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Removal of emerging contaminants from a primary effluent of municipal wastewater by means of sequential biological degradation-solar photocatalytic oxidation processes

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HIGHLIGHTS

- Sequential biodegradation-solar AOPs have been applied to remove ECs from MWWTP.
- Biological oxidation only removes caffeine and acetaminophen from wastewater.
- Ozonation system led to removal of ECs in less than 45 min.
- Solar photocatalytic ozonation with TiO_2 showed the highest TOC removal rate.

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ABSTRACT

Treatment of primary wastewater effluent containing a mixture of nine pharmaceuticals model compounds (acetaminophen ACM, antipyrine ANT, caffeine CAF, ketorolac KET, metoprolol MET, sulfamethoxazole SFX, carbamazepine CARB, hydrochlorothiazide HCT and diclofenac DIC) has been carried out by means of aerobic biodegradation followed by different advanced oxidation processes (solar heterogeneous photocatalysis with TiO_2, solar photo-Fenton and ozonation). Only ACM and CAF were completely removed from municipal wastewater in aerobic biological experiments. Apparently, the bacteriostatic nature of SFX could lead to some extent to bacterial growth inhibition. Photocatalytic ozonation allows for a higher degradation rate than simple photocatalytic oxidation in the presence of oxygen. Under the conditions investigated, emerging compounds (ECs) degradation (sum of concentrations) in the photocatalytic ozonation was in the range 80–100% depending on the system. Application of solar light (SL) Fe(III) photocatalytic ozonation, SL/O_3/Fe (III) (180 min) and ozonation (45 min) systems reduced the concentrations of the studied emerging contaminants below their detection limit (2 $\mu g\ L^{-1}$). Nevertheless, photocatalytic ozonation led to 41.3% mineralization compared to 34% achieved by single ozonation. Toxicity analyses by *Daphnia magna* showed no effluent toxicity after the application of the three tertiary treatments.

1. Introduction

A number of physical, biological, and chemical processes are used in wastewater treatment to deal with a variety of contaminants. However, some micropollutants found in wastewater, such as the catalogued as emerging contaminants, are recalcitrant to some extent to conventional applied wastewater treatment processes. Thus, although biological oxidation is likely one of the most advantageous technologies to deal with wastewater remediation, some biorefractory compounds are not effectively removed [1–3], remaining in solution after the secondary treatment has taken place. Alternative available technologies to deal with this kind of contaminants include the use of the so-called advanced oxidation processes (AOPs).

AOPs are based on the chemistry of hydroxyl radicals (·OH), which are non-selective reactive species, able to oxidize pollutants into harmless end-products, yielding CO_2 and inorganic ions [4–5]. The main drawback of these technologies relies on the economy of the process. Hence, operating costs associated to the use of AOPs are much higher than those considered in conventional biological treatments.

Accordingly, suitable application of AOPs should not consider, whenever possible, the replacement of the more economic biological

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processes [6], but the proper combination of both systems. AOPs can be used as pre- and/or post-treatment of biological systems. In the former case, AOPs aim at improving biological treatability of wastewaters, thus favouring their processing by means of common microorganisms [7]. In the latter situation, the oxidation step is directed towards the removal of those contaminants not completely degraded during the biological treatment [8].

In order to ensure the economic optimization of the combined process, it is necessary to limit the intensity and/or duration of the advanced treatment. In this sense, in recent years the attention of research has been focused on AOPs that can be driven by solar light as photo-Fenton and heterogeneous photocatalysis [9–11]. These technologies, a type of green oxidation systems, have also been recognized as energy saving and environmentally friendly processes. Green oxidation is an important challenge since this technology can effectively reduce the use of energy and consumables [12]. Solar radiation is an incessant source of energy in many regions, as a consequence, wastewater treatments developed under the idea of using solar radiation constitute an interesting research field from the economic point of view. The application of solar-enhanced AOPs in water/wastewater treatment is a relatively new area of research. The number of studies on the simultaneous removal of chemical pollutants and pathogens by solar AOPs is scarce [13].

Thus, in this study three different oxidation technologies have been tested in the degradation of some pharmaceutical compounds not eliminated in a previous biological oxidation step. The systems investigated were solar heterogeneous photocatalysis with TiO_2, solar photo Fenton (using Fe (III) and magnetite as aqueous iron source) and single ozonation.

Among light-based systems, heterogeneous photocatalysis with titanium dioxide as semiconductor is one of the promising AOPs using minimum energy input costs. Due to photochemical stability, low toxicity and low cost, powdered titanium dioxide has been efficiently used to eliminate a large variety of organic pollutants present in water [14]. Among the drawbacks, the difficult separation of fine particles of TiO_2 from the aqueous matrix and the wastage of radiation after electron–hole recombination can be listed.

Additionally, ozonation is a well-established and widely used technology. Ozone has already been applied at full-scale, but this process is an energy intensive treatment, characterized by high operating costs, mainly associated to ozone generation. In any case, comparison to solar AOPs efficiency is of interest.

Pharmaceuticals are usually non-volatile and often charged molecules, and many of them pass through treatment plants that are traditionally designed to get rid of more common pollutants [2–3]. They have been lurking in the environment since they have been in use, but it is only in the recent decades that analytical methods have advanced enough to detect them at the low levels–less than 1 μg/litre–found in very complex matrixes including liquid and solid states, in wastewater, and in surface and ground waters. Although these levels are becoming easier to quantify, the potential risk they pose is a more complex issue. Nowadays it is known that active pharmaceutical ingredients (APIs) and their biotransformation products are present in a range of habitats. Some of these compounds can bioaccumulate involving significant, but largely unstudied, consequences for individuals, populations and ecosystems [15]. Known environmental effects of some ECs include the reduction of macroinvertebrate diversity in rivers, behavioural changes in mosquito fish and reproductive disruption in fish, etc. [16].

The pharmaceuticals most frequently found in water treatment effluents are: antibiotics, steroids, antidepressants, analgesics, anti-inflammatories, antipyretics, beta-blockers, lipid-lowering drugs, tranquilizers, and stimulants [17]. Different water treatments and their effect on pharmaceutical compounds are described in the literature, focused on: adsorption/bioadsorption on activated carbon, ozonation, photooxidation, radiolysis and electrooxidation [17]. The simultaneous application of heterogeneous photocatalysis and ozonation has also great potential in pharmaceuticals abatement [18]. Various light sources have been employed in photocatalytic ozonation. Mercury lamp is one the most widely implemented technologies. Cooled xenon and black-light lampshave also been used. The replacement of UV lamps accounts for a relatively big part of the operation cost. Thus, the combination of solar light and ozone could be the ultimate objective from a practical point of view [18]. As far as the Authors knowledge is concerned, there are no publications in the specialised literature simultaneously dealing with biological treatment, solar photocatalytic ozonation, emerging contaminants, primary municipal wastewater effluent, magnetite and *in situ* generation of hydrogen peroxide for photo-Fenton processes.

Therefore, in this work, experiments of sequential aerobic biodegradation–AOPs have been conducted by using primary wastewater effluent containing a mixture of nine pharmaceutical model compounds. The ECs added to the domestic wastewater were acetaminophen (ACM, analgesic and antipyretic); antipyrine (ANT, analgesic and antipyretic); caffeine (CAF, stimulant drug); ketorolac (KET, nonsteroidal anti-inflammatory drug); metoprolol (MET, b1 receptor blocker); sulfamethoxazole (SFX, antibiotic); carbamazepine (CARB, anticonvulsant); hydrochlorothiazide (HCT, thiazide diuretic) and diclofenac (DIC, nonsteroidal anti-inflammatory drug). Concentration of pharmaceutical compounds, mineralization levels (as total organic carbon, TOC) and chemical oxygen demand (COD) were monitored to assess the extent of the oxidation. Also, the concentration of some intermediates and toxicity were measured.

2. Materials and methods

2.1. Primary wastewater effluent and chemicals

The Municipal Wastewater Treatment Plant (MWWTP) of Badajoz (Spain) has the following consecutive stages: physical pre-treatment, primary sedimentation units, aerobic biological process and secondary sedimentation units (water line). At this point, treated municipal wastewater is discharged into Guadiana River. Anaerobic digestion is only used for sludge treatment. Primary effluent samples from the Rincón de Caya (Badajoz) MWWTP were collected and spiked with the nine selected pharmaceuticals with a concentration of 200 $\mu g\ L^{-1}$ each. This concentration was higher than real levels found in some urban wastewater [19–20], but it allows for accurate and fast quantitative chemical analysis with available analytical equipments (see below). Nevertheless, sources concentration levels of pharmaceuticals (measured in raw municipal wastewater), up to 140 $\mu g\ L^{-1}$ have been reported in the literature [3,21–22]. The physical–chemical characterization of the wastewater used in this work was given in a previous article [23]. Pharmaceuticals and $Fe(ClO_4)_3.xH_2O$ were purchased from Sigma-Aldrich (Spain), Fe_3O_4 from Bendix (Spain) and TiO_2 Aeroxide®P25, from Evonik Industries AG, (Germany). All reagents were used as received. Other chemicals were at least reagent grade and also used as received.

The emerging contaminants used in this study were chosen from different pharmaceutical compound families (analgesic, beta-blockers, antiepileptic, antibiotic, etc) and their presence in different natural waters bodies has been reported (rivers, lakes, etc., [24–25]).

Conventional activated sludge was used as biomass for aerobic biological experiments and collected from the secondary aeration