Science of the Total Environment 569–570 (2016) 830–840

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Biological hazard evaluation of a pharmaceutical effluent before and after a photo-Fenton treatment

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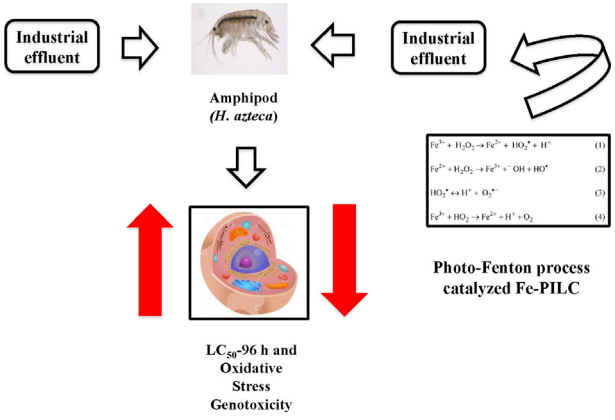
HIGHLIGHTS

- This study aimed to establish the biological efficiency of a photo-Fenton method.
- Acute toxicity test and biomarkers of oxidative stress were evaluated before and after treatment.
- The applied photo-Fenton process decreased oxidative stress and LC_{50} in *Hyalella azteca*.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 April 2016
Received in revised form 3 June 2016
Accepted 13 June 2016
Available online xxxx

Editor: D. Barcelo

Keywords:
Hyalella azteca

ABSTRACT

The aim of this study was to evaluate the biological hazard of a pharmaceutical effluent before and after treatment. For the former, the determined 96 h-LC_{50} value was 1.2%. The photo-Fenton treatment catalyzed with an iron-pillared clay reduced this parameter by 341.7%. Statistically significant increases with respect to the control group ($P < 0.05$) were observed at 12, 24, 48 and 72 h in HPC (50.2, 30.4, 66.9 and 43.3%), LPX (22, 83.2, 62.7 and 59.5%) and PCC (14.6, 23.6, 24.4 and 25.6%) and antioxidant enzymes SOD (29.4, 38.5, 32.7 and 49.5%) and CAT (48.4, 50.3, 38.8 and 46.1%) in *Hyalella azteca* before treatment. Also increases in damage index were observed before treatment of 53.1, 59.9, 66.6 and 72.1% at 12, 24, 48 and 72 h, respectively. After treatment the same biomarkers of oxidative stress decreased with respect to before treatment being to HPC (29.3, 22.5, 41.6 and 31.7%); LPX (14.2, 43.1, 30.7 and 35.5%); PCC (12.6, 21.3, 24.2 and 23.9%); SOD (39.2, 33.9, 49.5 and 37.9%)

Abbreviations: PCT, paracetamol; HPC, hydroperoxide content; LPX, lipid peroxidation; PCC, protein carbonyl content; SOD, superoxide dismutase; CAT, catalase; GPx, glutathione peroxidase; LC-MS/MS, liquid chromatography-tandem mass spectrometry; MS, mass spectrometer; LOAEL, lowest observed adverse effect level; NSAIDs, non-steroidal anti-inflammatory drug; NAPQI, *N*-acetyl-*p*-benzoquinoneimine; AOPs, advanced oxidation processes; STPs, sewage treatment plants; Fe-PILC, Fe-pillared clay.

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http://dx.doi.org/10.1016/j.scitotenv.2016.06.086
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Oxidative stress
Paracetamol
Photo-Fenton process
Amphipod
Fe-PILC

and CAT (28.6, 35.8, 33.7 and 31.7) at 12, 24, 48 and 72 h, respectively ($P < 0.05$). The damage index were decreased at 12, 24, 48 and 72 h in 48.9, 57.8, 67.3 and 72.1%, respectively. In conclusion, the obtained results demonstrate the need of performing bioassays in order to characterize an effluent before discharge and not base such a decision only upon current normativity. In addition, it was also concluded that the heterogeneous photo-Fenton process decreases the presence of PCT, oxidative stress, genotoxic damage and LC_{50} in *Hyalella azteca*.

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1. Introduction

Pharmaceuticals, by being routinely discharged into the aquatic ecosystem in amounts that roughly equal the environmental elimination rates, are considered pseudo-persistent pollutants (Zenker et al., 2014) and chronic effects are possible (Saucedo-Vence et al., 2015). Pharmaceuticals are known to have biological activity, which is the most important parameter when evaluating their toxicological impact in the wild (Miao et al., 2002). These contaminants are specifically designed to resist metabolic degradation, and, albeit being polar molecules, are lipophilic enough to be absorbed by target organisms (Brandão et al., 2014). Due to the conservative nature of physiological processes, many aquatic species possess similar target molecules/receptors to those drugs that are intended to interact solely with humans (Owen et al., 2007; Gunnarsson et al., 2008), favoring the exertion of pharmacological and toxicological effects on most aquatic organisms.

Pharmaceuticals are a class of "emerging contaminants", which comprise numerous prescription and over-the-counter medicines, including diverse groups, such as antibiotics, antiepileptics, blood-lipid regulators, antihistamines, β-blockers, antiulcer agents, anti-asthma drugs, serotonin re-uptake inhibitors, steroidal hormones and NSAIDs (Lubliner et al., 2010). The latter, is a heterogeneous group of pharmaceuticals with antiinflammatory, analgesic and antipyretic properties, are selective inhibitors of the enzyme cyclooxygenase (COX), inhibiting both cyclooxygenase-1 and 2 (COX-1 and COX-2) (Gonzalez-Rey and Bebianno, 2011; Vane and Botting, 2003) – which catalyzes the formation of prostaglandins, thromboxanes and leukotrienes from arachidonic acid. This group of pharmaceutical agents includes PCT (paracetamol), naproxen (NPX), diclofenac (DCF) and ibuprofen (IBP), among others. In Mexico, NSAIDs are among the most frequently sold and used medicinal remedies (Gómez-Oliván et al., 2009). They are marketed in diverse pharmaceutical forms and are immoderately used since they can be obtained without prescription.

One of the most used NSAIDs is PCT (also designated as acetaminophen) (Solé et al., 2010) due to its antipyretic and analgesic properties (Xu et al., 2008), especially for pediatric purposes (Pandolfini and Bonati, 2005). PCT has been found at concentrations of up to 6 μg L^{-1} in European effluent (Ternes, 1998), up to 10 μg L^{-1} in the USA (Kolpin et al., 2002), and >65 μg L^{-1} in the Tyne River in the UK (Roberts and Thomas, 2006). PCT is also reported as one of the most frequently detected pharmaceuticals in STPs effluents, drinking water, and also surface water (Kim et al., 2007). PCT has also been found in marine waters (namely in the Mediterranean Sea), in levels up to 3 μg L^{-1} (Nödler et al., 2014). Additional studies demonstrated that PCT is promptly accumulated by marine organisms, being one of the most common micropollutants found in sessile species, such as mussels (Will et al., 2011).

The European Agency for the Evaluation of Medicinal Products (EMEA, 2003) reports the cyto- and genotoxic potential of PCT at concentrations of 10.38 μg L^{-1} on zebra mussel. Similarly, mortality has been reported in hemocytes of these species at concentrations of 350 μg L^{-1} of PCT (Parolini et al., 2009).

Considering that its main toxicological outcomes in mammals result from oxidative stress (Letelier et al., 2011), it is likely that a similar response may occur in the exposed aquatic macroinvertebrates (Gómez-Oliván et al., 2012). PCT may be metabolized by conjugation with co-factors, forming the non-toxic conjugated metabolites PCT glucuronide and PCT sulfate (Jaeschke and Bajt, 2006; Xu et al., 2008). This pathway corresponds to a detoxification process, since the majority (circa 90%) of ingested PCT is converted into these two conjugate forms, which are promptly excreted. The remaining portion of absorbed PCT is oxidized via cytochrome P450 enzymes (primarily CYP 2E1, 1A2, and 3A4), into a highly reactive, oxidant, and electrophilic intermediate, NAPQI (Xu et al., 2008), which in turn is usually detoxified by conjugation with intracellular glutathione (Xu et al., 2008). However, higher PCT dosages are responsible for the exhaust of required cofactors for ulterior conjugation (both of PCT and, ultimately, NAPQI) and NAPQI is accumulated, exerting multiple toxic effects, such as covalent modifications of thiol groups on cellular proteins (Xu et al., 2008), DNA and RNA damage, and oxidation of membrane lipids, resulting in necrosis and cellular death (Hinson et al., 2004; Jaeschke and Bajt, 2006). Despite the absence of metabolic studies that corroborate this hypothesis, evidences point to the involvement of a similar oxidative pathway in aquatic organisms as *H. azteca* and *Cyprinus carpio* (Gómez-Oliván et al., 2012; Antunes et al., 2013; Nava-Alvarez et al., 2014; Ramos et al., 2014; Nunes et al., 2015).

On the other hand, the pharmaceutical industry generates large quantities of wastewater varying in characteristics and concentration as a function of the manufacturing process used and the year season. These effluents are mainly the result of machinery cleaning (Balcıoğlu and Ötker, 2003) and, in addition to residues of the pharmaceutical products manufactured, also contain other kinds of compounds used in the cleaning process, including solvents (ethanol) and detergents such as sodium dodecylbenzene sulfonate (SDBS). The pharmaceutical plant emanating the effluent analyzed in our study is used exclusively for NSAID manufacture and mainly PCT. Since the plant has no wastewater treatment system, the effluent contains PCT derived from the manufacturing process and goes to Lerma River. The importance of effective treatment of PCT containing effluents is related to toxicological effects in aquatic environment (Klamerth et al., 2010; Santos et al., 2010), since the degradation products of PCT are potentially toxics, causing in bioindicator species; oxidative stress, both cellular damage and death, and inhibition of reproduction (Gómez-Oliván et al., 2012; Nunes et al., 2014; SanJuan-Reyes et al., 2013).

Due to the potential ecotoxicological risk of the PCT for ecosystems, it must be removed from water, especially if it is intended for human consumption, and a solution to this problem might be the application of non-biological procedures, such as advanced oxidation processes (AOPs). The effectiveness of these techniques is based on the generation of hydroxyl radicals, which act as a powerful oxidizing agent with a high reactivity and low selectivity for the removal of organic compounds. Among AOPs, ozonation (Rodayan et al., 2014) and photo-oxidation processes such as photocatalysis with TiO_2 (Postigo et al., 2011a) and homogenous photo-Fenton with iron salts and hydrogen peroxide (Poyatos et al., 2009; Postigo et al., 2011a, 2011b) have been proposed as treatments for a variety of drugs (methadone, cocaine, benzoylecgonine, ketamine and oxycodone, among others). Although, the AOPs techniques such as Fenton, photo-Fenton and photo-like-Fenton processes are associated with problems such as excessive time requirements, high costs and high energy consumptions (Xu et al., 2012; Huang et al., 2015), however, these processes due to their highger efficiency and short reaction time could be considered as an alternative method in industrial applications (Irani et al., 2015; Rad et al., 2015a,b).

The extensive follow-up of degradation products and toxicity is important to ensure economically and ecologically safe applications of AOPs. The ecotoxicological characterization of AOPs during and after their application to treat industrial pollutants has attracted significant

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