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Removal of emerging contaminants in sewage water subjected to advanced oxidation with ozone

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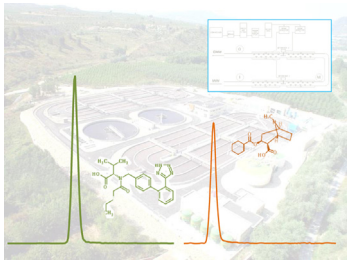
HIGHLIGHTS

- Several pharmaceuticals remain in sewage waters after conventional STP treatment.
- Advanced oxidation with ozone is investigated for pharmaceuticals removal.
- The study is made with on pharmaceuticals present in real-world sewage waters.
- Ozone treatment at a dose 7–12 mg/L is proven to be highly efficient.
- The use of ultrasounds did not lead to improved removal efficiencies.

GRAPHICAL ABSTRACT



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ABSTRACT

Advanced oxidation processes (AOP) based on ozone treatments, assisted by ultrasounds, have been investigated at a pilot-plant scale in order to evaluate the removal of emerging contaminants in sewage water. Around 60 emerging contaminants, mainly pharmaceuticals from different therapeutically classes and drugs of abuse, have been determined in urban wastewater samples (treated and untreated) by LC–MS/MS. In a first step, the removal efficiency of these contaminants in conventional sewage water treatment plants was evaluated. Our results indicate that most of the compounds were totally or partially removed during the treatment process of influent wastewater. Up to 30 contaminants were quantified in the influent and effluent samples analysed, being antibiotics, anti-inflammatories, cholesterol lowering statin drugs and angiotensin II receptor antagonists the most frequently detected. Regarding drugs of abuse, cocaine and its metabolite benzoylecgonine were the most frequent. In a second step, the effectiveness of AOP in the removal of emerging contaminants remaining in the effluent was evaluated. Ozone treatments have been proven to be highly efficient in the removal, notably decreasing the concentrations for most of the emerging contaminants present in the water samples. The use of ultrasounds, alone or assisting ozone treatments, has been shown less effective, being practically unnecessary.

1. Introduction

The worldwide use of pharmaceuticals and their increasing presence in the aquatic environment has generated a growing concern regarding possible ecological risks coming from pharmaceuticals released into the environment. These compounds are among the most frequently found in wastewaters and are considered as emerging contaminants, a group of diverse compounds that are not regulated despite their frequent detection in the aquatic

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environment. Other contaminants, like drugs of abuse or personal care products, are also considered as emerging contaminants and are matter of concern in the last few years. One of the main routes for these compounds to reach the aquatic ecosystem is from sewage treatment plants (STP). In fact, pharmaceuticals belonging to different therapeutic categories have been detected in urban wastewater effluents all over the world, showing the incomplete elimination of some compounds in conventional biological treatments [1–3]. Although the concentration levels found after sewage water treatment processes seem not to cause toxic effects on human health and on the aquatic environment, little is known about possible human and ecological adverse effects derived from long-term exposure to pharmaceuticals. Among them, antibiotics are of special concern because they can promote bacterial resistance in the environment due to continuous exposure [4–6]. This can affect flora and fauna, but also humans in those areas where treated effluents are used to supplement drinking water supplies [7]. As a result of their incomplete removal, residues of pharmaceuticals have been identified in surface waters [3,8–13] and even in drinkable water at the ng/L level [10,14–17].

STPs typically employ conventional sewage treatment consisting on primary sedimentation followed by secondary treatment and final sedimentation. Recently, research efforts have been made in the development of alternative water treatment technologies to decrease the concentration of pharmaceuticals in sewage water. Tertiary treatment or advanced treatment processes such as membrane filtration, activated carbon or oxidative processes (chlorination [18–20] and ultraviolet irradiation) seem to be rather efficient when they work under optimum conditions. Nevertheless, their use is not widespread yet due to some drawbacks, as the high cost in terms of energy consumption. Membrane bioreactors may also offer an improved potential to remove trace organics by biological means [21].

Another option is the use of ultrasounds. The chemical effect of the ultrasound is due to acoustic effects of cavitation [22]. Most studies on sonochemical degradation of pollutants, have adopted the “hot spot” model to explain their results. This model describes the structure of the reactions in two ways: thermal or pyrolytic decomposition reaction and attack and/or addition of hydroxyl radical. The breakage of bonds and/or dissociation of water molecules and other vapours, form free radicals or molecules in an excited state. These radicals and molecules react with each other, forming new species diffuse into the bulk liquid, to act as oxidants [23].

The aim of this work is to investigate the effectiveness of an advance oxidation process based on ozone treatment, which may be assisted by ultrasounds, in the removal of emerging contaminants (focused on pharmaceutical and drugs of abuse) present in “real” wastewater samples. The study has been carried out at pilot-plant scale. A total of 60 samples (untreated and treated urban wastewater samples) from two STPs have been analysed by LC–MS/MS, along three monitoring programmes (July 2010, November 2010 and July 2011). Fifty-two pharmaceuticals and eleven drugs of abuse were determined as target analytes in the samples. Data obtained have allowed us to estimate the occurrence and removal of these contaminants after conventional treatment as well as after oxidative-based process.

2. Materials and methods

2.1. Reagents and chemicals

Pharmaceutical reference standards were purchased from Sigma–Aldrich (St Louis, MO, USA), LGC Promochem (London, UK), Toronto Research Chemicals (Ontario, Canada), Across Organics (Geel, Belgium), Bayer Hispania (Barcelona, Spain), Fort Dodge Veterinaria (Gerona, Spain), Vetoquinol Industrial (Madrid Spain) and Aventis Pharma (Madrid, Spain). Isotopically-labelled internal standards (ILIS) were purchased from CDN Isotopes (Quebec, Canada), Toronto Research Chemicals (Toronto, Canada), Sigma–Aldrich and Isotope Cambridge Laboratories (Andover, MA, USA).

Illicit drugs and metabolites were obtained from Sigma–Aldrich (Madrid, Spain), Cerilliant (Round Rock, TX, USA) and the National Measurement Institute (Pymble, Australia). Deuterated compounds were all purchased from Cerilliant.

Details regarding preparation of standard solutions can be found elsewhere [24–26].

HPLC-grade methanol (MeOH) and HPLC-grade acetonitrile (ACN) were purchased from Scharlab (Barcelona, Spain). HPLC-grade water was obtained from purification of demineralised water in a Milli-Q Gradient A10 (Millipore, Bedford, MA, USA). Formic acid (HCOOH, content >98%), ammonium acetate (NH_4Ac, reagent grade) and sodium hydroxide (NaOH, >99%) were supplied by Scharlab (Barcelona, Spain).

SPE cartridges (Oasis-HLB; 6 mL, 200 mg) were purchased from Waters (Milford, MA, USA).

2.2. Instrumentation

Ultra-high performance liquid chromatography–tandem mass spectrometry (UHPLC) analysis was carried out using an Acquity UPLC system (Waters, Milford, MS, USA), equipped with a binary solvent pumping. For analysis of pharmaceuticals, an Acquity UPLC HSS T3 (100 mm × 2.1 mm i.d., particle size 1.8 μm) (Waters) was used. For determination of drugs of abuse, chromatographic separation was carried out using an Acquity UPLC BEH C18 column (50 mm × 2.1 mm i.d., particle size 1.7 μm) (Waters). The LC system was interfaced to a TQD (triple quadrupole) mass spectrometer with an orthogonal electrospray ionisation source Z-spray (Waters Corp.). MS/MS analysis was performed under selected reaction monitoring (SRM) mode, working in positive and negative ionisation modes simultaneously. Chromatographic and mass spectrometry conditions can be found elsewhere [24–26].

2.3. Analytical procedure

Water samples were extracted as described in [25,26]. Briefly, the procedure was as follows: 100 mL water sample (previously centrifuged at 3500 rpm for 10 min) was spiked with the ILIS working solution (100 μg/L) and passed through the Oasis HLB cartridge, previously conditioned with 3 mL MeOH and 3 mL water. Analytes were eluted with 5 mL MeOH and the extract was evaporated and reconstructed with 1 mL MeOH–water (10:90, v/v). Analysis of pharmaceuticals and drugs of abuse was performed separately. In both cases, 20 μL of the final extract were injected in the LC–MS/MS system.

Quantification was made using calibration standards prepared in solvent, based on relative responses analyte/ILIS or on absolute analyte responses, depending on whether ILIS was used for correction or not. The method applied for pharmaceuticals has been previously validated [25,26]. In the case of drugs of abuse, each compound was quantified using its corresponding analyte ILIS, except for norcocaine, which was quantified using a deuterated analogue (cocaine-d3), and norbenzoylecgonine, for which no adequate internal standard was available. This method, with a slight modification in the SPE procedure, has also been previously validated [24].

The list of target analytes investigated in this work can be found in Table S.1 (Supplementary Information).