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Enhancement and inhibition effects of water matrices during the sonochemical degradation of the antibiotic dicloxacillin

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ABSTRACT

The sonochemical degradation of dicloxacillin (DXC) was studied in both synthetic and natural waters. Degradation routes and the effect of experimental conditions such as pH, initial DXC concentration and ultrasonic power were evaluated. Experiments were carried out with a fixed frequency (600 kHz). The best performances were achieved using acidic media (pH = 3) and high power (60 W). The degradation process showed pseudo-first order kinetics as described by the Okitsu model. To evaluate water matrix effects, substrate degradation, in the presence of Fe^{2+} and organic compounds such as glucose and 2-propanol, was studied. A significant improvement was achieved with Fe^{2+} (1.0 mM). Inhibition of the degradation process was observed at a relatively high concentration of 2-propanol (4.9 mM), while glucose did not show any effect. Natural water showed an interesting effect: for a low concentration of DXC (6.4 μM), an improvement in the degradation process was observed, while at a higher concentration of DXC (0.43 mM), degradation was inhibited. Additionally, the extent of degradation of the process was evaluated through the analysis of chemical oxygen demand (COD), antimicrobial activity, total organic carbon (TOC) and biochemical oxygen demand (BOD_5). A 30% removal of COD was achieved after the treatment and no change in the TOC was observed. Antimicrobial activity was eliminated after 360 min of ultrasonic treatment. After 480 min of treatment, a biodegradable solution was obtained.

1. Introduction

Dicloxacillin (DXC) is a β-lactamic antibiotic of penicillin used against Gram positive bacterial infections [1]. Several penicillin compounds, including DXC, have been found in natural water sources and wastewater. This is the result of the low percentage of antibiotics metabolized by humans and animals [2,3], and the inefficiency of conventional water treatments at removing micro-pollutants. It has been recognized that the presence of antibiotics in the environment has a direct influence on bacterial resistance and consequently on the evolution of human illnesses [4–6]. The risk associated to the presence of DXC in the environment makes this compound a current environmental concern. Consequently, it is necessary to look for more efficient alternatives for drinking water and wastewater treatments. In recent years, advanced oxidation processes (AOPs) based on hydroxyl radical formation have shown to be highly efficient techniques for micro-pollutant degradation [7–10]. Hydroxyl radicals are highly reactive species due to their strong oxidative power, which makes them responsible for organic compound degradation [11]. These processes are known to be able to oxidize organic pollutants and in some cases achieve total mineralization of the compounds [12–14].

One of the most promising AOPs is ultrasound [15] since it is considered to be a selective technique in which toxic and/or recalcitrant hydrophobic compounds can be degraded faster than those hydrophilic compounds. This process involves the formation of cavitation bubbles due to the interaction between ultrasound waves and dissolved gas in aqueous solutions. Cavitation bubbles experience a successive growth and eventually achieve a critical size, which leads to their violent collapse. This is characterized by temperatures and pressures reaching up to 5000 K and 1000 atm, respectively [16]. As a consequence, dissolved gas and water vapor are dissociated, resulting in the formation of several

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reactive species including ·OH (Eqs. (1)–(5)). Three reactive zones are identified during the process: (I) inside cavitation bubbles where volatile pollutants and water vapor are pyrolysed; (II) the interface, the closest zone to the cavitation bubble, where non-volatile organic pollutants with hydrophobic characteristics easily react with hydroxyl radicals or are degraded via pyrolysis due to the high temperatures of this zone (around 1000 K); (III) the bulk solution, the main site of hydrophilic compounds degraded by hydroxyl radicals ejected from bubble implosions. Therefore, the ultrasound process is capable of promoting not only pollutant degradation through hydroxyl radicals, but also degradation through pyrolysis in accordance with the molecule properties:

$$H_2O \rightarrow H^{\cdot} + {}^{\cdot}OH \quad (1)$$

$$O_2 \rightarrow 2O^{\cdot} \quad (2)$$

$$H^{\cdot} + H_2O \rightarrow H_2 + {}^{\cdot}OH \quad (3)$$

$$O^{\cdot} + H_2O \rightarrow 2{}^{\cdot}OH \quad (4)$$

$$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot} \quad (5)$$

In the absence of any organic compounds, other reactions take place, which result in hydrogen peroxide formation (Eqs. (6) and (7)). Quantification of hydrogen peroxide is a helpful way to estimate hydroxyl radical production under different operational conditions. Moreover, under atmospheric conditions (dissolved air), secondary reactions take place (Eqs. (8)–(11)) where nitric species are produced by N_2 from the air, which compete for OH radicals and affect the accumulation of hydrogen peroxide [17,9,18]:

$$2{}^{\cdot}OH \rightarrow H_2O_2, \quad k = 5.5 \times 10^9\ M^{-1}\ s^{-1} \quad (6)$$

$$2{}^{\cdot}OOH \rightarrow H_2O_2 + O_2 \quad (7)$$

$$N_2 + O^{\cdot} \rightarrow NO + N^{\cdot} \quad (8)$$

$$N^{\cdot} + O_2 \rightarrow NO + O^{\cdot} \quad (9)$$

$$NO + {}^{\cdot}OH \rightarrow HNO_2 \quad (10)$$

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O \quad (11)$$

Despite the large number of sonochemical degradation studies that have been carried out, a limited number of them involve water matrix effects. Some studies dealing with organic pollutant degradation have described inhibition effects due to dissolved inorganic and organic matter [19–21], and a few have shown enhanced effects [22,23]. Both inorganic species and organic compounds are part of natural water and wastewater composition. Therefore, the evaluation of their effect on micro-pollutant degradation is of special interest.

Previous studies have also shown the viability of sonochemical processes to degrade pharmaceuticals [9,24,25]. However, to the authors' knowledge, none have investigated the removal of DXC. Therefore, the aim of this investigation is to study the sonochemical degradation of DXC, which has so far not been reported by any AOP. Degradation routes and the effect of different experimental conditions, such as pH, initial DXC concentration and ultrasonic power, were evaluated. The water matrix effect was studied using Fe^{2+} as an inorganic species, which is commonly found in natural waters and wastewater. Glucose and 2-propanol were chosen as the organic compounds. Glucose is widely used by the pharmaceutical industries and 2-propanol is an example of a volatile compound also known to be a hydroxyl radical scavenger. Finally, in order to provide information about the application of sonochemical processes, DXC degradation was evaluated in both synthetic water and natural water containing inorganic species.

2. Materials and methods

2.1. Reagents

Dicloxacillin (99.9% pure) was supplied by the Syntofarma company. Acetonitrile (HPLC gradient grade) was provided by Merck. Analysis grade nitric acid, sodium hydroxide, 2-propanol, glucose, ferrous sulfate, potassium iodide, sodium phosphate and ammonium heptamolybdate were also provided by Merck. Distilled water was used during the study for the aqueous preparations and Milli-Q water was employed as part of the mobile phase for high performance liquid chromatography (HPLC) analysis. Characterized natural water was used for the matrix evaluation.

2.2. Apparatus

A cylindrical 500 mL glass reactor equipped with a cooling jacket was used for the sonochemical process. Ultrasonic waves were emitted from the bottom of the reactor by a piezoelectric disc (diameter 4 cm) fixed on a Pyrex plate (diameter 5 cm). Ultrasonic electric power was adjustable from 20 to 60 W with a fixed 600 kHz frequency. The reactor temperature was controlled at 20 °C by a thermostatic bath. All experiments were carried out under atmospheric conditions (dissolved air). The ultrasonic energy dissipated in the reactor (~58% of electrical power input) was estimated using the calorimetric method [26]. A Spectronic Genesys 2.0 was used to measure hydrogen peroxide and chemical oxygen demand (COD). TOC analyses were carried out with a Shimadzu TOC 5000A.

2.3. Analysis

Quantitative analysis for DXC was carried out using a HPLC Agilent system with a C-18 column (Merck LiChosphere) and a phosphate buffer (0.02 mM; pH 5)-acetonitrile (70:30) in isocratic mode as the mobile phase. The injection volume was 10 μL and DXC quantification was performed with a UV detector (225 nm). Hydrogen peroxide was analytically determined employing the spectrophotometric method. Aliquots from the reactor were reacted with potassium iodide (0.1 M) using ammonium heptamolybdate (0.01 M) as a catalyst. After 5 min of reaction, the absorbance was recorded at 350 nm. COD was determined by analyzing the reaction between a potassium dichromatic solution and the aliquot samples in a strong acidic medium in accordance with the Standard Methods for the Examination of Water and Wastewater (5220). After two hours of digestion at 150 °C, absorbance was measured at 420 nm. In order to avoid interference from hydrogen peroxide, sodium bisulfite (1.0 mM) was added to each sample. Biochemical oxygen demand (BOD_5) analysis was carried out by the respirometric method in accordance with the Standard Methods for the Examination of Water and Wastewater (5210). Prior to testing, the pH samples were neutralized and hydrogen peroxide was removed. For TOC analyses, a potassium phthalate solution was used as the calibration standard. The antimicrobial activity was determined by employing the zone of inhibition test using *Staphylococcus aureus* (ATCC 6538) as the probe microorganism. After 24 h of incubation, the inhibitory halo was measured.

3. Results and discussion

3.1. Evaluation of chemical and operational parameters

3.1.1. Effect of initial DXC concentration

DXC degradation was evaluated using different initial concentrations, from 6.4 μM (3 ppm) to 0.85 mM (400 ppm), under the same experimental conditions (Fig. 1). As the concentration of DXC increased, it became easier for the sono-generated hydroxyl