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Elimination of drugs of abuse and their toxicity from natural waters by photo-Fenton treatment

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HIGHLIGHTS

- Photo-Fenton reactions eliminate drugs of abuse in natural fluvial water.
- High chemical degradation does not ensure toxicity elimination.
- Catalyst loading is critical for an efficient toxicity elimination.
- Toxicology testing is mandatory in decontamination assessment.

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ABSTRACT

This paper investigates the elimination of drugs of abuse from six different chemical classes and their metabolites in natural fluvial waters (nearby the output of a sewage system). Mineralization of these substances and toxicological characterization before and after treatment by a heterogeneous photo-Fenton system has been evaluated. This advanced oxidation technology was able to significantly reduce the concentration of the drugs of abuse in all the tested conditions (different hydrogen peroxide and catalyst loadings). However, toxicological analyses measured as inhibition of fern spore mitochondrial activity, showed only a complete elimination of acute and chronic toxicity when a higher solid catalyst loading was used (0.6 g/L). A lower catalyst loading of 0.2 g/L was not enough for toxicity elimination. These results evidence the need for combining toxicological tests and chemical analyses in order to establish the effectiveness of the water treatment technologies based on advanced oxidation processes.

1. Introduction

The presence of emerging microcontaminants, in particular drugs of abuse (DAs) (and/or their metabolites) in the water cycle as a consequence of their widespread consumption and poor elimination in the water treatment plants is an issue of important concern. As a result of their continuous introduction into the aquatic environment, these substances are behaving in a pseudo-persistent manner and currently represent a new class of environmental emerging pollutants that require emergency attention. In many cases, these substances are persistent, bioaccumulative and potentially toxic to aquatic organisms

Abbreviations: 6ACM, 6-acetylmorphine; ALCs, amphetamine-like compounds; ALP, alprazolam; AOP, advanced oxidation processes; BE, benzoylecgonine; CE, cocaethylene; CO, cocaine; DAs, drugs of abuse; DIAZ, diazepam; RW, raw water; EDDP, 2-ethylene 1,5-dimethyl 3,3-diphenylpyrrolidine; EPH, ephedrine; HER, heroin; LODet, limit of determination; LOR, lorazepam; LSD OXO, 2-oxo-3-hydroxy-LSD; LSD, lysergic acid diethylamide; MA, methamphetamine; MDMA, 3,4-methylenedioxymethamphetamine or ecstasy; MOR, morphine; OH-THC, 11-hydroxy-Δ^9-THC; PET, polyethylene terephthalate; SPE-LC–MS/MS, on-line solid phase extraction-liquid chromatography–tandem mass spectrometry; SRM, selected reaction monitoring; STP, sewage treatment plant; THC, Δ^9-tetrahydrocannabinol; THC-COOH, 11-nor-9-carboxy-Δ^9-THC; TOC, total organic carbon.

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(Boles and Wells, 2010). According to the last Spanish survey on alcohol and drugs (EDADES, 2012), a general decrease or stabilization of drug consumption has been observed with one exception, namely the family of sedatives, including benzodiazepines, consumed last year by 11.4% of the population. Among illicit drugs, cannabis continues to be the most consumed substance, followed by cocaine.

The presence of these substances and/or their metabolites in the sewage system following consumption, and thereafter in the receiving aquatic environment, is not surprising. To this end, their illegal condition and/or abused use comes to aggravate the problem by preventing their adequate disposal and the control of residues. This fact, as well as the recent development of advanced analytical methods for their determination in water, has led to their detection in surface water and even in tap waters, which is a significant concern for public health authorities. The occurrence of DAs and benzodiazepines has been reported in different European surface waters (Zuccato et al., 2008; van Nuijs et al., 2009, Kasprzyk-Hordern et al., 2008; Terzic et al., 2010). In Spain, the occurrence of DAs and benzodiazepines in surface waters has been evaluated in several zones (Postigo et al., 2010; Gros et al., 2010; Valcárcel et al., 2012; Mendoza et al., 2014a, 2014b). As for pharmaceutical residues, the main origin of these substances is the sewage treatment plant (STP) effluents due to their inefficient elimination.

Although there are very few studies on the occurrence of DAs in drinking waters (see Mendoza et al., 2014a, 2014b and references therein), some substances such as cocaine, benzoylecgonine, epinephrine, the group of benzodiazepines, methadone and 2-ethylene 1,5-dimethyl 3,3-diphenylpyrrolidine (EDDP) have been repeatedly found in low quantities such as 13–76 ng/L for cocaine or 50–150 ng/L for the group of benzodiazepines. Both the contamination of the sources of drinking water and the inefficacy of water treatment systems are pointed out as the main cause of this contamination. Albeit a human health risk is not expected from the concentrations detected, the lack of toxicological data regarding chronic exposure and mixture toxicity recommend the total elimination of any kind of micropollutant from drinking water (Mendoza et al., 2014a, 2014b). Currently, the potential effects of these components on the environment, at medium and long terms, are also unknown and their strong biological effects must not be overlooked. These biologically active substances are designed to exert specific effects on cells, and therefore can have numerous negative effects on ecosystems. Due to the potential ecotoxicological risk of the drugs of abuse for ecosystems, they need to 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 (Postigo et al., 2011a, 2011b) have been proposed as treatments for a variety of drugs (methadone, cocaine, benzoylecgonine, ketamine and oxycodone, among others). These processes, specially ozonation and homogeneous photo-Fenton showed a remarkable effect on drug degradation in simulated wastewaters or ultrapure water solutions at relatively high concentrations (100 μg/L–10 mg/L). On the other hand, the application of heterogeneous photo-Fenton treatment has been recently proposed as a remarkable effective technology for the degradation of drugs of abuse detected at low concentration (Valcárcel et al., 2012).

The quality of treated water requires the application of not only chemical but also biological methods to detect contaminants as well as to assess the possible effects on the environment and public health. Biological assays are presented as innovative and rapid tests and indicators of toxic effects of water contamination (Farré et al., 2007). The small number of taxa used in bioassays is currently one of the main concerns of environmental toxicology, since the use of an appropriate range of taxons allows ensuring ecologically relevant results. Some years ago, a novel microbioassay of phytotoxicity with fern spores has been published (Catalá et al., 2009). This method combines biological and ecological relevance with high sensitivity and simplicity, making it a low cost tool for ecotoxicological monitoring (Catalá et al., 2010). It has been successfully used in the assessment of the toxicity of polycyclic aromatic compounds, industrial pollutants (Marugán et al., 2012), environmental concentrations of pharmaceutical compounds (Feito et al., 2012), environmental water samples (Rodríguez-Gil et al., 2010; Esteban et al., 2012) as well as in the follow-up of water treatment technologies (Rodríguez-Gil et al., 2010; Marugán et al., 2012). Due to the use of selected robust biomarkers, this method has been demonstrated to improve sensitivity of validated methods to environmental micropollution (Esteban et al., 2012).

In this context, the main objective of this study was to evaluate the influence of a mesoporous Fe-based catalyst and hydrogen peroxide concentrations on a heterogeneous photo-Fenton system for the elimination of illicit drugs in complex natural fluvial waters. The assessment of the efficacy was performed by chemical analysis and also by acute and sub-chronic toxicity bioassays, as combined techniques to evaluate the removal of the DAs and by-products after the treatments.

2. Materials and methods

2.1. Environmental water sampling

The Madrid region, with 809 inhabitants per km^2, is the most densely populated region of Spain and one of the most densely populated in Europe. Its area, 8 028 km^2 (1.6% of the Spanish territory), is occupied by an estimated population of 6,495,551 inhabitants. A total of 86.94% of the population is concentrated in a conurbation composed of the city of Madrid (3,207,247 inhabitants) (49.9%) and the municipalities in the metropolitan area (2,370,678 inhabitants) (36.9%) (INE base, 2012). A surface water sample was collected in March 2012 from the Manzanares River, approximately 100 m downstream from the point of emission of Butarque STP due to its characteristics for drug presence observed in previous studies (Mendoza et al., 2014a, 2014b. This STP serves a population equivalent to 1,440,000, and treats 432,000 m^3/day with biological activated sludge. The samples were collected in 1 L of amber polyethylene terephthalate (PET) bottles, and the pH, conductivity and temperature were measured immediately after collection. Once collected and during shipment samples were kept frozen at −20 °C.

2.2. Photo-Fenton treatment

The experimental set-up for the photo-Fenton reactor was a batch-type reactor consisting of a vessel of 12 cm of diameter and 1 L in volume with the irradiation lamp axially immersed. The UV–Visible irradiation was provided by a 150 W medium pressure mercury lamp (Heraeus TQ-150). The lamp was surrounded by a quartz jacket in which a copper sulphate aqueous solution circulates to block radiation at wavelengths shorter than 313 nm. In a typical run, the vessel was filled with 1 L of the water sample. A powder silica-supported iron oxide (Fe_2O_3/SBA-15) was used as the heterogeneous photo-Fenton-like catalyst with an easy separation after the treatment. This catalyst was prepared following a method described elsewhere (Martínez et al., 2005). The Fe_2O_3/SBA-15 catalyst was characterized by containing crystalline iron oxides, in the form of hematite, supported on a mesostructured SBA-15 silica support. The iron catalyst was suspended into the aqueous solution (0.1 or 0.6 g/L) and the pH was initially adjusted to ca. 3 with H_2SO_4 (0.1 M) and left uncontrolled during the treatment. The initial hydrogen peroxide concentration used for the treatments was calculated according to the theoretical stoichiometric amount for the complete mineralization of the total organic carbon (TOC) of the water towards CO_2 and H_2O following reaction (1), one half and one quarter of that concentration (coded as 100%, 50% and 25%, respectively,