Benchmarking tertiary water treatments for the removal of micropollutants and pathogens based on operational and sustainability criteria

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A R T I C L E  I N F O

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A B S T R A C T

In a context of increasing water scarcity, it is essential to ensure an integrated watershed management, savings in the consumption of water as a finite resource and improve the performance of wastewater treatment plants to guarantee the quality of treated effluents. Therefore, advanced technologies for tertiary wastewater treatment have been widely studied in recent decades. These treatments have been reviewed over the years mainly providing comparisons from a technical perspective. However, there is a lack of a holistic evaluation considering environmental and economic aspects together with the aforementioned technical aspects. In this review, treatment alternatives for micropollutant and pathogen abatement have been identified based on technologies implemented on a large scale (ozonation, ultraviolet treatment, adsorption on activated carbon or membrane filtration) as well as those treatments in the process of implementation, such as electrochemical, Fenton-based or photocatalytic techniques. Thus, a systematic bibliographic search was performed considering works applying pilot and full-scale equipment, leaving lab-scale results out of the analysis. The description of each process allowed the identification of the technical feasibility, operating costs and associated environmental impacts, providing a comparative assessment that will help decision-making in the development and application of the different technologies. The benchmarking results reveal that the selected treatment should be chosen based on the source and specific pollutants present in the wastewater, as there is no single solution for the treatment of micropollutants and pathogens. In addition, recommendations are presented for the publication of reliable process-related data to facilitate comparison between different technologies and treatment scenarios.

1. Introduction

Population growth implies an increasing demand for natural resources such as water, energy and food [1]. In this context, one of the most serious problems to be faced is the increasing water scarcity [2]. This concept is defined as the imbalance between water demand and availability and is related to unbalanced consumption of water reserves, declining quality of drinking water due to contamination or saline intrusion of surface waters and aquifers and increased periods of drought [3]. The importance of access to safe drinking water and sanitation is highlighted and embedded in Goal 6 of the United Nations Sustainable Development Goals [4]. In order to address the problems related to water pollution, large investments have been made in wastewater treatment plants (WWTPs) [5]. Although WWTPs are capable of removing organic matter and nutrients (nitrogen and phosphorous), the occurrence of organic micropollutants (OMPs) such as personal care products, pesticides, endocrine disrupting chemicals or pharmaceuticals, in different environmental compartments requires changes in the design and operation of wastewater facilities to ensure their removal and the quality of the treated effluents [6,7].

As part of the implementation of the Water Framework Directive, the European Union defined a list of priority substances that could pose a risk to the environment and human health. The “Watch List” reported in 2015 included two pharmaceuticals, natural hormones, three macrolide antibiotics, pesticides, an ultraviolet filter and an antioxidant. Subsequently, three additional substances were added in 2018: an insecticide and two antibiotics. With the primary objective of OMPs removal, some tertiary treatment technologies, such as membrane filtration or adsorption on activated carbon, allow the retention of OMPs from the wastewater stream. However, the concentrated flow and the spent adsorbent have to be conveniently managed in a downstream process increasing the complexity of these techniques [8]. The possibility of

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implementing advanced oxidation processes (AOPs) based on non-
specific oxidation mechanisms [9] such as ozonation or UV radiation
are options that have had variable success since their large-scale oper-
aton involves high operating costs due to their high energy re-
quirements or lower kinetic rates.

Beyond organic micropollutants, special attention should be also paid
to contamination by heavy metals, which are generally classified as
inorganic micropollutants as they are present in treated effluents in trace
concentrations. Contamination due to heavy metals can occur naturally,
caused by the entrainment of geological material into surface waters
although most heavy metals pollution has been determined to be
anthropogenic, deriving from the use of pesticides and fungicides (As) or
pigments (As, Cd, Cr, Cu, Pb, Ni), as well as from the metallurgical (As,
Cd, Hg), petrochemical (Cd, Pb) or pyrotechnical (As) sectors [10]. In
this review, pathogen removal is also considered for benchmarking since
tertiary treatments are widely used as methods for pathogen abatement
[11]. The presence of pathogens is especially relevant in urban, hospital,
livestock and agricultural wastewater, since the release of microorgan-
isms into water bodies contributes to the spread of pathogens and
antibiotic resistances.

Several review articles have recently been published on the benefits
and drawbacks of advanced tertiary treatments for wastewater polish-
ing, mainly focusing on the technological aspects of treatments. For
instance, experts from NEREUS COST Action analyzed the best available
technologies for water reuse for crop irrigation considering ozonation,
activated carbon adsorption, chemical disinfectants, UV radiation,
advanced oxidation processes and membrane filtration [12]. The
conclusion of the expert group is that a single advanced treatment
method is not sufficient to minimize the release of chemicals of
emerging concern and antibiotic-resistant microorganisms. Luo et al.
analyzed the removal efficiency of the selected micropollutants in 14
countries and regions, analyzing different tertiary systems such as
coaugulation–floculation, activated carbon adsorption, advanced
oxidation processes, nanofiltration, reverse osmosis, and membrane
bioreactors [13]. Rizzo et al. analyzed consolidated versus new tertiary
treatment methods, concluding that the lack of comparative research
between the two categories complicates the evaluation of the most
suitable and cost-effective solution for the treatment of emerging con-
taminants [14]. Bui et al. performed a multicriteria assessment of
advanced treatment technologies for micropollutants removal,
including very brief references to environmental considerations and
only including some of the available tertiary treatments, i.e., adsorption,
ozonation, UV/H₂O₂, membrane processes and membrane bioreactors
[15].

The analyzed reviews are mainly focused on the technical aspects,
lacking the economic and environmental perspectives. The search for
new technological alternatives must meet the following objectives:
technological feasibility in the construction and operation of the
equipment, operational efficiency and reliability and reduction of
environmental impacts and costs. Based on the score in each of the
aforementioned sections, decision making will be better supported by
evidence and contrastable data [16]. In accordance with European di-
rectives, environmental and socioeconomic factors, including consid-
eration of human health, must be considered in the assessment of
advanced technologies. In this sense, the environmental impacts asso-
ciated with tertiary treatments can be elucidated using the interna-
tionally standardized Life Cycle Assessment (LCA) methodology.
Considering the environmental approach, Pesqueira et al. conducted a
literature review solely on the application of LCA in tertiary wastewater
treatment, however, the scope of the review focuses on the removal
of priority substances and pollutants of emerging concern mentioned in
European legislation, including a total of 18 papers [17]. In this study,
the focus was further extended to a total of 40 papers dealing with LCA
in tertiary treatments.

In consequence, the main objective of this keyword-based literature
review is to perform a holistic analysis of the main technological
developments in tertiary treatments from a sustainability perspective,
including not only efficiency variables, but also environmental impacts
and cost estimation. The key aspects of the technologies were identified
and evaluated for pilot and full-scale studies considering technical and
sustainability approaches, concluding that the combination of multiple
treatment processes is essential to meet the effluent requirements.
Moreover, the use of LCA methodology as a powerful tool for decision-
making can highlight specific hotspots of the technologies, com-
plementing the information provided by economical and technological
evaluation. Accordingly, the main challenge is to emphasize the key data
of each technology considering a joint technical, environmental, and
economic approach, providing useful information about the main
drawbacks of present studies and desirable targets for future research.

2. Bibliographic search methodology

The literature search was performed using the search tool provided
by the SCOPUS database in March 2021. The selection of manuscripts
addressing the efficiency of tertiary wastewater treatments for the
removal of micropollutants under technological, economic and envi-
ronmental criteria was conducted. Considering the scope of the review,
the search was limited to the technologies applied to wastewater treat-
ment, including the keywords “wastewater treatment” or “waste water
treatment” in the search string. In addition, since the goal of tertiary
treatments is the removal of micropollutants, heavy metals and patho-
genics, these words and their relevant abbreviations were considered in
the formulation of search parameters by including their respective
keywords. For this purpose, the search procedure used in the literature
review is summarized in Fig. 1, along with the specific keywords and
Boolean operators.

Tertiary treatments were classified into seven distinct groups to
facilitate the search process, i.e., ozonation, ultraviolet, catalyst-based,
pressure-driven, activated carbon adsorption, electrochemical and
irradiation treatments. Moreover, the results were filtered and reduced
considering their publication after 2010, written in English and in a final
step of publication. The obtained results applying each step are pre-
sentated in the Table S1 in the Electronic Support Material (ESM) 1. The
analysis of environmental indicators estimated by the LCA methodology
have been also analyzed performing a complementary search, using
specific keywords as “life cycle” or “LCA”.

The results of the bibliographic search are compiled in ESM 2 and
ESM 3 in the Supplementary Information. ESM 2 includes the biblio-
graphic information of all studies analyzed after the second refining step
along with their basic bibliographic data, while ESM 3 presents a stan-
dardized table with the technoeconomic data extracted from the
selected studies, focusing in micropollutant removal and operational
conditions.

3. Bibliometric analysis

The bibliometric analysis includes all the results after the manual
refinement obtained from Scopus using the methodology explained
above. These papers have been taken into account for the technological
and economic analysis performed during this review, and the keywords
were extracted and analyzed according to their occurrence and rel-
ationships, as shown in Fig. 2. To clarify the data and homogenize the
results, the substitution of keywords by synonyms or abbreviations was
conducted considering the formation of clusters involving keywords
with high similarity (ESM 4).

In view of the results, the keywords can be classified into four groups
considering the main topic addressed: (i) generic keywords: this group
formed by wastewater treatment, tertiary treatments, wastewater reuse
and domestic wastewater, terms that represent the target of the findings
and the definition of the field of study; (ii) target compound: the most
repeated keywords were pharmaceuticals and personal care products
(PPCPs), organic micropollutants (OMPs), compounds of emerging
Fig. 1. Search methodology for the different tertiary treatments.

Fig. 2. Map and network of keywords (elaborated with VosViewer®).
concern (CECs) and antibiotics (ABs) and represent the main target compounds evaluated; (iii) technologies: this group encompasses the different technologies used for tertiary wastewater treatment such as filtration, ozonation, UV or AOPs; and (iv) treatment effectiveness: this group includes the methods carried out for the evaluation of the technologies, such as removal, removal efficiency, by-products identification or toxicity.

Fig. 2 allows tertiary treatments to be classified between large-scale applied technologies and more innovative processes, and these trends are represented in the diagram. Focusing on the wastewater treatment circle and its relationships, this keyword usually appears together with adsorption techniques as granulated activated carbon or powdered activated carbon (GAC-PAC), ozonation, filtration and UV, indicating that the technologies most applied as advanced treatments for the removal of PPCPs and OMPs are those mentioned above.

On the other hand, there is an evident relationship between tertiary treatment and titania, photocatalysis and solar treatment, as well as a growing interest in pathogen removal. This keyword appears related to others such as disinfection or presence in water of antibiotic resistant bacteria (ARBs) and antibiotic resistance genes (ARGs), showing the current concerns regarding the transfer of antibiotic resistance to pathogens in the environment. Another issue to highlight is the close relationship between electrochemical methods and heavy metals (HMs), showing the preferences for the use of this type of processes for the treatment of wastewater containing heavy metals. Adsorption techniques such as GAC-PAC and filtration-based treatments to remove contaminants were usually studied together, as can be seen by the proximity of points and width of the relation line. In general, low presence of cross-sectional keywords as “economic assessment” was observed considering the significance criteria (only words with an occurrence of more than 3 were considered for the study). As a result, although some articles incorporate the economic evaluation of the technology, the analysis from the environmental point of view is missing.

4. Technological aspects of tertiary treatments

4.1. Ozone-based treatments

Ozonation (O₃) is a heterogeneous process applied for the oxidative
treatment of drinking water and more recently for wastewater. Conversely to fully water miscible oxidants (e.g., H₂O₂), mass transfer optimization from the gaseous to the aqueous phase must be considered. Typically, bubble column reactors are used to contact the ozone with the water stream (Fig. 3A). Ozonation has been studied mainly in continuous processes, whereas batch operation is the setup of choice at pilot scale to optimize reaction conditions [18–20]. Most of the reviewed studies considered the application of ozonation to effluents from conventional secondary treatment plants. However, since ozonation uses non-specific oxidation pathways to transform target compounds, the versatility of this process allows its wide application, such as for the removal of pollutants from surface groundwaters [21–23] as well as other types of wastewaters, e.g., industrial effluents [24,25] or reject streams from ultrafiltration and reverse osmosis units [26]. 70% of the reviewed studies were located in Europe, whereas none of them was in Africa, as depicted in Fig. 3C.

The typical temperature of ozonation-treated effluents ranges from 10 to 30 °C depending on climatic conditions and WWTP location, high temperatures can lead to volatilization of compounds facilitated by gas bubbling. In general, a pH above 8 favors ozone decomposition mediated by hydroxyl anions, but this condition is not met in most wastewaters, the pH values in the selected studies vary in the range of 6.0 to 10.5, respectively. To a much greater extent than hydroxyl anions, dissolved organic matter (e.g., phenols and amines) induces the formation of hydroxyl radicals through different pathways [27,28]. It should be noted that the efficiency of the process can be hampered by high loadings of radical scavenging species such as carbonates, halogen ions or nitrogen oxides [29,30]. Consequently, the abundance of these species implies not only a reduction of the treatment efficiency but also the formation of toxic oxidation products when halogen ions are present in the reaction matrix (bromate formation). In a typical configuration, relatively short removal times to achieve micropollutant removal vary from 5 to 30 min, but can extend to longer periods, as is the case for nonylphenol or bisphenol-A with treatment times up to 100 min [31]. In the case of organic matter removal, it has been established that the ozone dose varies depending on the stream flow to be treated between values of 1 to 200 mg O₃ L⁻¹. The typical parameters of ozonation are presented in Fig. 3B.

The electrophilic character of ozone and its high oxidation potential (E° = 2.07 V) enhance its reactivity towards compounds with low oxidation state such as deprotonated amines, sulfides, and aromatic rings with electron donor groups [29,32,33]. In addition to direct oxidation, there are indirect oxidation pathways in which reactive oxygen species (ROS), most notably *OH radicals, are produced [29,30], leading to the decomposition of water pollutants due to their high oxidation potential (E° = 2.80 V), as seen in Fig. 3D [34]. The studied pollutant concentrations are in the range of 0.1 ng L⁻¹ and 1.5 mg L⁻¹ for pharmaceuticals and pesticides, and from 1 mg L⁻¹ to 500 mg L⁻¹ for the combination of ozonation with an electrochemical method [25]. Although most authors focus their research on ozone-mediated micropollutant removal, some works have studied degradation pathways as well as the consequences of treatment on the treated effluent in terms of toxicity, estrogenicity or mutagenicity [31,35,36]. Different species have been considered for in vivo studies on the potential mutagenicity and toxicity of the treatment, in particular using *Daphnia magna* [37], *Aliivibrio fischeri* [37,38] and *Potamopyrgus antipodarum* [39]. Furthermore, the formation of intermediates [40] or the influence of ozonation on ARGs [41,42] have been studied. As a special case, the application of this process alone or in combination with GAC and sand filter against inactivation of microorganisms provided reductions of up to 4.3 log removal value (LRV) for Enterococci and Escherichia coli bacteria [41–43]. Unlike in chlorination, the formation of by-products affecting water quality such as halokalanes is prevented [44].

To improve its efficiency and pollutant removal performance, ozonation can be combined with UV irradiation [23,45] and hydrogen peroxide [26,37]. UV light at wavelengths up to 310 nm provokes the dissociation of O₃ into an oxygen molecule and hydrogen peroxide. Similarly, the peroxy process (O₃-H₂O₂) combines the oxidizing power of ozone with the decomposition of H₂O₂ to enhance the generation of *OH radicals and has been shown to be effective in reducing ozone-resistant micropollutants [27]. One of the most important factors to consider in the peroxy process is the ratio of O₃ to H₂O₂, which governs the reaction rate. However, the high capacity of H₂O₂ regarding the degradation of OMPs allows kinetic improvements even when present in trace amounts [46]. The H₂O₂-mediated generation of *OH can consume up to half the amount of available O₃ [47], therefore, the H₂O₂/O₃ ratio is generally set between 0.5 and 1.0. At pilot and full scale, the reaction is often carried out in gas-liquid reactors with a configuration similar to ozone bubbling columns. Alternatively, the decomposition of hydrogen peroxide in presence of UV irradiation leads the formation of additional *OH radicals [23,48]. Catalytic ozonation (O₃-CAT) makes use of a catalyst to promote the decomposition of ozone and the subsequent formation of ROS. Although many homogeneous catalysts based on transition metal ions, preferably bivalent, have been investigated, precipitation or lack of retention systems have prevented their large-scale application [49]. In the late 1990s, the first pilot plants applied heterogeneous catalysts to improve ozonation efficiency in leachate treatment [50]. Applicable materials are iron flakes, metal/metal oxide-coated ceramic membranes or clay minerals such as montmorillonite [49,51]. The application of alumina-based catalysts showed a significant enhancement of micropollutant removal compared to ozonation alone [52]. In contrast, the application of iron-based catalysts for the removal of sulfamethoxazole showed no improvement compared to the results with the results obtained for conventional ozonation [53]. On the other hand, the possibility of integrating ozonation with electrochemical methods aims at the coagulation of dissolved metals [25] and will be applicable for wastewaters of high content in heavy metals.

The combination of ozonation with different types of activated carbon such as GAC [54,55], biological activated carbon (BAC) [56,57], biofiltration [38,55] or sand filtration [43,58] has been successfully applied. As an example, Östman et al. [59] reported the improvement in benzothiazole removal from 30% to 82% by incorporating a GAC unit after the ozonation stage. However, in this study, the application of sand filtration to this effluent did not show a significant effect [56,58,59]. On the other hand, the use of biological filters has been studied by Knopp et al. [55] and Ternes et al. [38], showing similar results to those obtained by the application of ozonation.

4.2. Ultraviolet treatments

**Ultraviolet (UV)** irradiation is commonly applied as disinfection step after biological treatment. UV units for disinfection usually consist of cylindrical borosilicate modules housing mercury pressure lamps immersed in the wastewater stream (Fig. 4A). Both low pressure (LP) lamps, with a sharp emission peak at about 254 nm, and medium pressure (MP) lamps with a broader emission spectrum in the UV-C region (200–600 nm) are applied. The flow capacity of these full-scale modules can be up to 3000 m³ h⁻¹ [60] in single-pass mode for a residence time of less than 1 min. The influent treated in the revised studies was characterized by a pH in the range of 7.0–7.6 and a temperature ranging between 18 and 24 °C, and comparably low TSS and DOC values (Fig. 4B). Most of the considered studies were performed in Europe, with a concentration to the Mediterranean area, while the largest plants regarding treated flow were located in China, only one study was in Brazil, focusing on pathogen removal.

Pathogen removal by UV light typically ranges between 5 and 7 LRV at irradiance levels of 70 W m⁻². These high removal values are necessary to mitigate the effect of bacterial regrowth after UV treatment [61]. This possibility is of particular concern when reclaimed wastewater is stored in buffer tanks prior to use for agricultural purposes. It should be noted that certain species of bacteria show resistance to UV treatment. While the most commonly investigated *E. coli* bacteria are
effectively removed even within a short residence time, *Pseudomonas* strains are frequently detected in effluent from UV disinfection units [42]. Regarding the elimination of genetic patterns relevant to the evolution of antibiotic resistances, several studies reported that UV treatment only selectively eliminates ARGs, and reported removals of DNA or gene fragments was lower than for pathogens (ESM 6) [60,62]

Although many authors have studied OMP removal in full-scale modules designed for disinfection [63], these approaches only lead to slight removal efficiencies for applied irradiances up to 500 mJ cm$^{-2}$, even an irradiance of 4000 mJ cm$^{-2}$ only resulted in a removal of 0.77 LRV of micropollutants [64]. Similar removal percentages for endocrine disrupting chemicals (EDCs) were reported by Cédat et al. [65] at irradiance of 1000 mJ cm$^{-2}$. It was also shown that estrogenicity could not be satisfactorily removed, even though the parent compounds were partially transformed [66]. Regardless of the lamp intensity in the photolysis process, it is required that the target OMPs absorb the UV radiation in the range of the lamp spectrum to be abated. However, only a few organic micropollutants present in wastewater undergo photolysis at the applied wavelength of 245 nm. These are, for example, sulfamethoxazole with a removal efficiency between 22 and 70% [67], depending on the applied irradiance [63,68,69] and diclofenac between 45% and 100% [61,68] (Fig. 4D). Even if the target molecule is not susceptible to photolysis, it may undergo secondary radical transformation promoted by light-induced excitation of electrons from compounds present in the matrix. Generally, the studies reviewed were operated at dissolved organic carbon (DOC) values below 15 mg L$^{-1}$ with few exceptions. Still, most of the investigated OMPs are only degraded to a negligible extent [70] or even with negative removal efficiencies [71,72]. This may be related to several factors such as photolysis of coupling products towards the original compounds, errors in quantitative measurements due to matrix interference or desorption of residual particulate matter [66]. None of the investigated studies consider the fate of heavy metals during UV treatment, as UV irradiation is known to have no effect on their removal.

**UV-treatment combined with hydrogen peroxide (UV-H$_2$O$_2$)** produces reactive hydroxyl radicals as light with wavelengths $>254$ nm
induces photodissociation of H₂O₂ [70], resulting in enhanced micro-pollutant removal [73–75]. Typically, a H₂O₂ dose of 10 mg L⁻¹ is applied in photoreactors equipped with dosing-mixing systems that are already commercially available for large-scale applications [65,76]. Various reactor geometries have been evaluated to maximize mixing and irradiation [68]. However, the benefits of combining sunlight or UV with hydrogen peroxide are less prominent for antibiotic removal and disinfection [67]. Although H₂O₂ is the most used oxidant, it has been shown that the use of other oxidants considerably minimizes bacterial regrowth compared to UV treatment alone [61]. Regarding OMP, removal efficiencies are highly dependent on the type of contaminants, so variable energy efficiency values were obtained, ranging from 0.16–18 kW m⁻³ for ciprofloxacin and clarithromycin, respectively [10]. It is therefore necessary to evaluate and model the degradation kinetics of the expected micropollutants both in laboratory and at pilot scale [66,67,77]. Other oxidants such as ozone, chlorine, chlorine dioxide and persulfate in combination with UV treatment have been also investigated for OMP removal [73–75]. Compared to •OH radicals, Cl and SO₄ radicals have been reported to be less prone to deactivation by matrix constituents such as HCO₃⁻ or NO₃⁻ and to have less affinity towards natural organic matter [61,77]. The underlying mechanisms of radical formation and reaction with OMP are described in detail elsewhere [78,79].

4.3. Adsorption on activated carbon

Although advanced materials such as zeolites or carbon nanotubes are gaining interest as adsorbents in wastewater polishing, activated carbon is used as the predominant material, depending on the grain size, as powdered activated carbon (PAC) or granular activated carbon (GAC).

Powdered activated carbon is applied in grain sizes of 50–100 μm with a BET surface area between 900 and 1300 m² g⁻¹ [80]. PAC is usually added to the effluent of the biological treatment stage in a loading range between 10 and 20 mg L⁻¹. One of the constraints in the design of different process configurations must ensure the retention of spent PAC [84], achieved by (1) the implementation of a sedimentation unit [85,86] or by (2) sand, anthracite or expanded shale bed
filter columns or, in some cases, by (3) membrane filtration units (Fig. 5A). In the latter two options, PAC recycling can be achieved by backwashing to maximize the carbon usage rate. However, in the first case, it is necessary to improve PAC retention by coagulation-flocculation, which requires the addition of Fe\(^{3+}\)-based coagulants [83]. In some cases, an anionic polymer is additionally applied as a flocculant [85]. Alternatives where PAC is directly applied in membrane bioreactors (MBR) may pose problems in sludge management [87] as spent PAC is mixed with the sludge matrix and cannot be regenerated after use. A promising advance in process simplification is the development of µGAC, which is coarser and thus easier to separate and regenerate [88,89].

GAC units are mainly applied continuously in packed bed filter columns (Fig. 5A), which have to be replaced after the breakthrough threshold is reached. Several columns are applied in series or in parallel, while each configuration has drawbacks and advantages [90,91]. The same applies to the filtration direction, either downflow or upflow, which results in different head loss profiles, while the removal efficiency was reported only slightly higher in the upflow configuration [90]. In all cases, regular backwashing is required to impede pressure buildup and can increase the operation time of the filter columns. Based on experience during one year of pilot scale operation, Kärelid et al. [87] estimated the maintenance time to be 30–60 min per day. The most critical factors of the wastewater matrix that affect the stable performance of GAC filters are DOC and pH value, these values are between 6 and 11 mg L\(^{-1}\) (Q1-Q3) and 7.0–7.6 (Q1-Q3) respectively. TSS are considered to have a minor effect on the removal performance of GAC filters, but high levels require increased backwashing and range from 3 to 6 mg L\(^{-1}\) (Q1-Q3) in the reviewed studies [40,92] (Fig. 5B). Fig. 5C shows the geographical distribution of the revised studies based on activated carbon, indicating a focus of implementation in central and Western Europe and the USA. This is explainable by the stricter legislation regarding the presence of OMP in WWTP effluents implemented in Switzerland and local initiatives as in some German federal states (North Rheine Westphalia and Baden Wurttemberg). Both PAC and GAC can be considered as a strong barrier against most micropollutants [87,93].

Due to the numerous GAC products available, variable wastewater composition, and complex interaction mechanisms, a quantitative prediction of treatment capacity and GAC breakthrough values is not straightforward and must be performed on a case-by-case basis [89]. Another factor that adds complexity to the description of GAC processes and modeling of breakthrough behavior is the development of a biofilm in the GAC bed over a prolonged operating time, which ultimately turns them into BAC filters [55]. While adsorption-related removal efficiency will decrease during microbial evolution, biodegradation becomes more relevant [40,94,95]. As expected in relation to the larger surface area, a smaller GAC particle size is usually favorable for OMP removal [59]. The data obtained from the revised studies indicates that the GAC process can achieve higher maximal removals for all selected indicator compounds, but the data is more scattered than in the PAC process. Most critical compounds were diazepam, valsartan, acesulfame K and sulfamethoxazole, while atenolol, bezafibrate and metoprolol were removed below the detection limit, this is not the case for some compounds, especially small molecular weight [112]. For example, the small endocrine disruptor bisphenol-A or nitrosamines, such as N-nitrosodimethylamine (NDMA), and other ozonation/AOP byproducts are frequently found in RO permeates [111,113]. In this regard, it may be beneficial to apply RO/NF stages prior to AOP processes, as it has been shown that NDMA precursors such as ranitidine can be efficiently removed by NF and RO [114]. It should be noted that lower concentrations of OMP are more difficult to remove possibly due to slower reaction rates and/or matrix effects [112], which also emphasizes the need for investigations at environmental concentrations in order not to overestimate the efficiency of the process. Research studies rarely focus on pathogen removal by RO and NF stages, as they are usually preceded by an ultrafiltration unit to avoid biofilm growth. Although ultrafiltration membranes are a sufficient barrier against bacteria, viruses and OMPs are only sufficiently retained by NF and RO membranes [96,115]. NF and RO are also effective for heavy metal removal, but this feature is only relevant in special applications, e.g. highly contaminated landfill

**4.4. Pressure-driven membrane filtration treatments**

In reverse osmosis (RO) and nanofiltration (NF) processes, water is pumped through a variable set of pressurized membrane elements, yielding a treated permeate stream and a concentrated retentate stream. The percentage of the permeate flux regarding the influent flux is defined as recovery, ranging between 50 and 90% [18]. High recoveries can be achieved by applying two consecutive stages, feeding the second stage with retentate from the first stage, while higher permeate quality can be reached by a second pass through another stage (Fig. 6A). The most commonly applied polymeric membranes have a lifetime of about 5 years, depending on the quality of the treated water [96]. Recently, ceramic membranes are gaining interest despite higher manufacturing costs due to their longer lifetime, which can reach a duration 20 years [97,98]. In the reviewed studies, the operation of spiral wound polymeric modules in crossflow configuration is preferred over flat sheet configuration, while membrane areas between 2.2 and 14.0 m\(^2\) for pilot scale [99,100] and between 1000 and 3000 m\(^2\) for full scale were investigated. In both NF and RO processes, pressures in the range of 7–15 bar are applied, necessary to overcome the membrane resistance and the osmotic pressure between permeate and concentrate [18]. Pressure must be carefully monitored, as its sudden decrease reflects membrane damage, while continuous increase in pressure indicates membrane fouling/scaling due to the deposition of salts, colloids and organic matter clogging the pores [101–103]. Despite some exceptions where TSS concentrations were up of 1800 mg L\(^{-1}\) for pharmaceutical effluents [104] and 390 mg L\(^{-1}\) for primary treated municipal wastewater [105], TSS and DOC levels are lower with maximum concentrations of 15 mg L\(^{-1}\) [96] and 30 mg L\(^{-1}\) [106] respectively.

Considering the susceptibility to fouling, RO and NF systems are usually preceded by an ultrafiltration (UF) module or a membrane bioreactor (MBR). High water temperatures (>30 °C) usually lead to a decrease in membrane performance [107,108] (Fig. 6B). Despite the limitations imposed by influent quality, the implementation of RO/NF as an alternative to secondary biological treatment has already been applied as a decentralized treatment solution to produce high quality effluent [105]. Nevertheless, the main application at large scale is water reclamation in the range of 150,000–450,000 m\(^3\) d\(^{-1}\) in regions with high water scarcity [109]. The studies considered in this review were performed at smaller scale plants which ranged from 50 to 180 L h\(^{-1}\) (pilot) [96,110] and 24–168 m\(^3\) d\(^{-1}\) (full scale) [105,111]. A relevant share (39%) of the studies reviewed in our work were conducted in Spain, while studies were distributed worldwide, including studies from South Africa, Brazil, and India (Fig. 6C).

Focusing on the group of target contaminants, the most studied compounds in the reviewed publications are carbamazepine (CBZ), caffeine (CAF), diclofenac (DFC), ibuprofen (IBU) and sulfamethoxazole (SMX) are presented in Fig. 6D. The removal efficiency for both technologies is similar for the analyzed pollutants, except for carbamazepine, for which RO proved more effective. Retention of OMP is mainly governed by size exclusion, however several factors such as hydrophobicity, surface loading of contaminants, or biofilm formation can positively influence retention [111]. Although most studies report excellent removal of OMP (e.g., sulfamethoxazole, diclofenac, ibuprofen and atenolol) below the detection limit, this is not the case for some compounds, especially of small molecular weight [112]. For example, the small endocrine disruptor bisphenol-A or nitrosamines, such as N-nitrosodimethylamine (NDMA), and other ozonation/AOP byproducts are frequently found in RO permeates [111,113]. In this regard, it may be beneficial to apply RO/NF stages prior to AOP processes, as it has been shown that NDMA precursors such as ranitidine can be efficiently removed by NF and RO [114]. It should be noted that lower concentrations of OMP are more difficult to remove possibly due to slower reaction rates and/or matrix effects [112], which also emphasizes the need for investigations at environmental concentrations in order not to overestimate the efficiency of the process. Research studies rarely focus on pathogen removal by RO and NF stages, as they are usually preceded by an ultrafiltration unit to avoid biofilm growth. Although ultrafiltration membranes are a sufficient barrier against bacteria, viruses and OMPs are only sufficiently retained by NF and RO membranes [96,115]. NF and RO are also effective for heavy metal removal, but this feature is only relevant in special applications, e.g. highly contaminated landfill
leachate or construction site effluents [116,117], since heavy metals in municipal effluents are mostly successfully retained in secondary biological treatment.

4.5. Catalyst-based processes

Instead of directly using photon energy to decompose micropollutant structures, ROS are formed during photocatalytic processes using materials with semiconducting properties or based on light-driven decomposition of hydrogen peroxide (photo-Fenton). Due to the higher energy requirements of UV light compared to solar light, recent work focuses on the search for new materials capable of exploiting the advantages of this type of irradiation with a focus on reducing energy consumption resulting in greater technological feasibility for large-scale implementation (Fig. 7A). In photocatalysis processes, approximately half of the studies have used solar light and provide irradiance between 20 and 40 W m$^{-2}$ in lower latitude areas [118–120].

Heterogeneous photocatalysts (PC) in wastewater treatment are based on the use of solid-state metal oxides with semiconducting properties. In these materials, the valence and conduction bands (VB and CB) are separated by an energy band gap. Upon irradiation of photons with an energy equal to or higher than this energy, electrons in the VB are promoted to the CB. The formation of electron-hole pairs provides sites for the generation of ROS by oxidation and reduction reactions, acting as direct oxidant when an organic molecule serves as an electron donor, or as indirect oxidant by generation of $\cdot$OH which in turn attacks organic molecules [126]. In theory, organic micropollutants could be completely mineralized as the radical reactions are non-specific and are capable of degrading a wide range of compounds, however, the generation of by-products is a significant challenge. In practice, their mineralization efficiency is limited due to the presence of refractory compounds.

Economic and operational factors have driven the development of larger and more efficient plants, with the largest CPC plants for wastewater treatment having a treatment capacity around 100 L in batch operating mode [123–125]. The most frequent parameters studied with these techniques were depicted in Fig. 7B.

**Fig. 6.** A) Schematic representation of different configurations of membrane filtration unit: two-stage (green line boundary) and two-pass configuration (blue line boundary). B) Worldwide distribution of the analyzed studies (circle area is proportional to the treated flow rate and color represent the continent). C) Overview of the quality requirements of the influent and typical operational parameters of the analyzed studies D) Removal efficiencies for the five most investigated compounds for nanofiltration and reverse osmosis studies. Grey columns stand for RO and white columns stand for NF treatment results. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
products in the intermediate steps must be assessed [127].

The most widely applied photocatalyst in large-scale wastewater treatment is TiO$_2$ since it can be applicable for solar light absorption directly due to its absorption wavelengths [128]. However, modification of semiconductors by doping their structure with other metals has been studied to improve photo-efficiency [129]. Although the use of ZnO-based materials are potential candidates due to their higher electron mobility and similar properties compared to TiO$_2$, the undesired high electron-hole recombination is the main drawback for their application [130]. Furthermore, ZnO is more susceptible to photo-corrosion than TiO$_2$ the generated Zn$^{2+}$ ions can increase the toxicity of the effluent [131]. Materials with a narrower band gap and lower charge recombination rate have been developed to increase the share of usable solar spectrum.

One of the main drawbacks of heterogeneous photocatalysis is the limitation of reaction rates due to low mass transfer kinetics between phases. The use of nanostructured materials increases the surface-to-volume ratio, and electron-hole pairs are more exposed to the surface where they can act as a reactive center. Another challenge is that in most photocatalytic materials, the rapid electron-hole recombination process causes 90% of the active sites generated by photon absorption to be depleted before they can act as a catalytic site. This phenomenon can be partially avoided by the inclusion of certain components in the crystal structures, known as dopants, which improve catalytic efficiency [132]. In order to ensure efficient catalyst separation, numerous options have been evaluated such as immobilization on supports, like biopolymers [133], magnetite nanocomposites [134], glass plates [135], polymeric support materials [136] or membranes [137]. Hydroxyl radicals generated in photocatalytic systems enable pathogen elimination through non-specific mechanisms, which trigger the destruction of cell membranes and damage to genetic material [138].

In Fenton-based methods, ROS are generated by reductive and oxidative decomposition of H$_2$O$_2$ by Fe$^{2+}$ and Fe$^{3+}$ species at acidic pH, respectively. The limiting step in this process is the regeneration of Fe$^{3+}$ to Fe$^{2+}$. By irradiation with light of wavelength $<$ 580 nm, the regeneration of the catalyst by photochemical pathways is enhanced. Conventional Fenton (F) and photo-Fenton (PF) reactions produce a considerable amount of iron sludge. The increased turbidity caused by the abundance of Fe$^{3+}$ can further limit efficiency as light transmission decreases [70]. The fact that Fenton-based reactions require an acidic
pH implies subsequent neutralization of treated waters and increased salt concentration [14]. This can be minimized by the application of ligands that increase iron solubility even at circumneutral pH. Moreover, the photo-induced regeneration of Fe$^{3+}$ species reduces iron consumption and precipitation of iron oxides thus increasing the stability of photocatalyst [139]. Another way to stabilize catalysts at circumneutral pH values is the use of heterogeneous catalysts. Iron oxides can be applied as magnetite, which also allows the magnetic separation of the catalyst [261]. In this case, the use of nanostructured materials has the same advantages and disadvantages as in semiconductor photocatalysis.

In this context, the homogeneous photo-Fenton process is the most studied photocatalytic technology, using Fe (II) sulfate as catalyst at pH around 3 (Fig. 7C); alternatively, a larger range between 6 and 8 has been considered, stabilizing the solubilized iron with ligands such as ethylenediamine-N,N′-disuccinic acid (EDDS) [140,141], humic acid [140] or citrate [106] for circumneutral pH values. For both acidic and neutral conditions, the Fenton-based processes provided high removal percentages for most of the studied compounds for reaction times up to one hour. Following the same trends as the ozonation process, the most studied compounds were sulfamethoxazole and carbamazepine, followed by N-acetyl-4-aminophthalamide and trimethoprim. In most cases, the lowest removal percentages were obtained for sulfamethoxazole.

Pathogen removal was also evaluated, with studies focusing on the degradation of Escherichia coli [118,142] and Enterococcus species [123,143], reaching inactivation of 3.0 to 4.5 LRV.

Typical catalyst concentrations range from 1 to 20 mg L$^{-1}$ iron, although the most common concentration is 5 mg L$^{-1}$ and hydrogen peroxide is in the range of 10–100 mg L$^{-1}$ [121,123,144]. In contrast, in semiconductor-based catalysis, the catalyst loadings are higher, between 100 and 1000 mg L$^{-1}$. The different catalyst loadings are due to the type of reaction, as heterogeneous catalysis rates are governed by the interaction between the dissolved substances and the surface. Furthermore, the reaction times required for similar degradation percentages are significantly longer, being in the range of 1 to 7 h [47,145,146]. Modification of the TiO$_2$ catalyst using graphitic carbon nitrides [146], supports as poly(methyl methacrylate) [136] or metals [99] provided better results than the bare ones.

Considering the results obtained with solar simulators [122,146,147], variable irradiance, depending on weather conditions, latitude and solar incidence, poses a challenge for reactor efficiency and process regulation. Since irradiation energy is closely related to compound degradation, some authors report removal rates by comparing the results versus the total energy input to the system for solar processes where irradiance is a function of time of day [47,106,141]. Although the number of studies focused on the influence of degradation parameters in WWTP effluents is extensive, fewer studies focus on other types of waters such as industrial effluents with specific pollutants [145,148,149] or RO/NF concentrates [106]. In addition, the combination of these catalytic techniques with precipitation units [149] or electrochemical processes [141,146] has been studied for specific purposes such as metal removal. However, it is reported that drinking water resources contaminated with heavy metals of geogenic or industrial origin as well as waters containing OMP are not sufficiently removed with solar photocatalysis [150].

### 4.6. Electrochemical treatments

The classification of electrochemical treatments encompasses a wide number of methods grouped around the use of electrochemistry under different topologies and characteristics, as they can be used as a single stage or in combination with other techniques. For the techno-economic assessment, information was sought on eight distinct treatments (see Table S1): electrooxidation, electrodissolution, Fenton-based methods, photo-electrocatalysis, sono-electrochemical and electroperoxone techniques. Electrochemical wastewater treatments were originally proposed to remove heavy metals from mining wastewater by cathodic deposition. Two examples focus on the recovery of nickel and copper from pickling and electroplating wastewaters [149,151], but there are not many examples of full-scale experiments for the removal of micro-pollutants in wastewater (see Table S1). Since electrochemical methods comprise a wide variety of techniques, the number of publications per category is limited; thus, electrocoagulation, electrodialysis and Fenton-based electrochemical methods are the techniques with more publications, with 11, 9 and 6, respectively, as depicted in Fig. 8.

**Electrocoagulation (EC)** is particularly effective in the removal of heavy metals and is applied in the treatment of effluents from the mining, metallurgical and paper industries or landfill leachate [24,25,152–154]. During electrocoagulation, the sacrificial anodic material (e.g., iron or aluminum) releases metal ions that from hydroxides in the reaction medium. These species lead to neutralization of the surface charges of particulate organic or inorganic matter. Subsequently, aggregation occurs due to Van-der-Waals interactions, and the generated flocs can be removed by sedimentation or filtration [155,156]. For example, EC treatment resulted in up to 7 LRV of microorganisms and several pharmaceuticals, such as sulfamethoxazole (59%) or iopromide (31%) from tertiary-treated wastewater [157]. In addition to standard iron or aluminum electrodes, magnesium electrodes also demonstrated their technical feasibility at pilot scale, obtaining a removal efficiency of 65–85% for cephalosporin-based antibiotics [158]. EC accomplished arsenic removal from contaminated groundwater with a removal efficiency of 128.4 μg L$^{-1}$ per kWh in a plant operated for 2 years with iron electrodes [159]. EC has also been used in combination with ozonation or HO$_2$ to treat groundwater, resulting in an effective removal of arsenic, chromium, nickel and copper below detection limits [25,160].

**Electrodialysis (ED)** is an electrochemically assisted separation technique used to transport ions from solution across ion exchange membranes, usually alternating compartments separated by cation and anion exchange membranes, aided by an external electric field. The technique has high selectivity and is considered cost-effective, as it reduces the need for chemical consumption. In addition, it can be used for product recovery from waste streams. ED is implemented on an industrial scale but is mainly applied to desalinate brackish water. Guerrieri et al. [161] provided an excellent review of the fundamentals of the electrodialysis process along with a detailed description of its practical applications for wastewater treatment and resource recovery. Shen et al. [162] studied the recovery of 2-amino-1-propanol sulfate, an intermediate for the pharmaceutical industry, at pilot scale obtaining up to 98% recovery and a 15% reduction in operating cost compared to the conventional recovery procedure. However, the pilot scale plants found in the literature are only intended to treat water contaminated with heavy metals. For example, a 200 L plant installed in an electroplating wastewater treatment plant allowed reducing heavy metal concentration and conductivity [163]. Electrodialysis was also used for the treatment of municipal solid waste incineration residues in water suspension to reduce leaching of heavy metals [164,165] and for recycling contaminated wastewater for reuse in agriculture [166]. Although there are no pilot-scale experiments, the use of electrodialysis could be useful for the separation of pharmaceuticals and emerging contaminants. However, transport across membranes is reported to depend on hydrophobicity and electrostatic interactions between contaminants and ED membranes [167].

**Fenton-based processes** are also widely studied in combination with electrochemistry. For instance, Fenton and photo-Fenton processes can be upgraded to electro-Fenton (EF) and photoelectro-Fenton (PEF), enabling the on-line electro-generation of hydrogen peroxide using a gas diffusion electrode as the cathode by O$_2$ reduction. Additionally, Fe$^{3+}$ can be regenerated at the cathode from the reduction of Fe$^{2+}$; thus, reducing the amount of sludge production. There are several approaches to the process, as Fe ions can be produced by a sacrificial iron anode or, if a heterogeneous Fenton process is used, the anodic
process can be integrated with ELOX electrodes to foster a synergistic oxidation potential. Among other approaches, solar photoelectro-Fenton (SPEF) is gaining much attention because it uses solar radiation instead of artificial light, reducing energy consumption and associated treatment costs. More information on Fenton process and its different approaches can be found elsewhere [168,169]. The mineralization of chloramphenicol by EF and SPEF was studied in a 10 L pilot plant. SPEF was much more efficient than EF using the same conditions, resulting in 89% and 45% of the antibiotic degradation, respectively. However, SPEF presented an elevated energy consumption of 30.8 kWh m⁻³, with a current efficiency of 36% [170]. Furthermore, the authors note that the use of BDD anodes resulted in a much more efficient oxidation of chloramphenicol, based on previous experiments in a lab-scale stirred reactor. Complete mineralization of levofloxacin was achieved using a pre-pilot flow plant consisting of a filter-press reactor coupled to a photoreactor with very low specific energy consumption [171]. An electro-Fenton filtration system, based on iron nanoparticles attached to carbon felt electrodes, achieved only up to 85% degradation of diclofenac but at neutral pH and low electrical conductivity [172]. Additionally, a PEF-type process, based on the substitution of H₂O₂ by HClO and UV light for Fe²⁺ regeneration, achieved complete sulfamethoxazole degradation at relatively low current densities and without the generation of toxic chloro-organics [170].

**Electrooxidation (ELOX)** has the potential to remove a broad range of OMP and is especially promising in the abatement of perfluorocarboxylic acids, which are recalcitrant to other AOPs [173]. As the oxidation takes place at the surface of the anode, mass transfer limitations, due to low pollutant concentration in wastewater streams, may reduce the efficiency of the process. Therefore, it is preferable to use this technology in pre-concentrated streams, e.g., for leachate treatment (from hospitals, industries or landfills) or membrane filtration retentates. Heavy metals can be removed by electrodeposition on the cathode; however, this process can also lead to passivation [174]. The removal of 12 emerging contaminants from WWTP secondary effluents was evaluated in a pilot system to study the application of ELOX from reverse osmosis concentrate, reporting excellent results with degradation values between 94 and 97%, except for ibuprofen, for which only 70% abatement was achieved [175]. Salmeron et al. compared different Fenton-based technologies at natural pH (using a complexing agent to keep iron in solution) with anodic oxidation approaches for the treatment of
nanofiltration retentates [141]. Solar-assisted ELOX outperformed EF and SPEF due to the high chloride concentrations of the retentate, achieving a total degradation of 80%. However, a high concentration of chloride was detected in the treated effluents.

Another promising application is the enhancement of ozone treatment with the electrochemical generation of \( \text{H}_2\text{O}_2 \), the so-called electro-peroxone process, although only one pilot-scale example was found in the literature [23]. In this paper, the authors report the removal of 90% of selected pharmaceuticals at a flow rate of 113 L h\(^{-1}\), requiring an ozone dose of 9.3 mg L\(^{-1}\) and an electrical energy input of 0.135 kWh m\(^{-3}\). Furthermore, the electro-peroxone process has been shown to reduce bromate formation in bench- and pilot-scale operations due to reduced \( \text{O}_2 \) lifetimes and \( \text{H}_2\text{O}_2 \)-mediated quenching of relevant intermediates [23,176].

Electrochemical-coupled photocatalytic or ultrasonic techniques for pollutant degradation have not seen much use out of laboratory scale. Photo-electrocatalysis (PEC) improves the efficiency of photo-generated charge separation by increasing the lifetime of the electron-hole pairs created in the semiconductor. There are no pilot or large-scale investigations of photo-electrocatalytic degradation of pollutants in the literature. However, there is reasonable potential for large-scale treatment of water streams using the PEC process, as stable continuous operation at a 50 mL lab-scale reactor, achieving more than 80% degradation of tetracycline [146]. Sonoelectrochemical techniques include several methods, such as sonoelectrolysis or sonoelectro-Fenton, which have been successfully studied at laboratory scale [177]. As in the case of PEC, no examples of micropollutant removal at pilot or larger scale have been found in the literature review.

### 4.7. Irradiation treatments

The classification of irradiation techniques comprises ultrasonic and electromagnetic radiation application to treat contaminated waters. In the case of ultrasonic irradiation, sonochemical treatments use high-power ultrasound in three different approaches: formation of hydroxyl radicals, pyrolytic decomposition or supercritical water oxidation [178]. Regarding electromagnetic irradiation, two techniques have been used to some extent: (i) electron-beam treatments that produce highly reactive species formed from water radiolysis [179] and (ii) microwave treatments that degrade organic molecules mainly via thermal effects, caused by rapid heating at the molecular level [180].

The literature search shows the limited application of this group of techniques in the field of wastewater treatment. From the 169 initial results in the initial search (see Table S1), the number was reduced to 2 manuscripts in the selected papers exploring the combination of ozone with ultrasound [181] and ultrasonic-assisted UV treatment [182]. Therefore, the technological status of this group of treatment techniques is still far from actual pilot and real scale implementation.

### 5. Environmental aspects of tertiary treatments

As LCA is an internationally standardized method to identify environmental impacts throughout the life cycle of a technology, it can provide excellent insight into the environmental strengths and weaknesses of the different technologies and complement the technical and economic indicators of the systems under study. The publications assessing the environmental profile of tertiary water treatment plants are summarized in the supplementary information (ESM 5) together with some relevant data such as location, wastewater origin, functional unit or assessment methods, among others. Close to 50% of the manuscripts refer to lab-scale operation despite the idea that LCA is a methodology that is mostly applied to mature technologies, as there is a paradigm shift in which LCA is used prospectively to support decision making in the early phase of research and technology development to compare novel processes with existing commercial alternatives. However, there are some methodological and practical difficulties that need to be addressed, such as lack of data, uncertainty and how to deal with the extrapolation of laboratory data to full scale process [183]. Most of the studies analyzing the environmental impacts of tertiary treatments include UV techniques and ozonation, which account for more than 50% of the selected publications. In order of relevance, activated carbon units stand out, accounting for 25% of the total number of manuscripts. Among the innovative treatments, Fenton-based methods represent 25% of the publications, with solar photo-Fenton being the most evaluated approach. Surprisingly, reverse osmosis and nanofiltration, which are widely used tertiary treatment and drinking water purification technologies, are hardly studied using the LCA approach. Most of the reports have been conducted in Europe. There is limited evidence from Central and South America as well as from the African and Asian continents. In terms of the scope of LCAs, the operational phase is the most studied, as the main environmental impact is assumed to occur in this phase, as the construction and decommissioning phases are considered non-significant [8,184]. In contrast, the impact of the construction phase of the primary and secondary stages of a WWTP is widely studied [185]. Therefore, the construction phase of tertiary treatment is slowly starting to see more inclusion within the system boundaries in recent years [186,187].

Tertiary treatments were considered in many cases as an additional step for conventional WWTP effluents, either to reuse water or to improve effluent quality, as environmental benefits of water reuse through tertiary treatment in real WWTPs are identified [188–190]. Filtration techniques are already implemented for wastewater treatment, either alone or in combination with other techniques. In this context, Awad et al. [191] studied a basic tertiary treatment based on chemical coagulation followed by sand filtration, which improved global impact categories such as abiotic depletion, acidification, eutrophication or global warming. The key to impact reduction was water reuse without increasing energy consumption. Within the water reuse approach, another study was conducted in Tehran in which 20 different configurations were considered, including established treatments such as UV, UF or RO. However, the publication focuses more on the development of a method to aid decision-making on the type of water reuse (irrigation, industrial parks, etc.) and the configuration and associated costs of the technologies to choose for each case [192]. In France, several types of treatment trains, combining different types of filtration with UV treatments and disinfection, were evaluated to reuse water and comply with French legislation [193]. In this case, sand filtration with UV was the best alternative since it entailed the lowest energy consumption while still complying with quality regulations.

Ultraviolet treatments are commonly used in combination with oxidizing species or other treatment techniques to synergistically improve the efficiency. Foteniis et al. [194] analyzed different light-driven processes, such as solar and UV photolysis in combination with \( \text{H}_2\text{O}_2 \) and concluded that the main impact was due to electricity consumption and that chemicals did not affect negatively due to their low dosage. However, other studies reported environmental problems due to the addition of oxidants to UV treatments. For example, the removal of micropollutants in hospital wastewater treated by UV irradiation technology combined with \( \text{H}_2\text{O}_2 \) showed that the addition of peroxide has a great influence on the environmental impact due to its production process. Furthermore, it was shown that low-pressure lamps have a significantly lower impact than medium-pressure UV lamps [195]. Furthermore, a UV unit was applied to remove these contaminants, followed by the addition of sulfate-based oxidants. Apart from the promising economic data, the production of oxidizing agents is the main hot spot of these systems, which increases the impacts in several categories [196]. UV radiation was also combined with an electrochemical oxidation system to treat textile wastewater. This system demonstrated its technological feasibility and good environmental performance compared to conventional biological and tertiary treatment. Although the salts used as electrolyte had the greatest impact on the system, the addition of a reconstitution step to reuse water and salts proved to be...
beneficial to the process [197].

The environmental impacts of ozonation were less studied than those of UV, but there are studies reporting that ozonation impacts are reduced when compared to UV treatments [184,198], while others point out in the opposite direction, reporting high environmental impacts for ozonation when compared to UV treatments [199]. However, when compared to nanofiltration or adsorption on activated carbon, ozonation is less favored due to its inability to remove heavy metals and the production of harmful by-products [200]. Ozonation was also evaluated at laboratory scale to remove micropollutants in WWTP effluents noting that the amount of ozone applied and the type of columns play an important role for the environmental assessment. The toxicity of residual ozone in the effluent has to be taken into account, as there is a trade-off between the reduction of micropollutant toxicity and greenhouse gases (GHG) emissions from ozone production [201].

The environmental impacts of activated carbon adsorption technologies were evaluated in several investigations. For instance, different AC approaches were evaluated in a large-scale pilot fluidized bed. The results showed better performance of β-GAC compared to PAC, obtaining a similar outcome of GAC for a fixed bed in previous studies. The β-GAC technology also showed better environmental performance than regular GAC, generating impacts that are about ten times lower than bibliographic results [202]. Thompson et al. evaluated wood biochar as an alternative material to activated carbon in the removal of micropollutants [187]. A priori, it appears that wood biochar is more environmentally-friendly than activated carbon. However, the impacts were distributed between activated charcoal and biochar since the data were obtained through a laboratory-scale operation. The use of AC produced from local waste biomass in a large-scale WWTP was found to have a lower environmental impact for the removal of micropollutants compared to conventional AC [203]. However, it is reported that poorly designed systems and pre-treatment/drying of feedstocks could result in worse environmental footprints than conventional carbon [204].

Li et al. [205] compared ozonation, GAC and RO technologies with the main objective to remove micropollutants in domestic wastewater. While all technologies showed good micropollutant removal, reverse osmosis performed significantly worse when energy consumption is considered. In this study, the authors did not perform an LCA comparison for the different scenarios to obtain the alternative with the best environmental performance. Rahman et al. [206,207] conducted a comparative study between these treatments including the additional consideration of UV + H₂O₂. In terms of ecotoxicity and human toxicity, GAC and ozonation showed the best results, while, again, the worst results were obtained for the RO process. However, the advantage of AC adsorption compared to ozonation was found to be negligible although it could be significant depending on the profile of the electricity mix [202]. The electrical energy demand for GAC processes in WWTPs is 2–4 times lower compared to ozonation, but when cumulative energy demands (e.g., production and transport) are considered, the GAC process consumes 30% more energy and emits more GHGs than ozonation [59,208]. GHG emissions can be reduced by 80% if spent carbon is recycled. Although transport and dewatering costs and mass losses of 5–15% per regeneration cycle must be taken into account, recycling of spent carbon requires less energy and is more economical than producing fresh GAC, due to shorter pyrolysis times [209]. Moreover, Benston et al. could not observe an advantage of using virgin carbon over reused carbon in a meta-analysis [210].

Electrochemical processes are by far the least studied among those considered innovative tertiary treatments, especially when coupled to solar light. Despite the proven efficiency of solar photo-Fenton or photoelectro-Fenton, solar photo-Fenton was more environmentally friendly in terms of energy than photoelectro-Fenton [211,212]. Following these studies, Rodríguez et al. also considered the evaluation of heterogeneous and homogeneous Fenton processes at laboratory scale but using real wastewater of a pharmaceutical industry [213]. Although both configurations had acceptable efficiencies for micropollutant removal, the homogeneous Fenton had higher environmental impacts caused mainly by sludge production and higher operating temperature than the heterogeneous Fenton, which had problems related to chemical consumption. Ioannou-Ttofa et al. [186] evaluated the solar Fenton method in a pilot plant considering all system inputs (including the operational phase and the construction phase). The sustainability of this technology is very promising since its carbon footprint is only 8.7 kg CO₂ per cubic meter of treated wastewater. The environmental impact of Fenton-based removal processes was also compared with established tertiary technologies, such as ozonation or nanofiltration. Arzate et al. [214] compared ozonation, which is considered as an energy demanding process, with solar photo-Fenton, which a priori is considered a sustainable technology. The photo-Fenton process performed worse than ozonation due to the amount of chemicals required and the pH requirements. In addition, continuous operation is hampered by non-uniform irradiation; for example, additional storage technology would need to be installed to harvest solar energy for night-time operation.

Gallego-Schmid et al. [215] evaluated solar photo-Fenton at different pH and with and without the introduction of a nanofiltration technology. The results of Arzate et al. [214] showed a similar trend in which solar photo-Fenton had the worst impacts in most of the environmental categories analyzed. Furthermore, Tarpani and Azapagic (200) included more technologies in the comparison and analyzed the abovementioned processes (ozonation, solar photo-Fenton and nanofiltration) and GAC. As in the previous publications, solar photo-Fenton followed by ozonation had the most negative effects, while the NF unit was the best for between 13 and 18 impact categories. The photo-Fenton process also showed a negative impact compared to other solar-based AOPs. This negative environmental impact was confirmed by Pesqueira et al. [216] on the outcomes of the experiments conducted for pilot-scale treatments based on solar energy (photolysis, photocatalysis and photo-Fenton). It is concluded that the negative impact of the photo-Fenton process is caused by the acid pH required to avoid Fe precipitation and the consequent need for neutralization of the treated effluent. The negative environmental impact due to the use of chemicals in solar photo-Fenton was confirmed in the evaluation of a semi-industrial solar collector plant [217]. Surprisingly, in a study comparing heterogeneous photocatalysis and homogeneous photo-Fenton by Muñoz et al. [218], the solar photo-Fenton presents a lower environmental impact mainly due to the larger size of the solar collector field required for the photocatalytic process.

Beyond Fenton-based technologies, there are a couple of publications that evaluate the impacts of photocatalysis and electrooxidation. Gíménez et al. [219] compared photocatalysis and photo-Fenton processes at laboratory scale focusing on the removal of metoprolol. Photocatalysis showed a worse environmental impact related to energy consumption. In this study, electricity was disregarded for comparison and this can be considered problematic when extrapolating the results. Costamagna et al. [220] evaluated the degradation of phenol with photocatalysts based on zinc oxide doped with rare earth compounds. Zinc concentrations were modified to observe how they affect the environmental impact. Although the results related to pollutant removal were very promising, the process has issues related to the impact of zinc and electricity. The environmental impacts of the electrooxidation process were not compared with other tertiary processes, but in combination with other systems to improve its environmental profile. The intensification of the ELOX process with ultrasound and UV was evaluated in a bench-scale system with treated wastewater, with the ELOX-UV system being the option with the least impacts due to its lower energy requirements [221]. As the main problem related to electrochemical technologies is energy consumption, the coupling of electrochemical systems with renewable energy sources is being investigated. For example, ELOX has been coupled to wind and photovoltaic energy devices, showing an improvement of the impacts related to energy consumption, since it is estimated that 90% of the impact is caused by the associated fossil energy consumption [222].
The environmental evaluation of established tertiary technologies is also compared with several treatment methods outside the scope of the review, but the authors considered it relevant to look at the big picture in environmental comparisons of different treatment methods. For instance, Foglia et al. [223] compared the MBR technology with established treatments such as chemical and UV disinfection, showing better environmental performance in all impact categories except for freshwater eutrophication. On the other hand, Holloway et al. [224] reported that MBR treatment coupled with RO and UF have greater impacts than a treatment sequence composed of microfiltration, RO and UV for the generation of reclaimed water. The established treatments were also compared with other innovative non-abiotic methods such as algae growth [225] reporting 75–88% of efficiency in micropollutant removal and better environmental indicators than UV, ozonation or GAC due to the energy efficiency of algae. Other innovative techniques such as the application of bioaugmentation to sand filters [226] or the use of enzyme-coated membranes [227] were also compared to GAC adsorption, showing potential environmental and economic advantages.

6. Economic aspects of tertiary treatments

The implementation costs of advanced treatment technologies are composed of capital costs (CAPEX), which include land purchase, construction and decommissioning costs, and operating costs (OPEX), which are mainly influenced by energy and chemical consumption and the labor required for operation and maintenance [228]. Even when the technological parameters of a treatment technology are well studied at laboratory or even pilot scale, it is challenging to apply these results for cost estimation of new plants due to region-specific costs and variable wastewater characteristics and treatment goals.

The economic data for the ozonation process in the reviewed studies are heterogeneous and incomplete. This is because energy consumption is variable over a range of five orders of magnitude due to the complex interrelationships of individual rate constants, matrix composition and operating configuration. However, Mikkos et al. [229] found in a meta-analysis that ozonation has lowest median energy consumption values compared to other AOP processes, being lower than 1 kW m\(^{-3}\) operating configuration. However, Miklos et al. [229] found that energy demand was reported to be less than 1 kW m\(^{-3}\) and operational costs in the range of 0.12–0.16 € m\(^{-3}\) were indicated [65,70,229]. Based on pilot-scale data, Sbardella et al. [196] reported even lower costs for a UV/sulfate radical based treatment, showing a successful removal higher than 80% of micropollutants and a treatment cost of 0.088 € m\(^{-3}\).

Reina et al. [234] studied the operational and construction costs of photo-Fenton technology. The total costs ranged between 0.76 € m\(^{-3}\) and 1.39 € m\(^{-3}\), depending on the UV irradiance and the amount of iron. On the other hand, both CAPEX and OPEX were evaluated by Sánchez-Pérez et al. [120] for solar photo-Fenton process at pilot scale, providing a CAPEX of 0.067 € m\(^{-3}\) d\(^{-1}\) and an OPEX of 0.582 € m\(^{-3}\) for the process conducted at pH 3. When the process is performed at circumneutral pH, costs are reduced to 0.033 € m\(^{-3}\) d\(^{-1}\) and 0.206 € m\(^{-3}\), respectively. Moreover, solar photo-Fenton was compared with the ozonation process. The economic comparison (operational and construction costs) showed that solar photo-Fenton has higher costs (0.51–0.92 € m\(^{-3}\)) than ozonation (0.24–0.64 € m\(^{-3}\)) due to the large amount of chemicals consumed in the operational phase [235]. However, Prieto-Rodríguez et al. [47] studied the same treatments and their conclusion was exactly the opposite. Solar photo-Fenton was valued about 0.188–0.358 € m\(^{-3}\), whereas 0.450–0.560 € m\(^{-3}\) were the values for ozonation. This means that costs can change and must be carefully determined. The main function of the plant in terms of removal of micropollutants can change the costs for or against the technology. Strictly speaking, a comparison can only be made if the matrix composition and removal rate constants are similar. However, by comparing a sufficiently large data set, these uncertainties lose weight and general assumptions can be made about the efficiency of different treatments. Miklos et al. [229] found that reported energy consumption values for photo-Fenton, and electro-AOP were in the range of 1–100 kW m\(^{-3}\). Point-of-use solar disinfection (SODIS) of drinking water is an option for developing countries with high solar irradiance [236], as capital costs are mainly associated with the need for large irradiation areas and buffer tanks for downtime storage.

Detailed energy and cost evaluations for ozonation, GAC and PAC adsorption based on full-scale and pilot scale plants in Germany, have been presented in the literature [12,208]. The CAPEX values for ozonation and PAC adsorption are around 0.05 € m\(^{-3}\). While ozonation accounts for higher machinery costs (ozone generator), civil and electrical works are cheaper compared to the PAC process. The establishment of the GAC adsorption processes accounts only for 0.035 € m\(^{-3}\), provided that a filtration unit is already in place. The operating costs of the three treatment processes ranged around 0.04 € m\(^{-3}\), with different shares of individual contributors. While ozonation had highest electrical energy costs, PAC had the highest maintenance and personnel costs, while GAC techniques resulted in the highest and most variable material costs. This is also reflected in studies from other countries reporting variable process costs. Ek et al. [91] estimated the cost of GAC adsorption, accounting for the cost of the adsorbent to be around 0.14 € m\(^{-3}\). These costs could be decreased to 0.11 € m\(^{-3}\) when regenerated carbon was considered for application. The total system costs were estimated to be 0.31 € m\(^{-3}\). At the present stage of development, ozone treatment and activated carbon adsorption techniques with subsequent filtration steps are considered the most economically viable on a large scale in central Europe and are increasingly applied in Switzerland to comply with the current legislation [237].

Conversely to the abovementioned technologies, pressure-driven membrane filtration techniques account for significantly higher investment and operational costs due to expensive membranes and the high demand for pumping energy, respectively. Margot et al. [83] compared the influence of nanofiltration and sand filtration as...
alternative post-treatments to a PAC process, showing that the process costs with the implementation of nanofiltration comprised 0.80 € m\(^{-3}\) while sand filtration accounted only for 0.16 € m\(^{-3}\). Echevarría et al. [238] reported an OPEX of 0.31 € m\(^{-3}\) for a plant size of 15,000 m\(^3\) d\(^{-1}\) while assuming a membrane lifetime of 6 years and energy consumption of 1.3 kWh m\(^{-3}\). The CAPEX accounted for 662 € m\(^{-3}\) d\(^{-1}\) (translating to 0.044 € m\(^{-3}\) at peak flow). When treatment goals are less stringent, a common option for cost reduction is to divert the flow of wastewater, mixing with RO treated water. By producing a 50% blend, the OPEX could be reduced to 0.18 € m\(^{-3}\) on the expense that removal of selected OMP is reduced to 50%. Furthermore, since the energy demand of pumping scales almost linearly with membrane area and applied pressure, the size of the plant does not significantly reduce operating costs.

García et al. [96] calculated OPEX reaching 0.24 € m\(^{-3}\) while CAPEX decreased from 0.48–0.31 € m\(^{-3}\) comparing treatment capacities between 1 and 1000 ML d\(^{-1}\). Conversely, Hube et al. [239] argued that the rather simple configuration of membrane filtration can lead to low capital costs compared to other treatments. Thirty-nine percent of the reviewed studies investigating membrane treatments were conducted in Spain, while the rest of the studies were distributed worldwide, including publications from South Africa, Brazil and India. In contrast, only one pilot-scale study was presented for Germany [240]. This can be explained by the discrepant energy costs [241], as in 2020 household electric energy prices were 0.08 $ kWh\(^{-1}\) in India, the price in Germany was 0.38 $ kWh\(^{-1}\). Recently, the possibility of using energy-intensive but flexible processes, such as reverse osmosis, as a buffer in energy grids increasingly based on extractable energy has been proposed. Flexible operation patterns of WWTPs could compensate for the fluctuating production capacity of wind and solar energy [242].

Electrochemical treatments are usually regarded as energy intensive treatments. Although electrochemical treatments, such as electro-oxidation, present high energy consumptions [76], the use of electrochemical-assisted techniques presents competitive operational costs to be implemented in WWTPs. The use of electrodeposition is optimized by its extensive use in desalination and can be an effective method to remove heavy metals. For instance, a pilot plant with a productivity of 285 m\(^3\) h\(^{-1}\) integrating electrodeposition in a treatment train with ultrafiltration and reverse osmosis attained excellent reduction of copper concentration with an estimated total cost of 0.3–0.4 € per m\(^3\) of treated water [243]. The use of electrochemical technologies for the electro-generation of H\(_2\)O\(_2\) is also reported to reduce the costs compared to dosage. For instance, Wang et al. [100] estimate that the energy required for the in-situ generation of H\(_2\)O\(_2\) accounts for additional costs of between 0.4 and 0.8 USD kg\(^{-1}\)O\(_2\), while the dosage of H\(_2\)O\(_2\) involves costs of 1.2–1.5 USD kg\(^{-1}\).

For other innovative treatments, there is a lack of available data for cost calculations, as only laboratory-scale data are available. The energy consumption of UV-photocatalysis, ultrasound and microwave photocatalysis treatments have been reported to exceed even 100 kW m\(^{-3}\), however, calculations on this basis tend to overestimate energy consumption and thus costs [229]. Increasing energy efficiency with increasing plant size is a common concept in studies considering primary or secondary treatment plants. In the short-term perspective, these treatment options have potential to be further applied and investigated for the treatment of highly contaminated industrial wastewater, landfill leachate and RO/NF retentates. For example, the higher overall treatment costs of landfill leachate, even with conventional treatments, and the typically lower volumes treated, open up more options for the application of innovative treatment processes.

In terms of the costs and impacts of each technology, users and regulators must carefully balance the amount of investment, both economic and environmental, to achieve the goal of safer water resources. Muñoz et al. [244] propose an integrated approach to assess the eco-efficiency of a technology by weighing environmental and economic burdens. Based on their reasoning, ozonation was less favorable than photo Fenton or solar photo Fenton treatment. However, the costs assumed in this study were almost ten orders of magnitude higher than in the studies reviewed above. The centralized and distributed application of tertiary treatments was also studied for several established technologies. According to the results, centralized treatment is preferred for the disposal of pharmaceuticals [184], but more research would be needed to confirm this. In addition, social aspects will play a considerable role in the final steps of decision-making. In Switzerland, the public supported the decision to legally oblige WWTPs to guarantee the removal of certain indicator pollutants at 80%. This measure will increase treatment costs by 6% across the country. In addition, energy consumption is estimated to increase by around 0.1% with the most advanced technologies [237,245]. However, developing countries will not have the resources to implement such programs in the near future, as the prior objective is still to provide at least adequately disinfected water. Despite this difficult situation, the lack of infrastructure networks could also lead to the development of simple decentralized treatment options based on renewable energy sources more quickly than in developed countries.

7. Benchmarking of the technologies

As far as safe water reuse strategies are concerned, the tertiary treatment processes applied must fulfill several framework conditions. The treatment trains must be adaptable in size to the wastewater flow and pollutant load at the respective application site, while operation has to be reliable and provide redundancy in case of failure of individual units. Therefore, reproducible measurement schedules for indicator substances should be supported by fast online monitoring techniques such as fluorescence excitation emission matrices (FEEM), as well as by effect-based assays on (acute) toxicity, estrogenicity, mutagenicity or antibiotic susceptibility [246]. The integration of reasonable and standardized protocols in a “whole effluent” approach is currently an important research topic [247]. A sound assessment of the (avoided) risks of each technology is the basis of a comprehensive LCA study. Furthermore, regionalization of characterization factors was suggested as a key issue to represent an accurate toxicity impact in local environments [248]. It is also reported that the currently used assessment methods could provide different results and may not include some micropollutant factors [249].

In the following we summarize and qualitatively discuss the main strengths and weaknesses of each advanced treatment technology under technological, environmental and economic points of view, based on the findings of the studies selected. The technologies reviewed can be classified into (advanced) oxidation processes and physical retention treatments. While oxidation processes comprise traditional ozone treatment and emerging ancillary technologies, conventional UV treatment and enhancement technologies, as well as electrochemical treatments, physical treatments include adsorption processes mainly based on activated carbon and membrane filtration (Table 1).

One of the main drawbacks of ozonation is that, due to its high reactivity and instability, ozone must be generated on-site from oxygen by electrical discharge, with a yield of about 10%, which leads to high electrical energy consumption in the plant. In addition to the low ozone yield, the effectiveness of ozone treatment is limited by its slow dissolution rate and rapid decomposition. However, modifications to air diffusers that form micro-nano bubbles increase the treatment efficiency [46]. Furthermore, the high toxicity of ozone requires the design of ozone destruction units which remove unreacted ozone from the exhaust gas stream after treatment [250]. Trained personnel and strict safety protocols are necessary to minimize the risk of accidental release. In addition, the formation of toxic by-products such as bromates, which are potential human carcinogens, has been associated with this process [251]. Increased effluent toxicity after ozone treatment was reported by several studies and contributed to worsen environmental impacts from an LCA perspective. Despite these drawbacks, disinfection capacity and low operational costs are the main advantages of ozonation [252]. The
Table 1
Qualitative classification matrix of the investigated tertiary treatments regarding different feasibility criteria.

| Categories          | Oxidation | Electro | Adsorption | Filtration |
|---------------------|-----------|---------|------------|------------|
|                     | O₃        | EC      | GAC        | PAC        | NF         | RO         |
| Superior performance| O₃        | O₃      | O₃         | O₃         | O₃         | O₃         |
| Baseline technology | Cat       | Cat     | Cat        | Cat        | Cat        | Cat        |
| Poor performance    | UV        | UV      | UV         | UV         | UV         | UV         |
| OMP removal         | H₂O₂      | H₂O₂    | H₂O₂       | H₂O₂       | H₂O₂       | H₂O₂       |
| Heavy metal removal | H₂O₂      | H₂O₂    | H₂O₂       | H₂O₂       | H₂O₂       | H₂O₂       |
| Pathogen removal    | UV        | UV      | UV         | UV         | UV         | UV         |
| Additives           | UV        | UV      | UV         | UV         | UV         | UV         |
| Byproducts          | H₂O₂      | H₂O₂    | H₂O₂       | H₂O₂       | H₂O₂       | H₂O₂       |
| Waste               | UV        | UV      | UV         | UV         | UV         | UV         |
| Turbidity           | UV        | UV      | UV         | UV         | UV         | UV         |
| pH                  | UV        | UV      | UV         | UV         | UV         | UV         |
| TSS                 | UV        | UV      | UV         | UV         | UV         | UV         |
| DOC                 | UV        | UV      | UV         | UV         | UV         | UV         |
| Energy demand       | *         | *       | *          | *          | *          | *          |
| Operational risks   | *         | *       | *          | *          | *          | *          |
| Operational costs   | *         | *       | *          | *          | *          | *          |

*On-site energy demand.

The detrimental effects of induced toxicity can be circumvented when an additional filtration/adsorption step is applied after ozonation. In terms of applicability to wastewater matrix conditions, DOC is the most critical constituent that needs to be controlled prior to ozonation, while other characteristics such as TSS or turbidity have a minor influence as they are not related to DOC. The lowest removal rates were obtained for ibuprofen, oxazepam and sucralose, and their removal could be analyzed in the evaluation of operational conditions to increase the sensitivity of the method. Further research should focus on investigating effluent toxicity, elimination of antibiotic resistance genes, and decision-making based on operational costs and environmental impact.

Conventional UV treatment for pathogen removal requires irradiances of <500 mJ cm⁻² and short residence times, resulting in relatively low cumulative energy doses that minimize operating costs. However, these configurations are not efficient for OMP removal, not only because of the low transferred energies but also because of the intrinsic reactivity of most OMPs to direct UV photolysis. The first obstacle has been overcome with the development of high intensity photoreactor modules. To address the second problem, the dosing of additional oxidants has proven effective. While hydrogen peroxide in combination with high intensity UV treatment is already applied on a large scale, persulfate and chlorine dioxide are still under investigation, especially regarding the formation of toxic by-products. In addition, the environmental impact of their production and the possible risks associated with their unintentional release must be considered. All UV-based processes require water with low turbidity to maximize transmittance, so UV is usually applied after a clarification/filtration step.

Among the catalyst-based technologies, Fenton-based methods are the most studied. However, there is an agreement that the working pH of Fenton-based methods is a clear drawback, as chemicals are used both for acidification of the effluent and for pH correction before discharge or reuse. This drawback should be solved by improving the reaction at neutral pH to see its real use in WWTPs. From an environmental point of view, although the operational phase has worse impacts, Fenton-based methods could have less impacts if the construction phase is considered. Heterogeneous processes are favorable compared to homogeneous processes due to the easy recovery of the catalyst and the avoidance of changes in water composition. In addition, research focused on the development of new materials capable of improving light utilization, combined with a reusable catalyst operating under circum-neutral conditions, should be the main priority for further research work in this field. In relation to the high environmental impact of mercury pressure lamp manufacturing, alternative irradiation sources should be investigated. Although UV-LED irradiation is promising [253], it does not yet reach the energy efficiency of conventional lamps and cannot yet be considered an economically viable alternative. Moreover, according to available data, direct use of sunlight is more likely to remain a prospect for decentralized plants in the medium term. However, the indirect use of solar energy through photovoltaic plants could be an alternative worthy of consideration in remote areas [254].

Both GAC and PAC adsorption stages are effective against organic micropollutants, however, they do not achieve reliable removal of heavy metals, pathogens and ARGs. In direct comparison of GAC with RO, a similar range of OMP was removed by GAC, but RO was more efficient in removing heavy metals and volatile organic compounds [115]. In terms of on-site energy demand, GAC systems are preferable compared to energy-intensive processes such as membrane filtration and ozonation. However, when production is included in the assessment, GAC can be more energy intensive than ozonation, especially when adequate recycling systems are not applied. End-of-life scenarios also have a high environmental impact [256]. Depending on the treatment goals, GAC processes can be integrated into treatment trains to efficiently exploit the benefits of this treatment stage, for example, when targeting higher OMP removal in secondary effluents with high DOC loading, GAC can be used as a polishing step after ozone/AOP treatment [40,92]. In the case of PAC, recycling of spent adsorbent is currently not possible in most applications. In terms of improving the economic and environmental impact of PAC, not only efficient recirculation and recycling schemes need to be further investigated, but the materials applied must be renewable and not of fossil origin. In the short term, recycling of
industrial waste such as fly ash from coal plants could also be a possibility [257]. Spent activated carbon sludge must be properly handled to prevent soil and surface water contamination. Researchers are currently investigating the factors influencing OMP removal by activated carbon processes, as well as the application of control strategies, in order to increase the reliability of these processes. Reverse osmosis and nanofiltration processes an efficient barrier to retain most OMP, pathogens (including ARGs) and heavy metals. Depending on the configuration, desalination can be achieved, which is an important treatment objective, especially in reuse applications, and results in a clear benefit of this technology compared to others under review from which only electrodeislation is a considerable alternative for salt removal. The produced water can be provided with a reliable high quality, provided that a proper control and maintenance protocol is applied. Maintenance ensures the preservation of the expensive membrane modules against fouling and scaling, but requires backwashing procedures with antifoulants and antiscalants, which contributes negatively to the environmental impact. Although the RO/NF process is well established in regions with high water stress and comparatively low energy costs, from an LCA perspective, reverse osmosis is not recommended by any of the articles reviewed in this study, as the high energy consumption strongly impacts environmental indicators such as greenhouse gas emissions. Research should be directed towards the development of more durable and efficient membranes. This could lead to lower membrane and energy costs, as well as lower consumption of cleaning agents and thus lower environmental impact. Furthermore, the generation of a waste stream in the range of 10–20% of the originally treated stream increases the environmental burden and decreases the treated water yield [258]. Possible solutions for the management of retentate are its recirculation to WWTP headworks, evaporation ponds or AOP treatments [259]. For smaller volumes and higher intrinsic treated stream increases the environmental burden and decreases the treated water yield. Electrochemical methods have great potential to reduce the environmental impacts associated with micropollutant removal, as they mainly use electricity, which can be considered as a clean chemical. However, pilot-scale research is still scarce, and the different technologies need to reach larger scales of implementation in a significant number of publications to consolidate this potential. As highlighted in the LCA section, energy and chemical production are responsible for most of the environmental impacts in tertiary treatment. Electrochemical treatments could therefore be one of the keys in the quest to reduce chemical consumption. For example, electrooxidation does not use any chemical reagents, while electro-Fenton processes produce H₂O₂ by electroreduction of oxygen. As for energy consumption, electrochemical systems can be easily combined with renewable energy sources, but more studies are required to optimize the coupling [260]. The integration of renewable energy sources in combination with electrochemical wastewater treatments is proven to reduce the environmental impacts produced by energy consumption [222].

8. Concluding remarks

One of the drawbacks of the presented study is that peer-reviewed research articles are a limited source of operational data, given their specific focus and basic process parameters such as unit dimensions, critical conventional wastewater parameters and flow rates are not always reported. Regarding the rapidly evolving research on tertiary treatment schemes, more effort should be made in publishing reliable process-related data in the peer-reviewed literature. Nevertheless, the overview presented on the state of the art of tertiary treatments clearly identifies the key points of both full-scale processes already operated and innovative treatment processes based on these configurations and presents the solutions currently under development. To meet the requirements of water safety standards, a combination of different processes (multi-barrier approach) is often essential for each individual case.

In addition to economic and technological considerations, environmental constraints identified by a life cycle assessment must be incorporated into decision-making. Many authors point out that the key issues for most tertiary treatments are the electrical energy and chemicals consumption. More effort needs to be devoted to the characterization of the transformation products produced in the treatments to accurately assess the impact of the methods. The variability of influent quality needs to be monitored to take advantage of the high adjustability of chemicals and added energy in the AOP, which will reduce process costs. Risks to personnel and the environment should be assessed prior to implementation. For a complete risk assessment, which is necessary for any sound life cycle assessment, more attention should be paid to process evaluation based on toxicological data than to degradation efficiency alone. However, since so far, the application of effect-based effluent control is still under investigation, treatment efficacy is regulated and compared based on indicator substance removal targets. Many authors argue that the low concentrations of micropollutants and the lack of systematic assessment of their long-term effects when released into the environment mean that the environmental impact of new treatment trains outweighs the impacts of micropollutant discharge into the environment.

Faced with this problem, more environmental studies are needed to better understand the environmental profiles of tertiary treatments, preferably under real wastewater conditions and on a larger scale, to optimize construction and operation data, especially energy and chemical consumption. In addition, more work is needed on the analysis of innovative tertiary techniques, as the analyzed evaluations provided some contradictory results. In parallel, the characterization factors of micropollutants need to be revised and validated, to improve the accuracy of LCA results for effluents containing these pollutants.

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Availability of data and material

All data generated or analyzed during this study are included in this published article [and its supplementary information files].

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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