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Ozonation of hospital raw wastewaters for cytostatic compounds removal. Kinetic modelling and economic assessment of the process

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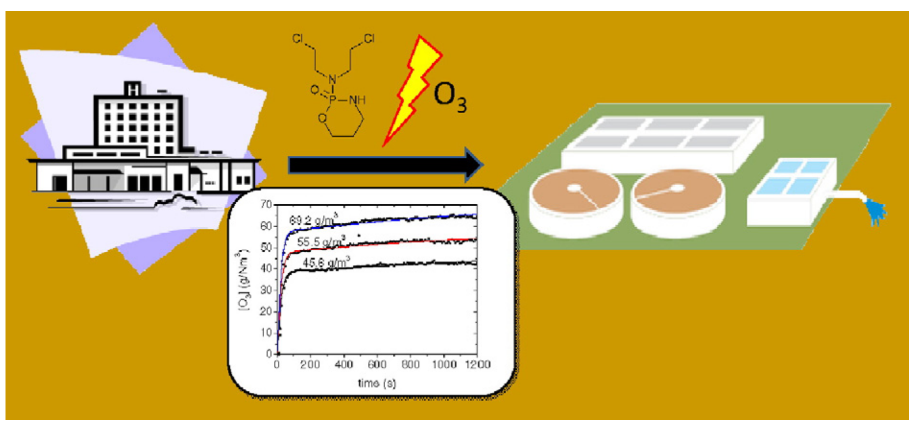
HIGHLIGHTS

- 17 cytostatic compounds were analysed and 4 detected by SPE-LC/MS-MS.
- The ozonation is 100% effective on the removal of the detected cytostatics.
- The kinetics of cytostatic ozonation reaction is modeled by competitive kinetics.
- The economic cost of the treatment of hospital wastewater was assessed.

GRAPHICAL ABSTRACT



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ABSTRACT

The kinetics of the ozone consumption for the pretreatment of hospital wastewater has been analysed in order to determine the reaction rate coefficients between the ozone and the readily oxidisabled organic matter and cytostatic compounds. The wastewater from a medium size hospital was treated with ozone and peroxone methodologies, varying the ozone concentration, the reaction time and the hydrogen peroxide doses. The analysis shows that there are four cytostatic compounds, i.e. irinotecan, ifosfamide, cyclophosphamide and capecitabine, detected in the wastewaters and they are completely removed with reasonably short times after the ozone treatment. Considering the reactor geometry, the gas hydrodynamics, the mass transfer of ozone from gas to liquid and the reaction of all oxidisable compounds of the wastewater it is possible to determine the chemical ozone demand, COzD, of the sample as 256 mg O_3 L^{-1} and the kinetic rate coefficient with the dissolved organic matter as 8.4 M^{-1} s^{-1}. The kinetic rate coefficient between the ozone and the cyclophosphamide is in the order of 34.7 M^{-1} s^{-1} and higher for the other cytostatics. The direct economic cost of the treatment was evaluated considering this reaction kinetics and it is below 0.3 €/m^3 under given circumstances.

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1. Introduction

Hospital wastewater effluents are characterized by a complex mixture of pharmaceutical products which belong to the groups of antibiotics, cytostatics, X-ray contrast substances and others. The cytostatic compounds are used in the treatment of some type of cancers, autoimmune diseases or as immune suppressants after the transplantation of organs, and the antibiotics and X-ray contrast media concentrations in the hospital wastewater can be 10–100 times higher than in municipal wastewater (Kovalova et al., 2013; Mauer et al., 2013; Putschew et al., 2013; Verlicchi et al., 2010; Verlicchi et al., 2012). The high metabolic activity of these compounds and their recalcitrancy to biodegradation in conventional municipal wastewater treatment plants (WWTPs) explains the environmental concerns associated to this kind of discharges (Ferrando-Climent et al., 2014; Negreira et al., 2014).

The conventional WWTPs are based on activated sludge or membrane bioreactors (MBR) technologies which are not specifically designed to eliminate those refractory pharmaceuticals which only a small fraction can be eliminated (Buerge et al., 2006; Ferrando-Climent et al., 2014; Steger-Hartmann et al., 1997; Zhang et al., 2013). For example, the application of the MBR technology to the abatement of some cytostatic products as ifosfamide and cyclophosphamide has been reported, with low removal rates (35% and 20%, respectively) (Nielsen et al., 2013). Other work did not register significant degradation in the two common cytostatic compounds (cyclophosphamide and ifosfamide) by activated sludge (Buerge et al., 2006).

Consequently, some residual pollutants reach the ecosystems, causing different types of problems. While the antibiotics contribute to increase the resistance of the microorganisms, the cytostatics are potentially ecotoxic, inhibiting the cell growth (Ferrando-Climent et al., 2014; Zhang et al., 2013). Therefore, it is necessary to upgrade the WWTPs technology with additional oxidative or other physicochemical treatment steps or/and implement a local treatment of hospital wastewaters with non-conventional technologies.

The Advanced Oxidation Processes are recognized as feasible technologies for the degradation of biologically persistent organic matter such as the pharmaceutical compounds. All these technologies are characterized by the production of hydroxyl radical on the wastewater in order to oxidize the organic substances. The radicals can be produced by chemical reactions (e.g. ozone, hydrogen peroxide), providing energy to the system (e.g. UV radiation, ultrasounds) or combining the chemical and the physical ways to generate the radicals (e.g. photocatalytic processes). Ozonation, in combination with hydrogen peroxide, catalysts or UV, is an advanced oxidation process in the sense that the ozone reaction radical pathway is enhanced and is a technology which has been tested (at laboratory-, pilot- and full-scale) to be adequate and economically acceptable for disinfection and the abatement of many types of organic pollutants. Among the organics are included those that are found in the hospital wastewaters, with different chemical structures and diluted in different types of wastewater matrices (Ikehata et al., 2006; Lee et al., 2014).

Ozone can react with the pharmaceuticals directly or through the generation of hydroxyl radicals. In the direct oxidation, the ozone attacks selectively the nucleophilic positions of the organic molecules and different scales of reactivity can be found depending on their molecular structure and the conditions of the reacting medium. On the other hand, the ozone can react indirectly with the organic molecules through the generation of hydroxyl radicals, resulting from the aqueous decomposition of ozone. The hydroxyl radicals are highly reactive and non-selective oxidants, although its concentration is lower than that of ozone and are easily scavenged by the medium. Their generation can be promoted by increasing the pH, adding hydrogen peroxide to the reaction media, applying UV radiation or using solid catalysts (Beltrán, 2004; Kovalova et al., 2013). Then, the ozonation is a potential alternative treatment for the removal of the cytostatic compounds but little information about the kinetics of their reaction with the ozone is available (Garcia-Ac et al., 2010; Lin et al., 2015; Lee et al., 2014), information which is fundamental for the economic assessment of this kind of treatments.

The objective of this work is the application of ozone, directly or in combination with hydrogen peroxide, for the abatement of some cytostatic products present in hospital wastewaters. Considering that the application of ozone to the reacting media is limited by the possible formation of undesired by-products, it is necessary to find the operation conditions and the dose of ozone for an efficient abatement of the cytostatic products. Our purpose is the direct treatment of the hospital wastewaters with the ozone before the mixing with the municipal wastewaters avoiding the dilution of pharmaceuticals arriving at wastewater treatment plants. An on-line solid-phase extraction-liquid chromatography-tandem mass spectrometry (SPE-LC-MS/MS) analytical methodology is used to determine the cytostatics concentration before and after the treatment (Negreira et al., 2013). A dynamic gas-liquid model is used for the determination of the rate constants of the reaction of the ozone with the dissolved organic matter and the direct reaction between some cytostatic compounds and the ozone. The rate constants allow the design of ozonation reactors working in-situ for the treatment of hospital wastewater and the developed gas-liquid model allows the economical assessment of the treatment.

2. Materials and methods

2.1. Wastewater sampling

The analysed and treated wastewater was sampled from a Hospital placed in Valencia City, the third largest city in Spain. The hospital has a Chemotherapy Treatment Unit, with 200 outpatient wards, 40 operating rooms, 1000 beds, 6 oncology outpatient wards for adults and 2 for children. All the wastewater generated by these units are collected together and sampled for this study before to discharge in the public sewer system. An automatic water sampler system collected the wastewater every four hours throughout 12 h, from 08:00 to 20:00 and mixed together; therefore the samples are representative of the integrated daily averages of the activity peak hours of the hospital. The sampling process was repeated for 5 consecutive days. 9 L of sampled water of the first day were sent to the ozonation laboratory, where treatments with ozone were applied to study the efficacy of this technology to remove cytostatics. These treatments were applied the next day after the sampling. The samples were sent from the Hospital in polyethylene-terephthalate (PET) bottles of 1 L and preserved at 4 °C until chemical analysis. After the ozonation of the wastewater, the treated water was sent to the analytical laboratory to quantify the remaining chemical species. An untreated sample of 2 L was sent to determine the initial concentration of the cytostatics in the raw wastewater. The pH and COT values of the raw wastewater was 8.89 and 87 mg/L respectively.

2.2. Analytical methodology.

2.2.1. Standards, reagents and materials

All solvents were of HPLC grade and all chemicals were of analytical reagent grade. Formic acid (98–100%), hydrochloric acid (HCl, 37%), methanol and ultrapure water were purchased from Merck (Darmstadt, Germany), while dimethyl sulfoxide (>99.9%) and sodium hydroxide (98%) were acquired from Aldrich (Milwaukee, WI, USA) and Carlo-Erba (Milan, Italy), respectively.

Standards of cytostatic compounds: gemcitabine hydrochloride (GEM), temozolomide (TMZ), methotrexate (MET), hydroxymethotrexate (OH-MET), irinotecan hydrochloride trihydrate (IRI), imatinib mesylate (IMA), ifosfamide (IF), cyclophosphamide (CP), erlotinib hydrochloride (ERL), etoposide (ETP), doxorubicin hydrochloride (DOX), capecitabine (CAP), endoxifen o 4-Hydroxy-*N*-