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Occurrence of organic microcontaminants in the wastewater treatment process. A mini review

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HIGHLIGHTS

- ► Ten-fold increase in the number of papers on PPCPs in WWTPs in ten years.
- ► Wastewater analysis can help tackle societal problems.
- ► PFCs in WWTPs present negative removal rates.

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ABSTRACT

A wastewater treatment plant may receive various types of wastewater namely, urban, industrial, agricultural, washout from the streets, wet or/and dry atmospheric deposition. As such, scientists have detected in wastewaters all major categories of pollutants like persistent organic pollutants (POPs), polycyclic aromatic hydrocarbons (PAHs) and pesticides, but also substances that are widely used as pharmaceuticals and cosmetics, classified as "PPCPs" (pharmaceuticals and personal care products). Finally, the latest categories of compounds to be looked upon in these types of matrices are illicit drugs (drugs of abuse, like cocaine, etc.) and doping substances.

This review article summarises major categories of organic microcontaminants that have been detected in wastewaters and studies their fate during the wastewater treatment process. Occurrence of these compounds in the influents and effluents are reported, as well as percents of removal, mass balances and phase distributions.

1. Introduction

Wastewater treatment plants (WWTPs) were initially designed to remove/decrease conventional pollution parameters (BOD_5, COD, total suspended solids, etc.) from the wastewater stream, so that the final effluent did not constitute a new source of pollution for the water body receiving it. However, it was soon found out that the wastewater organic load included high levels of a variety of hazardous organic pollutants and thus additional treatment steps and control measures became necessary. The quality of wastewater varies according to what types of influents the WWTP may receive, such as domestic wastewater, dry and wet atmospheric deposition, urban runoff containing traffic related pollution or agricultural runoff and the range of contaminants is even broader when industrial effluents are also included in the input wastewater [1–4].

WWTPs are also called "biological treatments" due to the secondary treatment step, during which the wastewater comes in contact with "activated sludge" and conventional contaminants are removed by means of biological degradation. Whilst this is the case for most of the organic load, for modern organic contaminants such as persistent organic pollutants (POPs), brominated flame retardants (BFRs), fluorinated compounds (PFCs) or pharmaceuticals among others, it has been shown that the biological treatment is not so efficient in their removal. These chemicals are not completely degraded and are either removed by sorption and deposition to the final sludge, by volatilisation, or by discharge onto a surface water body, if they remain in the wastewater effluent stream [7]. This last fraction is the most concerning, since it has been shown to be of relevant toxicity, readily bioavailable to living organisms, able to enter the food chain and hence ultimately exposing humans [5,6]. One of the most important factors that tend to keep organic microcontaminants in the wastewater stream is the dissolved organic carbon

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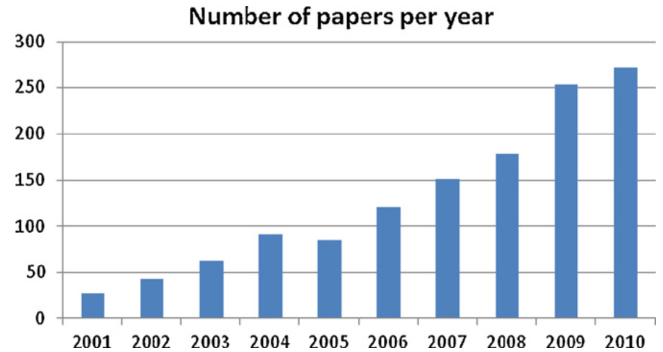

Fig. 1. Number of publications per year studying PPCPs in WWTPs. Source: SCOPUS™ Database.

(DOC) [7]. In particular, and due to its affinity with organic microcontaminants, DOC acts as an antagonist to sorption on particles and that way keeps organic microcontaminants in the wastewater stream.

In recent years, scientists have been considering as microcontaminants some compounds (or classes of compounds) that until some years ago were deemed safe or broadly supposed to be totally biodegradable, such as personal care products, pharmaceuticals or chemicals like caffeine, benzotriazole, etc. [8–13]. As a result of their broad usage, these microcontaminants have been detected in concentrations up to several μg/L in WWTP effluents and in surface waters.

Bearing in mind the aforementioned information, the scope of this paper is to present concentration levels, to describe the fate and trends and to discuss the respective implications of new categories of microcontaminants detected in wastewaters/WWTPs. These classes of chemicals include (a) pharmaceuticals and personal care products (b) illicit drugs (c) prohibited doping substances (d) persistent organic pollutants (e) perfluorinated compounds.

2. Methodology

Given the large number of studies present in literature, this study goes over some of the most important characteristics that govern the fate of OPs during the wastewater treatment process and presents interesting scientific aspects that derive from the chemical analysis of wastewaters for the aforementioned compounds.

3. Discussion

3.1. Pharmaceuticals and personal care products (PPCPs)

It has been known for over 20 years that pharmaceuticals and personal care products (PPCPs) enter into the environment through individual human activity and as residues from manufacturing, agribusiness, veterinary use, and hospitals and community use. Individuals may add PPCPs to the environment through waste excretion or bathing, as well as by directly disposing of unused medications into septic tanks, sewers, or trash containers. Their presence has been identified and quantified in WWTP effluents [14], surface waters [15], drinking water [150], groundwater [151], biosolids [152], agricultural manures [153] and biota [154]. With hundreds of different PPCPs in the market (see Table 1), WWTPs represent a key potential point source to the aquatic environment, but at the same time a major opportunity for centralised removal processes. This justifies the increasing number of studies dealing with pharmaceuticals in WWTPs in the last decade (Fig. 1). Summarizing research results in this area is not a simple task, given the large number of PPCPs found in WWTPs. The most common belong to the categories of antibiotics, analgesic and anti-inflammatory. However, other groups include diuretics, antibiotics, antidiabetics, anticoagulants, psychiatric drugs, lipid regulators, histamine H2 antagonists [14,15], anti-epileptic drugs [15,16], antifongics, antineoplasics, disinfectants, antidepressants, antiseptics, hormones, vascodilators [15], antifungics, vascodilators, barbiturates, anticancers, anticonvulsants [17], antihypersensitives and antilipidemics [18]. Recently, a review by Miege et al. [15] presented the concentrations of PPCPs in WWTP influents and effluents, their removal efficiency and their loads to the aquatic environment. Their database covered 184 PPCPs from 117 scientific publications until 2008.

It is difficult to discuss typical concentration levels (Table 1) of PPCPs as these can range from hundreds of pg/L up to hundreds of μg/L [13,15,19–25], depending on the target PPCP and the type of wastewater. Other important factors that play a role in the occurring levels are the types of products that can be found in the pharmaceutical market in each country, or the possibility in some countries to purchase medicines without a medical prescription [15]. As a matter of fact, reported average influent concentrations ranging between 0.1 ng/L for hormones and 34 μg/L for naproxen, whilst naproxen in a study by Nakada et al. [26] occurred in concentrations of only a few ng/L. If specific circumstances occur, the concentration levels of PPCPs in WWTPs can increase even further, to tens of mg/L. Such a case was the outbreak of the avian influenza, which led to concentrations of 20 mg/L for oseltamivir carboxylate in WWTPs with low flow and high population equivalents [20]. In the same study, it is stated that under normal conditions, the majority of PPCPs do not exhibit seasonality, but for some like antibiotics, temporal variation is observed due to increased winter usage.

Individual PPCPs have also distinct chemical and physical properties that suggest potentially different mechanisms and locations for removal/reduction in a WWTP. PPCPs can have octanol–water partition coefficients (K_{ow}) or water solubility (WS) values that vary up to 7–8 orders of magnitude. As an example, $\log K_{ow}$ of iopromide: −2.05 and $\log K_{ow}$ of mefenamin acid: 5.12 [23,27], or WS of roxithromycin: 0.0189 mg/mL and WS of diclofenac: 50 mg/mL. Many of the PPCPs are ionisable chemicals and it may not be appropriate to assess their lipophilicity based only on the K_{ow} value. Wells [171,172] addressed the latter issue underlining the value of using a different physical–chemical property which takes into account both hydrophobicity and ionogenicity (especially for the cases where $pK_a < pH$). Thus, Wells [171,172] suggested that the pH-dependent *n*-octanol–water partition coefficient D_{ow} should be used. High K_{ow} (or D_{ow}) values mean that PPCPs tend to sorb onto suspended particles and end up in the sewage sludge, whereas compounds with low K_{ow} and high WS are expected to remain in the wastewater stream and, if resistant against microbial degradation, to be discharged with the final effluents. Removal rates can also vary largely between various contaminants. For example diclofenac showed low removal rates (21.8 ± 28.5%), whereas ibuprofen showed a removal of 99.1 ± 1.8% [16]. Interestingly, in many cases PPCP loads increase during the wastewater treatment. Thus, diclofenac showed a raise of 105% in a sewage treatment plant of Sweden [28], and up to 300% in a WWTP in Korea [24]. In the latter study, other PPCPs showing a negative removal rate were acetylsalicylic acid, naproxen, ketoprofen and clofibric acid. A possible explanation for negative removal rates is the influent–effluent mismatching, or the formation of "conjugated compounds" throughout the treatment steps, like for example happens with glucuronic acid [172]. A review by Onesios et al. [17] reported removal rates for a very large number of PPCPs. Authors evidenced that removal rates may vary considerably even for the same PPCP, and intercomparisons are most of the times problematic, due to different definitions of removal, decrease or elimination rates, but also to different sampling strategies applied (integrated versus grab samples). In addition, the different treatment approaches described in