Journal of Hazardous Materials xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Hybrid Moving Bed Biofilm Reactor for the biodegradation of benzotriazoles and hydroxy-benzothiazole in wastewater

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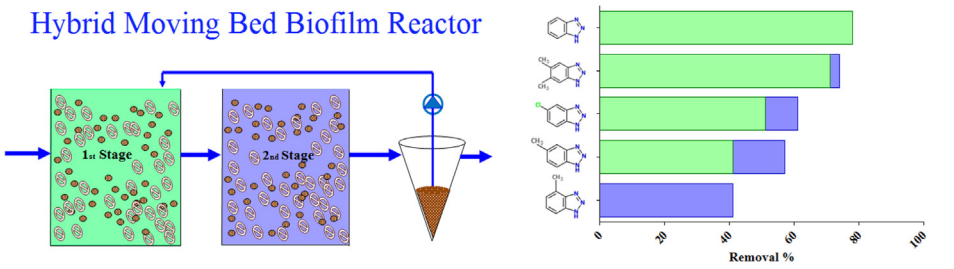
HIGHLIGHTS

- All target compounds were partially removed in hybrid Moving Bed Biofilm Reactor.
- 5 compounds were removed mainly in 1st stage, critical role of 2nd stage for 4TTR.
- AS and biocarriers contribute to different extent to micropollutants biodegradation.
- HMBBR and low loaded MBBR are the most efficient systems for studied compounds.
- 22 biotransformation products were tentatively identified.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 February 2016
Received in revised form 16 June 2016
Accepted 17 June 2016
Available online xxx

Keywords:
Micropollutants
Biological treatment
Sewage
Kinetics
Biotransformation
Biofilm

ABSTRACT

A laboratory scale Hybrid Moving Bed Biofilm Reactor (HMBBR) was used to study the removal of five benzotriazoles and one benzothiazole from municipal wastewater. The HMBBR system consisted of two serially connected fully aerated bioreactors that contained activated sludge (AS) and K3-biocarriers and a settling tank. The average removal of target compounds ranged between 41% (4-methyl-1H-benzotriazole; 4TTR) and 88% (2-hydroxybenzothiazole; OHBTH). Except for 4TTR, degradation mainly occurred in the first bioreactor. Calculation of biodegradation constants in batch experiments and application of a model for describing micropollutants removal in the examined system showed that AS is mainly involved in biodegradation of OHBTH, 1H-benzotriazole (BTR) and xylytriazole (XTR), carriers contribute significantly on 4TTR biodegradation, while both types of biomass participate on elimination of 5-chlorobenzotriazole (CBTR) and 5-methyl-1H-benzotriazole (5TTR). Comparison of the HMBBR system with MBBR or AS systems from literature showed that the HMBBR system was more efficient for the biodegradation of the investigated chemicals. Biotransformation products of target compounds were identified using ultra high-performance liquid chromatography, coupled with a quadrupole-time-of-flight high-resolution mass spectrometer (UHPLC-QToF-MS). Twenty two biotransformation products were tentatively identified, while retention time denoted the formation of more polar transformation products than the parent compounds.

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http://dx.doi.org/10.1016/j.jhazmat.2016.06.035
0304-3894/

1. Introduction

Growing demand for more efficient wastewater treatment is leading to new technologies for treatment as well as improvement of existing ones. Concerning biological treatment, the Hybrid Moving Bed Biofilm Reactor (HMBBR) is an approach that was introduced two decades ago for the first time in wastewater engineering [1]. The HMBBR is a combination of a typical activated sludge (AS) system with a Moving Bed Biofilm Reactor (MBBR), in which biofilm attached on biocarriers and AS flocs co-exist in the bioreactor, contributing to wastewater treatment. The main advantages of such a system compared to AS are the lower requirement for process volume, the increased nitrification capacity and the lower sludge load on the secondary clarifier [2]. Due to the above, HMBBR systems have been successfully used for upgrading of conventional AS systems [3,4].

So far, only few studies have focused on the ability of HMBBR systems to remove micropollutants from wastewater. Falås et al. [5] examined the elimination of 20 micropollutants from a large scale HMBBR in Switzerland and reported that the attached growth biomass can contribute significantly to the removal of specific compounds in such systems. Escolà Casas et al. [6] investigated the removal of 26 pharmaceuticals in hospital wastewater by a 4 staged pilot treatment plant consisting of AS, HMBBR and MBBR reactors in series and reported biodegradation kinetics in different bioreactors. Finally, Sfaelou et al. [7] recently examined the effects and removal of phenanthrene in sequencing batch reactors containing AS and biocarriers. To the best of our knowledge, no other studies have been published on the removal of micropollutants in HMBBR systems.

Benzotriazoles (BTRs) and Benzothiazoles (BTHs) are two groups of micropollutants that occur in wastewater from domestic and industrial activities [8]. BTRs are found in corrosion-inhibiting products, cooling fluids, de-icing fluids and dishwashing detergents [9], while BTHs are used as vulcanization accelerators and stabilizers in the photo industry [10]. Both groups are highly soluble in water and highly polar, leading to their persistence in the water cycle [11,12]. The partial removal of some of them in AS systems has been documented in monitoring studies [13–15] and laboratory biodegradation experiments [16,17]. Moreover, information on the biotransformation products of specific BTRs (1H-benzotriazole, BTR; 4-methyl-1H-benzotriazole, 4TTR; 5-methyl-1H-benzotriazole, 5TTR) has been reported in activated sludge experiments [16,18]. In a recent study, Mazioti et al. [19] compared the ability of AS and pure MBBR systems to biodegrade six of these compounds (BTR; 4TTR; 5TTR; xylytriazole, XTR; 5-chlorobenzotriazole, CBTR; 2-hydroxybenzothiazole, OHBTH) and reported that attached biomass had higher biodegradation potential compared to AS. To the best of our knowledge, no information is available on the removal of these compounds in HMBBR, on the contribution of co-existing types of biomass on their biodegradation and on the produced transformation by-products.

The aim of this study was to investigate the potential of a laboratory scale HMBBR system, consisting of two bioreactors in series, to remove BTR, 4TTR, 5TTR, XTR, CBTR and OHBTH from domestic wastewater. Concentrations of target compounds in different points of the hybrid system were monitored and the observed removal efficiencies were compared with those reported in a previous study using AS and MBBR systems [19]. Biodegradation kinetics of the target compounds were also determined using AS and biocarriers from the HMBBR system and a model was applied to describe the contribution to micropollutants removal by different mechanisms (biodegradation, sorption) and by different types of biomass (sludge, biofilm). Finally, batch experiments were conducted and for the first time biotransformation products formed in a HMBBR reactor were tentatively identified.

2. Materials and methods

2.1. Analytical standards and reagents

Analytical standards of XTR and CBTR were supplied by Sigma-Aldrich (USA). BTR was purchased from Merck (Germany), 4TTR by Fluka (Switzerland), 5TTR by Acros Organics (Belgium); whereas OHBTH was purchased from Alfa Aesar (USA). Stock solutions of individual compounds were prepared in methanol (MeOH) at 1000 mg L^{-1} and kept at −18 °C. Working solutions of 10 mg L^{-1} were prepared when needed and were kept at −18 °C for a time period not exceeding three months. Methanol (MeOH, HPLC–MS grade) and acetonitrile (ACN, HPLC grade) were purchased from Merck (Germany) and Fisher (USA), respectively. The solid phase extraction (SPE) cartridges used for samples' clean-up were polymer-based with surface modified styrene divinylbenzene phase (Strata-X, 33u Polymeric Reversed Phase 200 mg/6 mL) and they were supplied by Phenomenex (USA). HPLC grade water was prepared in the laboratory using a MilliQ/MilliRO Millipore system (USA). Ultra-pure HCl (32%), used for samples acidification, was purchased from Merck (Germany).

2.2. Continuous flow systems: set-up and operation

A small scale continuous flow system was installed and operated in the laboratory (Fig. 1), under constant room temperature controlled by central air-conditioning system. The HMBBR system consisted of two aerobic bioreactors (BC1 and BC2) connected in series, with a working volume of 3 L each. A settling tank, with a volume of 1 L, followed the BC2, from which AS was recirculated to BC1. Each bioreactor contained both biocarriers (type K3, AnoxKaldnes, at a filling ratio of 30%) and AS. The AS was collected from a nitrifying municipal STP (Mytilene, Greece), while the biocarriers were taken from a laboratory scale MBBR system that has been operated for six months and on which a mature biofilm was attached [19]. A hydraulic residence time (HRT) of 12.4 ± 0.6 h (for each reactor) was applied, providing a substrate organic loading equal to 0.64 ± 0.39 kg m^{-3} d^{-1} for BC1 and 0.11 ± 0.09 kg m^{-3} d^{-1} for BC2; whereas sludge residence time (SRT) of AS in the system was kept at 8 d, by daily removing equal amount of sludge from both reactors (Table S1). The HMBBR system was fed with raw wastewater collected from the STP of the University Campus in Mytilene, Greece (Table S2). In all bioreactors, the conservation of aerobic conditions and the adequate mixing of suspended and attached biomass were achieved by providing constant air supply, which ensured that the dissolved oxygen concentration (DO) was always higher than 4 mg L^{-1}.

An acclimatization period of 27 days took place (time almost equal to three times SRT), during which conventional pollutants removal (Chemical Oxygen Demand, COD; NH_4-N), concentration of suspended and attached biomass and values of pH, temperature (T) and DO were frequently examined in order to control the system's stability and efficiency. Afterwards, the target compounds were spiked to the raw wastewater using methanol solutions to obtain a daily stable inflow concentration of approximately 20 μg L^{-1} of each investigated chemical. To evaluate the removal of the target compounds in different bioreactors, 12 samples were taken during one week from different sampling points of the system (Fig. 1).

2.3. Batch biodegradation experiments for kinetics calculation

To determine the contribution of each type of biomass in the removal of target compounds, batch experiments were conducted and biodegradation kinetics was calculated. For this reason, four days after the end of spiking micropollutants to the HMBBR system

Please cite this article in press as: A.A. Mazioti, et al., Hybrid Moving Bed Biofilm Reactor for the biodegradation of benzotriazoles and hydroxy-benzothiazole in wastewater, J. Hazard. Mater. (2016), http://dx.doi.org/10.1016/j.jhazmat.2016.06.035