Journal of Environmental Management 370 (2024) 122728

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Comparative life cycle assessment of non-thermal plasma for the removal of pharmaceuticals from wastewater

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ARTICLE INFO

Keywords:
Life cycle analysis
Non-thermal plasma
Membrane technology
Advanced oxidation
Contaminants of emerging concern
Wastewater treatment

ABSTRACT

Wastewater effluents are a continuous source of pharmaceuticals in water bodies, which pose a serious environmental threat to aquatic ecosystems. This work provides a comprehensive technical, environmental and cost assessments of different advanced quaternary treatments for wastewater effluents, with special focus on novel Non-Thermal Plasma technology. For this porpouse Non-Thermal Plasma, Sand Filtration + Ozonation, Ultrafiltration, Ultrafiltration + Nanofiltration and Ultrafiltration + Reverse Osmosis technologies were compared with UV disinfection-based technology. This work applies the Life Cycle Analysis tool for the impact environmental assessment using both ReciPE 2016(H) method and, for a more detailed analysis of the contribution of pharmaceuticals to freshwater ecotoxicity category of impact, the USETOX method, which was integrated with 7 new characterisation factors. The results obtained showed overall removal efficiency of pharmaceuticals always higher than 80%, with performances in descending order of Ultrafiltration + Reverse Osmosis > Sand Filtration + Ozonation > Ultrafiltration + Nanofiltration > Non-Thermal Plasma, being Sand Filtration + Ultraviolet disinfection and standalone Ultrafiltration comparatively not suitable for pharmaceuticals removal. Regarding the target pharmaceuticals proposed on the EU Directive 271/91 revision, the Non-Thermal Plasma perform better towards venlafaxine than Sand Filtration + Ozonation, and towards diclofenac and carbamazepine than Ultrafiltration + Nanofiltration. Ultrafiltration + Nanofiltration and Non-Thermal Plasma showed better environmental performance than Sand Filtration + Ozonation and Ultrafiltration + Reverse Osmosis in 7 out of 18 categories of impact (ReciPe method), with Ultrafiltration + Nanofiltration being more advantageous than Non-Thermal Plasma in human and ecotoxicity-related categories of impact, and Non-Thermal Plasma more advantageous in Global Warming, Fossil Resource Scarcity, and Fine Particulate Matter Formation. Regrading Freshwater Ecotoxicity (USEtox method), the quaternary treatment configuration and its energy demand affect the Freshwater final value of impact more than the presence of pharmaceuticals. Under the conditions tested, the Non-Thermal Plasma provided the lower OPEX (0.24 € m^{-3}) than other tested technologies, showing an interesting compromise between pharmaceuticals removal efficiency, environmental impacts, and economic operational cost.

1. Introduction

With the advance of analytical techniques, over 600 different active ingredients of pharmaceuticals compounds (PhCs) have been detected in wastewater, drinking water, and aquatic environments (European Commission, 2023a; German Environment Agency, 2023; Norman Association, 2023) in 70 countries worldwide. These represent an increasing concern for water quality as PhCs can potentially affect plant photosynthesis (Taschina et al., 2022), be responsible for endocrine disrupting effects of aquatic species (Kwak et al., 2018), and, in the case of antibiotics, can act as promotors for antimicrobial resistance (Ajo et al., 2018; Manaia et al., 2018).

Urban wastewater effluents (WW) are a continuous source of PhCs in water bodies.This occurs because conventional Wastewater Treatment Plants (WWTP) have limited removal efficiency of these contaminants (Back et al., 2018; Rizzo et al., 2020), which on average in Europe does not exceed 45% in the absence of advanced treatment (van Dijk et al., 2023).

It is commonly accepted that monitoring every pharmaceutical

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https://doi.org/10.1016/j.jenvman.2024.122728
Received 4 May 2024; Received in revised form 13 September 2024; Accepted 29 September 2024

Abbreviations

AOP	adanced oxidation process
CBZ	carbamazepine
CIT	citalopram
CLAR	clarithromycin
DCF	diclofenac
DBD	dielectric barrier discharge
LCA	Life cycle assessment
NF	nanofiltration
NTP	non-thermal plasma
OZ	ozonation
PCD	pulsed corona discharge
PE	population equivalent
PhCs	pharmaceuticals compounds
RO	reverse osmosis
SF	sand filtration
UF	ultrafiltration
UV	ultraviolet disinfection
VFX	venlafaxine
WW	wastewater
WWTP	wastewater treatment plant
UWWTD	urban wastewater treatment directive

potentially present at WWTP discharge is neither feasible nor plausible, and a framework is needed to provide a short list of meaningful indicators that can address both ecosystems and human health relevance (Alcade-Sanz and Gawlik, 2017).The European Union (EU) has proposed, in the revision of the Urban Wastewater Treatment Directive (UWWTD) (European Commission, 2022), in the first stage, a minimum average removal efficiency of 80% for a defined set of harmful organic micro-pollutant substances at large-scale WWTP facilities (>100,000 PE). This set includes 10 PhCs, among them carbamazepine (CBZ), citalopram (CIT), clarithromycin (CLAR), diclofenac (DCF), and venlafaxine (VFX), which were considered meaningful indicators of pharmaceutical contamination. To achieve these forthcoming regulatory requirements, upgrading the existing WWTP with advanced quaternary treatment units is required (van Dijk et al., 2023).

It must also be noticed that 11% of Europeans are affected by water scarcity and that only 1 billion m^3 of treated WW is reused annually when there is potential to reuse 6 times more (European Commission, 2023b). Thus, the application of more stringent limits for treated WW discharge, as proposed by UWWTD (European Commission, 2022), can reduce WWTP PhCs discharge impacts and improve overall WW effluent quality, contributing to achieve the standard required by Dir 741/2020 (European Parliament and the Cuncil, 2020)European Parliament and the Cuncil, 2020 for later water recast.

Advanced wastewater treatment for PhCs removal has been explored through an array of technologies, such as UV-irradiation (Surra et al., 2021), adsorption (Verliefde et al., 2007), membrane separation (Giacobbo et al., 2023; Verliefde et al., 2007), and advanced oxidation processes (AOP)(Gerrity et al., 2010; Issaka et al., 2022; Rizzo et al., 2020). Among AOP, the research of atmospheric Non-Thermal Plasma (NTP) applications has recently gained visibility due to its potential to form a broad spectrum of physical and chemical phenomena, such as radicals (H•; O•; OH•) and other oxidizing species, shock waves and UV light, all without the use of chemical reagents (Hijosa-Valsero et al., 2014; Jiang et al., 2014; Vanraes et al., 2016). The combination of these phenomena allows a more effective and diversified action in treating various organic pollutants (Vanraes et al., 2016). Different NTP reactor configurations, based on dielectric barrier discharge (DBD) or pulsed corona discharge (PCD), have been successfully applied to remove PhCs (Ajo et al., 2018; Back et al., 2018). Despite being considered a competitive technology for treating PhCs in WW (Gerrity et al., 2010; Magureanu et al., 2015), NTP applications of NTP at significant scale and on real non-synthetic effluent matrixes for pharmaceutical removal in WW are still extremely limited (Ajo et al., 2018; Back et al., 2018; Gerrity et al., 2010).

The selection of the best technological solution must be based on the best trade-off between technical performance, environmental sustainability, and operating costs. Life cycle analysis (LCA) is a well-established and scientifically recognized tool for the assessment of the environmental impacts, thus the environmental sustainability, associated with a product, technology, or service (ISO, 2006a, 2006b). To the author's best knowledge, only 4 LCA studies are present in the literature analyzing pharmaceutical removal from WWTP effluents with advanced treatment technologies. Li et al. (2019) compared, through both the TRACI and USEtox methods, the environmental impacts associated with three advanced WW treatment processes designed to remove 126 PhCs and Personal Care Products (PCP) from WWTP effluent. Namely, ozonation (OZ) followed by sand filtration (SF) and disinfection (OZ + SF + D), was compared with granular activated carbons (GAC) followed by SF and disinfection (GAC + SF + D) and hallow fiber microfiltration (MF) followed by reverse osmosis (RO) (MF + RO). The results demonstrated that the 126 PCP contributed to toxicity-related categories of impact in all three configurations studied with an increase in ecotoxicity by 0.48%–5%, and human cancer and non-cancer toxicity increase by 1%–5%. Moreover, the scenario MF + RO was considered the least environmentally advantageous of all studied scenarios as it had the highest electricity and chemical consumption, whereas GAC + SF was considered the most advantageous one. Additionally, electricity was identified as the key factor and contributed with the highest percentage to acidification, global warming, ozone depletion, and smog air impact categories (Li et al., 2019). Similar results were obtained by Surra et al. (2021) that electricity consumption of the advanced oxidation treatment processes based on Anodic Oxidation has the most pronounced impact on the LCA results and that the use of renewable energy is the only way to reduce the overall environmental burdens of quaternary treatment for PhCs. Differences were, however, observed in the direct impacts associated with pharmaceutical emissions, since in Surra et al. (2021) the contribution of PhCs can be considered negligible, whereas, in the study of Li et al. (2019) the joint presence of PhCs and PCP represents a minor, but not a negligible contribution.

Zepon Tarpani and Azapagic (2018) elaborated a LCA (ReCiPe 2008 method) of GAC, NF, solar photo-fenton (SPF) and OZ technologies aimed at reducing the freshwater ecotoxicity potential of PhCs. Among them, on average, NF had the lowest impacts for 13 out of 18 categories considered. GAC was the best alternative for five impacts categories, including metals and water depletion, but it had the highest marine eutrophication. SPF and ozonation were considered the least sustainable for eight categories of impacts, including ecotoxicity and climate change.

On the other side, Gallego-Schmid et al. (2019) evaluated four advanced process options for the removal of micro-contaminants, among them the PhCs, from real effluents, and observed that SPF performed better environmentally with rather than without NF.

For the first time, this work compares (i) the technical performance, (ii) the environmental impact through LCA, and (iii) the operational costs of novel NTP technology and more consolidated advanced treatments of SF + OZ, UF, UF + NF, UF + RO, and with the SF + UV disinfection technology, providing key performance information that could be used for the future developments and applications of these technologies.

2. MATERIALS and METHODS

2.1. Selected WWTP

A NTP, UF, UF + NF, SF + OZ, and UF + RO pilot scale quaternary units were implemented at a municipal WWTP located in northern Portugal. This WWTP has secondary treatment, serves 300,000 PE, treats up to 66,700 m^3 of effluent per day, and discharges the treated effluent into the Atlantic Ocean. A fraction of this effluent (<10%) undergoes further SF + UV tertiary treatment for internal water reuse.

2.2. Tertiary and quaternary treatments set-up

The existing SF + UV tertiary treatment, used as a reference scenario, consists of two double-stage multilayer vertical SF in series (FV2B, Degrémont, France), and an UV open channel disinfection unit with low-pressure lamps (UV3000 Type B, Trojan Technologies Inc., Canada). This UV unit comprises a channel with 5 parallel banks x 8 lamps, with UV lamp unitary emission of 26.7 W and intensity of 190 μW cm^{-2} at 1 m. Aluminium sulphate was added as a coagulant agent (100 mg L^{-1}) to the SF stage. This unit operates intermittently with a 100 m^3 h^{-1} flowrate.

The NTP pilot unit consisted of a 50 L tank equipped with a dielectric barrier discharge (DBD) plasma generator (500Hz, 40W) (model IXS-500-KISS, SFC Umwelttechnik GmbH, Austria). The DBD plasma is generated in the gaseous phase in the presence of 20 L min^{-1} air flow, supplied by an air pump (model EL-250W, Secoh Shangai Mec. Ltd, China). The ionized gas is bubbled through the WW effluent by a 35 mm diffuser hose (Wagner Vertiebs GmbH, Germany) installed at the bottom of the tank. The NTP pilot unit was operated in batch for 1h. Fig. S1 reports the NTP unit set-up.

The UF unit was a containerized unit with an industrial scale (Model CONT-UF C001, AQUASMART- Water and Wastewater Treatment Solutions, Lda., Portugal), fed with WW effluent and equipped with 128 submerged UF modules of high-density polyethylene hollow fiber membranes of average pore size of 20 nm and active filtration surface of 768 m^2. The UF was operated at a continuous flow rate of 9 m^3 h^{-1} (average flux of 7.7 L m^{-2} h^{-1}). Backwashing was performed using sodium hypochlorite (NaOCl 13%) (1.5 g m^{-3} $_{WW}$), sodium hydroxide NaOH (32%) (0.014 mg m^{-3} $_{WW}$) and citric acid ($HOC(CH_2CO_2H)_2$ 40%) (0.43 g m^{-3} $_{WW}$) solutions.

The NF pilot unit (Model RBQ 002 NF, AST– Soluções e Serviços de Ambiente, Lda., Portugal), was implemented in series after the UF unit pre-treatment (UF + NF), according to the set-up in Fig. S2. NF unit is equipped with spiral-wound membrane modules, with pore size 150–300 Da and total active area of 26.4 m^2. The NF was operated in continuous, with a processing flow rate of 1.8 m^3 h^{-1} at 10 bar (average flux of 30.3 L m^{-2} h^{-1}). Membrane washing was performed using citric acid ($HOC(CH_2CO_2H)_2$ 40%) (7.15 μg m^{-3} $_{WW}$), alkaline agent (Ultrasil 11, Ecolab, Portugal) (2.41 g m_{WW}^{-3} NaOH, 2.41 g m_{WW}^{-3} ethylenediaminetetraacetic acid (ETDA), 0.38 g m^{-3} $_{WW}$ sodium bicarbonate, and 0.16 g m_{WW}^{-3} sodium dodecylbenzenesulfonate), and an antiscalant (Vitec 4000, Kurita, Germany) (0.054 g m^{-3} $_{WW}$).

The OZ pilot unit (Industrie De Nora S.p.A., Italy) comprises an ozone generator (Steriline MCP1-A), and a bubble column reactor where the ozone is introduced at the bottom through diffusers and mixed with the recirculated effluent. The OZ unit was operated continuously with an ozone dose of 88 g O_3 m^{-3} and a flowrate of 1.2 m^3 h^{-1}, with a contact time of 2 min.

The RO pilot unit was equipped with spiral-wound polymeric membrane modules (Borum rejection >90%) with a total installed active area of 57 m^2 (Model RBQ 002 OI, AST – Soluções e Serviços de Ambiente, Lda., Portugal). The average flux was 23.2 L m^{-2} h^{-1} at a pressure of 18 bar, with a flowrate of 2.2 m^3 h^{-1}. The RO was applied in continuous mode in series with the UF unit (UF + RO), according to the set-up in Fig. S3. Membrane washing was performed using citric acid ($HOC(CH_2CO_2H)_2$ 40%) (0.82 g m^{-3} $_{WW}$), alkaline agent (Ultrasil 11, Ecolab, Portugal) (34 g m^{-3} $_{WW}$ NaOH, 34 g m^{-3} $_{WW}$ EDTA, 5.2 g m^{-3} $_{WW}$ sodium bicarbonate, and 2.2 g m^{-3} $_{WW}$ sodium dodecylbenzenesulfonate), and an antiscalant (Vitec 4000, Kurita, Germany) (1.6 g m^{-3} $_{WW}$).

2.3. Wastewater sample Collection and analysis

Grab samples of the inlet and outlet effluent of the tertiary treatment studied were collected and refrigerated at 4 ° C until use. WW samples were submitted to physical-chemical analysis by an accredited external laboratory using standard methods for 5-days Biological Oxygen Demand (BOD_5), Total Suspended Solids (TSS), turbidity, Total Nitrogen (N-Total), Total Phosphorous (P-Total) and Ammonia (N-NH_4). The PhCs analysis was performed according to the method developed by Paíga et al. (2019). This method employs Solid Phase Extraction with a Strata-X cartridge for extraction. Analysis was performed using Ultra-High-Performance Liquid Chromatography coupled with Tandem Mass Spectrometry (UHPLC-MS/MS). UHPLC-MS/MS analysis was performed by injecting 5 μL of the extracted sample in a Shimadzu Nexera UHPLC system (Shimadzu Corporation, Kyoto, Japan) equipped with two LC-40D XS solvent delivery modules, a DGU-20A 5R degasser, a SIL-30 AC autosampler, a CTO-20 AC column oven, a CBM-20A system controller module, and coupled to a triple–quadrupole mass spectrometer detector LCMS–8030 with an electrospray ionization source. Chromatographic analysis was performed using a Cortecs®UPLC®C18+column (100 × 2.1 mm i.d.; 1.6 μm particle size) from Waters (Milford,MA, USA) for CBZ, CIT, CLAR, and VFX determination and a Kinetex C18 column (2.6 × 150 mm i.d., 1.7 μm particle size) from Phenomenex, Inc. (California, USA) for DCF determination. Quantification of PhCs was made by internal standard calibration method, based on linear regression.

2.4. Life cycle assessment

2.4.1. Goal and scope

Based on the obtained results of the pilot scale tests, which were properly adapted, upscaled, and integrated with literature data, a LCA was developed according to ISO 14040 (ISO, 2006a)and 14,044 (ISO, 2006b) standards. This LCA compares the environmental impacts generated by NTP, UF, UF + NF, SF + OZ, and UF + RO quaternary treatments, with SF + UV already present in the WWTP studied and taken as reference scenario (Fig. 1). For this comparison, 1 m^3 secondary effluent was chosen as a functional unit (FU), since it is consistent with the goal of the study and with the functions of the systems (Sills et al., 2020).

The reference scenario of this work applies to the SF + UV tertiary treatment unit currently operating at the WWTP for the disinfection of secondary effluent for WW internal reuse, considering 10% reuse of the WWTP treated effluent. It is assumed that the SF + UV unit operates continuously during 350 d y^{-1}, 24 h d^{-1}, including SF backwash and maintenance as the WWTP. The electric energy needed for SF + UV tertiary unit operation is bought from the national grid.

The LCA was performed according to a “cradle-to-gate” approach within the system boundaries reported in Fig. 1. This analysis did not include capital goods, but only spare parts such as UV lamps, UF and NF filtration modules, and chemical reagents used during ordinary maintenance activities. The allocation of the impacts was developed following the system expansion methodology according to the “avoided-burden method”, as proposed by Clift et al. (2000). This methodology consists of the identification of the products obtained, that can replace less sustainable products already present in the market or the depletion of a natural resource. In this study, this product is identified in the natural freshwater, whose depletion is avoided if treated WW is reused for urban or agricultural irrigation purposes. All the data used to calculate the impacts related to the five scenarios studied are of high

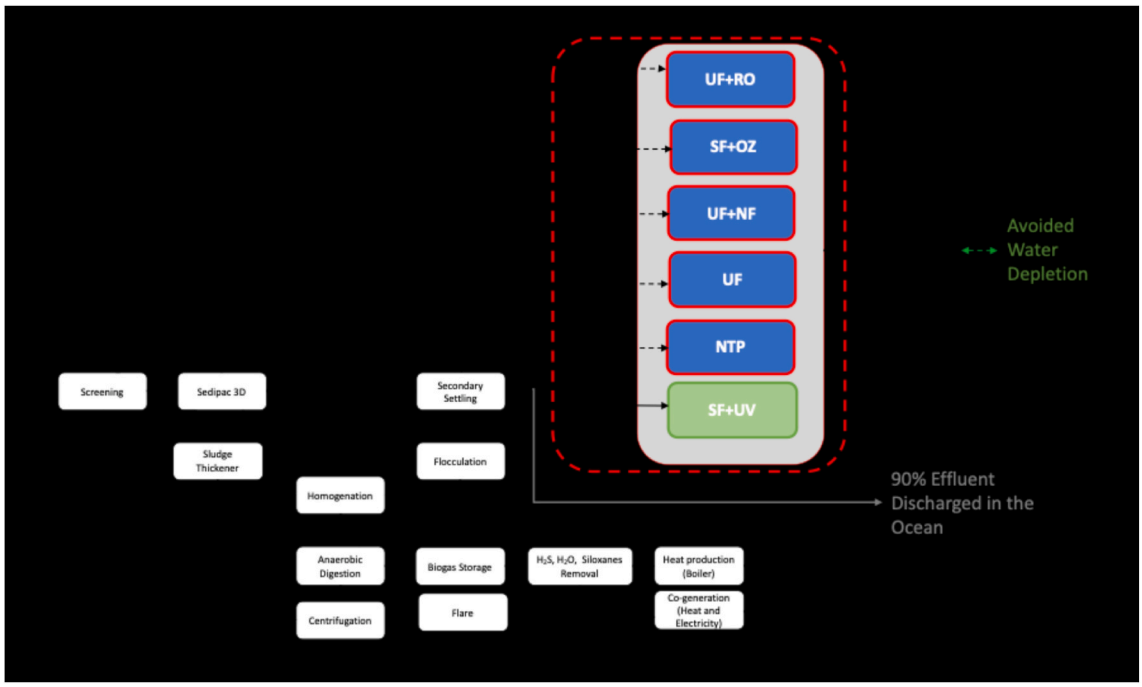

Fig. 1. Flowsheet of the system. Green box represents the base case scenario of Sand Filter (SF) coupled with UV-disinfection (SF + UV). Blue boxes are the alternative scenarios of Non-thermal Plasma (NTP), Ultrafiltration (UF), UF + Nanofiltration (UF + NF), SF + Ozonation (SF + OZ), and UF + Reverse Osmosis (UF + RO). The dashed red line represents the system boundary. Grey lines refer to the upstream WWTP. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Life Cycle Inventory of the scenarios Sand Filter + UV-disinfection (SF + UV), Non-Thermal Plasma (NTP), SF + Ozonation (SF + OZ), Ultrafiltration (UF), UF + Nanofiltration (UF + NF), SF + Ozonation (SF + OZ) and UF + Reverse Osmosis (UF + RO). All values are referred to the functional unit (1 m^3 secondary effluent).

	Unit	SF + UV	NTP	UF	UF + NF	SF + OZ	UF + RO
INPUT							
Secondary Effluent[a]	m^3	1	1	1	1	1	1
Spare parts							
UV Lamps	item	2.96×10^{-5}					
Membranes UF			–	2.18×10^{-4}	2.18×10^{-4}		2.18×10^{-4}
Membranes NF	m^2		–		2.83×10^{-3}		–
Membranes RO							1.29×10^{-3}
Reagents							
Aluminium Sulphate	kg	0.1				0.1	
Citric Acid (40%)			–	2.87×10^{-3}	3.69×10^{-3}		1.43×10^{-2}
Sodium Hydroxide (32%)			–	1.46×10^{-4}	2.56×10^{-3}		3.38×10^{-2}
Hypochlorite (13%)			–	2.95×10^{-2}	2.95×10^{-2}		2.95×10^{-2}
TAPwater			–	4.39×10^{-3}	4.47×10^{-3}		5.46×10^{-3}
Sodium bicarbonate					3.75×10^{-4}		5.23×10^{-3}
EDTA					2.41×10^{-3}		3.36×10^{-2}
Energy and Fuel							
Electric Energy	kWh	0.16	2.0	0.26	0.77	3.05	0.92
OUTPUT							
Tertiary Effluent [(a)]	m^3	1	1	1	1	1	1
Avoided Product/Resource							
Water/Natural Resource	m^3	1	1	1	1	1	1
Waste/Landfill/Treatment							
Hazardous waste for underground deposit (UV-lamp)	unit	2.96×10^{-5}					
Waste plastic, treatment of waste plastic, mixture, and sanitary landfill (UF, NF, RO membranes)	kg			1.7×10^{-3}	2.1×10^{-3}		2.96×10^{-3}

[a] The chemical composition of the WW (affluent and effluent) is reported in Table S3.

quality since they were obtained from pilot scale tests at the WWTP or derived from the laboratory assays.

This LCA study was developed using SimaPro 9.1.7 software package from PréConsultant, equipped with Ecoinvent v.3.1 database, applying the ReCiPe2016 Midpoint H v.1.04 (ReCiPe)(Huijbregts et al., 2016). For a more accurate assessment of Freshwater Ecotoxicity category of Impact, USEtox 2 (recommended + interim) v.1.04 (USEtox)(Bijster et al., 2018) was used since ReCiPe methodology does not include a representative list of Characterisation Factors (CF) for all the PhCs detected in the studied WW effluents.

Regarding CFs, 8 of the target PhCs were included in the USEtox method and 12 CFs were retrieved from literature (Li et al., 2019; Ortiz de García et al., 2017) and integrated into the method. 7 new CFs were calculated using the calculation sheet method USEtox 2.13 (USEtox, 2023). Physical-chemical properties, degradation rates, and data on bioaccumulation in fish were obtained with the Estimation Program Interface Suite v4.1 (from now on, EPISuite™) (USEPA, 2013). Ecotoxicological effects (avlogEC50) were calculated using experimental data taken from ECOTOX knowledge database (US EPA, 2023). The avlogEC_{50} was calculated using values of half maximal effective concentration (EC_{50}) or median lethal concentration (LC_{50}), preferably given for three different trophic levels: algae, crustacea, and fish. Tables S1 and S2 report the physical-chemical properties and degradation, bioaccumulation and ecotoxicity data, respectively, used for the calculation of the 7 new CFs. All CFs used, included 7 new CF_S are listed in Table S8.

2.4.2. Life Cycle Inventory

Table 1 summarizes the Life Cycle Inventory (LCI) of all the direct and indirect inputs, as well as the avoided product/resources and wastes associated with the SF + UV, SF + OZ, SF + RO, UF, UF + NF and NTP quaternary treatments studied. Table S3 reports the chemical characterization, which in this case corresponds to the LCI of the effluent before and after the quaternary treatments, and integrates Table 1.

Based on the information reported in section 2.1, since the tests of the UF, UF + NF, SF + OZ and UF + RO units were not normalized to the existing tertiary unit of SF + UV, used as reference base scenario (100 $m^3\ h^{-1}$), scale factors have been applied to the overall electric energy and reagents consumption measured during UF, UF + NF, SF + OZ and UF + RO operations, respectively. This approach can lead to some uncertainties in the results due to the scale effect but allows an initial comparison of the quaternary treatment studied at the current stage of development.

For the assessment of the indirect impacts associated with the production process of citric acid 40% v/v, sodium hydroxide 32% v/v, sodium hypochlorite 13% v/v, the corresponding production processes included in the Ecoinvent v.3.1 database were used. Since in the Ecoinvent v.3.2 database, these reagents are modelled at higher concentrations (i.e, citric acid 99% v/v, sodium hydroxide 50% v/v, sodium hypochlorite 15% v/v) the final amount of these reagents was recalculated considering an additional amount of ultrapure water (UP) for the dilution. The environmental impact associated to the use of antiscalant Vitec 4000 were kept out of the scope of the study due to the lack of reliable data for the main ingredient production process (1-hydroxyethylidene)bisphosphonic acid, sodium salt). The observed amont of concentrate resulting from UF + NF and UF + RO technologies was negligible, thus no further treatment was considered for these wastes in the present LCA.

2.5. Operating costs assessment

Operational costs (OPEX) associated with the treatment of 1 m^3 of WW secondary effluent, as accounted by the authors during the pilot scale experiments (Table S4), included the electric energy consumption cost, calculated on the Portuguese rates (0.12 € kWh^{-1}), and the unitary costs for the chemicals and for the spare parts (membranes and UV lamps) at the time of the experiments.

3. Results and Discussion

3.1. Removal efficiency of pharmaceuticals

Over 25 PhCs were frequently detected in the WWTP secondary effluent, with an average total pharmaceutical content of 16.8 μg L^{-1}. The overall removal efficiency of PhCs observed for the tested technologies was, in descending order, UF + RO > SF + OZ > UF + NF > NTP > UF > SF + UV, with average percentages removal of 98%, 92%, 89%, 86%, 29%, and −0.4%, respectively (Fig. 2a). These results demonstrate clearly that SF + UV and standalone UF technologies are not suitable for the pharmaceutical removal. UV irradiation as normally applied to disinfection processes at WWTP (10–80 mJ cm^{-2}) has been shown to have very low impact on PhCs removal (Kim et al., 2009; Noutsopoulos et al., 2014; Pablos et al., 2013). Several studies have also reported removals below 50% for UF applications (Acero et al., 2010; Ajo et al., 2018; Ferreiro et al., 2020), since UF membranes have molecular weight cut-off (MWCO) within the 10–100 kDa range, which is an order of magnitude higher than the molecular weight of most PhCs (<1 kDa) (Jermann et al., 2009).

Either AOP based on NTP or OZ, as well as NF and RO filtration, allowed overall average removal efficiencies higher than 80%, including for the detected UWWTD targeted compounds (Fig. 2b). These results are corroborated by previous literature data available for the more consolidated technologies such as ozonation and membrane-based ones (Ajo et al., 2018; Back et al., 2018; Gerrity et al., 2010; Giacobbo et al., 2023; Surra et al., 2021). Only for UF + NF less than 80% individual removal values were observed for CBZ and DCF, with 79% and 74%, respectively (Fig. 2b). Other studies performed with clooser (400–600 Da) and tighter (<200 Da) NF membranes, suggest that the MWCO of the membrane used could also justify these results for CBZ and DCF (Comerton et al., 2008; Yoon et al., 2007).

Although other PhCs properties, such as hydrophobicity, polarity, and water solubility, can also impact the PhCs rejection, in this study such correlations were not identified for the PhCs evaluated (Comerton et al., 2008; Yoon et al., 2007).

The NTP showed a high removal capacity for each of the individual UWWTD detected in the secondary effluent, with average removal of 87%, 100%, 100%, 97.5% and 84.7%, for CBZ, CIT, CLAR, DCF and VFX, respectively (Fig. 2b), which were comparable to the oxidation performance of SF + OZ pilot tested. For DCF and CBZ, these NTP values are higher than those reported by Back et al. (2018) for a continuous stand-alone DBD-based reactor treating secondary WW, with reported removal of 71% and 67% for DCF and CBM, respectively, achieved with lower electric energy per order (EEO) values (0.089 vs 0.49 kWh m^{-3} for DFC, and 0.081 vs 0.86 kWh m^{-3} for CBZ). Ajo et al. (2018) reported for a PCD-based batch recirculating reactor treating effluents from health institutions, complete removal of 17 PhCs detected, applying an energy level of 1 kWh m^{-3}, while comparatively in our study a lower level of 0.8 kWh m^{-3} was used for overall removal of 86%. It must be noticed that some PhCs showed poor removal with NTP, or even negative (Table S5). These results can be partly due to PhCs reformation of transformation products, as suggested for ibuprofen (Ajo et al., 2018), accumulation of intermediate species for a parent PhCs such as epoxicarbamazepine for CBZ oxidation, or PhCs subjected to hydrolysis, as possible for acetylsalicylic acid to salicylic acid (de Jesus Gaffney et al., 2017). Although these remaining PhCs combined were a small mass fraction of the initial total content (11%), there is room for further development and optimization of the NTP design used for the purpose of this LCA study, with a focus on gas-liquid mass transfer improvement, which is one the most frequent appointed limitations of NTP reactors (Nippatlapalli et al., 2022). Additionally, NTP had an impact on the reduction of TSS and CBO_5 in the treated effluent, with 13.4% and 19.8%, respectively, which is consistent with other NTP studies in WW (Back et al., 2018), which

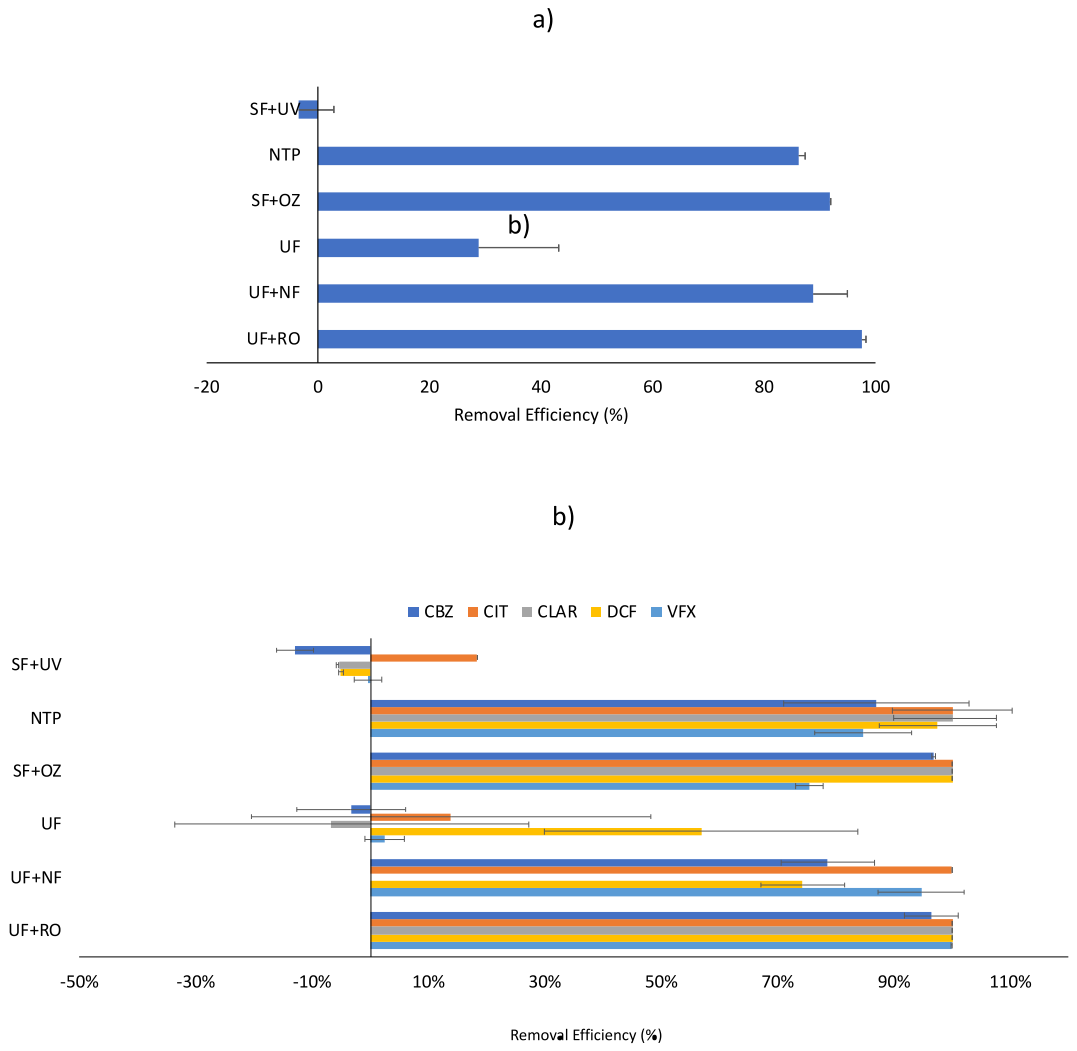

Fig. 2. Removal efficiency of pharmaceuticals (%) calculated on average and standard deviation ($\mu \pm \sigma$) for: a) total detected pharmaceuticals WW effluent, b) target UWWTD pharmaceuticals (CBZ, CIT, CLAR, DCF, VFX).

reported the occurrence of little mineralization of dissolved organic matter (chemical characterization data presented in Table S3). Further BOD_5 or nutrient removals with NTP could be acheived trhough additional pre-treatment processes, evethough this is not commonly expected for a WWTP quaternary treatment. These overall results obtained with real WW demonstrate that NTP can be an effective technology for quaternary treatment of urban effluents and compliance of UWWTD PhCs removal.The results obtained can be considered as reference for further scaling up, taking into consideration that the final integration into a WWTP is site and technology specific.

3.2. Life cycle assessment

3.2.1. Total environmental impacts assessment

Table 2 reports the results of the environmental impacts, calculated by ReCiPe method, in the 18 categories considering direct WW discharge ("Treated water discharged in the ocean") (columns 2–8, Table 2) and the reuse of 100% of the treated WW for urban or agricultural irrigation ("Treated water reused for irrigation") (columns 9–14, Table 2).

The results obtained for "Treated water discharged in the ocean" showed that at MidPoint Level, the quaternary treatments SF + UV and UF, which are those characterized by lower removal efficiency (Fig. 2a), provide the best environmental performance in 12 and 7 out of the 18 categories analyzed, respectively, with UF showing the second lowest values in the remaining 6 categories (column 3–4, Table 2). These environmental benefits are observed in the most relevant categories, which are: Terrestrial, Freshwater, and Marine Ecotoxicity, Human Non-Carcinogenic and Carcinogenic Toxicity, Global Warming, Fine Particulate Matter Formation, and Fossil Resource Scarcity. Analyzing the quaternary treatments with an average removal efficiency higher than 80% (UF + NF, NTP, SF + OZ and UF + RO), it is observed that UF + NF and NTP showed better environmental performance than SF + OZ and UF + RO in 7 out of 18 categories of impact, with UF + NF being more advantageous than NTP in human and ecotoxicity-related categories of impact, and NTP more advantageous in Global Warming, Fossil Resource Scarcity, and Fine Particulate Matter Formation. SF + OZ and UF + RO, which are the treatments which provided the highest removal efficiencies of PhCs, are, at the condition tested, characterized, as well, by higher environmental burdens than all other quaternary treatments (columns 7–8, Table 2). Among these latter, SF + OZ is more advantageous in the categories of the impact of Global Warming, Fine Particulate Matter Formation, Fossil Resource Scarcity, and Land Use, whereas UF + RO in the categories of impact related to Human and Ecosystems toxicity, which is intuitive due to the fact that OZ is a energy-based technology, when UF + RO are membrane-based.

The LCA literature related to advanced treatments for PhCs removal is currently very scarce. The few existing studies also differ significantly in terms of goals, boundaries, functional units, assumptions, and impact

Table 2
Total environmental impacts calculated with Recipe method for SF + UV, UF, UF + NF, NTP, SF + OZ, and UF + RO quaternary treatments considering direct discharge and water reuse. All values are referred to functional unit (1 m^3 treated water). A scale color is used to highlight the severity of impact in each category (red corresponds to the highest value of impact, and green cells correspond to the lowest ones).

Category of Impact	Unit	Treated water discharged in the ocean						Treated water reused for irrigation					
		SF+UV	UF	UF+NF	NTP	SF+OZ	UF+RO	SF+UV	UF	UF+NF	NTP	SF+OZ	UF+RO
Terrestrial ecotoxicity	kg 1.4-DCB	9.2×10^{-1}	1.2	2.4	4.1	6.9	3.8	5.4×10^{-1}	8.0×10^{-1}	2.0	3.7	6.5	3.4
Human non-carcinogenic toxicity	kg 1.4-DCB	2.8×10^{-1}	3.4×10^{-1}	6.0×10^{-1}	8.2×10^{-1}	1.5	1.6	1.2×10^{-1}	1.8×10^{-1}	4.4×10^{-1}	6.6×10^{-1}	1.3	9.9×10^{-1}
Marine ecotoxicity	kg 1.4-DCB	3.1×10^{-2}	4.1×10^{-2}	8.7×10^{-2}	1.7×10^{-1}	2.8×10^{-1}	1.3×10^{-1}	1.3×10^{-2}	2.4×10^{-2}	7.0×10^{-2}	1.5×10^{-1}	2.6×10^{-1}	1.2×10^{-1}
Global warming	kg CO_2 eq	6.2×10^{-2}	1.5×10^{-1}	5.0×10^{-1}	1.5×10^{-1}	2.8×10^{-1}	6.3×10^{-1}	-3.4×10^{-2}	5.8×10^{-2}	3.8×10^{-1}	5.3×10^{-2}	1.8×10^{-1}	5.3×10^{-1}
Freshwater ecotoxicity	kg 1.4-DCB	2.4×10^{-2}	3.7×10^{-2}	7.0×10^{-2}	1.4×10^{-1}	2.6×10^{-1}	1.1×10^{-1}	1.0×10^{-2}	1.9×10^{-2}	5.6×10^{-2}	1.3×10^{-1}	2.1×10^{-1}	9.1×10^{-2}
Fossil resource scarcity	kg oil eq	1.6×10^{-2}	3.8×10^{-2}	5.6×10^{-2}	3.4×10^{-2}	6.5×10^{-2}	1.4×10^{-1}	-1.2×10^{-2}	8.0×10^{-3}	2.6×10^{-2}	4.0×10^{-3}	3.5×10^{-2}	1.1×10^{-1}
Human carcinogenic toxicity	kg 1.4-DCB	3.2×10^{-2}	7.6×10^{-3}	1.3×10^{-2}	1.7×10^{-2}	5.7×10^{-2}	3.0×10^{-2}	2.7×10^{-2}	3.0×10^{-3}	8.0×10^{-3}	1.2×10^{-2}	5.2×10^{-2}	2.5×10^{-2}
Water consumption	m^3	1.003	1.005	1.009	1.012	1.021	1.018	2.0×10^{-3}	4.0×10^{-3}	8.0×10^{-3}	1.2×10^{-2}	2.0×10^{-2}	1.8×10^{-2}
Marine eutrophication	kg NOx eq	3.7×10^{-2}	3.5×10^{-2}	2.9×10^{-2}	1.7×10^{-2}	4.0×10^{-2}	1.8×10^{-3}	3.7×10^{-2}	3.5×10^{-2}	2.9×10^{-2}	1.7×10^{-2}	4.0×10^{-2}	2.0×10^{-3}
Land use	m^2a crop eq	5.0×10^{-3}	9.5×10^{-3}	1.4×10^{-2}	3.5×10^{-3}	3.5×10^{-3}	5.4×10^{-2}	-1.6×10^{-2}	-1.1×10^{-2}	-7.0×10^{-3}	-1.7×10^{-2}	-1.1×10^{-2}	3.3×10^{-2}
Mineral resource scarcity	kg Cu eq	2.7×10^{-3}	1.1×10^{-3}	1.8×10^{-3}	2.3×10^{-3}	6.0×10^{-3}	3.1×10^{-3}	2.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}	2.0×10^{-3}	6.0×10^{-3}	3.0×10^{-3}
Ionizing radiation	kBq Co-60 eq	5.0×10^{-3}	9.3×10^{-3}	9.3×10^{-3}	1.8×10^{-3}	7.6×10^{-3}	2.2×10^{-3}	-3.1×10^{-2}	-2.7×10^{-2}	-2.7×10^{-2}	-3.4×10^{-2}	-2.8×10^{-2}	-3.4×10^{-2}
Terrestrial acidification	kg SO_2 eq	6.0×10^{-4}	5.0×10^{-4}	9.0×10^{-4}	1.0×10^{-3}	2.1×10^{-3}	2.2×10^{-3}	2.0×10^{-4}	1.0×10^{-4}	5.0×10^{-4}	6.0×10^{-4}	1.7×10^{-3}	1.8×10^{-3}
Ozone formation, Human health	kg NOx eq	2.0×10^{-4}	3.0×10^{-4}	4.0×10^{-4}	4.0×10^{-4}	8.0×10^{-4}	1.0×10^{-3}	0.0	1.0×10^{-4}	2.0×10^{-4}	2.0×10^{-4}	6.0×10^{-4}	8.0×10^{-4}
Ozone formation, Terrestrial ecosystems	kg NOx eq	2.0×10^{-4}	3.0×10^{-4}	5.0×10^{-4}	4.0×10^{-4}	8.0×10^{-4}	1.0×10^{-3}	0.0	1.0×10^{-4}	2.0×10^{-4}	2.0×10^{-4}	6.0×10^{-4}	8.0×10^{-4}
Fine particulate matter formation	kg PM2.5 eq	2.0×10^{-4}	3.0×10^{-4}	5.0×10^{-4}	4.0×10^{-4}	8.0×10^{-4}	1.3×10^{-3}	0.0	1.0×10^{-4}	2.0×10^{-4}	2.0×10^{-4}	6.0×10^{-4}	1.0×10^{-4}
Freshwater eutrophication	Kg P eq	0.0	1.0×10^{-4}	1.0×10^{-4}	1.0×10^{-4}	2.0×10^{-4}	3.0×10^{-4}	0.0	0.0	1.0×10^{-4}	0.0	1.0×10^{-4}	3.0×10^{-4}
Stratospheric ozone depletion	kg CFC11 eq	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

assessment methodologies (Zepon Tarpani and Azapagic, 2018), and, but not less important, in the way the results are presented (absolute values or percentages of contribution), which limits the comparison. With the aim of providing some benchmarks, the comparison with Zepon Tarpani and Azapagic (2018) work, showed that ozonation is less advantageous than NF technology, confirming the results obtained in this work. The comparison of the absolute values of impact obtained, properly normalized to the same functional unit Zepon et al. refers the results to 1000 m^3 treated water, whereas in this study 1 m^3 is used as F. U.) showed that this work presents in the most relevant categories, values of impact similar to those observed by Zepon et al. either in NF (i.e, Global Warming 0.47 kg CO_2 eq *vs* 0.19 kg CO_2 eq, Freshwater ecotoxicity 0.07 kg 1.4 DCB eq *vs* 0.15 kg 1.4 DCB eq, Fossil Resource Scarcity 0.05 kg oil eq *vs* 0.06 kg oil eq) and in OZ (i.e, Global Warming 0.27 kg CO_2 eq *vs* 0.35 kg CO_2 eq, Freshwater ecotoxicity 0.22 kg 1.4 DCB eq *vs* 0.35 kg 1.4 DCB eq, and Fossil Resource Scarcity 0.06 kg oil eq *vs* 0.1 kg oil eq). The existing discrepancies may be due to the different energy and reagents consumption, to different system boundaries, and, not less important, to different calculation method (ReCiPe *vs* TRACI). It must be noticed that Zepon et al. retrieved the LCIA input data from several previous published literature and not directly measured on-site at pilot scale on the field at the same WWTP plant, as in the case of the present work, thus inevitably giving rise to some differences. The comparison of OZ treatment with membrane filtration associated to RO technology performed by Li et al. (2019) based on TRACI 2.0 methodology stated that membranes and RO treatment "appeared" to have a higher environmental burden than OZ, due to the high energy and material consumption during the treatment process. In this work both UF + RO and SF + OZ showed higher environmental burdens in 8 out of 18 of the impact categories analyzed, being UF + RO less advantageous in Global Warming and Fossil Resource Scarcity, whereas SF + OZ is less environmental advantageous in Ecosystem and Human Health Toxicity related categories of impact, thus setting the two technologies in an apparent position of equity, even if in this study UF + RO seems less advantageous in the categories of impact related directly to human health, thus more significant in the common adopted scale of values, confirming the Y. Li's et al. statement.

The comparison of the results obtained by Bordbar et al. (2022) for RO and NF + RO-based water desalinisation unit showed values higher in Global Warming and Fossil Resource Scarcity, due to significant discrepancies in the electric energy consumption between UF + RO unit of this work (0.97 $kWh.m^{-3}$) and Bordbar et al. (2022) work (3.11–4.22 $kWh.m^{-3}$), and lower in Human Toxicity and Marine Eutrophication categories of impact, due to the expected reduced amount of chemicals required for the desalinisation plant, rather than for a WW treatment unit, which is confirmed by the comparison of the life cycle inventories of this work with that of Bordbar et al. (2022).

The reuse of water allowed to reduce the total environmental impacts in all the categories of impact in the range from 62 % (SF + OZ) to 195% (NTP), with a reduction of 20%, 64%, 35% and 15%, and 53%, 89%, 47% and 21% in the categories of impact of Global Warming and Fossil Resource Scarcity (Columns 13–14, Table 2) for the UF + NF, NTP, SF + OZ, and UF + RO treatments, respectively.

In absolute values these results means that, taking as reference the WWTP studied in this work, 0.096 kg CO_2 eq, 0.014 kg 1.4 DCB eq, Freshwater ecotoxicity, 0.031 kg oil eq can be saved per m^3 of treated WW whatever technology is applied, thus means that 80.3 t CO_2 eq, 11.8 t 1.4 DCB eq, and 25.3 t oil eq can be saved per year at the reference WWTP. Thus, the reuse of treated WW has always to be preferred than direct discharge for its environmental benefits.

3.2.2. *Processes contribution to total environmental impacts*

Fig. 3a–d report the process contribution to the total impact of the quaternary treatments studied for the categories of impact of Global Warming (kg CO_2 eq), Fossil Resource Scarcity (kg oil eq), Freshwater, Marine and Terrestrial Ecotoxicity (kg 1.4 DCB eq) and Human Cancerogenic and Non-Carcinogenic Toxicity (kg 1.4 DCB, eq) according to ReCiPe method. The analysis reported in this section does not include the presence of PhCs.

In the Category of Global Warming impact, electricity consumption represents the 100% and 82% of the total impact value of oxidation-based technologies of NTP and SF + OZ, respectively, whereas the

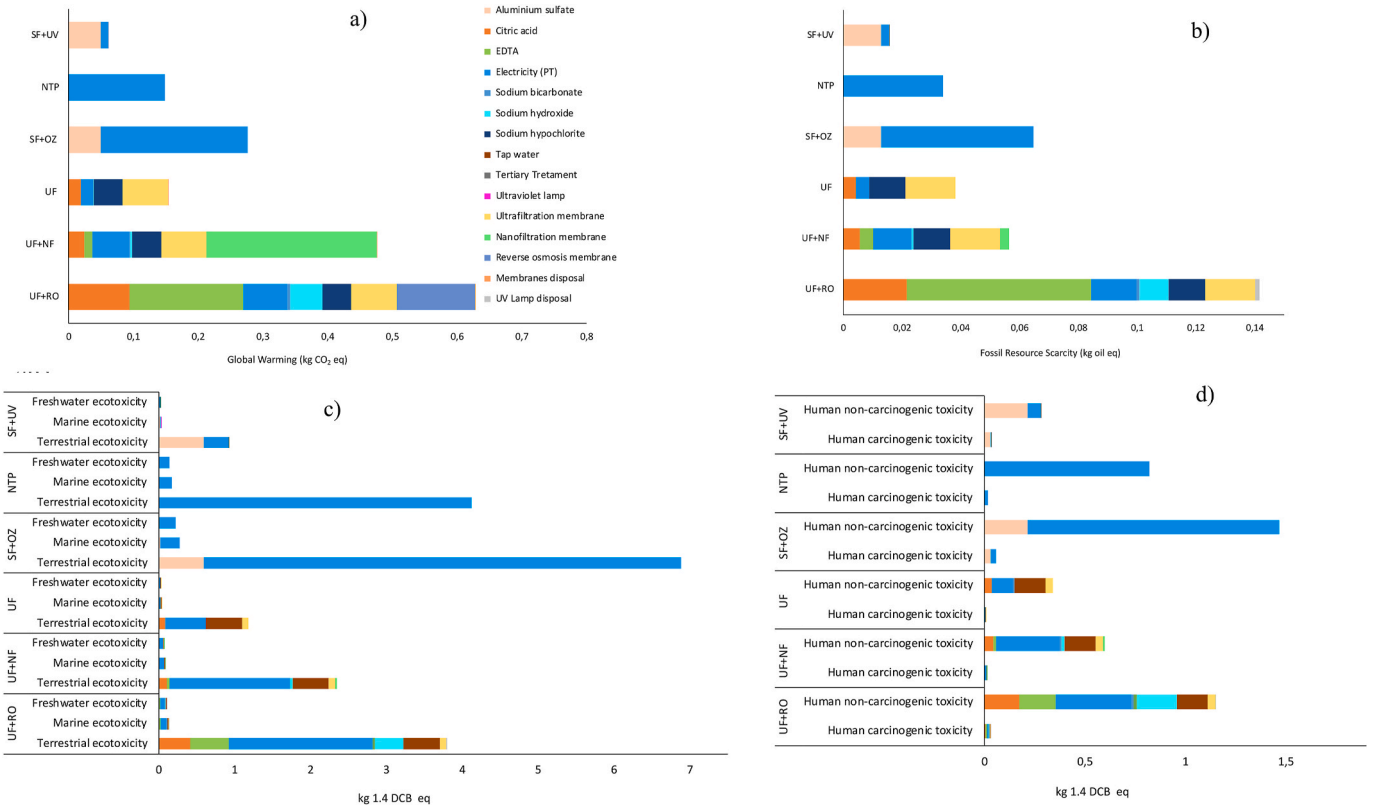

Fig. 3. Processes contribution to the total value of impact (ReCiPe) of SF + UV, NPT, SF + OZ, UF, UF + NF, and UF + RO in the categories of a) Global Warming; b) Fossil Resource Scarcity, c) Freshwater, Marine and Terrestrial Ecotoxicity, and d) Human Non-Carcinogenic and Cancerogenic toxicities. All values are referred to F. U. (1 m^3 treated water).

aluminum sulphate used as anticoagulant represents the 18% of this latter. Similar percentages were obtained by (Li et al., 2019) for SF + OZ configuration.

In membranes-based technologies, characterized by removal efficiency higher than 80%, the electricity consumption represents a minor contribution, with percentages ranging from 12% (UF + NF) to 10.9% (UF + RO), in UF + NF and UF + RO the indirect impacts associated to the production of filtration modules contribute by total percentages of 69.9% and 30.4%, respectively (Fig. 3a). The use of sodium hydroxide, EDTA, citric acid, and sodium hypochlorite for membranes cleaning and anti-scaling represent 17.9% of the total value of Global Warming impact in UF + NF, whereas in the case of UF + RO they account for 58.6%, being EDTA responsible for 27.9% of the total value of Global Warming.

In all configurations, waste disposal makes a negligible contribution to Global Warming's impact value, always lower than 1%, as confirmed by previous literature data (Zepon Tarpani and Azapagic, 2018).

Similar results of Global Warming in terms of relative percentage of contribution are obtained in the category of impact of Fossil Resource Scarcity, where electricity represents the main contribution of oxidation-based technologies, and reagents and membranes modules represent the main contribution in membrane-based technologies (UF + NF and UF + RO). In the UF + RO treatments UF and RO membranes contributed by 13% and the reagents by 76%, being ETDA and citric acid the chemicals which provided the highest associated fossil depletion impact value with percentages of 44.2% and 15.21%, respectively.

In the case of UF + NF membranes account for 35.4%, and reagents for the remaining 46.7% (Fig. 3b).

In this work, the contribution to the final value of the impact of membrane-based technologies associated with the electric energy seems lower than that provided by membrane production and chemicals, which is due mainly to the low electric energy demand of UF + RO unit, as it is measured at the pilot scale plant. This evidence agrees with the contribution percentages reported by Li et al. (2019) for UF + RO treatments. Different relative contributions were observed by Bordbar et al. (2022), which studied a treatment characterized by energy consumption 4-fold higher than that of the present work. Thus, energy is the main responsible for the final value of impact.

Analyzing Ecotoxicity categories of impact, reported in Fig. 3c, the electric energy is the most relevant contribution for all the high removal efficiency quaternary treatments, contributing from percentages of 49.9% in Terrestrial ecotoxicity for UF + RO up to 99.9% in Freshwater, Marine and Terrestrial ecotoxicities categories of impact of NTP treatment. Membranes modules represent a minor contribution either in UF + RO, and UF + NF quaternary treatments, never exceeding 4% of the total value, when chemicals represent 23% on average in UF + RO and 30% in NF + UF (Fig. 3c). Similar results were obtained for Human Carcinogenic and Non-Carcinogenic Toxicity (Fig. 3d). It must be noticed that the Freshwater, Marine, and Terrestrial ecotoxicity associated to SF + UV tertiary treatment is affected mainly using the coagulant in 54%, rather than by the electric energy consumption. This evidence is observed as well in Human Toxicity related categories as well as in Global Warming and Fossil Resource Scarcity, where the use of this chemical brought a higher environmental burden than the use of electricity itself in SF + UV.

The analysis of the substance's contribution to freshwater ecotoxicity and human cancerogenic toxicity categories of impact (Table S6), analyzed with 0.02% cut-off showed that it is mainly associated to the emission (water compartment, ocean) of copper, vanadium, zinc, nickel and chromium VI and nickel. The emission of these metals is related firstly to the electric energy production processes and secondly to membranes and chemicals. In contrast, Human Carcinogenic Toxicity is associated with chromium VI, arsenic, and nickel emitted in water and air compartments, respectively, again during the electric energy

production process. These results demonstrated how the use of renewable energy source, as well as sustainable energy production process is of key importance for driving the WW treatments studied towards higher environmental levels of sustainability. This evidence was already observed by several authors (Li et al., 2019; Surra et al., 2021).

3.3. Contribution of pharmaceuticals to the freshwater ecotoxicity category of impact

3.3.1. Calculation of missing CF by USEtox

Table S7 reports the CFs used in this work; in green, the new 7 CFs calculated for this work are reported.

The results obtained showed, as expected, that the CFs associated with emission to the compartment of river are always higher than those associated with the emission in seawater (i.e. trazodone 2.47×10^4 PAF.m^3.day/kg vs 5.28×10^{-9} PAF.m^3.day/kg) (Table S7). It is interesting that analyzing all the CFs used for the freshwater ecotoxicity assessment, it can be concluded that the first 10 PhCs with higher associated CFs in freshwater compartment are, in descending order: ofloxacin, clarithromycin, atorvastatin, azithromycin, trazodone, fluoxetine, bupropion, sertraline, sulfadiazine, ciprofloxacin, desmethylvenlafaxine, and sulfamethoxazole. The fact they showed the highest associated CFs suggests that they potentially provide higher environmental impacts in the freshwater ecotoxicity category than the other PhCs detected at similar concentrations, since the impact value of each pharmaceutical is calculated as the product of its concentration ($M_{x,i}$) with the respective $CF_{x,I}$ (Bijster et al., 2018). It must be noted that, among them, only the clarithromycin (CLA) is included in the proposal of UWWTD for 80% removal at WW discharge. Moreover, according to the calculation made in this work, the metabolites desmethylvenlafaxine and hydroxibuprofen presented higher CFs than the original compound venlafaxine and ibuprofen, with values of 5.25×10^3 PAF.m^3.dia/kg and 1.42×10^3 PAF.m^3.dia/kg *vs* 4.74×10^2 PAF.m^3.day/kg, and 2.33×10^2 PAF.m^3.day/kg, respectively. This result suggests that the potential ecotoxicity of these metabolites is higher than that of the parental compounds venlafaxine and ibuprofen, which were both detected in the UWWTD. These results agree with previous literature ecotoxicological data (Ortiz de García et al., 2017). According to CFs calculation, epoxicarbamazepine seem to be slightly less environmental harmful than its corresponding original compound, providing CFs of 607 PAF.m^3.day/kg towards 780 PAF.m^3.day/kg of their correspondent parental compound (Table S7). Obviously, these results must be taken with caution since the parameter used for CFs calculation derives from modeling performed in EPISUIte software, thus can be associated to an intrinsic uncertainty, but the point is that applying the USEtox model, which is one with the highest associated scientific consensus and take into consideration fate, exposure and effects factors associated to each contaminants, it is clear that a larger set of PhCs, and of their metabolites deserve at least as much attention as those included in the UWWTD Proposal.

3.3.2. Freshwater ecotoxicity calculated through USEtox method

Fig. 4 reports the results of the total impacts in the category of Freshwater ecotoxicity calculated by USETOX method, including ("Pharm") and excluding ("No Pharm") in the presence of the pharmaceuticals in the WW effluent, and considering the discharge of WW either into the ocean and into the river as receptor compartments.

The results confirmed those already obtained by the ReCiPe method for this impact category. Among the treatments with higher removal efficiency (>80%), SF + OZ is the less environmentally advantageous treatment and UF + NF is the most advantageous one. Fig. 4 showed that no significant differences are observed if the treated WW is discharged in the ocean or in the river (Fig. 4). Moreover, the presence of PhCs affects the total value of Freshwater ecotoxicity impact by maximum percentages of 0.017% and 0.012% in SF + UV and UF treatments when the WW effluent is discharged into the river, whereas the impact values associated to PhCs are negligible when the WW effluents are discharged into the ocean (percentage of contribution of PhCs $<6.0 \times 10^{-5}$%), whatever technology is used to remove them. This result agrees with the previous data reported in literature (Surra et al., 2021), which confirmed that PhCs have negligible contribution to the environmental impact in the category of Freshwater ecotoxicity. This does not mean that the presence of PhCs in WW effluents cannot be considered a relevant environmental issue, it means that the ecotoxicity associated with their removal is currently somehow higher than the ecotoxicity associated to PhCs themselves. This poses the serious question about how the sustainability of all the process can be systematically and drastically reduced, starting from its main contributor, which is the electric energy production process.

Fig. 5 reports the contribution of the most relevant substances to the final value of freshwater ecotoxicity according to USEtox method, including the presence of PhCs considering as final water receptor body the "Ocean" and the "River" (*cut-off* of 2.0×10^{-5}%).

The results showed that the PhCs whose impact in freshwater is still accountable at the applied *cut-off* 2.0×10^{-5}% are strictly associated with the efficiency of the treatments.

In the case of SF + UV and UF treatments, the PhCs, whose impact is still accountable after treatment at the *cut-off* of 2.0×10^{-5}%) are in descending order are bupropion, atorvastatin, azithromycin, clarithromycin, diclofenac and desmethylvenlafaxine. It must be noticed that if the WW is discharged in the Ocean the value of impact is always lower

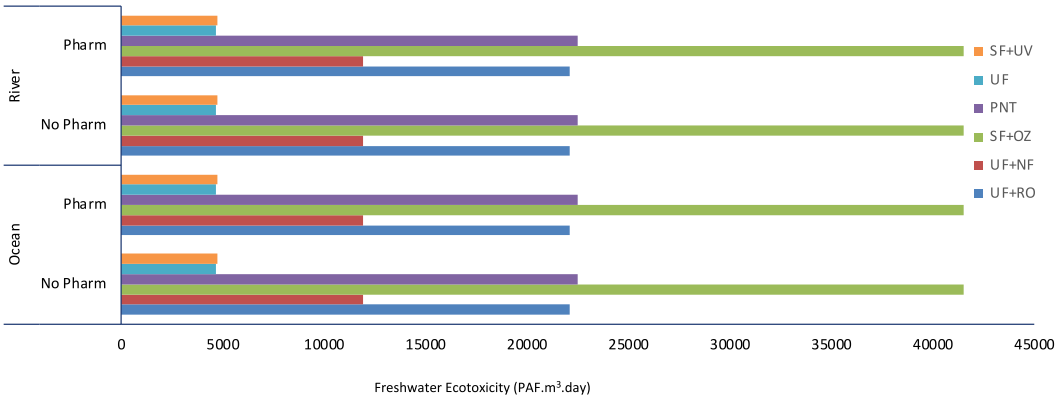

Fig. 4. Total Impacts in Freshwater Ecotoxicity category of impact (USEtox method) in presence and in absence of pharmaceuticals considering the WW discharge in "Ocean" and "River" compartments.

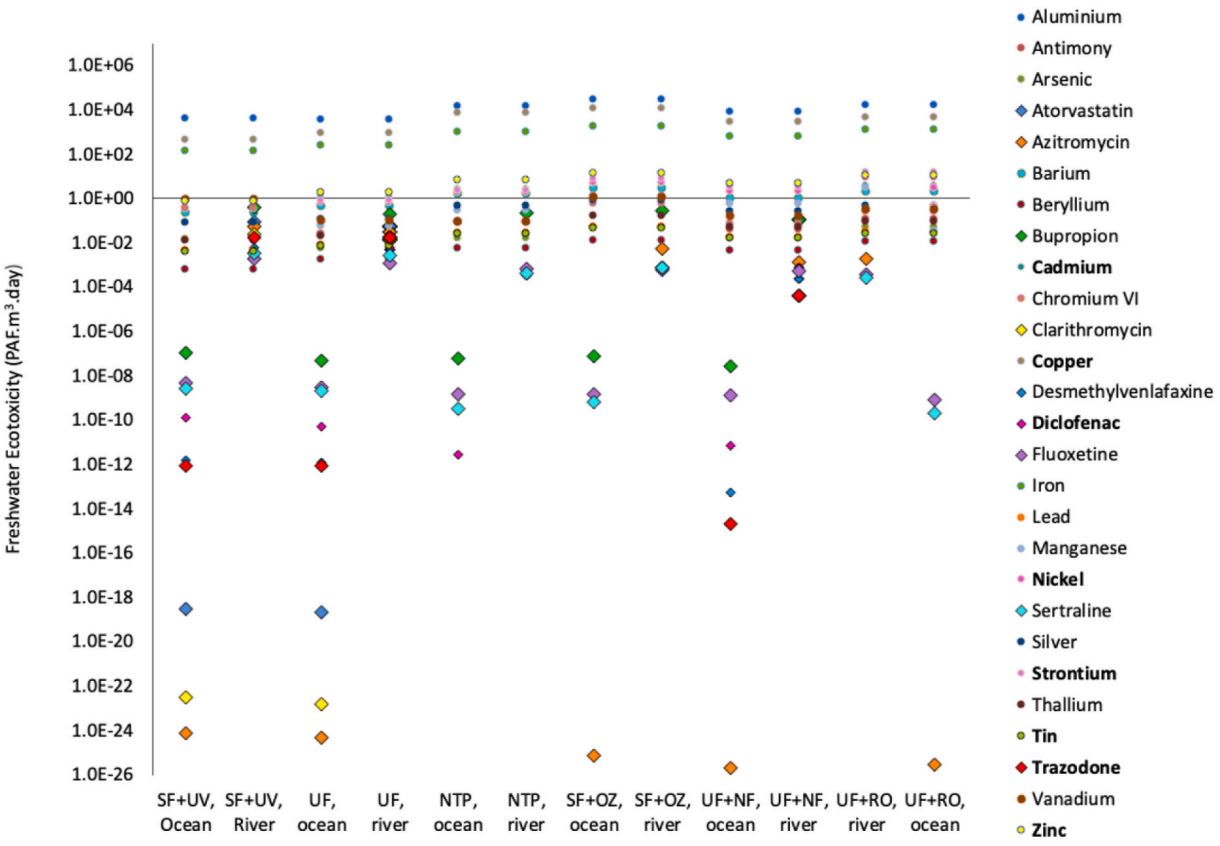

Fig. 5. Substances contribution to Freshwater Ecotoxicity (USEtox method). Al values are referred to F.U. (1 m^3 treated water).

than 1 $\times 10^{-7}$. When NTP, UF + NF, UF + RO or SF + OZ are applied (average removal efficiency higher than 80%), the only pharmaceutical, whose freshwater environmental impact was still reasonably accountable (>0.01 PAF.m^3.day) in the environment after treatment is bupropion. In the presence of UF + RO the freshwater ecotoxicity associated to pharmaceutical can be considered non-existent (<0.002 PAF.m^3.day). Fig. 5 clearly shows that the environmental burden associated with PhCs is very low in comparison to those provided by aluminium, iron, and copper. Fig. 5 suggests that different environmental threats can be expected from the presence of pharmaceuticals according to the final water receptor body, being more severe in the case of rivers.

3.4. Operating costs and energy analysis

From the best performing technologies for pharmaceutical removal, FA + OZ showed the highest OPEX (0.41 € m^{-3}), followed by UF + NF (0.33 € m^{-3}) and UF + RO (0.31 € m^{-3}). The NTP provided the lower OPEX (0.24 € m^{-3}) at the conditions tested, showing its potential competitiveness with commercially mature technologies (Gerrity et al., 2010). However, NTP is not yet a commercial technology, and the final value of OPEX for its full-scale configuration, can undergo to possible adjustments. One of the important advantages of NTP technology is that its operation does not require any chemical reagents or consumables, unlike other treatments. The SF + UV provided the lowest OPEX (0.05 € m^{-1}) but did not show any significant impact on the PhCs removal.

For SF + OZ, the OPEX is dominated by energy costs (96%), while for membrane-based technologies, energy accounts for 39–50% of OPEX, with reagents and membrane maintenance accounting for the remaining.

SF + OZ and NTP showed the highest energy consumption, with 3.1 kWh m^{-3} and 2 kWh m^{-3}, respectively. The reported SF + OZ energy consumption is significantly higher than that of other reports (Pistocchi et al., 2022), which places this requirement between 0.1 and 0.3 kWh m^{-3}. This could be since a higher ozone dose was used in this study (88 gO_3 m^{-3}), due to reactor contact time limitations, while typically doses below 10 gO_3 m^{-3} are generally applied at full scale (Pistocchi et al., 2022; Rizzo et al., 2019). It must be noticed that larger scale OZ units can exhibit better energy efficiency, thus lower operating costs (Rizzo et al., 2019). Literature data (Ajo et al., 2018; Gerrity et al., 2010) for NTP batch treatment of PhCs from WW reported lower energy consumption than in this work (0.5–1 kWh m^{-3} *vs* 2 kWh m^{-3} (this work)). These studies only account energy for the plasma generation and not for the overall set-up, which in this study accounts for 0.8 kWh m^{-3} (without air pump) for 86% removal, a consumption closer to the reported values.UF + RO and UF + NF followed with similar energy consumptions of 0.77 kWh m^{-3} and 0.92 kWh m^{-3}, respectively, consistent with literature data (0.74 and 1.2 kWh m^{-3}, respectively) (Kehrein et al., 2021; Pearce, 2008).

4. Conclusions

This work compared for the first time the NTP advanced quaternary treatment for PhCs removal from WW secondary effluent, in its technical, environmental and operating cost performances with four consolidated advanced technologies, SF + OZ, UF, UF + NF, UF + RO, and one tertiary SF + UV treatment, this latter being commonly devoted to final microbiological disinfection. Based on the results obtained, neither SF + UV nor standalone UF can be considered adequate for PhCs removal. The analysis of the removal efficiencies observed on real WW effluents showed that either NPT, UF + NF, SF + OZ or UF + RO provided an average removal efficiency always higher than 80%, including targeted PhCs included in UWWTD revision proposal (CBZ, CIT, VFX, DCF, and CLAR), with NTP performing better towards VFX than SF + OZ, and towards DCF and CBZ, than UF + NF.

The analysis of the environmental impacts showed that the technologies with higher removal efficiency are those with higher

environmental associated burdens (SF + OZ, UF + RO), highlighting NTP as an interesting compromise between removal efficiency and environmental impacts. The application of the USEtox method for freshwater ecotoxicity assessment confirmed the results obtained with Recipe method, highlighting that the presence (or absence) of PhCs in the WW effluent after treatment has very low/negligible impacts to the final value of freshwater ecotoxicity, independently to the technology used for PhCs removal, suggesting that the highest efforts have to be applied to reduce indirect environmental impacts associated to quaternary treatments operation, acting firstly on electric energy production, transport and supply, secondly in the choice of reagents and membranes used in the quaternary treatments in the case of filtration-based technologies. According to the analysis of the CFs of the detected PhCs, it is observed that these compounds represent a higher environmental threat when discharged in the river rather than in the ocean, and that among them, ofloxacin, clarithromycin, atorvastatin, azithromycin, trazodone, and fluoxetine, are the most potentially hazardous for freshwater ecosystems, being the metabolite desmethylvenlafaxine more dangerous than the venlafaxine.

When high efficiency quaternary treatments are applied (NTP, UF + NF, UF + RO or SF + OZ), bupropion is the only pharmaceutical, whose freshwater environmental impact is still accountable (>0.01 PAF.m^3.day) applying a cut-off of 2.0 $\times 10^{-5}$ %. In the presence of UF + RO the freshwater ecotoxicity impact value associated to PhCs can be considered negligible (<0.002 PAF.m^3.day).

Although NTP showed the highest energy consumption after SF + OZ, its OPEX (0.24 € m^{-3}) is lower than UF + NF andUF + RO membrane configurations, since NTP has no demand for chemical reagents or significant replacement parts. The NTP is still at pilot scale but the treatment performance and OPEX analysis clearly demonstrate that NTP has the potential to be an efficient and competitive technology for quaternary treatment of PhCs in from WW.

Considering the lack of NTP pilot studies at the pilot scale with WW, this study provided valuable knowledge about the application of NTP technology in the removal of PhCs in real WW effluents and an innovative insight into the environmental assessment.

Funding

This work received financial support from Fundação para a Ciencia e Tecnologia e MInisterio da Ciencia tecnologia e Ensino Superior (FCT/MCTES) (UIDP/50006/2020 DOI 10.54499/UIDP/50,006/2020) through national funds.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Elena Surra reports financial support was provided by Polytechnic Institute of Porto School of Engineering. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgements

This work received support and help from Fundação para a Ciencia e Tecnologia e MInisterio da Ciencia tecnologia e Ensino Superior (FCT/MCTES) (LA/P/0008/2020 DOI 10.54499/LA/P/0008/2020, UIDP/50006/2020 DOI 10.54499/UIDP/50006/2020 and UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020), through national funds and project FARMASENSE (NORTE-01-0247-FEDER-039957) sponsored by Sistema de Incentivos à Investigação e Desenvolvimento Tecnológico de Portugal 2020, by Programa Operacional do Norte (NORTE 2020) and Fundo Europeu de Desenvolvimento Regional (FEDER). Authors also acknowledge SIMDOURO S.A. for providing access to the urban WWTP where the pilot scale tests were performed.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2024.122728.

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