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Degradation of benzotriazole and benzothiazole in treatment wetlands and by artificial sunlight

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ABSTRACT

Laboratory-scale experiments were performed using unsaturated subsurface-flow treatment wetlands and artificial sunlight (with and without TiO_2) to study the efficiency of benzotriazole and benzothiazole removal and possible integration of these treatment methods. Transformation products in the effluent from the treatment wetlands and the artificial sunlight reactor were identified by high performance liquid chromatography coupled with tandem mass spectrometry. The removal of benzothiazole in the vegetated treatment wetlands was 99.7%, whereas the removal of benzotriazole was 82.8%. The vegetation positively affected only the removal of benzothiazole. The major transformation products in the effluents from the treatment wetlands were methylated and hydroxylated derivatives of benzotriazole, and hydroxylated derivatives of benzothiazole. Hydroxylation was found to be the main process governing the transformation pathway for both compounds in the artificial sunlight experiment (with and without TiO_2). Benzotriazole was not found to be susceptible to photodegradation in the absence of TiO_2. The integration of the sunlight-induced processes (with TiO_2) with subsurface-flow treatment wetlands caused further elimination of the compounds (42% for benzotriazole and 58% for benzothiazole). This was especially significant for the elimination of benzotriazole, because the removal of this compound was 96% in the coupled processes.

1. Introduction

Benzotriazoles (BTAs) and benzothiazoles (BTs) are high production volume substances that are widely used in various industrial processes and in households (Weiss and Reemtsma, 2005; Jover et al., 2009; Matamoros et al., 2010; Herrero et al., 2014). BTAs are heterocyclic compounds based on the structure of benzotriazole (BTA), which contains two fused rings (benzene and triazole) and three nitrogen atoms. The most common BTAs are the parent compound and tolyltriazole, which is a mixture of the isomers 4- and 5-methyl-BTA (Herrero et al., 2014). BTAs due to their complexing properties are used as corrosion inhibitors (Giger, 2006; Ding et al., 2010; Herrero et al., 2014). In households, BTAs are used as components of dishwasher detergents (Giger, 2006; Ding et al., 2010). BTAs have been classified as being toxic to aquatic organisms, potentially carcinogenic and showing estrogenic activities (Giger, 2006; Matamoros et al., 2010; Asimakopoulos et al., 2013).

The structure of benzothiazole (BT) and its derivatives (BTs) are based on two fused rings – benzene and thiazole. BTs are very often used as vulcanization accelerators in rubber production, and as antifungal agents in paper and leather manufacturing (Matamoros et al., 2010). The commonly used BTs include the parent compound, 2-morpholin-4-yl-BT, 2-hydroxy-BT and 2-methylthio-BT (Reemtsma et al., 1995; Herrero et al., 2014). Asimakopoulos et al. (2013), additionally mentioned 2-(mercapto)-BT as one of the most widely used BT derivatives, which is used as a biocorrosion inhibitor in various industries.

Only in the US the annual production of BTAs exceeds 9000 tons and the production of BT was reported to be in the range of 4.5–450 tons (Asimakopoulos et al., 2013). Because of their

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widespread application, both BTAs and BTs have been identified in different environmental compartments, especially in the aquatic environment. The major sources of BTAs and BTs in the aquatic environment are wastewater treatment plants' (WWTPs) effluents and runoff from urbanized areas (Ni et al., 2008; Janna et al., 2011). Municipal and domestic WWTPs are not optimized for the removal of organic micropollutants (Huntscha et al., 2014). In the case of BTAs and BTs, their removal efficiency in conventional activated sludge system ranged from 0 to 74% for BTAs and 5–28% for BTs (Kloepfer et al., 2005; Voutsa et al., 2006). BTA has been proposed as a proxy compound for assessing compliance to removal targets in Swiss WWTPs (Eggen et al., 2014). Both BTAs and BTs are relatively high water-soluble and do not partition significantly into organic phases or the atmosphere, and are found in average concentrations of up to 10 μg/L in WWTP effluents (Stasinakis et al., 2013; Huntscha et al., 2014) and at 0.1–6.0 μg/L in surface waters (Matamoros et al., 2010). The highest concentrations of BTAs (5-methyl-BTA) were found in the runoff water from several airports in the US and were in the range of 1.1–90 mg/L (Sulej et al., 2011). The conventional activated sludge WWTPs are not efficient in the removal of BTs and BTAs, but it was found that treatment wetlands (TWs) can be more suitable for the removal of these and other organic pollutants as they support co-existence of more diverse degradation processes: photodegradation, microbial degradation, sorption and plant uptake (Matamoros et al., 2010). Indeed, Miksch et al. (2015) indicated the elucidation of the removal and fate of corrosion inhibitors in TWs as one of the research needs.

Only several articles address the removal of BTs and BTAs in TWs but their transformation products (TPs) were not identified. Castro et al. (2005) stated that TWs have the potential for the removal of BTAs especially by the vegetation-induced processes. High removal (98%) of 2-methylthio-BT in an activated soil filter planted with common reed operated as a continuous down-flow (DF) system was attributed to sorption by peat (Bester and Schäfer, 2009). The removal of BT and BTA in a surface flow TW was approximately 80% and 50% during warm season, but negative or equal to 0% during cold season, respectively (Matamoros et al., 2010). On the other hand, in a waste stabilization pond even during cold season the removal of BT and BTA was 72% and 45%, respectively, and was markedly less affected by the seasonality (Matamoros et al., 2016). Pilot-scale vertical DF bed ensured removal efficiency within 80–90% for both compounds (measured only during the warm season) (Matamoros et al., 2010). The elimination of BTA in horizontal flow TWs was found to be very low (<5%) during both cold and warm season, and the removal of BT was moderate and was affected by the seasonality, this is, 63% for the warm season and 39% for the cold season (Matamoros et al., 2016). Aerobic conditions prevailing in unsaturated vertical flow TWs and photodegradation in open water surface systems seems to be conducive to BT and BTA removal. In the case of subsurface-flow TWs, which were applied in the present study, the photodegradation is not a major factor (Matamoros et al., 2010), but this type of TW can be coupled with a system with open water surface systems to promote sunlight-induced processes (Vymazal, 2013).

Indeed, photochemical processes induced by sunlight are mentioned as an effective tool for the removal of persistent micropollutants from biologically treated wastewater (Lin and Reinhard, 2005; Klavarioti et al., 2009; Oller et al., 2011; Gan et al., 2014). In most cases, the sunlight-induced processes were accelerated by the addition of a semiconductor (predominantly TiO_2) to a reaction solution during the irradiation process (Lin and Reinhard, 2005; Pereira et al., 2011; De la Cruz et al., 2013). As a result of an excitation of TiO_2 molecule by means of the sunlight (in an aqueous environment and in the presence of oxygen), hydroxyl radicals are generated, which react indiscriminately with most of organic contaminants. There are only several studies, in which the photochemical degradation of BTA and BT is discussed (Andreozzi et al., 1998; Benitez et al., 2013; Bahnmüller et al., 2015), but none of them described application of both suspended TiO_2 and UV radiation in the solar range for BTA and BT decay. Importantly, TiO_2-based photocatalysis process was suggested as a post-treatment method for the TW-treated effluents, in which the turbidity would not reduce radiation penetration (Liu et al., 2015).

The main objective of the present study was to determine the effect of the processes occurring in TWs and the processes induced by solar light on the degradation and transformation of BT and BTA in the wastewater.

2. Materials and methods

2.1. Chemicals

Analytical standards of 1H-benzotriazole (BTA) and benzothiazole (BT) were purchased in highest available purity from Sigma Aldrich (Poland). Acetonitrile Chromoscan® for HPLC analysis was purchased from POCH S.A. (Poland). Acetonitrile Ultra CHROMASOLV® from Sigma Aldrich (Poland) was used for LC/MS-MS analyses. Titanium (IV) oxide (CAS number 1317-70-0) was purchased from Sigma-Aldrich. In the experiments, TiO_2 was used as powdered anatase (particle size < 5 μm; purity = 99.8%).

2.2. Laboratory-scale TWs

The experimental system consisted of twelve PVC columns filled up to 70 cm with three layers of bed media: 4–8 mm gravel (0–5 cm from the bottom), 0.5–1 mm sand (5–65 cm) and sand mixed with organic soil (65–70 cm). Polyester mesh was used to separate the layers and to protect the outlet from clogging. The dimensions of the columns are shown in Fig. S1 (Supplementary data). The experimental system was operated under laboratory conditions. In order to enable plant growth, the experimental system was illuminated using high pressure sodium lighting system (400 W; photosynthetic photon flux 750 μmoL/s) with various light/dark conditions to mimic seasonal changes: for summer 16 h of light and 8 h of dark (16/8), for fall 9/15, and winter 8/16. The duration of the experiment was 23 weeks (162 days; 10 days of summer, 68 days of fall, 64 days of winter), but this period was preceded by a 3-month adaptation period when the columns were fed with the influent without BT and BTA. The mean min. and max. temperature during the experiment was 23.0 °C and 28.7 °C, and the humidity was 50.3–76.4%. Selected columns were planted with the seedlings of reed canary grass 'Picta' (*Phalaris arundinacea* var. picta L.) 3 months before the experiment. The seedling plants were rooted in organic soil, therefore the top most layers of all the columns contained a mixture of organic soil and sand. This mixed layer was also present in the unplanted columns.

The types of columns (in duplicate) used in the experiment were selected based on the presence or absence of vegetation in the columns and the presence or absence of BT or BTA in the influent. This combination yielded six types of columns: columns fed with simulated wastewater (control columns, CTRL), respectively planted (CTRL-P) and unplanted (CTRL-U); columns fed with wastewater spiked with BT, respectively planted (BT-P) and unplanted (BT-U) and columns fed with wastewater spiked with BTA, respectively planted (BTA-P) and unplanted (BTA-U).

The columns were operated in an intermittent DF unsaturated mode and fed by simulated municipal wastewater prepared based on the modified protocol by Nowrotek et al. (2016). The detailed information on the composition of the wastewater used in the study is given in Table S1. The influent for the BTA-U and BTA-P