Current Technologies to Remove Organic Micropollutants from Wastewater

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Micropollutants are organic and mineral contaminants, including industrial chemicals, pharmaceuticals, pesticides, and personal hygiene products, that enter the water cycle (ground and surface waters) from human activities. They are found in trace concentrations and do not completely break down, accumulating and posing a risk to the aquatic environment and water resources . Pharmaceutical residues are of environmental concern since they are found in several environmental compartments, including surface, ground and waste waters. However, the effect of pharmaceuticals on ecosystems is still under investigation. To date, the removal of these micropollutants by conventional treatment plants is generally ineffective, in addition to producing a considerable carbon footprint.

Keywords: wastewater ; diclofenac ; carbon footprint

1. Introduction

Micropollutants such as pharmaceuticals and personal-hygiene products have been detected in different matrices (e.g., wastewater, natural water, groundwater) [1][2][3]; in spite of this, a large number of them are often not yet included in regulations [4]. Moreover, prioritized micropollutants in different countries (e.g., the UK and USA) could be varied according to the individual studies [5]. Apart from instrumentation constraints, the diverse sources of these micropollutants to the environment can lead to large uncertainties in the identification/quantification of them. The procedures for micropollutant analyses are generally expensive, and most of the studies focus on the quantification of pre-selected targeted analytes rather than the identification of all the compounds present in the natural matrices [2].

Evidence that traces of pharmaceuticals in the environment, in particular in water and soil, could have an adverse impact on wildlife such as fish, birds, and insects and knock-on effects on wider ecosystems, including antimicrobial resistance, has been widely reported [6][7][8][9]. Pharmaceutical residues have been found across Europe’s soils, sediments, surface waters and wastewaters and have even reached the drinking water, although not in quantities that cause immediate concern [10]. A wealth of ongoing research focuses on the development of suitable wastewater treatment to reduce the discharge of pharmaceuticals into the environment [11][12][13]. Typically, upstream (prior to release) and downstream (post-release) strategies may be adopted for pollution control, with the first being preferred and more effective. However, in the case of pharmaceuticals, although some improvements may be made upstream (e.g., manufacturing, distribution, prescription, consumption or management), and albeit education and awareness campaigns are very important [14], restrictions cannot be applied using a similar approach to that for other micropollutants, since pharmaceuticals are essential to satisfy the population’s healthcare needs.

In addition, the zero-pollution ambition for a toxic-free environment, as expressed in the European Green Deal [15], aims to protect both public health and ecosystems through avoiding the negative effects of chemical substances, including certain pharmaceutical residues in air, soil and water. The recently adopted Farm to Fork Strategy [16] includes the target to reduce overall EU sales of antimicrobials for farmed animals and in aquaculture by 50% by 2030, thus reducing this source of environmental contamination. Other initiatives, including the 8th Environment Action Programme [17], the Circular Economy Action Plan [18], the Chemicals Strategy for Sustainability [19] and the Biodiversity Strategy [20], set a framework for generating an overall shift to a production and consumption of resources, materials and chemicals, which is safe and sustainable by design and creates the lowest possible impact on the environment, including considering pollutants of emerging concern. Work is ongoing on a variety of interlinked topics, which includes the improvement of wastewater treatment at sewage treatment works (STW). In March 2019, the European Commission adopted the European Union Strategic Approach to Pharmaceuticals in the Environment (PiE), which focuses on actions to address the environmental implications of all phases of the lifecycle of (both human and veterinary) pharmaceuticals, from design and production through use to disposal [21].

The EU water law is under evaluation, and the 2019 evaluation of the Urban Wastewater Treatment Directive (UWWTD) highlights that it has delivered a reduction in loads and thereby contributed to the improvement of water quality as compared to 1990 [22]. However, it has also addressed the presence of contaminants of emerging concern (e.g., microplastics and pharmaceuticals) as well as the energy use during wastewater treatment (0.8% of all energy consumed in the EU) and associated sludge management [23][24]. A revised and modernised UWWTD should be a key legal instrument to properly address the European ambitions and the UN Sustainable Development Goals (SDG) for the coming decades [25].

The Water Framework Directive (WFD)—Directive 2000/60/EC—launched a strategy to define high-risk substances to be prioritized, with 33 priority substances and their corresponding environmental quality standards being ratified by Directive 2008/105/EC. This directive also set up the establishment of a watch list of 10 substances, in the first instance, to be monitored across the EU to gather support information for future prioritization exercises, and to be dynamic and updated every two years to respond to new information on the potential risks. Then, Directive 2013/39/EU established that the non-steroid anti-inflammatory diclofenac, the synthetic hormone 17-alpha-ethinylestradiol (EE2), and the natural estrogen 17-beta-estradiol (E2) should be included in the first watch list. Accordingly, Decision 2015/495/EU set the definite first watch list, which, besides the referred substances, also contained three macrolide antibiotics, namely azithromycin, clarithromycin, erythromycin, and another natural estrogen, viz. estrone (E1). Decision 2018/840/EU indicated that sufficient high-quality monitoring data were only available on diclofenac, which was removed from the list; the rest of the pharmaceuticals remained on the second watch list, which also added the antibiotics amoxicillin and ciprofloxacin. Most recently, Decision 2020/1161/EU established that, since four years is the maximum that any substance may be on the watch list, EE2, E2, E1, and macrolide antibiotics should be removed, while amoxicillin and ciprofloxacin should be maintained in the third watch list. This Decision, in agreement with the EU Strategic Approach to PiE and with the European One Health Action Plan against Antimicrobial Resistance (AMR), also set the inclusion of the sulfonamide antibiotic sulfamethoxazole, the diaminopyrimidine antibiotic trimethoprim, the antidepressant venlafaxine together with its metabolite O-desmethylvenlafaxine, and a group of ten azole pharmaceuticals [26].

The Green Deal [15] and the evaluation of the WFD [26] and UWWTD [24] identified the main challenges for the future: climate change (mitigation and adaptation) and energy consumption, zero pollution, circular economy, biodiversity, protection of aquatic ecosystems, protection of water resources, contaminants of emerging concern and other pollutants, and the speed of implementation of EU water directives. For example, a recent review by the Scientific Committee on Health, Environmental and Emerging Risks (SCHEER) is endorsing concentrations of diclofenac of 0.04 μg/L (40 ng/L) for freshwater and 0.004 μg/L (4 ng/L) for saltwater as the annual average evaluation of quality standards (EQS). These challenges are strong drivers to change approaches, technologies, and governance of water in Europe.

To date, conventional WWTPs are still not able to eliminate many micropollutants found in wastewaters [4], and based on the above information, greener technologies are urgently needed for the effective removal of pharmaceuticals in wastewater treatment plants without having a detrimental impact in the environment. Despite advances in wastewater treatment for pharmaceutical removal through the use of adsorption technologies, advanced oxidation processes (AOPs), and multiple treatment processes [27], researchers still face limitations in terms of cost and carbon footprint. Based on this, researchers have globally sought efforts to introduce and/or improve natural-based technologies with the potential to be consistent with the demands of a low-carbon future. Some technologies that are receiving particular interest for the removal of a variety of pharmaceuticals are discussed further in this work. They are: (i) constructed wetlands (CWs), which consist of a plant-based technology, offering low maintenance and operation costs, in addition to low energy demand [28][29][30]; (ii) anaerobic membrane bioreactor (AnMBR), an integrated system of anaerobic bioreactor and ultrafiltration (or microfiltration) considered as a low-energy-footprint technology and capable of efficiently producing biogas, with different recovery paths, and is used for energy neutrality of the system [31][32]; and (iii) enzymes, which are basically alternative biologically made catalysts with high efficiency for the removal of micropollutants and certain pharmaceuticals [33][34].

The framework of this work aims at providing information on the approaches being currently used for the removal of micropollutants in general and, in particular, pharmaceuticals, suggesting new approaches that could be used, either alternatively or to complement existing ones, and taking into consideration the potential reduction in carbon emissions in race to zero carbon.

2. Current Technologies: Efficiency and Carbon Footprint

Pharmaceuticals (and many micropollutants of emerging concern) are only partially removed from wastewater during biological treatment [35]. Therefore, usually an oxidant and/or adsorbent process is required, activated carbon and ozonation being the most common processes used by the water industry. Their efficiency in the removal of target micropollutants and carbon footprint require particular attention prior to the wider adoption by the global water industry.

There are several review documents on the use of ozonation and activated carbon, including specifics on operational parameters, capacity of plants, and removal efficiencies. The purpose of this section is not to repeat what has already been published in the literature but to provide enough information to the reader to understand why there is a need to search for alternative and less energy-consuming processes to remove micropollutants from wastewater.

2.1. Ozonation

One frequently applied process option to remove micropollutants from wastewater is oxidation, typically using ozone (O_3). In the existing large-scale plants, O_3 is generated from synthetic air on site and then dispersed into oxidation reactors at wastewater concentrations of 4–15 mg/L. Micropollutants are rapidly degraded by O_3 molecules or hydroxyl radicals formed by ozone. While the chemical reaction is generally non-selective, electron-rich compounds have been found to be reduced to a higher degree [21][22]. Pharmaceuticals that are particularly well degradable by ozone are, e.g., diclofenac, sotalol, sulfamethoxazole, and gemfibrozil [22]. The major drawback of ozonation is the formation of mostly unknown and potentially toxic oxidation by-products, e.g., bromate in bromide-rich wastewaters. To overcome this issue, ozonation is typically combined with a post-treatment for by-product removal, either by adsorption, e.g., GAC, or biological degradation, e.g., sand (bio-) filtration [16].

The carbon footprint of ozonation processes mainly originates from the on-site electricity use to generate O_3 from synthetic air. The typical energy consumption for ozone generation is estimated around 0.06 kWh/m^3 wastewater but will highly depend on the required O_3 dose (**Table 1**). In the ozone generating unit, 90% of this energy is converted into heat, which could potentially be recovered for heating purposes on site [23]. Apart from that, a considerable amount of energy is used for the production of synthetic air and for the operation of a post-treatment stage. The production of construction materials and activities to build the necessary infrastructure (e.g., reactors, piping) account for ca. 20% of the total carbon footprint of an ozonation stage [24]. The more sustainable the generation of electricity is, the higher the fraction of infrastructure carbon footprint becomes. In total, the carbon footprint of an ozonation stage is estimated to be in the range 5–60 g CO_2-equiv./m^3 of treated wastewater, depending on the operating conditions and energy sources.

Table 1. Estimated on-site and primary energy consumption of advanced treatment technologies, assuming average Swiss (182 g CO_2-eq per kWh) and EU (450 g CO_2-eq per kWh) energy sources and the following operating conditions: O_3 dose of 5 mg/L, PAC dose of 12 mg/L and GAC lifetime of 30,000 bed volumes [18][23].

Parameters	Unit	Ozonation	PAC	GAC
On-site electricity consumers		**Ozone generation, heating and aeration, pumping, post-treatment**	**Stirring and pumping, post-filtration**	**Pumping**
On-site electricity consumption	**kWh/m^3**	**0.06**	**0.02**	**0.01–0.05**
	kWh/p.e. and p.a.	**8–27**	**2.5–9**	**1–5**
On-site carbon footprint	**g CO_2-eq per m^3**	**10.9–27**	**3.6–9**	**1.8–22.5**
Primary energy consumption	**kWh/m^3**	**0.28**	**0.37**	**0.15**
	kWh/p.e. and p.a.	**34**	**46**	**19**
Primary carbon footprint	**g CO_2-eq per m^3**	**51–126**	**67.3–166.5**	**27.3–67.5**

2.2. Activated Carbon

The most frequently used adsorbent to remove micropollutants from wastewater is activated carbon, which is produced from carbonaceous raw materials, e.g., coal or coconut husks. After chemical and/or thermal activation, activated carbon is an excellent adsorption material with a large inner surface of 800–1800 m^2/g and hydrophobic surface properties [36]. Activated carbon has been found to preferably remove non-polar compounds that are positively charged or neutral at wastewater pH. Pharmaceuticals that are particularly efficiently removed by activated carbon processes are, e.g., ibuprofen, ketoprofen, atrazine, and metoprolol [22]. In advanced municipal STWs, activated carbon is applied either in the form of powdered activated carbon (PAC) with particle sizes of 50–100 μm, or as granular activated carbon (GAC) with particle size of 0.5–4 mm. PAC is dosed into wastewater at concentrations of 10–20 mg/L and, after adsorption has taken place, separated from the water stream and typically incinerated together with the sewage sludge. GAC, in contrast, is continuously applied in a fluidized or fixed bed reactor and, once its adsorption capacity is exhausted, can be thermally regenerated and partially reused [25].

The on-site energy consumption for PAC and GAC processes is comparably low, as they only require pumping and/or stirring. The highest carbon emissions are attributed, by far, to the production of activated carbon materials, particularly to the raw material extraction, combustion, and activation [24]. Depending on the raw material used, the carbon footprint of these processes varies between 5 g CO_2-eq per kg PAC in the case of coconut husk as a raw material and 18 g CO_2-eq per kg PAC if lignite or coal is used [23][24]. In GAC processes, used adsorbent can be regenerated and reused up to 90%, which significantly reduces the total carbon footprint of GAC compared to PAC processes. Generally, the major influencing factor for the advanced treatment's carbon intensity is the required PAC doses and the GAC bed lifetime, respectively. Approximately 19–27% of the overall carbon footprint is related to the production of construction materials and to construction activities for the process infrastructure (e.g., concrete basins, piping), depending on the specific plant design [24].

A recent study has used a life-cycle assessment framework to assess net environmental efficiencies for ozone systems and granular activated carbon on the removal of micropollutants with proven removal efficiency values and toxicity and/or ecotoxicity potentials. The results showed that the direct water quality benefits obtained from advanced water treatment were outweighed by greater increases in indirect impacts from energy and resource demands [37].

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