Laboratory scale study of photolytic and photooxidative treatment for removal of pharmaceutical residues from water matrices

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Abstract
Photolytic and photooxidative degradations of diclofenac (DICL), naproxen (NAPR) and carbamazepine (CARB) were studied applying a batch photo-reactor containing low-pressure mercury lamp emitting at 185 and 254 nm. The drugs were added in concentration of 5×10^{-6} M to ultra-pure water (UPW) and biologically treated wastewater (BTWW). Almost complete photolytic and photooxidative degradations were observed by VUV irradiation for DICL, NAPR and CARB in UPW within 1.0, 1,0 and 1.5 min, respectively. But in the spiked BTWW matrix, the efficient degradation of DICL, NAPR and CARB were achieved within 1, 2 and 10 min, respectively. Several aromatic degradation products of DICL, NAPR and CARB were identified by quadrupole time-of-flight mass spectrometer hyphenated to an ultra-high performance liquid chromatograph after preconcentration with off-line solid phase extraction upon irradiation of the UPW matrix spiked with the selected drugs at 254 nm. For several degradation products, chemical structures differing from those previously reported have been proposed. Moreover, acridine has not yet been reported as photodegradation product for DICL. . Almost complete degradation of DICL, NAPR and CARB as well as their degradation products by VUV+PhO in BTWW took place in 5, 10 and 30 min, respectively applying only one 50 cm long photo-reactor and oxygen stream. The efficiency of this technology can be increased by simultaneous application of more photoreactors in a flowing system.
Keywords: Diclofenac; Naproxen, Carbamazepine, UV irradiation; Low-pressure mercury lamp

1. Introduction

Persistent micropollutants, such as active pharmaceutical ingredients are permanently detected worldwide in different water matrices, e.g., drinking water, surface water, influent and effluent wastewater (WW) from ng/L to µg/L concentration range Oliveira et al 2015, Paiga et al 2017). The main source of pollution is anthropogenic through human excretion or direct discharge of pharmaceuticals into the communal WW system. Diclofenac (DICL) and naproxen (NAPR) are nonsteroidal anti-inflammatory drugs, while carbamazepine (CARB) is an anticonvulsant. They are considered as persistent micropollutants that are ubiquitously present in the aquatic environment. Globally, the mean concentrations of DICL, NAPR and CARB in surface waters are 50, 32, 187 ng/L, respectively (aus der Beek et al. 2016). These drugs are mainly excreted in the form of metabolites and conjugates. Although excretion rate in unchanged form is low, excessive intake of these pharmaceuticals leads to their occurrence in detectable quantities in raw and treated wastewater.

The conventional three-step wastewater treatment plants (WWTPs) have low removal efficiencies for these compounds, which leads to the contamination of the surface water reservoirs. This can also affect the drinking water quality in the case of riverbank filtration (Bradley et al 2014). Therefore recently, various types of quaternary steps for WW clarification are being implemented. These include several advanced oxidation processes (AOPs) based on ozonation, Fenton and photo-Fenton reactions, UV photolysis (PhL) and photooxidation (PhO), photocatalytic processes (Carabin et al 2015, Martinez et al 2011) activated carbon filtration and nanofiltration or reverse osmosis.

In the case of visible light and UV irradiations, free radicals are generated from the molecules after photon absorption in primary photochemical processes. The benefit of using VUV irradiation compared to UV is the higher photon energy that is sufficient to cleave most covalent bonds in organic compounds. Moreover, it is capable of water photodissociation generating ·H and ·OH radicals leading to a faster degradation *via* radical and molecule reactions. The disadvantage of using VUV is that VUV photons are only absorbed by a thin layer of water, thus the mode of stirring of the irradiated solution can largely influence the efficiency of the irradiation.

2. Materials and Methods

For the identification of the photodegradation products, an Elute ultra-high performance liquid chromatograph (UHPLC) was coupled to a Compact quadrupole time-of-flight mass spectrometer (Q-TOF-MS), both purchased from Bruker Daltonik GmbH (Bremen, Germany).

3. Results

The degradation of drug molecules at the same treatment conditions increased in the following order: CAR<NAP<DICL. Due to the relatively high TOC content of biologically treated wastewater, a strong matrix effect can be observed (*Fig. 1.)* during both the photolytic and the photooxidative treatments, therefore a filtration step before the radiation of water samples can improve the efficiency of the water treatment procedure. The possible by-products and degradation pathways will be demonstrated at the conference.

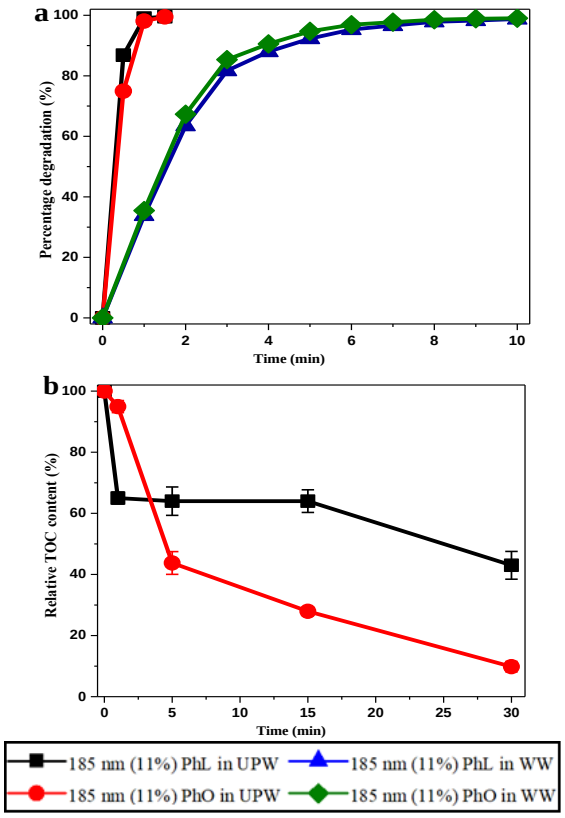

Fig. 1 The change of degradation rates of drug molecules and the TOC reduction during the photolytic and photooxidative treatments

4. Conclusions

Protection and conservation of the water resources are key issues for the future of mankind that require development of strategies taking into account efficient wastewater treatment technologies. With this respect, UV photolytic and photooxidative degradation of such persistent micropollutants like pharmaceutical residues seems to be an efficient way as a future quaternary water treatment step for wastewater originating from small and medium sized settlements. However, efficiency of this proposed procedure relies on the mixing of the sample with an adequate O_2 or air stream. Ecotoxicological investigation should be performed in the future to strengthen the outcomes of the present study. Moreover, due to its disinfection potential, the proposed photooxidative procedure can be recommended even for irrigation or drinking water production.

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