Science of the Total Environment 612 (2018) 192–201

Contents lists available at ScienceDirect

Science of the Total Environment

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

Potential of biochar filters for onsite sewage treatment: Adsorption and biological degradation of pharmaceuticals in laboratory filters with active, inactive and no biofilm

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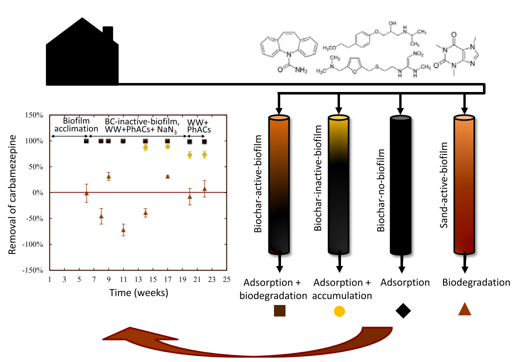
HIGHLIGHTS

- Carbamazepine removal in biochar with no biofilm is high due to adsorption.
- Inactivation of biofilm in biochar filters impairs removal of carbamazepine.
- Inactivation of biofilm in biochar filters does not affect removal of metoprolol.
- Ranitidine and caffeine are efficiently removed by adsorption and biodegradation.
- Biochar is a promising medium for pharmaceutical removal in onsite sewage systems.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 July 2017
Received in revised form 16 August 2017
Accepted 17 August 2017
Available online xxxx

Editor: D. Barcelo

Keywords:
Active biofilm
Adsorption
Biochar
Biodegradation
Inactive biofilm
Pharmaceuticals
Onsite sewage facilities

ABSTRACT

This study investigated the potential of biochar filters as a replacement or complement for sand filters for removal of pharmaceutically active compounds (PhACs) from wastewater in onsite sewage facilities (OSSF). Specifically, the study investigated the effects of biodegradation, adsorption and a combination of these processes on removal of four model PhACs from wastewater in biochar filters operated under hydraulic loading conditions mimicking those found in onsite infiltration beds. Concentrations and removal of the four PhACs (i.e. carbamazepine, metoprolol, ranitidine and caffeine) were investigated over 22 weeks in four treatments: biochar (BC) with active or inactive biofilm (BC-active-biofilm, BC-inactive-biofilm), biochar without biofilm (BC-no-biofilm) and sand with active biofilm (Sand-active-biofilm). The adsorption of carbamazepine was high in BC-no-biofilm (99% removal after 22 weeks), while biodegradation was very low in Sand-active-biofilm (7% removal after 22 weeks). Removal of carbamazepine in BC-active-biofilm was high and stable over the 22 weeks (>98%), showing a significant role of biofilm in filter biogeneration. However, carbamazepine removal declined over time in BC-inactive-biofilm, from 99% in week 13 to 73% in week 22. Metoprolol was poorly degraded in Sand-active-biofilm (37% after 22 weeks), while adsorption seemed to be the major pathway for removal of metoprolol in biochar. Ranitidine and caffeine were efficiently removed by either adsorption (97% and 98%, respectively, after 22 weeks) or biodegradation (99% and >99%, respectively, after 22 weeks). In conclusion, biochar is a promising filter medium for OSSF, especially for persistent PhACs such as carbamazepine and metoprolol.

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http://dx.doi.org/10.1016/j.scitotenv.2017.08.178

1. Introduction

Onsite sewage facilities (OSSFs) have recently been recognised as a significant source of hazardous micropollutants such as pharmaceutically active compounds (PhACs) and polyfluorinated alkyl substances (Ejhed et al., 2011; Ejhed et al., 2016). Conventional OSSF treatment techniques, such as sand filter and soil infiltration treatment systems, have been proven to be only partially efficient or even inefficient in removal of different types of organic micropollutants, including PhACs. For example, Gros et al. (2016) reported intermediate to low removal of PhACs in soil beds used for OSSF (e.g. 46% removal for ibuprofen, 86% for diclofenac, 44% for metoprolol and 73% for caffeine), while Blum et al. (2017) reported insignificant (<10%) removal of e.g. acetaminophen in soil beds. Matamoros et al. (2009) found that well-functioning sand filters achieved removal efficiency of >80% for the PhACs salicylic acid, ibuprofen and carboxy-ibuprofen, but failed to remove carbamazepine, diclofenac and ketoprofen. Processes such as advanced oxidation can transform PhACs or even mineralise them completely, but these processes are expensive to apply in OSSF (Mehrjouei et al., 2014) and difficult to maintain by household inhabitants. The adsorption process is efficient and easy to operate (Hao et al., 2012; Zhou et al., 2012), relatively inexpensive and unaffected by the toxicity effects which have been reported in biologically-based processes (Ahmaruzzaman, 2008).

Biochar is a material of organic origin which is pyrolysed at high temperatures (300–800 °C) in the absence of oxygen, and it is characterised by large specific surface and high porosity (Downie et al., 2009). Previous studies have demonstrated the efficiency of biochar as an adsorbent and biofilm carrier for removing organic matter, surfactants, phosphorus (P) and nitrogen (N) from onsite wastewater and greywater treatment systems (Dalahmeh, 2016; Dalahmeh et al., 2014; Niwagaba et al., 2014). Use of biochar for adsorption and immobilisation of PhACs from different waste streams, e.g. sludge (Bair et al., 2016), urine (Solanki and Boyer, 2017) and other liquid solutions (Guo et al., 2016; Rajapaksha et al., 2015), has been investigated. Bair et al. (2016) showed that addition of walnut biochar to sludge-amended soil increased immobilisation of ciprofloxacin in the soil. Solanki and Boyer (2017) achieved high removal (>90%) of acetyl salicylic acid, paracetamol, ibuprofen, naproxen, citalopram, carbamazepine and diclofenac from synthetic urine using bamboo and southern yellow pine biochar adsorbents. In addition, Guo et al. (2016) showed that adsorption of the antibiotic tylosin from liquid solution using goethite biochar was rapid, with an adsorption capacity of 8100 L kg^{-1}. Im et al. (2014) tested biochar and activated carbon as catalysts in an ultrasonic process to degrade acetaminophen and naproxen and found that biochar was more efficient in degrading PhACs than activated carbon under ultrasonic radiation.

Besides adsorption, biofilms can play an important role in biodegradation of certain PhACs. In fact, adsorption and biodegradation through co-metabolism in biologically active carbon has been used for removal of metoprolol in a study which found that easily degradable organic substances such as acetate enhanced the removal rate (Abromaitis et al., 2016). In contrast, Saravia and Frimmel (2008) showed that the presence of organic matter reduced adsorption of the PhAC carbamazepine on activated carbon, due to competitive adsorption between the carbamazepine and organic matter. Synergetic removal of PhACs, organic matter and nutrients in biochar filters in a system in which a combination of adsorption and biodegradation processes is utilised and sustained by self-biogeneration of the filter is a novel technology which can be developed for OSSF treatment. While the biodegradation mechanism itself can be similar in different filter systems and media, the combination of biofilm-enhanced degradation and adsorption varies widely depending on the type and characteristics of the media used and the physicochemical properties of the micropollutant (Ahmed et al., 2017; Dalahmeh et al., 2014; Sun et al., 2016). Thus a better understanding of the effects of biofilm on PhACs removal via adsorption and biodegradation processes in biochar filters is essential for the development of biochar filter-based OSSF for removal of PhACs together with organic matter and nutrients. To our knowledge, no previous study has investigated the potential of biochar filters as a replacement or complement for sand/soil filters for concurrent and synergetic removal of PhACs, organics and nutrients in OSSFs.

This study investigated the potential of biochar filters for removal of PhACs, organics and nutrients in OSSF. Specific objectives were to (i) investigate the effects of biodegradation, adsorption and a combination of these two processes on the removal of four model PhACs (viz. carbamazepine, metoprolol, ranitidine and caffeine) from wastewater using biochar filters and (ii) assess the efficiency of biochar filters with and without active biofilm in removal of PhACs, organics and nutrients from wastewater.

2. Materials and methods

2.1. Chemicals and materials

Standards for carbamazepine, metoprolol (as tartrate salt), ranitidine (as hydrochloride salt) and caffeine were purchased from Sigma-Aldrich (Stockholm, Sweden, purity >95%). Physical and chemical properties of the PhACs tested are summarised in Table S1 in the Supporting Information. Isotopically labelled standards of carbamazepine-d_{10} and atenolol-d_7 (used for metoprolol determination) were acquired from Sigma-Aldrich (Stockholm, Sweden), while ranitidine-d_6 was purchased from Toronto Research Chemicals (Toronto, Canada).

The filter media consisted of non-activated hard wood biochar (biochar) and sand (Table 1). The particle size distribution, effective size (d_{10}) and uniformity coefficient (d_{60}/d_{10}) of the media were determined according to ASTM (1998). Specific surface area of the media was determined according to Brunauer et al. (1938). Bulk density was determined by dividing the dry weight of the filter medium by the volume occupied by the medium. The particle density and porosity of biochar and sand were determined according to methods described previously (Dalahmeh et al., 2012). The internal structure, surface topography and surface chemistry of the biochar and sand were identified before packing using elemental scanning electron microscopy (SEM). The SEM micrographs and energy dispersive X-ray spectrographs (EDS) of the samples were obtained using a HITACHI TM-1000 scanning electron microscope equipped with an Oxford Instruments EDX detector. To obtain reliable statistics in the elemental analysis, the average of three individual measurements was used for each point. The scanned surface was mapped by moving over the sample with steps of 10 μm. The SEM image of the biochar showed longitudinal hollow tubes with high porosity (Fig. S1A), while sand particles showed a solid structure, with limited occurrence of micropores (Fig. S1B).

2.2. Experimental set-up

Removal of the target PhACs (carbamazepine, metoprolol, ranitidine and caffeine) and other chemical parameters (chemical oxygen demand (COD), nitrate nitrogen (NO_3-N), total nitrogen (Tot-N) and phosphate phosphorus (PO_4-P) was investigated in four different treatments (T1–T4) using biochar (BC) and sand as filter materials with and without biofilm (Fig. 1). The aforementioned PhACs were selected due to their frequent occurrence in surface water and wastewater in Sweden

Table 1
Physical characteristics of the biochar and sand used as filter materials in the different treatments.

Parameter	Biochar treatments 1–3	Sand treatment 4
Particle size (mm)	1–5	1–5
Effective size (mm)	1.5	1.4
Uniformity coefficient	2.1	2.2
Specific surface area ($m^2\ g^{-1}$)	184	0.14
Bulk density (kg m^{-3})	187	1700
Total porosity (%)	72–74	40