Chemosphere 148 (2016) 473–480

Contents lists available at ScienceDirect

Chemosphere

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

Use of solar advanced oxidation processes for wastewater treatment: Follow-up on degradation products, acute toxicity, genotoxicity and estrogenicity

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HIGHLIGHTS

- 53 micropollutants detected in wastewater effluent.
- The most used toxicity tests as well as other methods are tested and discussed.
- Genotoxicity and Estrogenic response are complementary to other bioassays.
- Successful follow-up of wastewater treatment processes by solar AOPs.

ARTICLE INFO

Article history:
Received 27 May 2015
Received in revised form
8 January 2016
Accepted 18 January 2016
Available online 4 February 2016

Handling Editor: Frederic Leusch

Keywords:
Wastewater
Micropollutants
Toxicity
Estrogenic activity
Genotoxicity
Solar advanced oxidation processes

ABSTRACT

Wastewater tertiary treatment by advanced oxidation processes is thought to produce a treated effluent with lower toxicity than the initial influent. Here we performed tertiary treatment of a secondary effluent collected from a Waste Water Treatment Plant via homogeneous (solar/HSO_5^-/Fe^{2+}) and heterogeneous (solar/TiO_2) solar advanced oxidation aiming at the assessment of their effectiveness in terms of contaminants' and toxicity abatement in a plain solar reactor. A total of 53 organic contaminants were qualitatively identified by liquid chromatography coupled to high-resolution mass spectrometry after solid phase extraction. Solar advanced oxidation totally or partially removed the major part of contaminants detected within 4.5 h. Standard toxicity tests were performed using *Vibrio fischeri*, *Daphnia magna*, *Pseudokirchneriella subcapitata* and *Brachionus calyciflorus* organisms to evaluate acute and chronic toxicity in the secondary or tertiary effluents, and the EC_{50}% was calculated. Estrogenic and genotoxic tests were carried out in an attempt to obtain an even sharper evaluation of potential hazardous effects due to micropollutants or their degradation by-products in wastewater. Genotoxic effects were not detected in effluent before or after treatment. However, we observed relevant estrogenic activity due to the high sensitivity of the HELN ERα cell line.

1. Introduction

Water scarcity is becoming an increasingly acute issue in many regions of the world. Taking cognizance of the need for this crucial resource, wastewater treatment plants (WWTPs) offer the most promising source of recycled water. Obviously, reusable wastewater should not contain any toxic or xenobiotic substances like pharmaceuticals, pesticides and, especially, endocrine-disrupting compounds (Köck-Schulmeyer et al., 2013). Most of these recalcitrant compounds count among the so-called 'emerging contaminants' (ECs). In view of their widespread presence and potential impact, ECs must be removed from wastewater before discharge or reuse.

Recent studies report that WWTPs fail to remove ECs and other pollutants normally present in the ng–μg L^{-1} range of

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http://dx.doi.org/10.1016/j.chemosphere.2016.01.070
0045-6535/

concentration (Lacey et al., 2008; Göbel et al., 2005). Hansen (2007) and Pal et al. (2010) reported the ecological risk that ECs may cause via continuous penetration in the aquatic environment. Major consequences are: feminization of higher organisms, microbiological resistance and accumulation in soil, plants and animals, short-term and long-term toxicity, endocrine-disrupting effects, and antibiotic resistance of microorganisms (Bolong et al., 2009; Fent et al., 2006). The hazard of these micropollutants in the environment does not only depend on their concentrations but also their metabolites or degradation by-products, which can sometimes prove more harmful that the parent compounds (Vulliet et al., 2001; Scrano et al., 2002, 2004). Cocktails of compounds represent an issue that had to be addressed because the toxicity of a mixture cannot be easily determined by summing up individual toxicities of the mixture components. Thus, predicting the impact of a wastewater stream on the ecology of a receiving body hinges on determining the toxicity of the outlet effluent.

There is currently no scientifically recognized definition of toxicity, but a lay of definition would sum up the adverse effects posed by a substance to living organisms (European Union, 2012). Toxicity research focuses on organisms from bacteria to algae, invertebrates, and others. Wastewater contains a cocktail of organic compounds, some of which maybe toxicant. For this reason, biomonitors have been developed and standardized to detect toxicity in water samples, by analyzing usually response patterns in living organisms, such as inhibition of luminescence or inhibition of growth (Calleja et al., 1986). However, these methods are not always sensitive at low concentration of contaminants (Rizzo et al., 2005), making it necessary to accurately plan a selection of assays that may have to be used simultaneously to adequately assess toxicity (Rizzo, 2011).

The EU Water Framework Directive requires a “good chemical and biological status” of all water bodies by 2015 (Water Framework Directive, 2000/60/EC). To achieve this objective, hinges on developing efficient technologies to create effective wastewater treatment protocols is necessary. Advanced oxidation processes (AOPs) are emerging as lead candidates for removing ECs in wastewater as unselective radicals (hydroxyl or sulfate) can mineralize organic matter at high reaction rates. A disadvantage regarding the use of AOPs is the additional cost of producing radicals, i.e. the reagent and/or energy consumption needed to activate the mechanisms. Some AOPs, like photo-Fenton and heterogeneous photocatalysis with TiO_2 can be driven by solar irradiation (Malato et al., 2009; Plantard et al., 2012; Brienza et al., 2014; Quiñones et al., 2015). Several reports suggest that AOPs may produce an effluent with higher toxicity than the initial wastewater influent due to the formation of oxidation intermediate products, which highlights the need to carry out toxicity tests when applying AOPs (Li et al., 2013; Garcia-Käufer et al., 2012).

Here we set out to take a snapshot of the issues currently questionable. No doubt exists that it is necessary to determine what kind of contaminant residues are persisting in wastewater secondary effluents before their discharge, and assess the toxicity of an effluent also in the presence of great dilutions. But, what kind of bioassay might be more effective to do that? By adopting a specific tertiary treatment is it possible to foresee a real abatement of toxicity? Are AOPs the most relevant and efficient treatment technologies for micropollutants’ degradation and toxicity abatement?

To try to answer these questions, we proceeded through several steps: (i) identification of the micropollutants present in the wastewater; (ii) assessment of the toxic potential of wastewater based on different standard assays; (iii) evaluation of the estrogenic and genotoxicity potential of wastewater; (iv) comparison of efficiency of two solar AOPs according to two major criteria: destruction of contaminants and evolution of toxicity.

2. Materials and methods

2.1. Reagents and wastewater

Wastewater (WW) was taken from a WWTP in southern France designed to treat 35,227 $m^3\ day^{-1}$ of inlet flow. Real WW effluent collected downstream of the WWTP secondary biological treatment stage had the following mean characteristics: pH = 7.2 ± 0.2; conductivity = 669 ± 21 μS cm^{-1}; [TOC] = 26.3 ± 0.6 mg L^{-1}; [Cl^-] = 77.9 ± 0.3 mg L^{-1}; [NO_3^-] = 9.9 ± 0.2 mg L^{-1}; [HCO_3^-] = 108.8 ± 7.2 mg L^{-1}; [Ca^{2+}] = 52 ± 4 mg L^{-1}; [Na^+] = 67 ± 3 mg L^{-1}; [K^+] = 15 ± 2 mg L^{-1}. Sampled effluent was used on the same day as it was collected.

All reagents used for chromatographic analyses were LC/MS grade.

Solar heterogeneous photocatalytic experiments were carried out using a slurry suspension (0.7 g L^{-1}) of Evonik P-25 titanium dioxide (surface area 54 $m^2\ g^{-1}$). Solar photo-Fenton experiments were performed using iron sulfate (100 μM of $FeSO_4 \times 7H_2O$), Oxone®(PMS) monopersulfate (200 μM of $HKSO_5 \times 0.5\ HKSO_4 \times 0.5\ K_2SO_4$) and sulfuric acid, obtained from Sigma Aldrich. To avoid the precipitation of iron during solar photo-Fenton processes, pH was adjusted to 2.6 with sulfuric acid.

The free concentration of Fe (II) was determined at the beginning and the end of process by potentiometric micro-titration (Abulkibasha et al., 2013). The loss of Fe (II) free concentration was less than 10%.

2.2. Analytical equipment and methods

Contaminant concentrations were measured by liquid chromatography–electrospray–orbitrap mass spectrometry (Exactive Plus Orbitrap, ThermoScientific) using an ion spray source in positive and in negative mode. Separation was done on a HPLC system (Accelera 1250 pump, ThermoScientific) equipped with a Betabasic C-18 analytical column (150 mm × 2.1 i.d., 3.5 μm particle size) at 0.2 mL min^{-1} flow rate. The mobile phase consisted of a binary mixture of solvent A (0.1% formic acid/water) and B (acetonitrile). The gradient was operated from 10 to 30% A for 10 min, 30–90% A for 5 min, held at 100% for 5 min, then back to initial conditions in 5 min.

A solid phase extraction procedure was applied to the wastewater sample using Oasis HLB LP cartridges (500 mg, 6 mL, Waters). Pre-concentration was performed according to Bueno et al. (2009), and a final concentration factor of 100:1 was obtained.

2.3. Toxicity analyses

Ecotoxicological evaluation was performed on sampled effluent using *Vibrio fischeri*, *Daphnia magna*, *Pseudokirchneriella subcapitata* and *Brachionus calyciflorus* as test organisms to evaluate acute and chronic aquatic toxicity according to standard procedures: (i) bioluminescence inhibition of marine bacterium *V. fischeri* after 30-min exposure (ISO 1134-3:2007); (ii) 48-h immobilization of *D. magna* (ISO 6341:1996); (iii) 72-h growth inhibition of *Pseudokirchneriella subcapitata* green algae (ISO 8692:2012); (iv) 48-h growth inhibition of *B. calyciflorus* rotifers (ISO, 20666:2008). Assays with *V. fischeri* and *D. magna* are considered acute toxicity tests while assays with *P. subcapitata and B. calyciflorus* as are chronic toxicity tests. Samples were classified according to their toxicity using EC_{50} values as established by Calleja et al. (1986). This classification system is based on wider ranges of outcome percentages of effect, considering the concentration where 50% of maximal