxidation" system for the treatment of domestic wastewater by coupling membrane bioreactor (MBR), nanofiltration (NF) and ozonation. Five contaminants were selected (acetaminophen, carbamazepin, sulfamethoxazole, tetracyclin and terbutryn). The MBR effluent samples have been fully characterized using conventional analysis (COD, TOC, UV254, ionic chromatography…) and advanced characterization analyses (3D fluorescence excitation–emission matrices (3DEEM)) before being spiked with 1ppm of each of the selected pharmaceuticals. NF process experiments were carried out in batch and semi-batch mode using a flat sheet membrane system (NF-90). Selected OMPs were well rejected by NF (between 84% and 98%) and the main fouling mechanisms observed were pore blocking and gel layer formation. MBR effluent was then pre-treated in an ozonation pilot unit's with ozone gas inlet fixed at 5g.Nm^{-3}.The complete degradation by ozonation of carbamazepine and sulfamethoxazole took 15 to 20 min and more than 30 min for terbutryn. Acetaminophen, tetracyclin and dissolved organic matter were almost totally ozonated in 5 min. The overall mineralization rate was low. The pre-ozonation enables the NF fouling resistance to be decreased by almost 40%.

Keywords: Wastewater reuse, Organic micropollutants, Nanofiltration, pre-Ozonation

List of symbol

$[O_3]_{gas}$: applied gas ozone concentration (gO_3/Nm^3)
ACT: acetaminophen
CBZ: carbamazepin
COD: chemical oxygen demand (gO_2/m^3)
Da: Dalton
DCOM: dissolved and colloidal organic matter
DWW: domestic wastewater
HPLC: high performance liquid chromatography
LC-MS/MS: liquid chromatography tandem mass spectrometry
MBR: membrane bioreactor
MWCO: molecular weight cut-off
NF: Nanofiltration
OMPs: organic micropollutants
RO: reverse osmosis
SUL: sulfamethoxazole
TER: terbutryn
TET: tetracyclin
TMP: transmembrane pressure (bar)
TOC: total organic carbon
TSS : Total Suspended Solid (mg/L)
UPW: ultrapure water
UV_{254}: ultra-violet absorbance at 254 nm
v: tangential velocity (m/s)
$V_{reactor}$: volume of reactor (m^3)
v_{stir}: stiring velocity (m/s)
WWTP : wastewater treatment plant
Y: permeate recovery rate (%)

1. Introduction

To overcome water shortage which is becoming a growing worldwide challenge, domestic wastewater (DWW) must be considered as a promising water resource instead of mere waste. Indeed, wastewater can be reused for different applications among which agricultural, industrial and municipal uses but also for ground water recharge (Kellis et al. 2013). Even though, occurrence of organic micropollutants (OMPs) in municipal wastewater constitutes an important limiting factor pointed out by many authors (Bollmann et al. 2014; Dong et al. 2016; Gogoi et al. 2018). According to Ganiyu et al., most of the pharmaceuticals administered for both human and animal uses are excreted unmodified via urine and feces and directly introduced into sewage systems (Ganiyu et al. 2015). An important factor limiting the wastewater reuse is the inefficiency of conventional waste water treatment plant (WWTP) in

removing OMPs (Martin Ruel et al. 2010). Even in the case of secondary treatment processes improved by MBR, OMPs are not fully removed and some specific compounds showed really low removal efficiencies (between 8 and 32% for pesticides such as atrazine and fenoprop) (Ahmed et al. 2017). Consequently, pharmaceuticals and antibiotics have been found widespread in different environmental compartments due to their persistence and low biodegradability (Terzić et al. 2008).

To fulfill public regulations requirements and achieve sustainable development goals in terms of ensuring safe and sustainable access to water (SDG 6, UN) (Costanza, Fioramonti, and Kubiszewski 2016), tertiary treatment processes capable of removing bio-resistant compounds are being developed and investigated. Activated carbon adsorption, ozonation and membrane separation processes, such as NF and RO, have been investigated in wastewater treatment schemes. Tight nanofiltration and reverse osmosis remove well the majority of organic micropollutants (above 95%). The efficiency of such membrane processes depends mainly on the type of membrane, the effluent matrix and the micropollutants physico-chemical properties (Cartagena et al. 2013; Garcia-Ivars et al. 2017, Licona et al. 2018). These last years, some authors have demonstrated that nanofiltration (NF) could be a good alternative to reverse osmosis (RO) for urban wastewater reuse (Yangali-Quintanilla et al. 2010; Bellona et al. 2012; Azaïs et al. 2017). Indeed, it offers a very good compromise between permeability and selectivity. Due to the more important permeate flux compared to RO while having an acceptable OMPs removal, nanofiltration requires less energy and seems more appropriate in an economical point of view for the treatment of such refractory effluents (Nikbakht Fini, Madsen, and Muff 2019; Song, Lee, and Ng 2020). However, there is still the problem of the brine management and the propensity to fouling which both represent an object for many researchers mobilization (Contreras, Kim, and Li 2009; Gan et al. 2019). Lan *et al.* have investigated the performances of NF on MBR effluent and pointed out that colloidal organic fouling played a major role in flux decline (Lan et al. 2018). Moreover, According to Mänttäri *et al.* (2000), the humic-like substances adsorb onto the polyamide-based thin film composite and cellulose acetate NF membrane surface forming a gel layer which induces an additional resistance to the flux passage (Mänttäri et al. 2000; Azaïs et al. 2014; 2016a). Fersi *et al.* distinguished two stages in fouling related to gel layer in filtration process: the gel layer formation and the gel layer compression (Fersi, Gzara, and Dhahbi 2009). Because of a decrease in porosity, the second stage accelerates the flux decline and this phenomenon was observed after 60% of recovery rate.

Beside the membrane processes, advanced oxidation processes are also investigated for OMPs elimination (Deng 2020). They offer the advantages in degrading well micropollutants (Mizuno et al. 2018). Ozone is the second most powerful oxidizing agent after hydroxyl radicals and is much more stable than hydroxyl radicals. Ozonation was firstly used as final treatment process for effluent disinfection and to oxidize iron and manganese in the end of 19th century (Langlais, Reckhow, and Brink 2019). Nowadays, ozonation is subject to many investigation as promising treatment process to eliminate emerging OMPs (Esplugas et al. 2007; Mizuno et al. 2018; Azaïs et al. 2017). However, oxidation sometimes leads to more toxic byproducts than parent compounds and an additional treatment must be added to remove this new toxicity from the final effluent (Le et al. 2016; 2017; Oropesa et al. 2017).

The aim of this study was to combine pre-ozonation and NF processes to eliminate selected OMPs in real MBR secondary effluent. Combining ozonation with NF seems an appropriate synergetic solution to take advantages of these processes while limiting their drawbacks (Byun, Taurozzi, and Tarabara 2015; Vatankhah et al. 2018; Ghernaout 2020). Indeed, while NF membrane act as an efficient physical barrier against toxicity due to OMPs and their by-products, pre-ozonation can efficiently degrades these refractory pollutants and also maintain the good flux performances of the NF process by limiting membrane fouling.

The specific objectives were to investigate the fouling propensity and OMPs removal mechanisms in NF, to study the effect of the matrix composition on ozonation process and to evaluate the effect of pre-ozonation on fouling and flux evolution in NF.

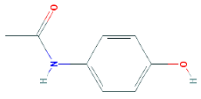
2. Materials and methods

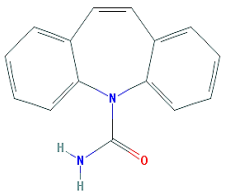
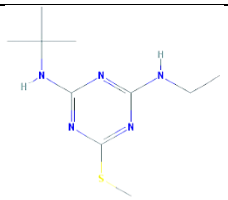
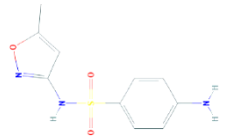
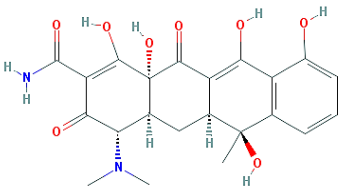
2.1 Micropollutants and matrix selection

2.1.1 Selection of micropollutants

Four pharmaceuticals, acetaminophen (ACT), carbamazepine (CBZ), sulfamethoxazole (SUL) and tetracyclin (TET) and one herbicide, terbutryn (TER) have been selected for this study.

Table 1 : Physico-chemical characteristics of selected micropollutants.

Compounds	MW $g.mol^{-1}$	kO_3 $mol.l^{-1}.S^{-1}$	Log-K_{ow}	Charge at pH7	semi-structural formula
Acetaminophen (ACT) $C_8H_9NO_2$	151	$6.5 .10^{6}$ [a]	0.45	neutral	

Carbamazepin (CBZ) $C_{15}H_{12}N_2O$	236	$3.0 .10^{5}$ [b]	2.45	neutral	
Terbutryn (TER) $C_{10}H_{19}N_5S$	241	-	3.50	neutral	
Sulfamethoxazole (SUL) $C_{10}H_{11}N_3O_3S$	253	$2.5 .10^{6}$ [b]	0.89	negative	
Tetracyclin (TET) $C_{22}H_{24}N_2O_8$	444	$1.9 .10^{6}$ [c]	-1.37	neutral	

a. (Hamdi El Najjar et al. 2014) b. (Huber et al. 2003) c. (Khan, Bae, and Jung 2010)

These molecules were selected because of their representativeness for different class of emerging contaminants found widespread in WWTP secondary effluent (Terzić et al. 2008; Leung et al. 2012; Nguyen et al. 2013; Yang et al. 2017; Barbosa et al. 2016), the diversity of their MW, hydrophobicity (Log K_{ow}) and oxidation rates (kO_3). Some of these molecules especially the terbutryn, are in the list of the 15 new priority substances which have to be completely removed from all treated WW by 2020 (DIRECTIVE 2013/39/EU). In order to be able to determine low concentrations in permeate when high rejection rate of the membrane are achieved, the feed solution was spiked with 1000 μgL^{-1} of each OMP. All the products were purchased from Sigma-Aldrich France, and were of analytical grade.

2.1.2 Synthetic effluent

As reference matrix, ultrapure water was spiked with 1000 μgL^{-1} of each targeted micropollutants. Before running any experiment with the real MBR effluent, this matrix was used first and served as comparison baseline.

2.1.3 Real effluent

The real effluent was taken from a full scale domestic WWTP equipped with MBR, located close to Montpellier, France. The plant was designed to treat 13,000 m^3/d of domestic wastewater and was performing biological nitrogen removal (nitrification/denitrification).

MBR was equipped with KUBOTA Submerged Membrane Unit (SMU RW400) (KUBOTA, Japan) flat sheet microporous membranes made of chlorinated polyethylene (total surface of 16,240 m²), with an average pore size of 0.2 µm. The characteristics of the MBR permeate are presented in Table 2. The effluent was immediately stored at nearly 4°C after sampling in order to limit the variation of the composition and rewarm at room temperature (20°C ± 1°C) before conducting the experiments. No significant change was observed in the sample characteristics after the storage period.

Table 2: Characteristics of real MBR effluent.

Parameters	unit	Average	Minimum	Maximum
pH		7.40	7.10	7.80
Electric conductivity	µS/cm	3300	2460	3940
TOC	mgC /L	6.70	5.50	8.60
COD	mg O_2/L	19.10	13.60	23.00
Absorbance at 254 nm	cm^{-1}	0.14	0.13	0.16
$SUVA_{254}$	L/mg/m	2.1	1.9	2.4
TSS	mg /L	2.50	2.30	2.70
Ammonium NH_4^+	mg /L	2.00	0.12	4.10
Bromure Br^-	mg /L	1.20	0.95	1.50
Calcium Ca^{2+}	mg /L	134.70	100.70	156.00
Chloride Cl^-	mg /L	602.10	498.40	754.00
Magnesium Mg^{2+}	mg /L	48.50	33.20	67.00
Nitrate NO_3^-	mg /L	9.00	3.00	30.20
Nitrate NO_2^-	mg /L	7.70	0.08	8.00
Orthophosphate PO_4^{3-}	mg /L	10.00	7.94	12.00
Potassium K^+	mg /L	34.10	22.50	44.00
Sodium Na^+	mg /L	321.90	287.00	370.60
Sulfate SO_4^{2-}	mg /L	153.70	144.50	559.50

2.2 Membranes selection and nanofiltration protocol

2.2.1 Membranes selection and characterization

The NF-90 polyamide membrane from DOW Filmtec has been selected for this study. This membrane is considered as a “tight” NF membrane with an estimated MWCO around 150 Da which seems appropriate for the retention of the selected micropollutant. Before experimentation, each membrane has been firstly soaked in ultrapure water to remove preservative agent then compacted at 18 bars for one hour at least or still stability of the flux was reached. Thereafter, these membranes have been fully characterized in terms of permeability and sodium chloride retention.

The NF-90 membrane permeability was determined at 10 bars at 8.4 ± 1.0 L h^{-1} m^{-2} bar^{-1} with a NaCl rejection close to 88 ± 4 %. After experiments, membranes were stored in a 200 mg L^{-1} Na_2SO_3 solution at 4°C.

2.2.2 Cross-flow nanofiltration unit and experimental protocol

An Osmonics Sepa CF II cell (Sterlitech Corp.) was used to carry out the filtration experiments using flat sheet membrane coupons with an effective membrane area of 140 cm^2. A pump (Hydra-Cell, Wanner Engineering, Inc.) was used to feed the Sepa cell with the solution from a 16 L feed vessel. A cryothermostat (F32, Julabo) maintained constant the feed water temperature (20 ± 1 °C) to prevent an increase in liquid flow temperature. During this study, the transmembrane pressure (TMP) was regulated using a micrometric pressure control valve located on the retentate outlet. Experiments were performed at a cross-flow velocity (v_T) of 0.5 m s^{-1} with a spacer in feed channel of 47 Mil (1.194 mm). The bench-scale NF system was operated at a constant TMP of 10 bars all along the filtration experiment until reaching 80% of water recovery (or at least the maximum water recovery reachable). The effect of the pressure on the NF membrane efficiency has been examined at different water recovery rates corresponding to ~0%, 15%, 40% and 60% at 6, 8 and 10 bar pressure. It has to be noted that in order to evaluate the effect of the pressure at a fixed water recovery, the concentrate and permeate was both recirculated into the feed tank.

Finally, after each filtration experiment the NF unit was cleaned by first recirculating caustic soda (NaOH, 2%) solution then acid (HNO_3, 2 %) solution. After each base and acid cleaning, the system is fully rinsed with deionized water until a conductivity of 50 µS cm^{-1} and a neutral pH were reached.

Before the experiment, the feed water was placed in the storage tank and recirculated for 24 h (V_T = 0.5 m s^{-1}) without TMP to ensure that compound adsorption onto pipes and membrane had reached a steady-state. The flux was recording all along the experiment by measuring the permeate weight every 30 second using a scale connected to a computer. Samples were collected from each compartment (feed, concentrated and permeate) for analysis. The volume of the collected sample for different analysis was considered in the mass balance and the apparent rejection calculation. Considering that the NF system is made of stainless steel material, it was assumed that compound (micropollutant or organic matter) adsorption is exclusively occurring on membrane material.

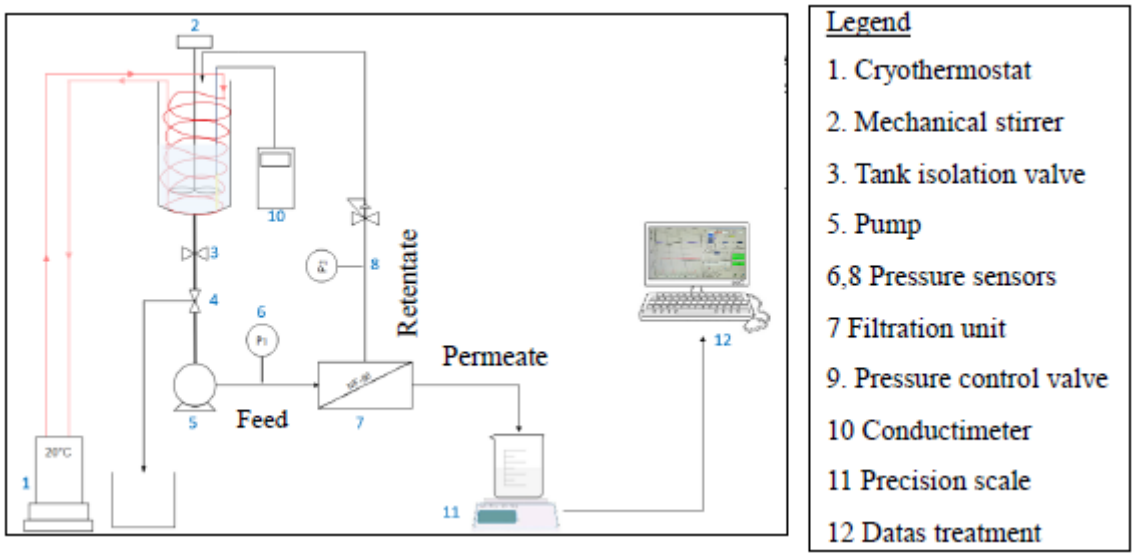


Figure 1: Experimental setup of nanofiltration bench scale pilot.

2.2.3 Fouling characterization

Membrane fouling was estimated considering the flux recovery after different type of washing procedure. Reversible fouling was evaluated first (immediately after experiments) by conducting ultrapure water cleaning. Then, the irreversible organic fouling was evaluated by the determination of flux recovery after 6h of sodium hydroxide (0.1N) cleaning. Finally, the inorganic fouling (scaling) was determined after 6h recirculation of hydrochloride acid (0.1N) cleaning solution. The flux recovery is given by the following equation:.

$$Flux_{recovery} = \frac{J_{initial} - J_{cleaning}}{J_{initial} - J_{final}} \qquad \textit{Equation 1}$$

With:

$J_{initial}$: initial flux measured before the experiment (LMH)

$J_{cleaning}$: flux measured after different cleaning steps (LMH)

J_{final}: final flux measured after the experiment and before the cleaning (LMH)

2.3 Ozone pilot semi-batch ozonation protocol

The ozonation lab-scale pilot consists of a glass stirred batch reactor ($V_{reactor}$ = 3 L) under thermostatic control (20°C) continuously feed by an ozone generator (BMT 803 N) from a

lab-grade pure oxygen tank. Before diffusion in the reactor, the ozone is diluted with the oxygen to achieve a gas flow of 60 L h^{-1} and introduced from the bottom of the reactor through a porous diffuser. An ozone gas analyzer (BMT 964) is used to monitor the gas ozone concentration ($[O_3]_{gas,in}$) after dehumidification. The effect of pre-ozonation on NF process is studied for two different reaction contact times (15 and 30 min) for which indigo method (Bader and Hoigné 1981) was used to determine the dissolved ozone concentration.

Two electro valves connected to a computer are used to determine the desired concentration for the mix oxygen/ozone. During the reaction an agitator is used to homogenized (400 rpm) and increase the ozone dissolution rate in the solution. A recirculating pump is used for sampling. The experiment consists in applying an ozone gas concentration and to determine the transferred ozone doze. Finally the specific ozone doze was defined on a well characterized effluent. Different contact times were tested depending on the parameter the experiment aimed to monitor (0 min to 5 hours).

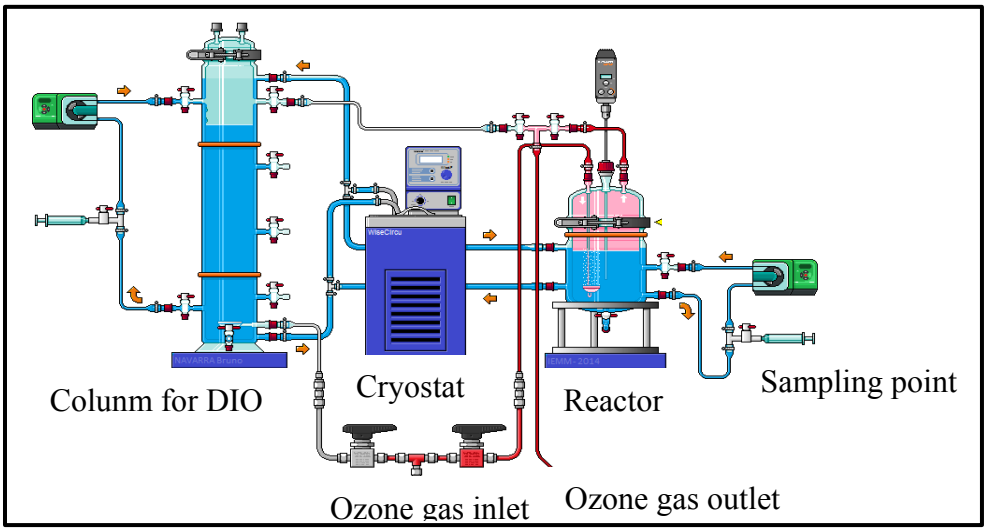


Figure 2: experimental setup of ozonation labscale pilot.

2.4 Evaluation of the nanofiltration (NF) and Ozonation systems performance

2.4.1 Micropollutant analysis by direct LC-MS/MS

Liquid chromatography-tandem mass spectrometry (LC-MS/MS) were used to quantify OMPs and was performed with a Waters 2695 pump, autosampler with a 20 µl loop, a Waters 2695 separation module (HPLC), and a Waters Micromass (Wythenshawe, Manchester, UK) Quattro Micro mass spectrometer equipped with ESI in positive mode. A C18 column (HSS-T3 (100 mm * 2.1 mm, 3.5 µm)) was used with eluent A (90 % HPLC grade water + 10 % HPLC grade acetonitrile (ACN) + 0.1% formic acid) and eluent B (ACN + 0.1% formic acid). The flow-rate was 0.25 mL min^{-1} and the injection volume was fixed at 5 µL. To achieve the

best sensitivity, the MS was adjusted to facilitate the ionization process and the detection conditions were: capillary potential 3.5 kV, cone voltage 25 V, source temperature 120°C, desolvation temperature 450°C, cone gas flow 50 NL h^{-1}, and desolvation gas flow of 450 NL h^{-1}. Nitrogen was used as a nebulizer gas and argon as a collision gas. The collision energy was optimized for each compound (between 14 to 22 V according to the compounds). Each calibration curves were made in the same matrices as the analyte samples to avoid matrix effects on detection (external calibration). Two calibration curves were made, by analyzing standard samples before and after analyte samples, to avoid instrumental drift. Each sample was analyzed in duplicate. The instrument quantification limit (IQL) and the instrument detection limit (IDL) were determined according to a detection limit method based on a signal to noise of 3 and 10 for five replicates. The IQL and IDL obtained in ultrapure water are presented in Table 3.

Table 3: The instrument detection limit (IDL) and quantification limit (IQL) of selected micropollutants analysis in HPLC-MS/MS.

	IDL (µg/L)	IQL (µg/L)
ACT	4.00	11.00
CBZ	3.00	10.00
TER	22.00	65.00
SUL	0.13	0.74
TET	0.40	2.09

2.4.2 Global indicator for pollution monitoring : TOC, UV254 and SUVA analysis

The specific UV absorbance ($SUVA_{254}$) corresponds to the ratio of UV254 absorbance, measured in a 1 cm quartz cuvette using a UV–vis spectrophotometer (UV-2401PC, Shimadzu, Japan) and TOC value (Weishaar et al. 2003). TOC analysis was performed using a TOC-VCSN Shimadzu analyzer (Shimadzu Japan).

2.4.3 NF Removal rate determination

The NF removal rate of any parameter is determined by the difference between the feed and permeate concentrations. It is then divided by feed concentration and expressed in percentage:

$$R = \frac{C_{feed} - C_p}{C_{feed}} \qquad \textit{Equation 2}$$

With:

R : removal rate (%)

C_{feed} : concentration in feed stream

C_p : concentration in permeate stream

2.4.4 Dissolved organic matter (DOM) characterization using 3DEEM fluorescence

A Perkin-Elmer LS-55 spectrometer (USA) was used to produce 3DEEM spectra. Measurements set-up and data analysis were described in details in Jacquin et al. (Jacquin et al. 2017). Samples were scanned in ranges of 200–500 nm and 280–600 nm in excitation (Ex) and emission (Em) respectively at the speed of 1500 nm/min and the increment at 10 nm, while slit width was fixed at 10 nm in excitation and emission. The 3DEEM spectra were divided into five fractions: Region I + II corresponded to aromatic protein-like fluorophores (tyrosine) ranging from Ex = 200–250 nm/Em m = 280–380 nm, Region III was associated tfulvic acid-like fluorophores (Ex = 200–250 nm/Em m = 380–600 nm), Region IV and V corresponded to proteins main derived from soluble microbial product fluorophores (tryptophane) (Ex = 250–350 nm/Em m = 280–380 nm) anhumic acid-like fluorophores and their hydrolysates (Ex = 380–600 nm/Em m = 250–500 nm), respective (Jacquin et al. 2018; 2017; Chen et al. 2003). A MilliQ water control spectra was used to normalize all spectra.

3. Results and discussions

3.1 Performances of NF system

The performances of the NF system has been evaluated on both synthetic and real effluents taking into account the permeate flux and OMPs retention. The experimentations have been conducted during 15-25 hours in order to reach at least 80 % of water recovery (Y=80%). Removal rates of TOC and ions in real MBR effluent have been presented in a previous study (Azais et al. 2014). Depending of the stage of fouling by real MBR effluent (with virgin membrane or with fouled membranes), NF-90 membranes are able to reject between 92% and 98% of TOC, between 83% and 97% of monovalent ions (Cl^-, Na^+, K^+ and NO_3^-) and between 93% and 100% of divalent ions (SO_4^{2-}, Mg^{2+}, Ca^{2+}).

3.1.1 Flux evolution

As a reference baseline, an experiment was conducted on ultrapure water spiked with 1000 µg/L of each selected OMPS. Thereafter, same experiment was conducted (with a new membrane coupon) on real MBR effluent also spiked with OMPS in order to evaluate the

impact of such matrix on water flux decline. The results of these experiments are presented in Figure 3 with the relative flux (ratio between the actual flux and the initial flux) on the y-axis according to the recovery rates on the x-axis:

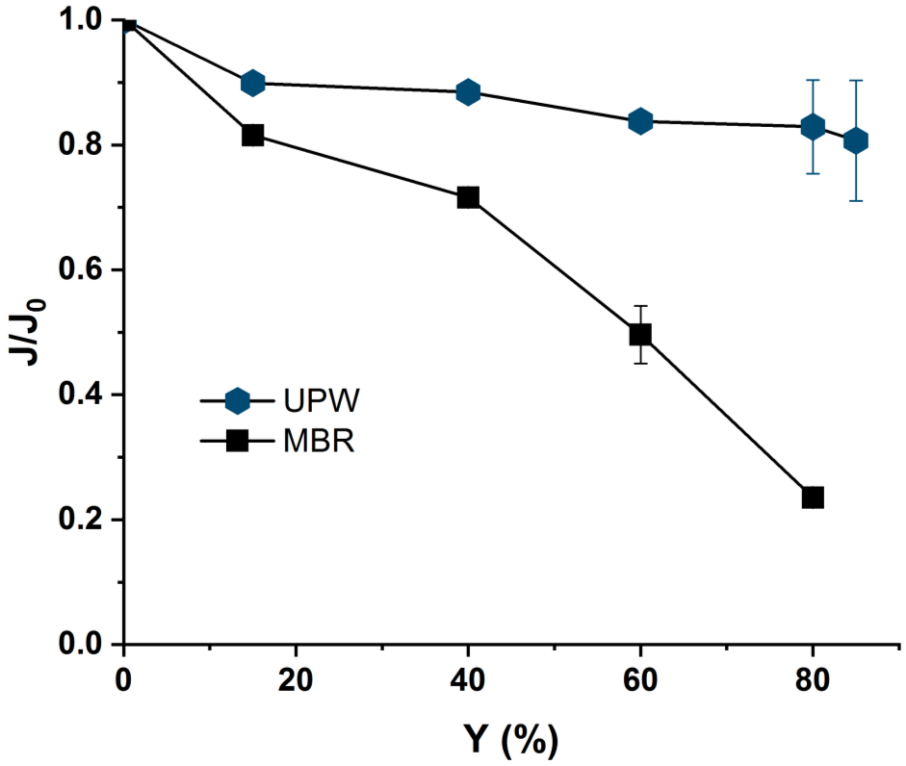


Figure 3: Relative flux evolution for real MBR effluent (MBR eff) and ultra-pure water (UPW): TMP = 10 bars, pH = 7, V = 0.5 $m.s^{-1}$, $J_{0,MBR}$ = 53 LMH, $J_{0,UPW}$ = 63 LMH, Y = 0.1%; 15%; 40%; 60%, 80% and 85%.

The flux decline evolution associated to the filtration of the synthetic solution (the reference baseline) displays only a slight decrease in the flux, 24 % after 17 hours corresponding of 85% water recovery. This might be explained by steric hindrance of higher MW OMPs and adsorption of the most hydrophobic OMPS which reduce slightly the flux. Concerning the real MBR effluent filtration, the flux decrease is much more pronounced up to 68% reduction of the initial flux after 25 hours experiment corresponding to 80% of water recovery. The major factor leading to the flux drop could come from dissolved and colloidal organic matter (DCOM) fouling associated to high molecular weight compounds such as protein-like, fulvic and humic-like substances. Such substances have been identified as revealed by the 3DEEM fluorescence spectrometry (Figure 7).

In addition to the colloidal fouling, the real MBR effluent contains non negligible salts concentration (see Table 2). Considering that tight NF membrane such as NF-90 has relatively high salt rejection, it induces inevitably a difference of salt concentration on both side of the

membrane resulting in a decrease of the driving force due to osmotic pressure difference. Salt concentration increase in the feed compartment with the water recovery resulting in an increasing osmotic pressure.

3.1.2 Monitoring of removal performances during NF: OMPs removal mechanisms

During the previous experiment, samples were taken from NF feed and permeate streams to monitor the influence of recovery rate on selected micropollutants removal. Moreover, to assess the impact of the TMP on micropollutants removal, samples were also picked for each recovery rate at different pressures (6, 8 and 10 bars). Removal rates at 0.1 and 80% recovery rates are shown in Figure 4.

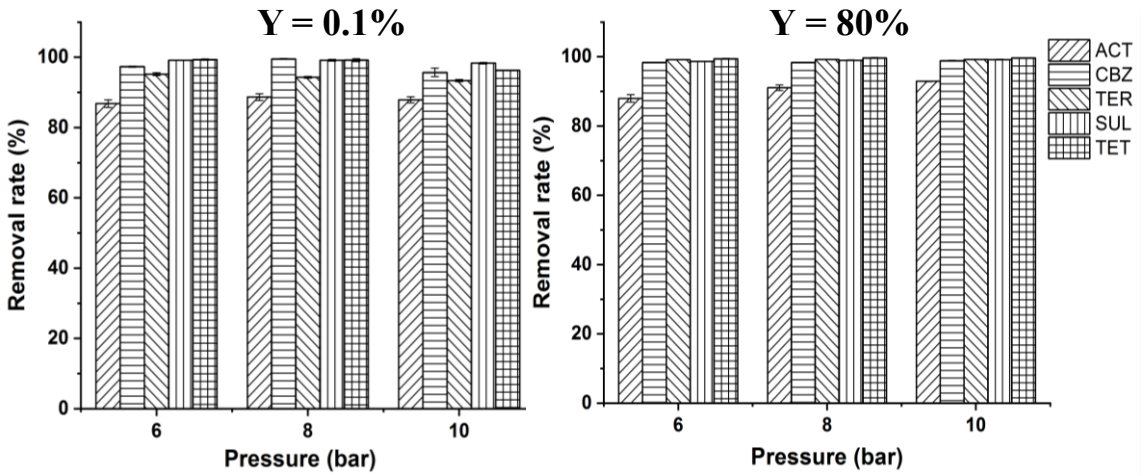


Figure 4: Micropollutants removal efficiency from real MBR effluent using NF-90, TMP = 10 bars, v = 0.5 $m.s^{-1}$, Y = 0.1% and 80%.

Removal rate of micropollutants is related to its molecular weight. The bigger it is, the better the removal is. Except for ACT for which the molecular weight (151 Da) is on the limit of the MWCO of the membrane (estimated to 150-200 Da), a very good removal rate has been observed for all the other selected micropollutants. So the main removal mechanism seems to be steric hindrance as it was also observed by other authors (Garcia-Ivars et al. 2017). These authors noticed an impact of real effluent matrix on the retention of uncharged micropollutants. In our study, additionally to the size exclusion, an adsorption competition test using calcium revealed that the tetracyclin was also adsorbed on the effluent organic matter and that adsorption on organic matter may improve its retention. For the most hydrophobic compounds (Carbamazepin and Terbutryn), interactions with fouled membrane surface might contribute to their removal (Ganiyu et al. 2015). Sulfamethoxazol is charged

negatively and might undergo in electrostatic repulsive interactions with the membrane surface. Thus, electrostatic repulsion could contribute to enhance its removal.

As shown on Figure 4, OMPs removal rate is also linked to the fouling state of the membrane. OMPs removal is lower at 0.1% water recovery where the membrane was unfouled than for the fouled membrane at 80% water recovery. As already observed by other authors, fouling layer constitutes a second barrier to improve the NF membrane removal ability (Azaïs et al. 2014; Azaïs et al. 2016a; Lan et al. 2018).

3.2 Ozonation of MBR real effluent

The ozone-based degradation of dissolved organic matter (DOM) and selected micropollutants was investigated and in this aim, the instantaneous ozone demand (IOD) constitutes a key parameter which was first determined.

3.2.1 Instantaneous ozone demand determination

In order to optimize the specific ozone dose to apply, the IOD and consumption coefficient (k) were firstly determined. The IOD corresponds to the transferred ozone dose (TOD) that is instantaneously consumed by the organic matter of the effluent, with k (mn-1) the consumption kinetics, before any remaining ozone is detected in the outlet liquid phase. The two parameters were determined according to Roustan et al. method and their values are 3.76 mgO_3 / mgDOC (Figure 5) corresponding to a specific ozone doze of 0.56 mgO_3/mgC and 0.064 mn^{-1} respectively (Roustan et al. 1998).

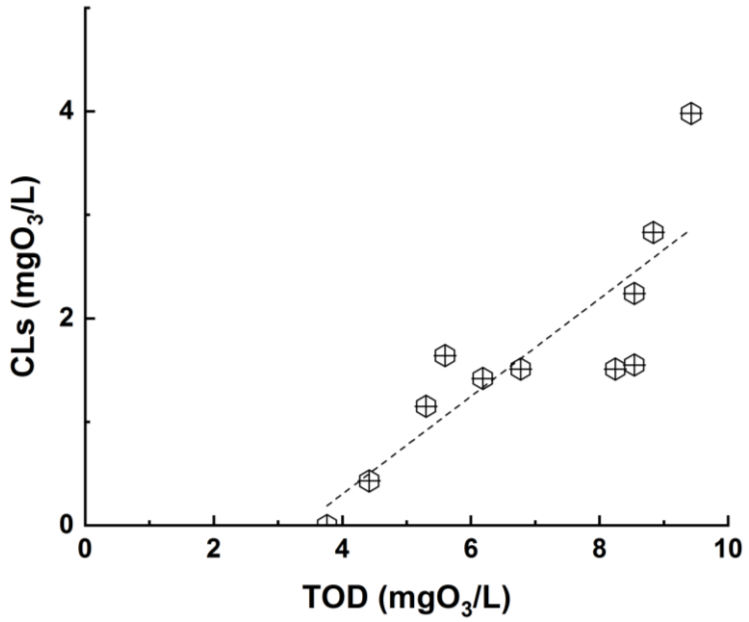


Figure 5: Determination of the instantaneous ozone demand (DIO) with: x-axis : transfered ozone doze and y-axis : dissolved ozone in the outlet liquid phase quantifed by indigo-method. $V_{reactor}$ = 4L, liquid flow rate = 6.7 $.10^{-2}$ m^3/s. contact-time = 10 min.

3.2.2 Ozonation of real wastewater

The ozonation of the real wastewater were monitored through following parameters: UV_{254}, COD and TOC. In order to better understand the phenomenon, the experiments were run for 5 hours, Figure 6 shows the evolution of sub mentioned parameters as a function of both time and ratio TOD/TOC:

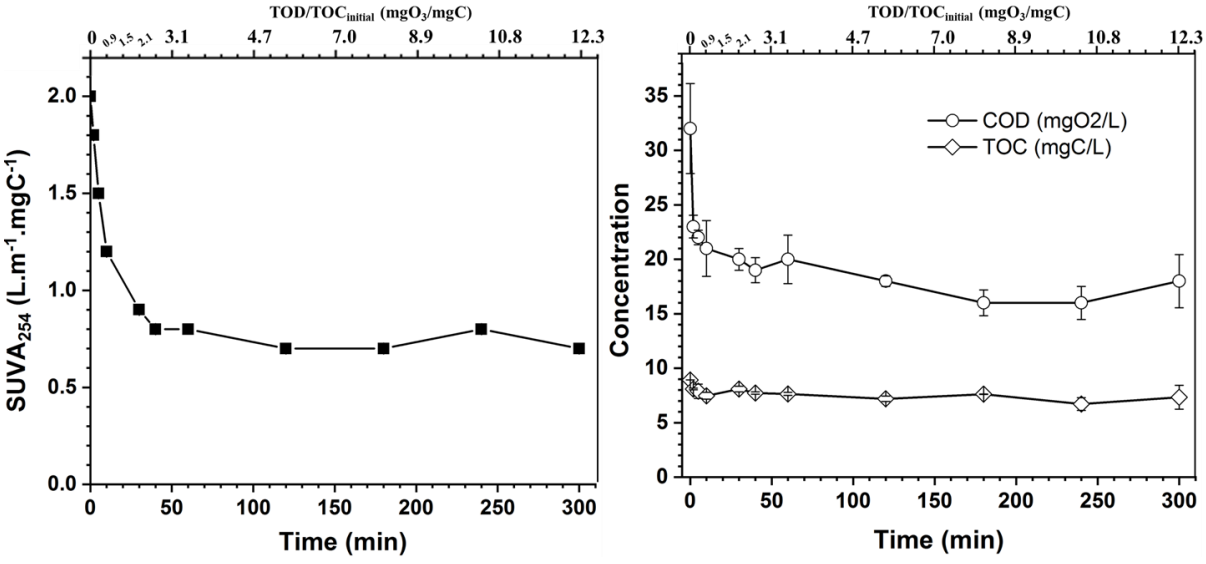


Figure 6: Evolution of global parameter of the real matrix during ozonation. left: $SUVA_{254}$, right: COD and TOC removal, T° = 20 °C, $V_{reactor}$ = 3 L, V_{stir} = 400 rpm, $[O_3]_{gas}$ = 5 gO_3/Nm^3.

It can be seen in Figure 6 that the specific UV absorbance at 254 nm drastically decreases since the beginning of the reaction to stabilize after 30 min (2.1 mgO_3/mgC**)**. Indeed, by attacking the double-bound of the carbon chain monitored throughout the UV absorbance at 254nm, the ozonation process is known to be efficient in aromaticity degradation (Azaïs et al. 2017; Cheng et al. 2016).

Moreover, the COD decreases for 40% from its initial value of 32 mgO_2 /L in the first 15 min to 20 min (1.2 to 1.5 mgO_3/mgC**)** to stabilize around 50%.

As revealed by previous studies (Byun, Taurozzi, and Tarabara 2015; Azaïs et al. 2016b), the curve of TOC degradation over time, confirms the inefficiency of ozone in terms of organic matter mineralization, with only a very slight decrease even after five hours of ozonation (Byun, Taurozzi, and Tarabara 2015). The low change in TOC is not detrimental, because ozonation main goal is to limit the fouling of NF by transforming DCOM into lower MW compounds. The second goal of ozone at this stage is to transform bio-refractory molecules into more biodegradable compounds that should be further biodegraded (after recirculation of NF concentrate to the MBR).

Furthermore, the evolution of organic matter was characterized through three dimensional emission-excitation fluorescence (3DEEM). 3DEEM spectra and the percentage of fractions are illustrated in Figure 7.

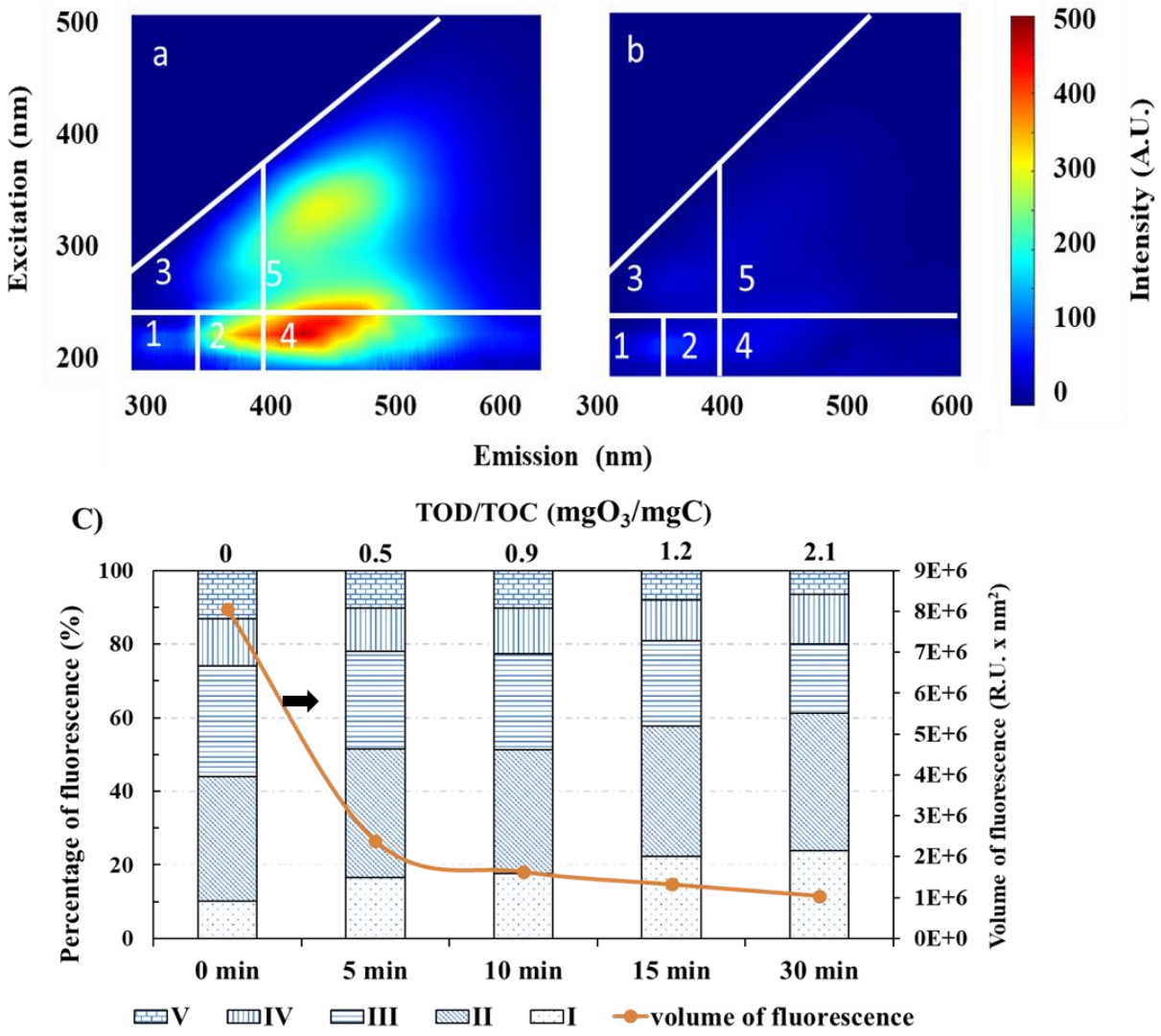


Figure 7: 3DEEM fluorescence spectra and volumes of fluorescence for different fractions of DCOM during ozonation (T° = 20 °C, $V_{reactor}$ = 3 L, V_{stir} = 400 rpm, $[O_3]_{gas}$ = 5 gO_3/Nm^3). a) 3DEEM spectra after 0 min of ozonation; b) 3DEEM spectra after 30 min of ozonation; c) volume and % volume of the five 3DEEM regions. Region I, region II, region III, region IV and region V correspond to aromatic proteins-like type I, aromatic proteins-like type II, fulvic-like, SMP-like and humic-like fluorophores, respectively.

3DEEM spectrum presented in Figure 7.a. demonstrate that MBR permeate is mainly constituted of fluorescent molecules located in the protein-like and SMP-like regions (zones II and III), as well as in the fulvic-like and humic-like substances regions (zones IV and V). Figure 7c shows that DOM repartition in fractions does not change significantly during 30 min ozonation time (2.1 mgO_3/mgC). However, an important decrease of the overall volume of fluorescence was observed after only 5 min ozonation contact time with almost 70% drop, then a slight linearly decrease over time to reach almost 90 % drop after 30min of ozonation (Figure 7.b.). The differences between Figure 7.a. and Figure 7.b. is due to the first 5 min of reaction (0.5 mgO_3/mgC). These results are concordant with the observation of Liu *et al.* who

monitored the evolution of DCOM during ozonation and noticed a significant decrease in the intensities of all DCOM fluorophores after 30 min ozonation contact time (2.1 mgO_3/mgC) (Liu et al. 2016).

3.2.3 Ozonation of micropollutants in real wastewater

During the ozonation of real MBR effluent before coupling with NF, the degradation rate of five selected micropollutants has been monitored for 30 min and the results are presented in Figure 8.

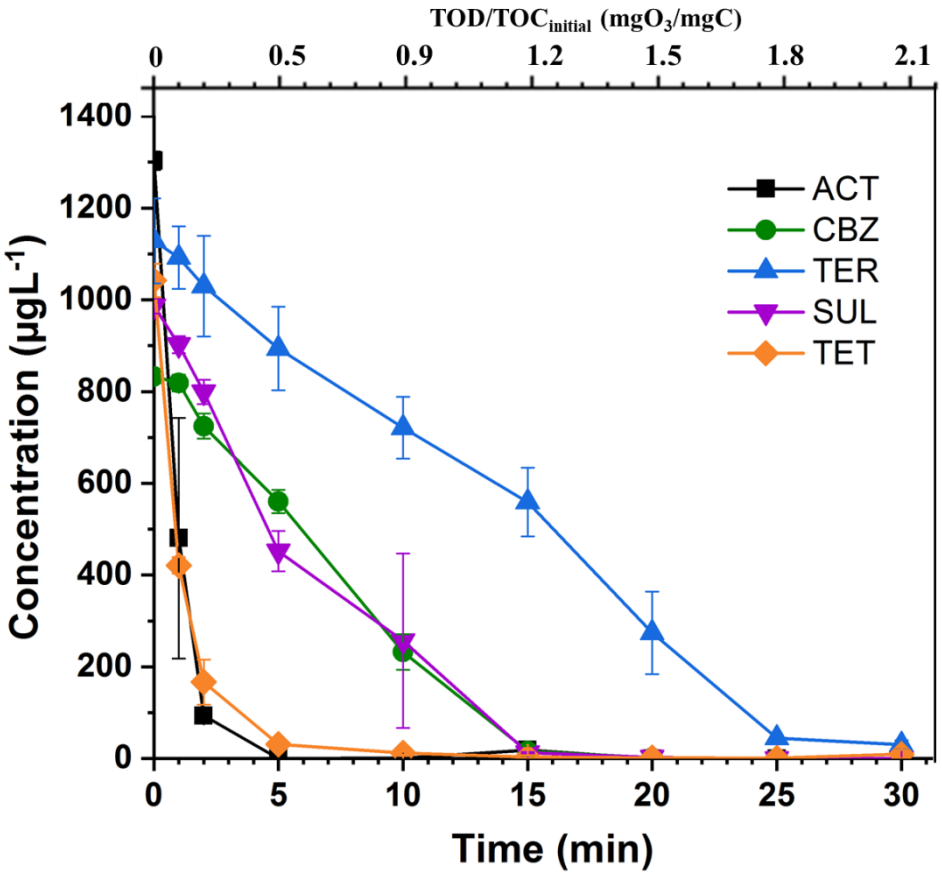


Figure 8: Evolution of OMPs concentration in doped real MBR effluent in function of time of ozonation. $V_{reactor}$ = 3 L, V_{stir} = 400 rpm, $[O_3]_{gas}$ = 5 gO_3/Nm^3.

The monitoring of the degradation of the selected micropollutants revealed three categories of micropollutants: the first group constituted by ACT and TET which shows 90% degradation rate in the first 5 min (0.5 mgO_3/mgC) and total degradation after 10 min (0.9 mgO_3/mgC) of ozonation reaction time. This has been confirmed by some authors who have determined the ozone reactivity kinetics constants (k_{O3}) for these molecules (Hamdi El Najjar et al. 2014; Huber et al. 2003; Khan, Bae, and Jung 2010). For ACT, Najjar et al. obtained 2.6 x 10^6 M^{-1} s^{-1} in pure water and for TET, Khan et al., evaluated the ozone reactivity kinetics constant at 1.9 x 10^6 $M^{-1.}$ s^{-1},(Najjar et al. 2014; Khan, Bae, and Jung 2010). The second

group composed of CBZ and SUL shows 70% degradation in the first 10 min and almost total degradation after 15 min (1.2 mgO_3/mgC) to 20 min (1.5 mgO_3/mgC) of ozonation reaction time. The ozone reactivity kinetics coefficients have been determined in literature for this second group as well. 3.0 x 10^5 $M^{-1.}$ s^{-1} and 2.5 x 10^6 M^{-1} s^{-1} were obtained for CBZ and SUL respectively (Huber et al. 2003). Finally, the third category including TER is the less reactive compound to ozone. 70% of the initial concentration is degraded by ozone after 20 min and only a degradation of 90% to 95% of the initial concentration is achieved after 25 min to 30 min (2.1 mgO_3/mgC) reaction time. Terbutryn is part of a class of micropollutants (triazins) known to be more resistant to ozone degradation; the low reactivity towards ozone of the compound may be explained by stability of triazinic rings (Ormad et al. 2008).

3.3 Impact of pre-ozonation on NF performances

In order to investigate the impact of the pre-ozonation on the nanofiltration performances, some experiments were conducted immediately after MBR effluent ozonation. The performances were compared to that of non-ozonated matrix. As the micropollutants were almost totally degraded during ozonation, their removal was not monitored in ozonated matrix except for the terbutryn which is still present at significant concentration (30 µg/L) but totally eliminated at 80% of water recovery. So the impact of pre-ozonation on NF is limited to the flux and the fouling study.

3.3.1 Impact of pre-ozonation on NF flux evolution

In this section, the impact of ozonation on nanofiltration efficiency (permeability) has been studied. The flux evolution for both reference and real MBR effluent, ozonated and non-ozonated, are presented in Figure 9.

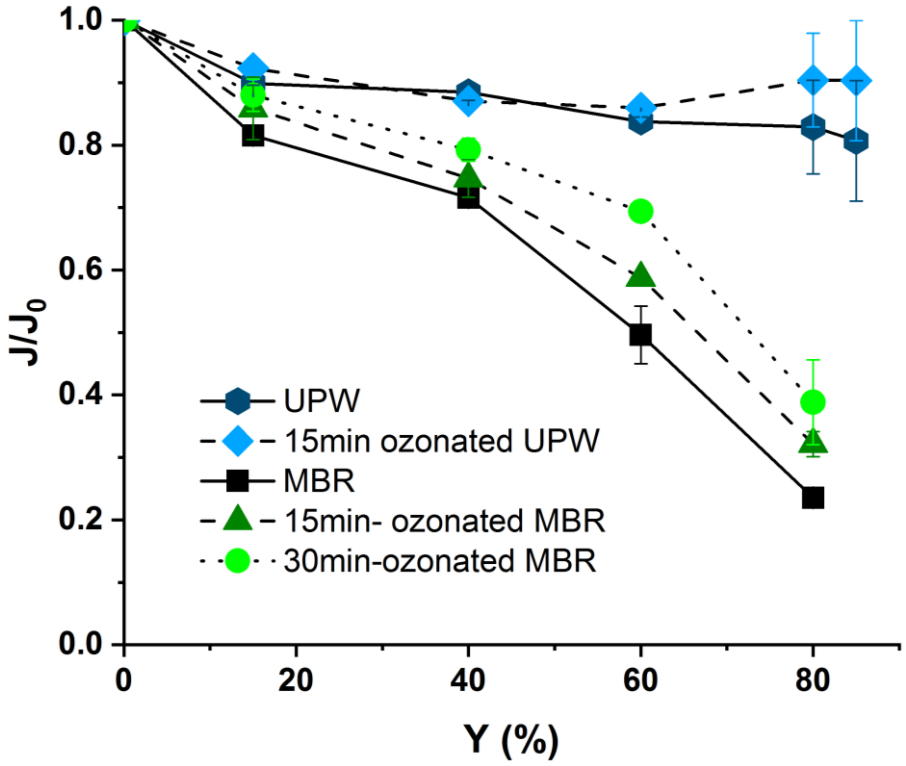


Figure 9 : Monitoring of flux evolution for different ozonated matrixes spiked with micropollutants (1000 µg/L). TMP = 10 bars, v = 0.5 m.s^{-1}. $J_{0,UPW}$ = 63 LMH, $J_{0,UPW+15minO3}$ = 74 LMH, $J_{0,MBR}$ = 53 LMH, $J_{0,MBR+15minO3}$ = 57 LMH, $J_{0,MBR+30minO3}$ =53 LMH. Ozonation conditions: T° = 20 °C, $[O_3]_{gas}$ = 5 gO_3/Nm^3, ozone contact time = 15 min and 30 min corresponding to 1.2 and 2.1 mgO_3/mgC, respectively.

Figure 9 reveals that due to the degradation of DOM (see 3DEEM on figure 7) during the pre-ozonation, the flux decline is always lower in case of ozonated matrix than that of non-ozonated matrix. When the real effluent matrix has been ozonated for 15 min, the flux is slightly improved and the decrease in the initial flux is about 65% (Y=80%). Indeed, nearly 3% and 8% of flux improvement (average) can be observed after 15min and 30min ozonation respectively. These flux improvement on real ozonated effluent can be attributed to the oxidation of the protein-like, fulvic and humic-like substances as revealed by the 3DEEM fluorescence spectrometry (figure 7). Ozonation induced a structural change in DOM by decomposing carbon-carbon double bonds and aromatic rings of humic substances (Cheng et al. 2016; Stylianou et al. 2015). Concerning UPW, no significant change of flux is observed with pre-ozonation, which is logical due to the absence of DOM. It has to be noted that the evolution of the flux in case of UPW spiked or not, indicate that the presence of micropollutants induced a drop flux of about 20% for Y= 80%.

3.4 Fouling and resistance of the NF membrane.

In order to better investigate the impact of the pre-ozonation, the resistance to the flux for both reference and real MBR effluent ozonated and non-ozonated are recapitulated in Table4.

Table 4: Membrane, fouling and total resistances of ozonated and non-ozonated MBR effluents and ultra pure water (UPW) after NF-90 filtrations : TMP = 10 bars, v = 0.5 $m.s^{-1}$, Y = 80%. Ozonation: $[O_3]$gas = 5 gO_3/Nm^3, ozone contact time = 15 min, $[O_3]_{specific}$= 1.2 mgO_3/mgC.

Resistances ($x10^{13}$ m^{-1})	UPW	Ozonated UPW	MBR	Ozonated MBR
R_m	4.06	4.00	4.04	4.08
R_f	3.63	2.33	9.99	6.51
R_{tot}	7.69	6.33	14.03	10.6

Table 4 revealed that the ozonation induced for both matrixes a decrease in the overall resistance. The reduction of the resistance mainly comes from fouling which was structurally modified by the ozonation as shown in Figure 10-a. Moreover, according to the type of washing and subsequent flux recovered, the percentages of reversible and irreversible fouling for reference and real MBR effluent matrixes spiked with micropollutants, ozonated and non-ozonated, were also determined and presented in Figure 10-b.

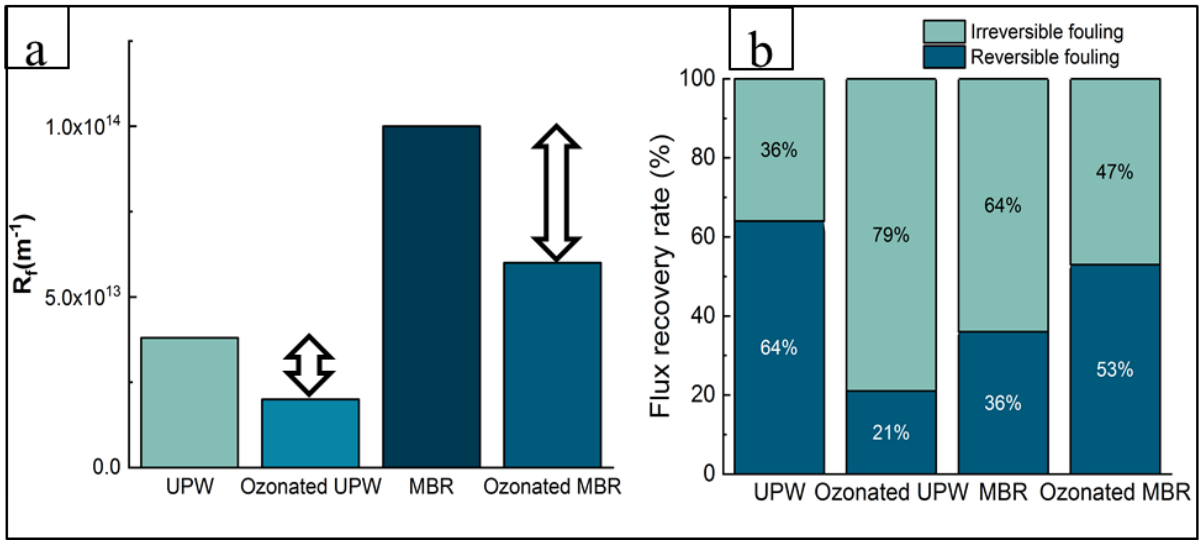


Figure 10: a. Effect of ozonation on fouling and b. resistance in NF-90: TMP = 10 bars, v = 0.5 $m.s^{-1}$, Y = 80%. Ozonation conditions: T° = 20 °C, $[O_3]_{gas}$ = 5 gO_3/Nm^3, ozone contact time = 15 min, $[O_3]_{specific}$= 1.2 mgO_3/mgC.

Figure 10-a revealed that the pre-ozonation induced a decrease of about 40% of the fouling resistance for both matrixes. For instance, from a fouling resistance of 10^{14} m^{-1}, after ozonation of real MBR effluent, the fouling resistance is only about 6.0 x 10^{13} m^{-1}. The fouling characterization confirmed that the pre-ozonation enable a mitigation of the fouling

propensity during NF especially in the case of real MBR effluent, by modifying the DCOM structure which led to a DCOM more hydrophilic and with less propensity to promote irreversible fouling (Park et al. 2017; Vatankhah et al. 2018). In fact, while for the non ozonated MBR effluent only 36% of the initial flux was recovered, up to 53% of the initial flux were recovered by a mere ultrapure water cleaning for membrane fouled by ozonated real MBR effluent (Figure 10-b). The opposite effect was observed in the case of UPW because the fouling mainly came from OMPs. After ozonation, the OMPs were degraded except the terbutryn which might induce a slightly higher irreversible fouling.

4 Conclusion

The overall objective of the paper was to investigate the impact of a pre-ozonation on NF process performances during tertiary treatment of a MBR secondary effluent. Fouling and micropollutants removal mechanisms during nanofiltration experiments with real MBR effluent have been investigated. Degradation of a mixture of five micropollutants and DOM during ozonation were also studied. Fouling investigation revealed that size exclusion was the main mechanism of micropollutants rejection. In addition, gel layer onto fouled membrane formed a supplementary barrier which contributed to enhance micropollutants retention. The micropollutants were globally well retained by NF-90 membrane.

During ozonation, relatively high degardation rates were achieved for micropollutants, requiring different specific ozone doses. In fact, while CBZ and SUL require a specific ozone doze of 1.2 mgO_3/mgC and TER require a specific ozone dose of 1.5 mgO_3/mgC to be degraded, 0.5 mgO_3/mgC are suficient for the degradation of ACT and TET. The dissolved organic matter was significantly degraded as well, by ozone but the overall mineralization rate was low. A forecoming study will investigate the rejection of ozonation by-products by NF-90.

A pre-ozonation enables the fouling resistance to be decreased by almost 40%. To sum up, it was demonstrated that coupling NF to a pre-ozonation process is twicly benefic. Firstly, it degrades well the micropollutants preventing from expensive specific processes in NF retentates management. Secondly, it also mitigates NF fouling by degrading the DOM inducing concomitantly to flux improvement a decrease in membrane cleanning frequency and a subsequent improve of membrane lifetime.

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