Removal and transformation of citalopram and 4 of its biotransformation products during ozonation

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EXTENDED ABSTRACT

The continuous discharge of pharmaceuticals in effluents from production facilities, hospitals, and private households, improper disposal of unused drugs, and the direct discharge of veterinary medicines all lead to contamination of environmental waters [Kümmeler (2001)]. Many pharmaceuticals are not entirely removed even through wastewater or drinking water treatment processes, thus, they are consequently detected at various concentrations (from ng to μg per liter) in effluent samples of wastewater treatment plants (WWTPs) and drinking water supplies [Kumar and Xagoraraki (2010)]. Citalopram (CTR), a selective serotonin re-uptake inhibitor, is a compound of interest due to its worldwide high consumption for the treatment of depression. Several studies carried out worldwide reported the occurrence of CTR in different environmental matrices, including influent and effluent wastewaters, sewage sludge, surface waters and biota [Beretsou (2016)]. The treatment sequence applied in WWTPs encompasses the following steps: a primary gravity settling, a secondary biological treatment and finally a tertiary step, including advanced oxidation processes for disinfection and removal of micropollutants [Escher and Fenn (2011)]. Treatment with ozone appears to be one of the most promising disinfection technologies for the removal of these compounds. Although the removal of many pollutants may be significant, often total mineralization is not achieved. Since the reactivity of ozone towards organic compounds is high, transformation products (TPs), with unknown physicochemical properties and toxicity, may be produced.

So far, studies concerning the transformation of emerging contaminants during a disinfection method (ozonation, chlorination, UV treatment), have been focused on the probable transformation of known contaminants and less frequently on their known human metabolites [García-Galán (2010)]. Since recent literature has revealed the formation of biotransformation products of emerging contaminants during secondary biological treatment, their probable transformation during tertiary treatment should not be overlooked.

The aim of this study is to investigate the removal and transformation of CTR and four of its biotransformation products during ozonation. These biodegradation TPs, N-desmethyl CTR, CTR amide, CTR carboxylic acid and 3-oxo-CTR, were identified in a previous study [Beretsou (2016)] by means of high resolution mass spectrometric techniques and their structure was confirmed through the analysis of the corresponding reference standard. These compounds were also detected through retrospective analysis in real secondary treated wastewater samples, underlying the need for further investigation. Five ozonation TPs of CTR have been reported by Hörsing et al. (2012) using low resolution MS analysis. High resolution analytical instruments, like quadrupole time-of-flight (Q-ToF) mass spectrometry, are extensively used for real time detection and identification of oxidation products, due to their high confirmatory capabilities, derived from the high resolving power and the mass accuracy in MS and MS/MS modes, along with the developed sophisticated software.

Lab-scale ozonation experiments were performed for the five tested compounds (2 mg/L), with different initial ozone concentrations ranging from 0.06 to 12 mg/L at neutral pH. Moreover, a batch of experiments (with 3 mg/L of ozone) was also performed at pH 4 and 10. The samples were analyzed by reversed-phase liquid chromatography quadrupole-time-of-flight mass spectrometry (RPLC-QToF-MS) in positive ionization mode.

All tested compounds reacted with O₃, reaching total removal when 3 mg/L of O₃ was applied. TrendTrAMS, an in-house developed software, was used to detect any m/z that showed a specific trend (formation profile) with increasing O₃ concentration. These m/z were attributed to ozonation TPs and were further treated through suspect and non-target screening approaches, for their structure elucidation. Furthermore, the TPs that were formed only under a certain pH were revealed by XCMS online, using pairwise comparison.

Several TPs were identified for citalopram and its 4 tested biodegradation products. Among them, N-oxides were the most abundant TPs, which were found to be more toxic than their parent compounds in aquatic environment towards daphnia magna after 48 h of exposure using ToxTrAMS program [Aalizadeh (2017)]. The findings of this study highlight the need for systematic investigation of the fate of biodegradation products during treatment with ozone.

References


Keywords: ozonation, citalopram, emerging pollutants, transformation products, trend analysis