Science of the Total Environment 551–552 (2016) 640–648

Contents lists available at ScienceDirect

Science of the Total Environment

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

Understanding the fate of organic micropollutants in sand and granular activated carbon biofiltration systems

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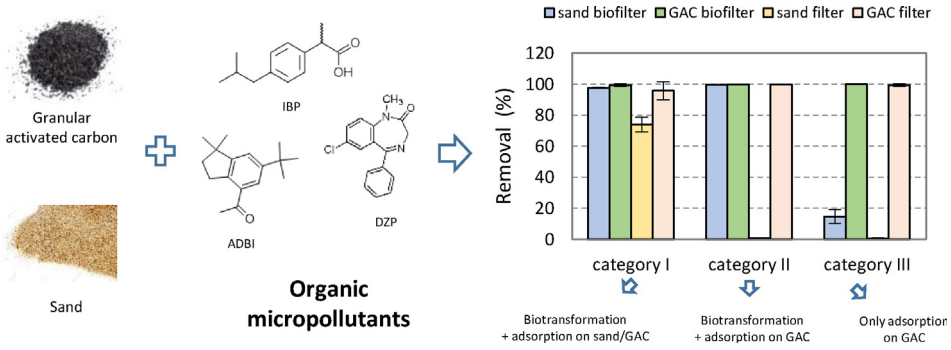
HIGHLIGHTS

- OMP removal was comparatively assessed in sand and GAC biofilters.
- The contribution of adsorption and biotransformation in OMP removal was identified.
- The filtering material did not affect the biological activities in biofilters.
- There is no direct correlation between EBCT and OMP removal in biofilters.
- The type of secondary effluent determines the lifespan of filtering material.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 December 2015
Received in revised form 1 February 2016
Accepted 2 February 2016
Available online xxxx

Editor: D. Barcelo

Keywords:
Adsorption
Biotransformation
Empty bed contact time
Granular activated carbon
Organic micropollutant
Sand filtration

ABSTRACT

In this study, sand and granular activated carbon (GAC) biofilters were comparatively assessed as post-treatment technologies of secondary effluents, including the fate of 18 organic micropollutants (OMPs). To determine the contribution of adsorption and biotransformation in OMP removal, four reactors were operated (two biofilters (with biological activity) and two filters (without biological activity)). In addition, the influence of empty bed contact time (EBCT), ranging from 0.012 to 3.2 d, and type of secondary effluent (anaerobic and aerobic) were evaluated. Organic matter, ammonium and nitrate were removed in both biofilters, being their adsorption higher on GAC than on sand. According to the behaviour exhibited, OMPs were classified in three different categories: I) biotransformation and high adsorption on GAC and sand (galaxolide, tonalide, celestolide and triclosan), II) biotransformation, high adsorption on GAC but low or null adsorption on sand (ibuprofen, naproxen, fluoxetine, erythromycin, roxythromycin, sulfamethoxazole, trimethoprim, bisphenol A, estrone, 17β-estradiol and 17α-ethinylestradiol), and, III) only adsorption on GAC (carbamazepine, diazepam and diclofenac). No influence of EBCT (in the range tested) and type of secondary effluent was observed in GAC reactors, whereas saturation and kinetic limitation of biotransformation were observed in sand reactors. Taking into account that most of the organic micropollutants studied (around 60%) fell into category II, biotransformation is crucial for the elimination of OMPs in sand biofilters.

Abbreviations: AC, activated carbon; ACB, activated carbon biofilter; ACF, activated carbon filter; ADBI, celestolide; AHTN, tonalide; AOP, advanced oxidation process; ATU, allylthiourea; BPA, bisphenol A; CBZ, carbamazepine; COD, chemical oxygen demand; DCF, diclofenac; DO, dissolved oxygen; DZP, diazepam; E1, estrone; E2, 17β-estradiol; EBCT, empty bed contact time; EE2, 17α-ethinylestradiol; ERY, erythromycin; FLX, fluoxetine; GAC, granular activated carbon; HHCB, galaxolide; IBP, ibuprofen; k_{biol}, biodegradation kinetic constant; NaN_3, sodium azide; NLR, nitrogen loading rate; NPX, naproxen; OLR, organic loading rate; OMP, organic micropollutant; PAC, powdered activated carbon; PPCP, pharmaceutical and personal care product; ROX, roxithromycin; S, sand; SB, sand biofilter; SF, sand filter; SHA, specific heterotrophic activity; SMX, sulfamethoxazole; SNA, specific nitrifying activity; TCS, triclosan; TMP, trimethoprim; VSS, volatile suspended solid; WWTP, wastewater treatment plant.

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http://dx.doi.org/10.1016/j.scitotenv.2016.02.008
0048-9697/

1. Introduction

The presence of organic micropollutants (OMPs) in aquatic environment has seen increased scientific interest in recent years. Since they have not been considered during the design of wastewater treatment plants (WWTPs), their removal during the conventional wastewater treatment is only partial, thus being discharged into receiving water bodies (Joss et al., 2008). Although nowadays concentrations of pharmaceutical and personal care products (PPCPs) in treated effluents are not regulated, the concern about the potential risk of these compounds on the environment has increased due to the demonstration of some evidences about their adverse effect on aquatic organisms (Fent et al., 2006; Roig, 2010; Schwindt et al., 2014). As a first step, European Commission incorporated five of these compounds (17α-ethinylestradiol, 17β-estradiol, diclofenac, estrone and erythromycin) to the watch list of substances in the field of water policy pursuant to Directive 2008/105/EC.

In order to improve the quality of the WWTP effluents and to reduce their potential environmental impact, post-treatment systems are recommended (Verlicchi et al., 2012; Rivera-Utrilla et al., 2013; Sudhakaran et al., 2013). Most studies are focused on advanced oxidation processes (AOPs), membrane systems and activated carbon adsorption. Although AOPs have been shown to remove most OMPs with high removal efficiencies (>90%), including recalcitrant compounds, the complete mineralization of micropollutants is not achieved (Luo et al., 2014), leading to the formation of a wide number of oxidation byproducts. This fact, together with the high energy consumption required, hampers the full-scale implementation of these systems (Stalter et al., 2010). An alternative strategy proposed by other authors is the use of AOPs as a pre-treatment stage to transform initially biorecalcitrant compounds to more readily biodegradable intermediates which will be treated further in a biological post-treatment (Klavarioti et al., 2009; Lee et al., 2012).

Membrane systems rely on physical mechanisms (size exclusion, adsorption onto membrane and charge repulsion) to remove the micropollutants (Jacob et al., 2010). Removal efficiencies higher than 60% were obtained for diclofenac, naproxen and 17α-ethinylestradiol during nanofiltration, while the use of reverse osmosis increased the elimination up to 95% (Urtiaga et al., 2013). High energy consumption and fouling are the main factors limiting the full-scale application of membranes (Lee et al., 2012).

Granular activated carbon (GAC) and powdered activated carbon (PAC) are employed in post-treatment systems to remove OMPs by adsorption without the generation of transformation products (Hernandez-Leal et al., 2011; Ruhl et al., 2014). The need of regenerating the filtering material supposes the main disadvantage of this technology (Kennedy et al., 2015). Recently, the use of biological filters to remove OMPs has been proposed due to their numerous advantages: low space requirement (Guo et al., 2012), low energy input (Pipe-Martin et al., 2010), improved effluent quality due to lower levels of organic matter and ammonium (Fernandez-Polanco et al., 2000) and minimising the presence of transformation products (Lee et al., 2012). It is especially interesting the possibility that biofilters offer for their in situ bioregeneration due to the biological transformation of the pollutants previously adsorbed on the filter media, thus increasing its lifespan (Çeçen and Aktas, 2012).

There are already some studies in the literature focused on the application of biofiltration systems to remove OMPs (Matamoros et al., 2007; Reungoat et al., 2011; Zearley and Summers, 2012; Kennedy et al., 2015). Most of these works deal with drinking water treatment, whereas the number of publications about the post-treatment of secondary wastewater effluents is more limited, and none studied effluents from anaerobic reactors. Different materials (granular activated carbon, anthracite, sand) have been tested as filtering media, but activated carbon displays several advantages due to its great potential to adsorb OMPs of different nature (Reungoat et al., 2011). Sand biofiltration is considered a promising technology due to the lowest cost of sand (Moser, 2008). However, the efficiency to eliminate OMPs is not clear yet. Some works have observed the removal of recalcitrant compounds, such as diclofenac, with removal efficiencies above 40% (Escolà and Bester, 2015), whereas others have showed no elimination (<20%) (Reungoat et al., 2011). In addition, most published works assessed the overall OMP elimination, without discerning between the two main mechanisms involved in OMP removal in sand/activated carbon biofilters: adsorption and biotransformation. Only Rattier et al. (2014) have evaluated the contribution of nitrifying bacteria to OMP biotransformation in anthracite biofilters. Also, there is a lack of knowledge about the influence of operational parameters, such as empty bed contact time (EBCT) or the type of secondary effluent, on OMP sorption and biotransformation in sand/activated carbon biofilters.

Therefore, the main objective of this study was to identify the main mechanisms responsible of the removal of 18 selected OMPs in sand and granular activated carbon biofilters during the post-treatment of secondary effluents. In addition, the influence of the type of effluent and empty bed contact time (EBCT) was evaluated.

2. Materials and methods

2.1. Organic micropollutants

Three antiphlogistics (ibuprofen (IBP), naproxen (NPX) and diclofenac (DCF)), four antibiotics (erythromycin (ERY), roxithromycin (ROX), sulfamethoxazole (SMX) and trimethoprim (TMP)), an antidepressant (fluoxetine (FLX)), an antiepileptic (carbamazepine (CBZ)), a tranquillizer (diazepam (DZP)), three musk fragrances (galaxolide (HHCB), tonalide (AHTN) and celestolide (ADBI)) and five endocrine disruptor compounds (estrone (E1), 17β-estradiol (E2), 17α-ethinylestradiol (EE2), bisphenol A (BPA) and triclosan (TCS)), were selected in this work. These substances were spiked into the reactor feedings at concentrations ranging between 1 and 40 $\mu g \cdot L^{-1}$.

2.2. Secondary effluent characteristics

Two synthetic secondary effluents from sewage treatment were tested: effluent from anaerobic treatment in an up-flow sludge bed reactor (experiment 1) and effluent from conventional activated sludge reactor (experiments 2 and 3). Their characteristics are shown in Table 1.

2.3. Experimental set-up

Three experiments with a duration of around 100 days each were performed. Experiments 1 and 2 were designed to evaluate the influence of the type of secondary effluent (anaerobic and aerobic, respectively), whereas experiment 3 aimed at determining the critical EBCT.

Four column reactors with 110 cm of height and 7.3 cm of internal diameter giving a total volume of 4.6 L (3 L of filtering bed) were employed in experiments 1 and 2 (Fig. S1A). Granular activated carbon (AC) and sand (S) were used as filtering media (Table S1), which

Table 1
Average characteristics of the secondary effluents used in the experiments.

	Anaerobic effluent (experiment 1)	Aerobic effluent (experiments 2 and 3)
pH	7.0–7.5	7.3–7.8
COD ($mg \cdot L^{-1}$)	450–600	40–130
N-NH_4^+ ($mg \cdot L^{-1}$)	8.5–11.5	0.6–1.4
N-NO_3^- ($mg \cdot L^{-1}$)	0.3–5.3[a]	4.7–11.8
P-PO_4^{-3} ($mg \cdot L^{-1}$)	10–11	0.5–1.5
Alkalinity ($mg\ CaCO_3 \cdot L^{-1}$)	450–550	6.5–8.5

[a] The presence of nitrate in the anaerobic effluent is due to the use of inhibitors (filters) and tap water in the preparation of synthetic feeding.