Use of suspended and attached growth wastewater treatment systems for the removal of benzotriazoles and benzothiazoles

Aikaterini A. Mazioti*, Agapi Taka*, EvdoxiaChroni*, Athanasios S. Stasinakis*, Nikolaos S. Thomaidis**, Henrik R. Andersen***

* Department of Environment, University of the Aegean, 81100 Mytilene, Greece
**Department of Chemistry, National and Kapodistrian University of Athens, 15771 Athens, Greece
***Department of Environmental Engineering, Technical University of Denmark, Denmark

Abstract
Three lab-scale biological wastewater treatment systems (an Activated Sludge, AS system, a pure Moving Bed Biofilm Reactor, MBBR and a hybrid Moving Bed Biofilm Reactor, HMBBR) were used in order to investigate five benzotriazoles (BTRs) and 2-hydroxybenzothiazole (OHBTH) removal from wastewater. According to the results, target compounds removal was ranged between 2 and 97% depending on the compound and the system used. The main mechanism of removal was biodegradation, while among tested systems HMBBR was proved to be the more efficient regarding micropollutants removal. Regarding the MBBR and HMBBR systems, the greater part of the compounds elimination occurred in the first bioreactor.

Keywords
micropollutants, activated sludge, MBBR, HMBBR

INTRODUCTION

Benzotriazoles (BTRs) and benzothiazoles (BTHs) are two classes of emerging contaminants that have been extensively detected in the aquatic environment, worldwide (Nödler et al., 2014). BTRs are found in corrosion-inhibiting products, cooling fluids, de-icing fluids and dishwashing detergents (Reemtsma et al., 2010), while BTHs are used as vulcanization accelerators and stabilizers in the photo industry (Herrero et al., 2014). As they are polar compounds with a high solubility in water they persist in the water cycle and are frequently find in surface and underground water (Loos et al., 2009). The concentrations of these compounds in raw sewage vary from some hundred ng L^{-1} to some tens μg L^{-1}, and as they are partially removed in wastewater treatment plants there is need for investigation and optimization of their elimination from wastewater.

Regarding technologies available for biological wastewater treatment, activated sludge systems (AS) is the most frequently used. The partial removal of selected micropollutants has been documented for AS systems (Asimakopoulos et al., 2013; Stasinakis et al., 2013; Molins-Delgado et al., 2015). On the other hand, systems using attached biomass have not been thoroughly investigated regarding their capacity to eliminate micropollutants. For example, only few researches are focusing on the use of Moving Bed Biofilm Reactors (MBBR) or Hybrid Moving Biofilm Reactors (HMBBR) (Falås et al., 2013; Escolà Casas et al., 2015). In both cases, these two systems may be a promising way of treating emerging micro contaminants as they present many advantages, such as robustness, low volume requirements and low sludge production (Di Trapani et al., 2013).

In this study three different lab-scale biological wastewater treatment systems (AS, MBBR, HMBBR) were used to investigate the removal efficiency of five BTRs (1H-benzotriazole, BTR; xylytriazole, XTR; 4-methyl-1H-benzotriazole, 4TTR; 5-methyl-1H-benzotriazole, 5TTR; 5-chlorobenzotriazole, CBTR) and one BTH (2-hydroxybenzothiazole, OHBTH). All systems were operated under continuous flow mode, similar operational parameters and were fed with raw municipal wastewater. After the appropriate time period, needed for the systems to achieve sufficient wastewater treatment, the target compounds were spiked inflow and samples were collected from various points of each system in order to calculate each compound's elimination.

MATERIALS AND METHODS

Continuous flow systems

The AS system consisted of an aerobic bioreactor (AB), with a working volume of 4.5 L, and a settling tank with a working volume of 1 L, from which sludge was recirculating to the bioreactor. The MBBR system consisted of two aerobic bioreactors (BC1 and BC2) connected in series, with a working volume of 4.5 L each. Each bioreactor contained biocarriers (type K3, AnoxKaldnes) at a filling ratio of 30%. The MBBR system was operated at two HRTs, in two different experimental cycles. An HRT of 26.4 ± 3.6 h (for each reactor) was applied in the first experimental cycle (MBBR-low; organic loading: 0.25 ± 0.16 kg m^{-3} d^{-1} for BC1 and 0.05 ± 0.03 kg m^{-3} d^{-1} for BC2). A lower HRT of 10.8 ± 1.2 h (for each reactor) was applied in the second experimental cycle (MBBR-high; organic loading: 0.60 ± 0.40 kg m^{-3} d^{-1} for BC1 and 0.17 ± 0.11 kg m^{-3} d^{-1} for BC2). 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. An hydraulic residence time (HRT) of 12.4 ± 0.6 h (for each reactor) was applied (organic loading: 0.64 ± 0.39 kg m^{-3} d^{-1} for BC1 and 0.11 ± 0.09 kg m^{-3} d^{-1} for BC2). An acclimatization phase of approximately four weeks took place for all systems, during which conventional pollutants removal was frequently examined. Afterwards, the target compounds were spiked in raw wastewater in order to obtain an inflow concentration of approximately 20 μg L^{-1}. From all systems, samples were collected from different points and analyzed in order to determine the concentration of target micropollutants.

Analytical Methods

The performance of lab-scale systems was periodically monitored measuring T, DO, pH, COD, NH4-N, NO3-N, TSS and MLSS. For the investigation of target compounds fate, analysis of target compounds in the dissolved phase was based on previously developed method (Mazioti et al. 2015) and included solid phase extraction (SPE). Chromatographic analysis was performed by a Shimatzu (Japan) LC20-AD prominence liquid chromatographer associated with a SPD-M20A prominence diode array detector and a SIL-20AC auto sampler.

Equations

The removal efficiency of target compounds in each bioreactor was calculated as the difference between mass flux entering (m_i) and that leaving (m_{out}) each bioreactor, divided by the mass flux of the substance entering the system (M_{in}), as indicated in Eq. (1):

$$Removal\ (\%) = \frac{m_i - m_{out}}{M_{in}} \times 100 \quad (1)$$

RESULTS

Systems performance for conventional pollutants

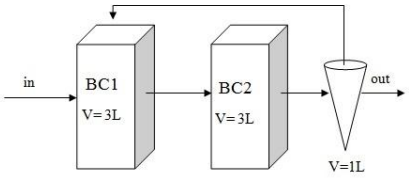
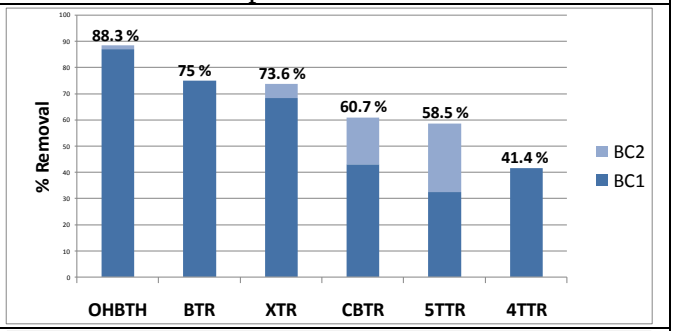
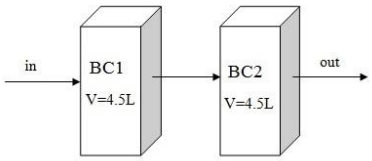
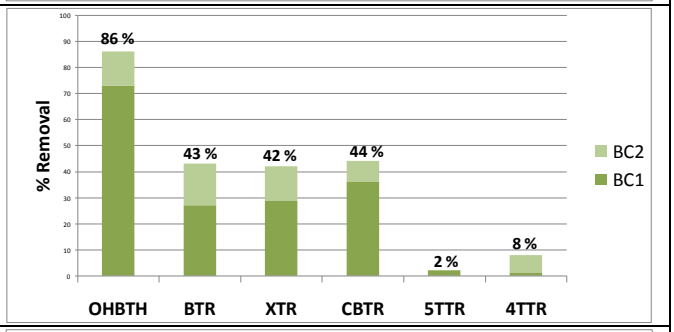
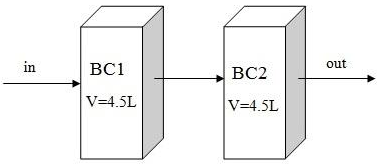
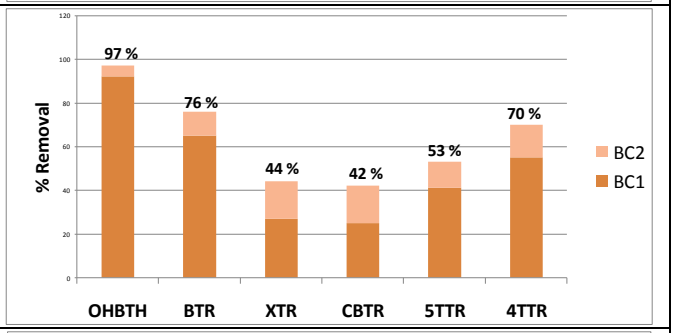
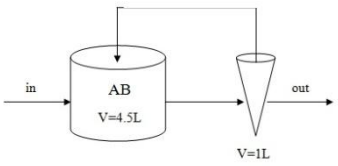
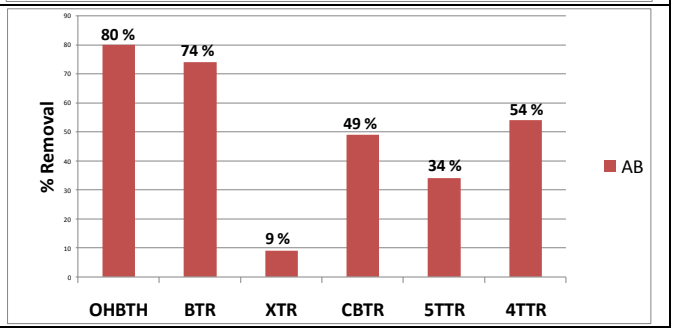
All systems were stable during the whole experimental period and achieved sufficient removal of dissolved COD (between 86%, for MBBR-low and 91%, for MBBR-high) and NH_4-N (between 93% for MBBR-low and AS and 98% for HMBBR). Regarding systems composed of two reactors, the major part of conventional pollutants was removed in BC1, whereas the use of BC2 improved further the quality of treated wastewater. All systems preserved a stable concentration of biomass during the acclimatization and experimental phase. The pH also remained stable and close to neutral through the whole experimental phase.

Removal of target compounds

All micropollutants were removed to some extend during biological treatment with the examined

lab-scale systems. OHBTH was the only compound that was removed on a rate higher than 80% in all systems. BTR removal was recorded from 43 to 76%, XTR from 9 to 73.6%, CBTR from 42 to 60.7%, 5TTR from 2 to 58.5% and 4TTR from 8 to 54%. In all examined systems, the greater part of elimination occurred in the first bioreactor of the system, while in some cases the second one contributed with the further elimination of some compounds. Detailed results on each compounds removal are shown in Table 1.

Table 1. Schematic set-up and percent average removal of target compounds in each examined system.

System	Set-up	Micropollutants removal
HMBBR		
MBBR-high		
MBBR-low		
AS		

Comparison of the removal efficiency of target compounds in the AS, pure MBBR and HMBBR system showed that the HMBBR system achieved similar or statistically higher elimination for 5 out of 6 examined chemicals. Only 4TTR was removed more efficiently in a pure MBBR system that operated under lower organic loading conditions. It is worth mentioned that the performance of

the HMBBR system is higher when compared to a pure MBBR system operated under similar organic loading and HRT condition. Finally, the hybrid system achieved statistically higher removal efficiencies for XTR and 5TTR and similar removal for the other compounds comparing to the AS system operated at the double HRT and the same concentration of suspended biomass. In a previous study, Di Trapani et al. reported that HMBBR systems can achieve similar performance in terms of organic and nitrogen removal as a traditional AS system operating at lower hydraulic loading (Di Trapani et al., 2010), however, to the best of our knowledge, this it is the first time that this is described for micropollutants removal.

CONCLUSIONS

All systems were able to eliminate target compounds from wastewater to some extent. Only OHBTH was removed to an extent higher than 80%. All other compounds demonstrated variations in removal, depending on the system used. The HMBBR system was proved to achieve higher elimination rates compared to other systems. At the same time, the HMBBR system was operated under realistic operational parameters, rendering this system highly suitable for the biological elimination of examined compounds.

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