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Photodegradation of micropollutants using V-UV/UV-C processes; Triclosan as a model compound

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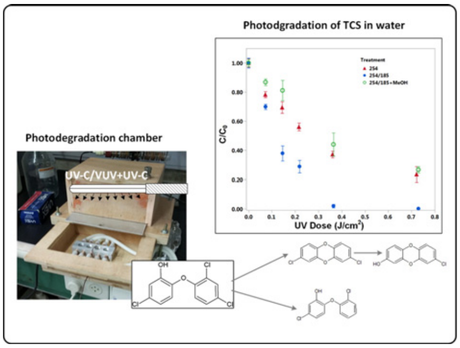
HIGHLIGHTS

- Triclosan (TCS) photodegradation was faster in aqueous solution than in dry thin films.
- Degradation kinetics of aqueous TCS was faster under combined V-UV/UV-C radiation.
- Transformation products were identified and their formation/degradation kinetics was quantified.
- Toxicity and biodegradability were predicted by QSAR.

GRAPHICAL ABSTRACT



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ABSTRACT

Non-potable reuse of treated wastewater is becoming widespread as means to address growing water scarcity. Removal of micropollutants (MPs) from such water often requires advanced oxidation processes using •OH radicals. •OH can be generated in-situ via water photolysis under vacuum-UV ($\lambda < 200$ nm) irradiation.

The aim of this study was to investigate the potential of unmasking V-UV radiation from low pressure Hg lamps (emitting at 185 and 254 nm), commonly used in decentralized treatment systems, for enhancing MPs removal efficiency. Triclosan, a biocide of limited biodegradability, served as a model compound for MPs that are not very biodegradable. Its degradation kinetics and identification of intermediate products were investigated under 254 nm and under combined 254/185 nm irradiation both in dry thin films and in aqueous solutions. In the latter, degradation was faster under combined 254/185 nm radiation, although the 185 nm radiation accounted for only 4% of the total UV light intensity. In contrast, triclosan photodegradation in dry film did not show significant differences between these irradiation wavelengths, suggesting that the enhanced degradation of dissolved triclosan under combined radiation is mainly due to oxidation by •OH formed via water photolysis under V-UV. This conclusion was supported by slower TCS degradation in aqueous solution when methanol was added as •OH scavenger. Under both irradiation types (254, 254/185 nm) three transformation products (TPs) were identified: 2,8-dichlorodibenzo-p-dioxin, 5-chloro-2-(4- or 2-chlorophenoxy)phenol, and 2-hydroxy-8-chlorodibenzodioxin. *In-silico* QSAR toxicity assessment predicted potential toxicity and moderate-to-low biodegradability of these TPs. Removal of these TPs was faster under 254/185 nm irradiation.

Considering the low cost, simple operation (i.e. no chemicals addition) and small size of such low-pressure mercury lamps, this is a promising direction. Further investigation of the process in flow-through reactors and real

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wastewater/greywater effluent is needed for its future implementation in small on-site systems for post-treatment of persistent pollutants.

1. Introduction

Growing demand for freshwater together with depleting natural water sources increase the reuse of treated wastewater (e.g., greywater, municipal wastewater) for non-potable applications. Wastewater reuse can be implemented either by centralized municipal wastewater treatment plants or through decentralized facilities, where greywater (GW) reuse is a preferred alternative (Maimon et al., 2010).

A major challenge of both decentralized and centralized wastewater treatment, is the removal of micropollutants (MPs) that are not efficiently removed by conventional treatment. The most widely spread MPs in wastewater are pharmaceuticals and personal care products (PCP's) (e.g. shampoos, soaps, toothpastes and creams) that contain preservatives, biocides, musks and UV-filters. As some of the MPs found are toxic/endocrine disrupters and/or persistent in the environment, water containing them needs to be properly treated prior to its reuse or release to the environment.

Advanced oxidation processes (AOPs) seem promising methods to eliminate MPs residues that were not removed during conventional treatment (De la Cruz et al., 2012; Herrmann et al., 2015).

In wastewater treatment by AOPs, •OH radicals are usually generated via photolysis of H_2O_2 under 254 nm light (UV-C). However, •OH and other radicals can also be generated in situ via photolysis of water and dissolved O_2 using vacuum-UV (V-UV, $\lambda < 200$ nm) (Gonzalez et al., 2004; Zoschke et al., 2014 and reference therein). Such generation of •OH (see detailed reactions in Supplementary Material S1) eliminates the need of chemicals (H_2O_2) or catalysts (TiO_2 or Fe^{3+}) addition. This is very important for decentralized and small-scale wastewater treatment units (e.g., greywater treatment), as it simplifies their operation and maintenance (Zoschke et al., 2014). Furthermore, decentralized systems that treat small volumes of water can easily overcome the limited penetration of V-UV light in water, resulting from the strong absorption of V-UV by the water itself.

As many organic compounds are likely to absorb V-UV radiation (Gonzalez et al., 2004), UV light may also lead to direct photolysis of MPs. However, very little information is currently available regarding the spectral properties and quantum yields of MPs in V-UV range.

In recent years there is growing interest in using V-UV irradiation for MPs and natural organic matter removal from water (Zoschke et al., 2014 and references therein), but there are still many knowledge gaps regarding it. Studies on the removal of PCP-related MPs by V-UV are very scarce. Kim et al. (2009) compared the removal of 30 PCPs and pharmceticals in water by UV-C and by combined V-UV/UV-C irridation. The study revealed that the combined irradiation was more efficient than UV-C alone, but was unable to determine if this was a result of fast direct photolysis under V-UV irradiation and/or oxidation by •OH that formed only under V-UV irradiation.

It should be noted that as long as full mineralization is not achieved, AOPs may form transformation products (TPs) that may continue to pose environmental or health concerns (Fatta-Kassinos et al., 2011; Khaleel et al., 2017). Thus, special attention should be given also to the toxicity and persistence of such products (which in some cases are more toxic than their parent compound). However, many of the previous studies on V-UV water treatment have not addressed this issue (see review by Zoschke et al., 2014).

Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol) (TCS) is a biocide added to PCPs (e.g. antibacterial soaps, deodorants, toothpastes) and used in several other household products (e.g. kitchenware or functional clothing). Hence, it occurs in wastewater effluent, and due to it is persistence, it is frequently detected in surface waters and sediments (Bock et al., 2010; Cantwell et al., 2010; Kolpin et al., 2002; Singer et al., 2002). The median effective concentration (EC_{50}) of TCS lies between 0.96 and 390 μg L^{-1} (depending on the species tested) (Orvos et al., 2002). The major transformation process affecting TCS fate in surface waters is likely to be direct photolysis (Anger et al., 2013; Kliegman et al., 2013; Lindström et al., 2002; Singer et al., 2002), as biodegradation and hydrolysis are ineffective for TCS (Singer et al., 2002). In water treatment, TCS was shown to be efficiently removed via direct photolysis under UV-C light (254 nm) as well as via oxidation by •OH (Gao et al., 2014; Sirés et al., 2007; Wong-Wah-Chung et al., 2007). Nevertheless, its photolysis under such UV-C radiation, was accompanied by formation of undesired intermediates, such as dibenzo-p-dioxin (Anger et al., 2013; Kliegman et al., 2013; Latch et al., 2003; Mezcua et al., 2004; Wong-Wah-Chung et al., 2007).

The aim of this study was to investigate the potential of unmasking the V-UV radiation from low pressure Hg lamps (emitting at 185 and 254 nm), commonly used in decentralized treatment systems, for enhancing MPs removal efficiency. TCS served as a model compound for MPs that are not very biodegradable. Its photodegradation under UV-C and combined V-UV/UV-C irradiation was investigated, including both kinetics and intermediate products identification. In order to understand whether V-UV contributed to TCS degradation by direct photolysis or by reaction with photo-induced radicals (generated via water photolysis), its removal was examined both in aqueous solution and in dry thin films (in which •OH are not formed). Finally, established Quantitative structure-activity-relationship (QSAR) models were used for *in-silico* analysis in order to provide preliminary indication for fate and toxicity of new and unknown TPs of TCS.

2. Material and methods

2.1. Chemicals and reagents

All chemicals used were analytical or HPLC grade: 5-Chloro-2-(2,4-dichlorophenoxy)phenol (TCS, >97%) was purchased from Sigma (Steinheim, Germany); methanol (>99.8) and hydrochloric acid (32%) from Bio-Lab ltd. (Jerusalem, Israel); acetone (>98%) and sulfuric acid (>98%) from Gadot ltd. (Netanya, Israel); N_2 gas (>99.999%) and air from Maxima (Israel). Deionized (DI) water 18.2 MΩ was obtained by MilliPore system (Direct Q3, Merck, Germany).

2.2. UV-C and V-UV light source

Low-pressure mercury lamp ($\lambda = 254$ nm or $\lambda = 254 + 185$ nm) were used (Jelight; 7″, double-bore, PN: 78–2046-7 or 81–3306-7, respectively). According to the manufacturer, both lamps have an input power of 6 W and output intensity (on lamp's surface) of ~30 mW cm^{-2} at 254 nm and (for the combined lamp) 1.3 mW cm^{-2} at 185 nm. UV-C irradiation intensity was measured using spectroradiometer (USB2000 + UV-VIS-ES, Ocean Optics, USA); whereas photon flux at 185 nm was measured in batch experiments using methanol photolysis as an actinometer (Oppenländer and Schwarzwälder, 2002). Samples of 80 mM of methanol were placed in the temperature-controlled wells (as above), and exposed to 254/185 nm UV-C/V-UV. The photon flux was calculated from the methanol photodegradation rate.