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Economic valuation of environmental benefits of removing pharmaceutical and personal care products from WWTP effluents by ozonation

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HIGHLIGHTS

- Environmental Benefit Analysis of PPCPs
- PPCPs' removal depends on their functional group and molecular structures.
- Shadow prices as a proxy of the environmental benefits from ozonation process
- HHCB and AHTN have the lowest shadow prices.
- The greatest environmental benefit is associated with the removal of DCF.

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ABSTRACT

Continuous release of pharmaceutical and personal care products (PPCPs) present in effluents from wastewater treatment plants (WWTPs) is nowadays leading to the adoption of specific measures within the framework of the Directive 2000/60/EC (Water Framework Directive). The ozonation process, normally employed for drinking water production, has also proven its potential to eliminate PPCPs from secondary effluents in spite of their low concentrations. However, there is a significant drawback related with the costs associated with its implementation. This lack of studies is especially pronounced regarding the economic valuation of the environmental benefits associated to avoid the discharge of these pollutants into water bodies. For the first time the shadow prices of 5 PPCPs which are ethynilestradiol, sulfamethoxazole, diclofenac, tonalide and galaxolide from treated effluent using a pilot-scale ozonation reactor have been estimated. From non-sensitive areas their values are −73.73; −34.95; −42.20; −10.98; and −8.67 respectively and expressed in €/kg. They represent a proxy to the economic value of the environmental benefits arisen from undischarged pollutants. This paper contributes to value the environmental benefits of implementing post-treatment processes aimed to achieve the quality standards required by the Priority Substances Directive.

1. Introduction

In accordance with the Water Framework Directive (WFD) 2000/60/EC, the European States should implement measures aimed to achieve good ecological status for all water bodies. Consequently the European Parliament adopted the Directive 2008/105/EC which lays down environmental quality standards for priority substances and certain other pollutants, aimed to achieve good surface water chemical status. Following the precautionary principle, the European Commission has included for the first time three pharmaceutical compounds in the proposal for amending the list of priority substances, based on the potential risk they pose to the environment: the anti-inflammatory diclofenac, the sex hormone estradiol and the contraceptive pill ingredient ethynilestradiol.[2] This statement is a

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direct consequence of the increasing concern derivative from the ubiquitous presence of many different pharmaceutical and personal care products (PPCPs) in water bodies worldwide (Camacho-Muñoz et al., 2010; Chase et al., 2012; Comeau et al., 2008). These substances follow different pathways before reaching surface waters, being the effluent from Wastewater Treatment Plants (WWTPs) identified as their most relevant source (Clara et al., 2012; Reif et al., 2011). A consequence of the inclusion of pharmaceuticals in the priority substance list is that member states have to ensure that their monitoring and specific environmental quality standards should be met by 2021 (deadline of the 2nd River Basin Management Plan). This leads to direct consequences in terms of overall cost due to the economic impact associated with the upgrade of treatment facilities, currently unable to eliminate these and many other emerging contaminants (pesticides, surfactants, flame-retardants, nanomaterials, disinfection by-products, etc.). An increasing number of papers and reviews dealing with the efficiency of different secondary treatment alternatives (Gabet-Giraud et al., 2010; Verlicchi et al., 2012; Petrovic et al., 2009) have been published throughout the last decade. According to them, it is obvious that biological treatments (with conventional or modern configurations such as the membrane bioreactors) are inefficient to achieve the complete elimination of PPCPs from sewage, although the adoption of specific operational strategies might contribute to increase their effectiveness. Therefore, research efforts are also focused on more effective post-treatment alternatives, more concretely, technologies such as nanofiltration, reverse/forward osmosis membranes, activated carbon, ozonation and advanced oxidation processes (AOPs). Such processes were able to reach eliminations up to 90% or even above for the majority of PPCPs detected in effluents (Dolar et al., 2011; Suarez et al., 2007; Lopez-Muñoz et al., 2012; De La Cruz et al., 2012). However, it is a complicated task to identify the best post-treatment alternatives for specific scenarios, given the high number of substances of concern. In general, the main drawback for the quick widespread of post-treatment technologies is based on their high investment, operation & maintenance costs. Jones et al. (2007) anticipated these issues estimating costs of different alternatives and concluded that they might be economically and environmentally undesirable. According to Owen and Jobling (2012), the upgrade of a facility serving a town of about 250,000 people with a post-treatment system based on granular activated carbon (GAC), efficient to cut ethynilestradiol (EE2) levels, might cost about €8 million with a further €800,000/year being needed to operate the system. Despite its effectiveness for the elimination of EE2, GAC is not always the best option in case a wider number of compounds have to be removed. In this sense, reverse osmosis (RO) and oxidation processes based in ozone have proven to be suitable for removing a higher number of compounds (Radjenovic et al., 2008; Lee et al., 2012; Snyder et al., 2006). For example, Lee et al. (2012) carried out a direct comparison between ozone treatment and RO, and found that despite their similar costs and performance in terms of PPCPs' elimination, when wider environmental impacts (energy consumption and waste production) were considered, ozone treatment appeared to be a more suitable technology for urban wastewater applications. Ozonation effectiveness for PPCPs' removal is based on two different reactive processes: direct oxidation with the highly selective ozone and the secondary reactions with the more powerful and unspecific hydroxil radical simultaneously produced during the ozonation process (Dodd et al., 2009). It is also necessary to mention known disadvantages such as the generation of intermediate products more toxic than the parent compound as well as the possible interferences between the oxidation of bulk organic matter and target pollutants. However, these issues might be overcome as long as the economic feasibility of the overall process is granted. For example, Stalter et al. (2010) found that a further sand-filtration step reduces toxication effects of ozonated effluents.

Focusing on economic aspects, estimations carried out in previous works have not considered the quantification of the environmental benefits of preventing the discharge of pollutants into water bodies. Nowadays, such interest has been stirred up motivated mainly by two facts:

i) An increased awareness of the society on environmental protection (Caballero et al., 2008). In this sense, pioneering methodologies applied to wastewater management have slightly improved the perception of post-treatment strategies as environmentally friendly processes.
ii) The WFD allows temporal derogation or less stringent objectives based on the concept of disproportionate costs. Hence, the costs and the benefits of the measures to achieve the good ecological status should be assessed including the economic valuation of the environmental benefits.

In this context, the work of Hernández-Sancho et al. (2010) was pioneering since based on the methodology developed by Färe et al. (1993) it quantified the shadow prices of some wastewater pollutants. These shadow prices can be interpreted as the economic value of the environmental benefits for avoiding the discharge of contaminants into water bodies. The subsequent developments carried out (Molinos-Senante et al., 2010a, 2011a) have proven that this methodology, named in this work as “Environmental Benefit Analysis” (EBA) is a very suitable approach for this purpose. Despite the usefulness of these previous works, their main limitation is that EBA has been applied only for the main wastewater pollutants such as chemical oxygen demand, suspended solids, nitrogen and phosphorus. In this sense and taken into account the Directive 2008/105/CE, the aim of this research is to value the economic benefits of removing 5 different PPCPs from WWTP effluent by ozonation. Moreover, the performance of this post-treatment for removing such compounds has been also evaluated.

2. Materials and methods

2.1. PPCPs' selection and analytical methodologies

The 5 PPCPs studied in this work (diclofenac, ethynilestradiol, sulfamethoxazole, tonalide and galaxolide) were selected according to their different physical chemical properties being also representative of different therapeutic groups and uses (Table 1). Thus, they are expected to show different behaviors when undergoing ozone treatment. The five compounds are frequently found in WWTP effluents and therefore, they truly represent the vast number of compounds which can be found in the aquatic environment. PPCPs' analysis was performed adapting methods already published (Rodríguez et al., 2003; Vanderford et al., 2003). Briefly, the content of galaxolide, diclofenac and tonalide was determined after solid-phase extraction (SPE) of 300 mL samples using 60 mg OASIS HLB cartridges (Waters, Milford, MA, USA) and then quantitatively eluted from the cartridge using 3 mL of ethyl acetate. Meclofenamic acid was spiked to the samples as surrogate standard. The extract was divided into two fractions: one of them was used for the direct determination of tonalide and galaxolide; the second one was employed for the determination of diclofenac, as a tert-butyldimethylsilyl derivative. Detection was carried out by GC/MS using a Varian CP 3900 chromatograph (Walnut Creek, CA, USA) equipped with a split-splitless injector and connected to an ion-trap mass spectrometer (GC/MS). To measure ethynilestradiol and sulfamethoxazole, SPE was done as described for the previous compounds, although the elution step was performed with a mixture of 1.5 mL of methanol and the same amount of methyl tert-butyl ether. Final detection and quantification were performed by LC/MS/MS, using an Agilent Liquid Chromatograph API 400 GI312A) equipped with a binary pump and autosampler HTC-PAL and with a triple quadruple mass spectrometer (ESI + mode).