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Sorption and biodegradation of selected benzotriazoles and hydroxybenzothiazole in activated sludge and estimation of their fate during wastewater treatment

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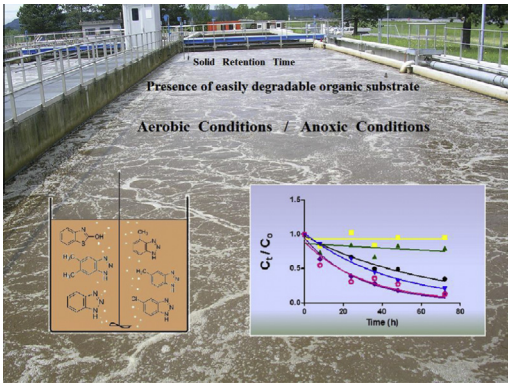
HIGHLIGHTS

- The sorption and biodegradation of selected BTRs and OHBTH was studied.
- Anoxic, aerobic conditions, SRT and organic substrate were investigated.
- BTR, CBTR, XTR and OHBTH were biodegraded under aerobic, anoxic conditions.
- With one exception, Sludge Retention Time did not affect biodegradation kinetics.
- Partial removal of investigated compounds expected in STPs, mainly by biodegradation.

GRAPHICAL ABSTRACT



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ABSTRACT

Biodegradation of benzotriazole (BTR), 5-chlorobenzotriazole (CBTR), xylytriazole (XTR), 4-methyl-1H-benzotriazole (4TTR), 5-methy-1H-lbenzotriazole (5TTR) and 2-hydroxybenzothiazole (OHBTH) was studied in activated sludge batch experiments under aerobic and anoxic conditions, presence of organic substrate and different sludge residence times (SRTs). Their sludge-water distribution coefficients were also calculated in sorption experiments and ranged between 87 and 220 L kg^{-1}. Significant biodegradation of BTR, CBTR, XTR and OHBTH was observed in all biotic experiments. Half-life values ranged between 23 and 45 h (BTR), 18 and 47 h (CBTR), 14 and 26 h (XTR), 6.5 and 24 h (OHBTH). The addition of substrate did not suppress biodegradation kinetics; whereas in some cases accelerated biodegradation of microcontaminants. Except for CBTR, no effect of SRT on biodegradation constants was observed. Prediction of micropollutants removal in Sewage Treatment Plants (STPs) indicated that they will be partially removed, mainly due to aerobic biodegradation. Higher removal is expected at STPs operating at higher SRT and higher suspended solids concentrations.

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1. Introduction

Benzotriazoles (BTRs) and benzothiazoles (BTHs) are two classes of emerging contaminants that have been extensively detected in the aquatic environment, worldwide (Loos et al., 2009; Nödler et al., 2014). BTRs consist of a benzene ring fused with a triazole ring, they are soluble in water, slightly basic (pK_a 8.2–8.8) and have a weak tendency to sorb onto organic matter (Weiss et al., 2006). They are widely used in several industrial applications for protection of metal mechanical parts, as well as in everyday products and dishwashing detergents (Janna et al., 2011; Kiss and Fries, 2012). In the case of BTHs, a benzene ring is fused with a thiazole ring. These compounds are also polar, they are used in tire and rubber manufacturing industries and they are found in biocides, drugs and food flavors (Llompart et al., 2013).

During the last decade, the occurrence of BTRs and BTHs in Sewage Treatment Plants (STPs) has been documented around the world (Reemtsma et al., 2010; Liu et al., 2012; Stasinakis et al., 2013). The concentrations of these compounds in raw sewage vary from some hundred ng L^{-1} to some tens μg L^{-1}, while they are partially removed during conventional wastewater treatment (Weiss et al., 2006; Stasinakis et al., 2013). Despite the frequent detection of BTRs and BTHs in STPs, so far, there is little information on their fate in activated sludge processes and the role of sorption and biodegradation on their removal. Previous research has mainly focused on benzotriazole (BTR), 4-methyl-1H-benzotriazole (4TTR), and 5-methy-1H-lbenzotriazole (5TTR), while in most cases the experiments have been conducted at much higher concentrations than that is found in wastewater. Specifically, in experiments with activated sludge and initial concentration of target compounds equal to 1 mg L^{-1}, Liu et al. (2011) studied the biodegradation potential of BTR, 5TTR and 5-chlorobenzotriazole (CBTR) under aerobic conditions and proposed their biotransformation pathways. In a recent study, Huntscha et al. (2014) investigated the biotransformation of BTR, 4TTR, and 5TTR under aerobic conditions (initial concentrations: 0.5–2.4 mg L^{-1}), determined their half-lives and identified the major biotransformation products. Finally, Herzog et al. (2014a, b) studied the removal efficiency of BTR, 4TTR and 5TTR under different experimental conditions at initial concentrations ranging between 0.2 and 34 mg L^{-1}, and reported that sludge acclimatization enhanced biodegradation of some compounds. To the best of our knowledge, no data is available for the fate of xylytriazole (XTR) and 2-hydroxybenzothiazole (OHBTH) in activated sludge processes. On the contrary, it is known that the biodegradation of micropollutants during activated sludge process is affected by factors such as the redox conditions, the sludge residence time (SRT) and the presence of supplementary substrate (Joss et al., 2004; Stasinakis et al., 2009; Falås et al., 2012; Vasiliadou et al., 2014). Except for BTR, 4TTR and 5TTR (Herzog et al., 2014a,b), no data is available for the effects of these parameters on biodegradation of BTRs and BTHs. Moreover, there is a lack of data for sorption of these compounds to sludge, as well as for the contribution of biodegradation and sorption on their removal from STPs.

Therefore, the main objectives of this study were to investigate biodegradation and sorption potential of five BTRs (BTR, CBTR, XTR, 5TTR and 4TTR) and 2-hydroxybenzothiazole (OHBTH) in activated sludge processes (Table S1). Batch biodegradation experiments were conducted at target compounds concentration levels similar to those reported in the literature for domestic wastewater (ppb level). The effect of aerobic and anoxic conditions, presence of easily degradable substrate and SRT on BTRs and OHBTH biotransformation kinetics was investigated. Additionally, batch experiments were conducted to calculate sludge-water distribution coefficients (K_d) of target compounds. Finally, a model was developed to predict the removal of target compounds during activated sludge processes and to investigate the contribution of biodegradation and sorption to their elimination.

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 by Merck (Germany), 4TTR by Fluka (Switzerland), 5TTR by Acros Organics (Belgium) and OHBTH by Alfa Aesar (USA). Stock solutions of individual compounds were prepared in methanol (MeOH) at 1000 mg L^{-1} and kept at −18 °C. MeOH (HPLC-MS grade) and acetonitrile (ACN, HPLC grade) were purchased by Merck (Germany) and Fisher (USA), respectively. The solid phase extraction (SPE) cartridges used for samples' clean-up were 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%) was purchased by Merck (Germany).

2.2. Sorption experiments

Sorption experiments were conducted with frieze-dried sludge and tap water and were based on previous studies (Andersen et al., 2005; Arvaniti et al., 2014). In brief, activated sludge was washed three times using tap water, centrifuged to remove water soluble constituents and frozen at −18 °C for 24 h. Afterwards, sludge was gently freeze dried to preserve its structure, sterilized by heating at 103 °C for minimum 3 h and stored at 4 °C.

To determine K_d values of the investigated compounds, batch experiments were conducted for a range of initial concentrations of each compound (10, 40, 80, 150, 300 and 500 μg L^{-1}) to 3 g L^{-1} sludge and 100 mL tap water. Flasks were covered in order to inhibit photodegradation, agitated at 120 rpm on a shaking plate and samples were taken at the end of the experiment (24 h) for analysis of compounds in the water phase. All the experiments were performed at 22.0 ± 1.0 °C, while pH was 7.3 ± 0.2.

2.3. Biodegradation experiments

Activated sludge from a nitrifying municipal STP (STP A, Mytilene, Greece), operating at a SRT of 18 d, was used for most biodegradation experiments. After being collected, biomass was left to settle and the supernatant was rejected and replaced with tap water. Afterwards, sludge was aerated for 48 h and diluted to achieve the desired concentration.

The experimental conditions used in different biodegradation batch experiments (A to G) are presented in Table 1. Experiments were conducted in stoppered glass bottles that were constantly agitated on a shaking plate. The working volume in each reactor was 1 L and the mixed liquor suspended solids (MLSS) concentration 3000 ± 200 mg L^{-1}. The investigated compounds were spiked using methanol solutions to obtain an initial concentration of around 30 μg L^{-1} for each microcontaminant in the reactors. The addition of methanol (100 μL in each reactor) resulted to a theoretical oxygen demand of 120 mg L^{-1}. To quantify biodegradation of micropollutants, homogenized samples of mixed liquor (10 mL) were collected after 0, 8, 24, 36, 48 and 72 h. The concentrations of target compounds were determined in the dissolved and particulate phase using the analytical methods described below.

In aerobic experiments (Experiments A, C, E), dissolved oxygen concentrations higher than 4 mg L^{-1} were achieved by constantly

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