WATER RESEARCH 54 (2014) 89–99

Available online at www.sciencedirect.com

ScienceDirect

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

# Removal of micropollutants during tertiary wastewater treatment by biofiltration: Role of nitrifiers and removal mechanisms

*M. Rattier, J. Reungoat, J. Keller, W. Gernjak**

*The University of Queensland, Advanced Water Management Centre (AWMC), Brisbane, Qld 4072, Australia*

ARTICLE INFO

*Article history:*
Received 15 October 2013
Received in revised form
12 January 2014
Accepted 13 January 2014
Available online 6 February 2014

*Keywords:*
Ammonia oxidizing microorganisms
Biodegradation
Biofiltration
Micropollutants
Tertiary wastewater treatment

ABSTRACT

The objective of this study was to determine the extent to which a suite of organic micropollutants (MPs) can be removed by biological filtration and the role of bioavailability and ammonia oxidizing microorganisms (AOMs) in the biodegradation process. During approximately one year, laboratory-scale columns with 8 min empty bed contact time (EBCT) and packed with anthracite as filter media were used for treating a tertiary effluent spiked with a broad range of MPs at a target concentration of 2 μg $L^{-1}$. In parallel columns, aerobic biomass growth was inhibited by using either the biocide sodium azide (500 mg $L^{-1}$ $NaN_3$) or allylthiourea (5 mg $L^{-1}$ ATU), specifically inhibiting nitrifying bacteria. Once the biomass had colonized the media, around 15% of the dissolved organic carbon (DOC) contained in the untreated tertiary effluent was removed by non-inhibited columns. The removal of several MPs increased over time indicating the relevance of biological activity for the removal of MPs, while the negative control, the $NaN_3$ inhibited column, showed no significant removal. Out of 33 MPs, 19 were recalcitrant (<25%) to biodegradation under aerobic conditions with the others exhibiting a diverse range of removal efficiency up to 95%. Through inhibition by ATU it was shown that nitrifying bacteria were clearly having a role in the degradation of several MPs, whereas the removal of other MPs was not affected by the presence of the nitrification inhibitor. A relationship between the qualitative assessment of sorption of MPs on granular activated carbon (GAC) and their removal efficiency by biodegradation on anthracite was observed. This result suggested that the affinity of the MPs for GAC media could be a useful indicator of the bioavailability of compounds during biofiltration on anthracite.



*Abbreviations:* AMO, ammonia monooxygenase; AOM, ammonia oxidizing microorganism; ATU, allylthiourea; CAS, conventional activated sludge; DAFF, dissolved air flotation-sand filtration; DO, dissolved oxygen; DOC, dissolved organic carbon; EBCT, empty bed contact time; GAC, granular activated carbon; LOQ, limit of quantification; MBR, membrane bioreactor; MP, micropollutant; MS, mass spectrometry; MW, molecular weight; $NaN_3$, sodium azide; NPOC, non-purgeable organic carbon; SIL, stable isotope labelled; SPE, solid phase extraction; SRT, solids retention times; WWTP, wastewater treatment plant.

* *Corresponding author*. Tel.: +61 7 3346 3219.
E-mail addresses: w.gernjak@awmc.uq.edu.au, w.gernjak@uq.edu.au (W. Gernjak).

0043-1354/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.watres.2014.01.030

## 1. Introduction

The removal of emerging contaminants such as endocrine disrupting compounds, pharmaceuticals, personal care products is an increasingly adopted goal for wastewater treatment. State-of-the-art biological wastewater treatment designed for nutrient removal achieves only partial MP removal, and is deemed to generate an insufficient effluent quality to avoid environmental impact (Ort et al., 2009). Partial removal of MPs in wastewater treatment plants (WWTPs) occurs through abiotic and biotic processes including stripping, sorption and biological and/or chemical transformation. The behaviour of a substance depends on its biodegradability, adsorbability, volatility and inhibitory properties. Previous studies have indicated significant variation in removal depending on the MPs in conventional activated sludge (CAS), membrane bioreactors (MBRs) or soil aquifer treatment, ranging from near complete removal for some compounds (e.g. ibuprofen and gemfibrozil) to almost no removal for others (e.g. carbamazepine) (Onesios et al., 2009; Petrovic et al., 2009; Rauch-Williams et al., 2010).

The fundamental strategy of aerobic microorganisms to activate hydrocarbons by initial hydroxylation may, however, be inefficient with certain synthetic compounds that carry electron withdrawing substituents. Structural elements such as halo-, nitro- or azo-substituents are rare in natural compounds and create a relatively high redox potential rendering molecules less susceptible to activated oxygen species generated by mono- or dioxygenase (Rieger et al., 2002). The presence of such electron-withdrawing groups in the molecular structure was associated with low removal of MPs in biological processes previously (Hai et al., 2011b; Tadkaew et al., 2011). However, an absolute definition of a xenobiotic structural element that prevents a synthetic chemical from being biodegraded cannot be given.

Interestingly, the longer solids retention time (SRT) in CAS treatment has a positive effect on the elimination of MPs (Clara et al., 2005; Gerrity et al., 2013). The combination of longer SRT and lower food to microorganisms ratio achieved in MBR compared to CAS treatment, also have a positive effect on the elimination of MPs (Bo et al., 2009; Petrovic et al., 2009). Sorption onto particulate matter is an important removal mechanism when the tendency of an MP to partition onto particulate matter is high. Biosorption of trace contaminants, driven primarily by hydrophobic interaction, appears to be one of the key mechanisms controlling removal efficiency during MBR and CAS treatments (Radjenović et al., 2009). For instance, apparent improvement in removal efficiency of certain acidic trace organics such as ibuprofen, ketoprofen, and diclofenac has been observed when MBRs are operated under acidic conditions rather than neutral conditions (Urase et al., 2005; Tadkaew et al., 2010). This phenomenon was explained by the speciation of the compounds from hydrophilic ionic forms to much more hydrophobic forms at pH lower than their acid dissociation constant ($pK_a$) making the compounds more readily available for biomass sorption.

To minimise effluent MP load additional measures need to be implemented for improved environmental protection. Therefore, novel tertiary treatment processes based on low cost and easy to operate engineered solutions that can be easily added to WWTPs require investigation (Jones et al., 2007; Joss et al., 2008). This has led to a renewed interest in biofilm-based techniques serving the useful purpose of converting organic and inorganic materials into energy and biomass before reaching the environment. Bacteria can naturally attach to granular media and wetland vegetation and subsequently develop into a biofilm which acts as a filter that attenuate and concentrate certain MPs from secondary or tertiary effluent and natural waters (Gullicks et al., 2011). Biofilms provide a habitat for microbiota that graze on associated organics (Herzberg et al., 2003). Several studies investigated the potential of engineered biofilters employing a variety of filter media; sand, anthracite, activated carbon (LeChevallier et al., 1992; Snyder et al., 2003; Reungoat et al., 2011), and increasing efforts have been undertaken to understand MP removal during biofiltration recently (Reungoat et al., 2011; Zearley and Summers, 2012; Rossi et al., 2013).

Biodegradation of MPs occurs at specific rates which are a function of prevailing environmental factors such as availability of nutrients, oxygen concentration, pH value, concentration and bioavailability of contaminants, physical and chemical characteristics of the biomass. Organic compounds are assumed to be biodegraded in biofilters either by direct catabolism or cometabolism (Zearley and Summers, 2012; Benner et al., 2013). Primary and secondary substrates can be catabolized by enzymes and used as carbon and energy sources for the microorganisms. If an organic compound (primary substrate) is available in larger quantities, biomass and catabolic activity increases until an essential nutrient becomes limiting. In contrast the transformation rate of a secondary substrate and the number of active cells in the population remains constant and does not yield energy for growth. Under these conditions the fate of MPs embedded in the DOC matrix is essentially determined by the gratuitous process named cometabolism (Rieger et al., 2002). Cometabolized compounds are biodegraded by nonspecific enzymes generated by the primary substrate metabolism. A high efficiency of biodegradation was related in previous studies to the biodegradable DOC content in the wastewater and to the presence of nitrifying conditions, which create environments suitable for biological activity, and the development of stable microbial communities able to degrade contaminants (Zearley and Summers, 2012). In addition to the ammonia oxidation, ammonia monooxygenase (AMO) enzymes are known to oxidize a wide range of aliphatic and aromatic hydrocarbons (Roh et al., 2009). Shi et al. (2004) reported that *Nitrosomonas europaea*, was capable of degrading steroidal estrogens in wastewater. In a more recent study (Roh et al., 2009), *N. europaea* was shown to degrade triclosan and bisphenol A, but not ibuprofen. Moreover, AMO enzymes have been postulated to be responsible for the degradation of certain MPs (Helbling et al., 2012).

The extent of biodegradation depends on the nature, concentration and chemical properties of the MP as well as filter residence time. In the presence of a sorbent such as the filtration media or biofilm support media, a constraint is implied in space and time, potentially preventing the organism from gaining access to the sorbed MP. Compounds which