COUPLING TERTIARY WASTEWATER TREATMENTS FOR WATER REUSE: MICROPOLLUTANTS ELIMINATION USING NANOFILTRATION, OZONATION AND NATURAL REACTIVE BARRIERS

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Water, a vital resource for the environment, human well-being, and economic development, is increasingly threatened by anthropic activities. Global freshwater use has surged sixfold over the last century, with developed countries showing a remarkably high per capita consumption. Unequal global freshwater distribution results in water stress for over two billion people (UNESCO and Economic Commission for Europe, 2021). Global warming worsens the situation by increasing water demands and decreasing river flows. Water quality also faces threats with the usage of numerous chemical compounds in water by economic activities like agriculture (pesticides and pharmaceutical products), industry or households (pharmaceutical and personal care products, disinfectants, and other chemicals) (Luo et al., 2014).

Wastewater (WW) reuse after adapted treatment represents one of the existing solutions to decrease tension over water resources (Angelakis and Gikas, 2014). However, it is associated with possible health and environmental risks caused by the presence of micropollutants (MPs) and pathogens. Tertiary WW treatments such as ozonation and nanofiltration (NF) are considered effective for the elimination of these pollutants. Indeed, ozone has a strong oxidation capacity and leads to hydroxyl radicals generation during the process (Kwarciak-Kozłowska, 2019). NF membranes have shown excellent organic pollutants, organic matter and pathogens retention abilities. Although effective, these intensive treatments may be energy consuming and expensive. Reactive Barriers (RB) based on low-cost natural materials may also show significant water epuration abilities, strongly depending on their composition. Based on these observations, the coupling between intensive and low-cost treatments appears as promising for WW reuse.

The aim of this study was to evaluate treatment strategies at varying costs to remove MPs and organic matter in the context of WW reuse in Claira (southern France). Firstly, we individually characterized the efficiency of ozonation, NF, and RB, operating under cost-effective conditions, utilizing either low ozone concentrations, low-pressure NF or local natural materials. Then, three combinations of unit operations were tested (Ozonation + RB, NF+ RB, RB only). Three types of RB column experiments were implemented: the first utilized water directly from Claira wastewater treatment plant (WWTP), the second followed ozonation treatment, and the third followed NF treatment. We investigated the elimination of eight pharmaceuticals (native concentrations without spiking) from WW effluent for the three different strategies and at each treatment step.

Treated wastewater (TWW) used in every experiment has been sampled at Claira's city (France) WWTP in december 2023. It is a small plant with a treatment capacity of 4 750 inhabitants equivalent. Treatment train is based on classical pretreatments followed by activated sludge treatment.

Ozonation experiments were performed for 90 minutes in a 3 L ozonation reactor glass stirred semibatch reactor under thermostatic control (20 ± 0.5 °C). The total gas flow was 50 $NL.h^{-1}$ and the inlet ozone gas concentration ($[O_3]_{G,inlet}$) was 5 $g.Nm^{-3}$ to estimate the evolution of the global water quality parameters (COD, Abs_{254}, BOD_5..) and 3 $g.Nm^{-3}$ for micropollutants degradation experiments. Inlet and outlet ozone gas concentration were monitored by an ozone gas analyzer (BMT 964, BMT). The ozone enriched oxygen gas was immediately injected in the glass

reactor by the action of solenoid electrovalves. Dissolved ozone in water was monitored using an ozone sensor (Orbispher C1100, Hach), values were acquired every 30 s. Specific transferred ozone dose ($g_{O3}.g_C^{-1}$) was back calculated after every experiment. The maximum specific transferred ozone dose was 5.8 $g_{O3}.g_C^{-1}$.
NF experiments were performed with a Mexplorer® unit (NX Filtration) using dNF 40® (NX Filtration), a lab scale hollow fiber NF membrane module. The membrane was made of modified polyethersulfone, modification was made through layer-by-layer technique. The module was made of 120 fibers of 19 cm length and 0.7 mm inner diameter, for an average surface filtration of 0.050 m^2. Module operates in inside-out crossflow filtration mode. Feed wastewater was pre-filtered at 100 µm, continuously sitrred and maintained under thermostatic control (20 ± 0.5 °C). The feed flow was fixed at 83 $L.h^{-1}$ (crossflow velocity: 0.5 $m.s^{-1}$). Samples were collected at pressures of 4, 5 and 6 bar for recoveries of 0, 50 and 80 %.
RB were made of materials collected in the vicinity of Claira WWTP, namely alluvial sand, vegetal compost and plane tree sawdust. Materials were crushed and sieved between 200 µm and 2 mm, then mixed with respective volumic proportions of 60%, 25% and 15% for sand, compost and wood. The plexiglass columns had a length of 30 cm and a diameter of 5 cm. Columns were filled with RB from above while they were flooded from the bottom with ultrapure water to avoid air entrapment. Glass balls layers of 5 cm thickness and 100 µm nylon filter disks were placed under and above RB to avoid particles loss and prevent localized water feed inflow onto materials. Feed water was distributed from top to columns bottom at a flow of 0.5 $L.day^{-1}$ using a peristaltic pump (Minipuls 3, GILSON) for 30 days. Temporal monitoring was conducted to study outlet water quality.
Water quality analysis were conducted based on global parameters, including Dissolved Organic Carbon (DOC), $UV_{254\ nm}$ absorption, Biological Oxyen Demand in 5 days (BOD_5), Chemical Oxygen Demand (COD), and Total Suspended Solids (TSS).
MPs were analyzed using High-Performance Liquid-Chromatography coupled to a High-Resolution Mass Spectrometer (HPLC-HRMS) in positive electrospray ionisation mode (ESI +).

Although the elimination kinetics vary from compound to compound, ozonation treatment is highly effective even at low ozone doses. Indeed, after 8 minutes of ozonation (TOD = 0.64 ± 0.06 $g_{O3}.g_C^{-1}$), seven of the eight compounds studied were eliminated over 50%. In 20 minutes (TOD = 1.25 ± 0.10 $g_{O3}.g_C^{-1}$), these same compounds are eliminated over 90%, with only fluconazole being eliminated to a lesser extent (62%). Some of the results obtained are shown below (Fig. 1).

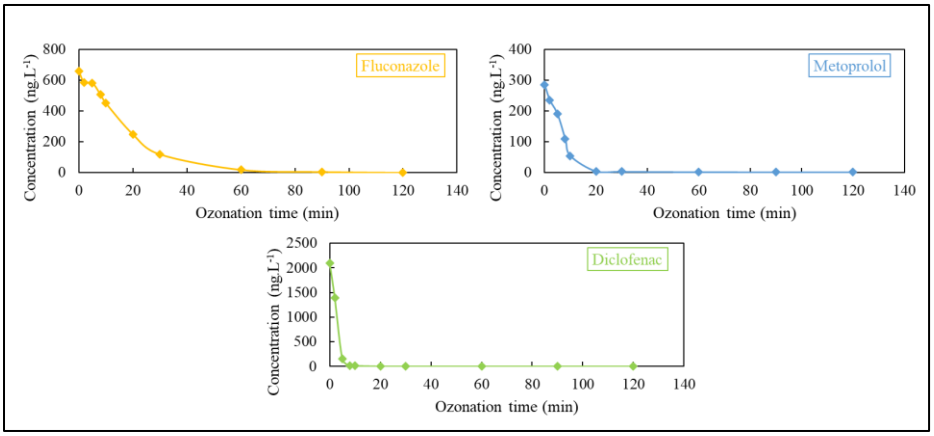

Fig.1: Concentration of micropollutants from TWW during ozonation (Q_g = 50 $L.h^{-1}$, $[O_3]_{G,E}$ = 3 $g.m^{-3}$)

We can distinguish 3 types of compounds according to their reactivity constant with molecular ozone. Fluconazole is a molecule with low reactivity to molecular ozone (k_{O3}=2 $M^{-1}.s^{-1}$), and its elimination is moderate during the initial ozonation phase. Metoprolol (k_{O3}=2.10^3 $M^{-1}.s^{-1}$) and diclofenac (k_{O3}=10^5 $M^{-1}.s^{-1}$) have intermediate and high molecular ozone reactivity respectively and are therefore eliminated more rapidly. Considering these

results, it is obvious that the greater the micropollutant affinity for molecular ozone, the more rapidly it should be eliminated during ozonation. However, for other MPs, competition mechanisms may come into play, particularly considering complex matrices such as TWW. This is notably the case for sulfamethoxazole, whose elimination kinetics are close to those of metoprolol despite its high reactivity to molecular ozone. Conversely, irbesartan has been quickly eliminated: decreasing from 8425 ± 383 ng.L^{-1} to 79 ± 28 ng.L^{-1} in 30 minutes of ozonation despite its low reactivity to ozone (k_{O3}=23 M^{-1}.s^{-1}),suggesting a joint radical mechanism.

Nanofiltration process was also very effective. MPs retention was higher than 75 % for every compound we monitored, carbamazepine excepted (Fig.2)

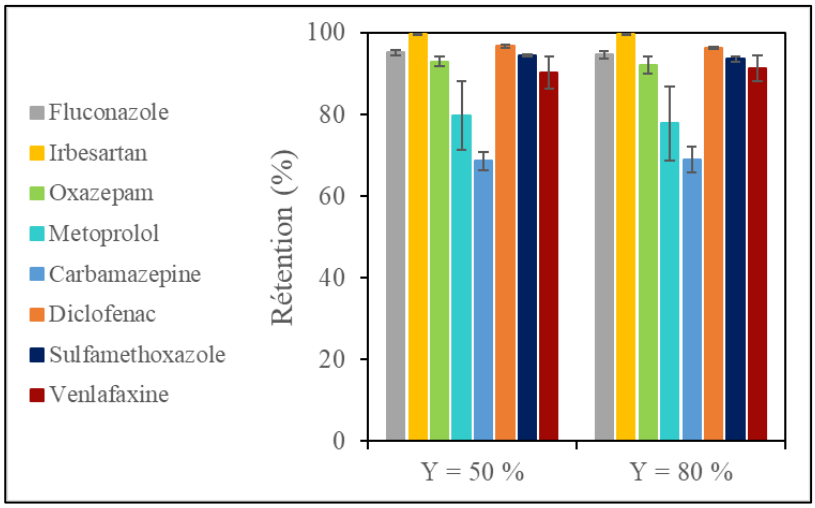

Fig.2: Retention of micropollutants from TWW depending on the NF process recovery (TMP= 5 bars, Permeate flux =55,4 LMH ; 52,6 LMH, Crossflow velocity = 0.5 m.s^{-1})

The only micropollutant with a molar mass above the dNF 40 membrane cut-off (400 g.mol^{-1}) was irbesartan, which, in addition to its negative charge, would explain its very high retention. The retention of other micropollutants may therefore be linked to polar interactions, adsorption phenomena and feed water composition. As the membrane is negatively charged at pH 7-8, it seems consistent that negatively charged molecules in the TWW, such as diclofenac and sulfamethoxazole, are strongly retained due to charge repulsion. Conversely, the positively charged metoprolol is less retained due to weak membrane repulsion. The high retention of venlafaxine, which is also a positively charged molecule with a mass close to metoprolol, remains to be explained. For the other compounds, neutral in the TWW, retention is mostly governed by steric exclusion (de Grooth et al., 2014). In that case, the higher the molar mass, the greater the retention. As neutral micropollutants are below the membrane molecular weight cut-off value indicated by the manufacturer, it is possible that this value has been overestimated. It is also well-known that MPs can interact with the organic matter in the TWW to form larger complexes that are better retained (Azaïs et al., 2016).

RB efficiency was diverse, highly depending on MPs characteristics. Tracer experiments were conducted before real water injection started. It allowed us to determine micropollutants behaviors in the columns, such as adsorption or biodegradation. Feed water composition must be considered when interpreting these results, as saturation of adsorption sites is more likely to happen for TWW, rather than NF permeate or ozonated TWW. Moreover, using non treated materials has clearly favored microbial growth, as biofilms were detected during the first days of injection. Eventually, this microbial growth led to intensified biodegradation comparing to other studies using materials bought in stores.

Operating in cost-effective conditions, ozonation and NF can still be very effective. They decrease the WW effluent organic load and lead to a substantial reduction of micropollutants. Although they can very well remove certain MPs, RB efficiency is more tributary of contaminants characeristics. As when working in cost effective conditions, intensive processes do not eliminate the entire micropollutant load, RB could be very relevant as a final WW treatment step.

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