Comparative study of ceftriaxone removal by UVc photolysis and UVc based oxidation processes (UVc/H_2O_2 and UVc/PS)

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Abstract

The removal of ceftriaxone in aqueous solutions by three UV based photolytic processes (direct UVc photolysis, UVc/H_2O_2, UVc/Persulfate (UV/PS)) was investigated. UVc irradiation was provided by a low pressure mercury lamp emitting predominately at 254 nm. The objective of this study was to assess the performance of the above treatments on the removal of ceftriaxone from water, and evaluate the effects of factors in the treatment efficiency.

Keywords: UV/H_2O_2 oxidation processes, UV/persulfate oxidation processes, ceftriaxone

1. Introduction

The presence of antibiotics in the environment is an issue of increasing importance (Kummerer, 2003). High consumption of antibiotics and the inability of waste water treatment plants of removing these pharmaceuticals from wastewater have caused their release to the aquatic environments. Penicillins, cephalosporin and fluoroquinolones are the most used antibiotics around the world (Kummerer, 2009). Antibiotics in the environment have been reported worldwide and their presence has been associated with the evolution of "bacteria resistance", as well as with chronic toxicity to some non-target organisms. Ceftriaxone (Figure 1) is a third generation semi-synthetic cephalosporin antibiotic which has a broad antibacterial spectrum including gram-positive and especially gram-negative bacteria (Glaria et al., 2003).
The aim of the present work was to assess the performance of UV-C (i.e. λ=254 nm) irradiation, either alone or in the presence of H_2O_2 and Persulfate ($Na_2S_2O_8$) on the degradation of the cephalosporin ceftriaxone, in aqueous solutions.

2. Materials and methods

2.1. Chemicals and reagents

The experiments were conducted using ceftriaxone Disodium Salt Hemiheptahydrate（CAS Number 104376-79-6) purchased from Tokyo Chemical Industry- TCI. Phosphate salts, such as $Na_2HPO_4{\cdot}H_2O$ and KH_2PO_4 (both obtained from Merck) were employed for the preparation of aqueous buffer solutions. Sodium phosphate monobasic monohydrate ($NaH_2PO_4{\cdot}H_2O$) was obtained from Sigma-Aldrich and acetonitrile was purchased from Merck and both were used as solvents for high performance liquid chromatography (HPLC). All aqueous solutions were prepared with ultrapure water from the purification system Simplicity UV supplied by Millipore.

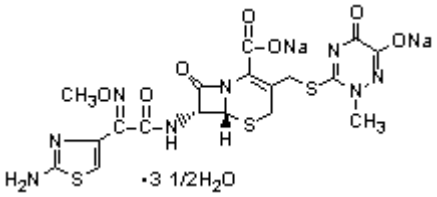

Figure 1. Structural form of ceftriaxone

2.2 UV-irradiation experiment

UV-C irradiation was provided by an 11 W, low pressure mercury lamp (Philips TUV, PL-S, G23), which emits predominately at 254 nm. UV-C irradiation experiments were conducted in an

immersion well, batch type, laboratory scale photochemical reactor. It consists of an inner cylindrical quartz glass vessel, housing the lamp (length: 250 mm, outer diameter: 36 mm) and an external double-walled, cylindrical, borosilicate glass, reaction vessel (length: 230 mm, internal diameter: 63 mm, volume capacity: 450 mL). The reaction mixture was placed in the external cylindrical reaction vessel and the inner cylindrical quartz glass vessel was immersed inside the reaction mixture. The UV-C lamp was placed inside the inner cylindrical quartz glass. The external double-walled, cylindrical, borosilicate glass, reaction vessel was effectively cooled by a water circulation stream through the double-walled compartment, acting as a cooling water jacket. During photolysis experiments, temperature was maintained constant at 22±2ºC. This reaction geometry is ideal for full exploitation of the UV-C irradiation emitted from the lamp. In a typical photolysis run, 450 mL of the aqueous solution containing the desired concentration of ceftriaxone was loaded in the reaction vessel and a measured volume of the concentrated H_2O_2 solution or $Na_2S_2O_8$ solution was added in the reaction mixture to achieve the desired concentration of each oxidant in the reaction mixture when experiments for testing the indirect photolysis of ceftriaxone were conducted. Immediately after the addition of the reaction mixture, the UV-C lamp was placed inside the inner quartz vessel of the photochemical reactor and the reaction mixture was continuously stirred with a magnetic stir bar and a magnetic stirrer.

2.3. Analytical Methods

Ceftriaxone concentration was determined at 242 nm using HPLC (Alliance 2695 Waters with a Diode Array (PDA Detector)) and a Luna C-18 column (5μm, 250mm x 4.6 mm) and a security guard column (4mm x 3mm) both purchased by Phenomenex. The mobile phase was a mixture of phosphate buffer 20mM and acetonitrile using a gradient program with a flow rate of 1 mL·min^{-1}. The gradient started with 90% phosphate buffer and this composition was held constant for the 1st minute. After the 1st minute the composition of phosphate buffer proceeded to 80% till the 8th minute and then returned to the initial conditions for a further 3 minutes. The temperature of the column compartment was 30°C, and the injected volume for HPLC analysis was 100 μL.

H_2O_2 concentrations were determined using a spectrometric method at 410nm and $Na_2S_2O_8$ concentrations were also determined by using a spectrometric method at 352nm.

Total organic carbon concentration was measured on a Shimadzu 5000A TOC analyzer.

3. Results and discussion

In an initial set of direct photolysis experiments under UV-C radiation, the effect of varying the initial concentration of ceftriaxone was studied in the range from 0.45 μmol·L^{-1} to 22.7 μmol·L^{-1} in buffer solution at pH = 7. The results are shown in Figure 2, which shows the normalized remaining concentration of ceftriaxone versus time.

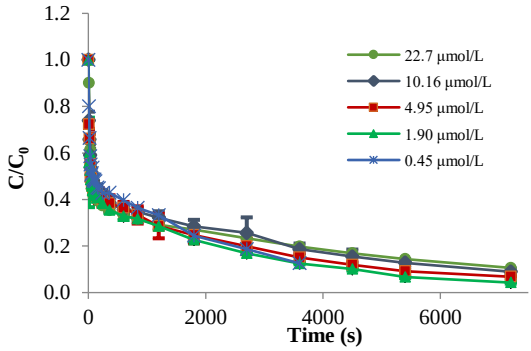

Figure 2. Direct UV-C photolysis of ceftriaxone. [[Ceftriaxone] =22.7 μmol L^{-1} to 0.45 μmol L^{-1}, phosphate buffer pH~7]

As can been seen in Figure 2, UV-C irradiation was able to accomplish 90-95% degradation of ceftriaxone in about 120 minutes, at any of the examined concentrations. Furthermore, the concentration of the total organic carbon (TOC) was measured, and it was found that the TOC of these solutions remained practically constant (data not shown).Thus it is obvious that the direct photolysis of ceftriaxone lead to the formation of transformation products which were relatively stable.

In further experiments, the photochemical degradation of ceftriaxone was studied under UV-C irradiation in the presence of either H_2O_2 or $Na_2S_2O_8$. More specifically, the concentration of H_2O_2 or $S_2O_8^{2-}$ varied from 0.05 to 10 mmol·L^{-1}, while the initial concentration of ceftriaxone was 22.7 μmol L^{-1} at pH 7. The results are shown in Figures 3, 4. UV-C irradiation in the presence of common oxidants such as hydrogen peroxide or $Na_2S_2O_8$ was much more powerful due to the generation of the reactive radicals $HO^{\cdot}$ or $SO_4^{\cdot-}$ (Xu et al., 2016). The addition of oxidants decreased the required time for the total removal of the ceftriaxone. Furthermore, as the initial concentration of each oxidant was increased the faster was the degradation of ceftriaxone. In the presence of H_2O_2 or $Na_2S_2O_8$, the overall degradation of ceftriaxone was attributed to both direct and indirect photolysis mainly due to hydroxyl radicals or sulphate radicals produced during the process.

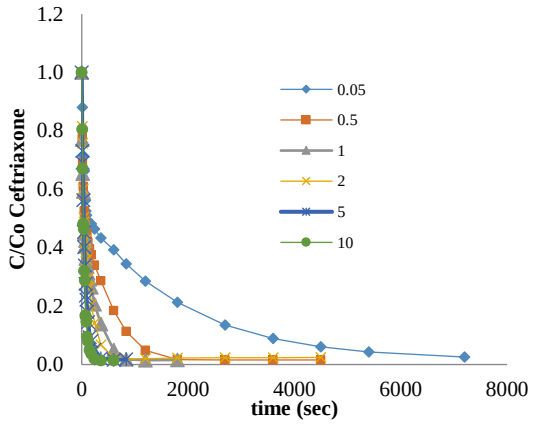

Figure 3. H_2O_2/UV-C photochemical oxidation of ceftriaxone. [[Ceftriaxone] =22.7 μmol L^{-1}, phosphate buffer pH~7, H_2O_2 dosage: 0.05 mmol L^{-1} to 10 mmol L^{-1}]

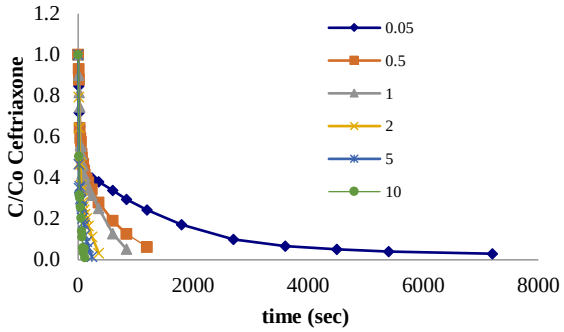

Figure 4.$Na_2S_2O_8$/UV-C photochemical oxidation of ceftriaxone. [[Ceftriaxone] =22.7 μmol L^{-1}, phosphate buffer pH~7, $Na_2S_2O_8$ dosage: 0.05 mmol L^{-1} to 10 mmol L^{-1}].

In addition, during UV-C/H_2O_2 or UV-C/$S_2O_8^{2-}$ treatment, the effect of the concentration of each oxidant on TOC removal was investigated. Figure 5 and 6 demonstrates TOC removal during the photochemical degradation of ceftriaxone at pH 7 and at various initial concentrations of oxidants. The removal of TOC was an important parameter during the combined processes because of the formation of byproducts thus TOC measurements can be related to mineralization of ceftriaxone. The TOC removal time was obvious longer than the time of total removal of ceftriaxone, implying that ceftriaxone had converted to lower molecular weight compounds and the intermediates still contribute to the TOC of the solution.

As can be seen in the Figures 5 and 6, the increase of the initial concentration of both oxidants leads to decrease of TOC concentration, compared to the direct UV-C photolysis of the substance where the TOC is stable. It is obvious that the addition of $Na_2S_2O_8$ achieved higher removal of TOC.

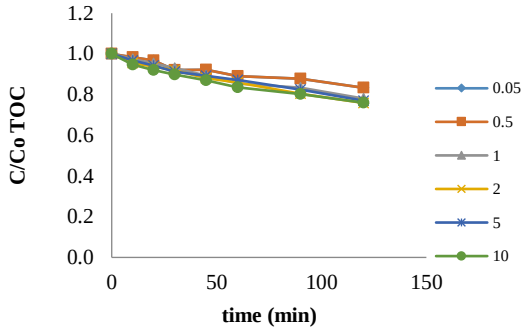

Figure 5. Effect of different H_2O_2 concentration on TOC concentration [Experimental Conditions: [Ceftriaxone] =22.7 μmol L^{-1}, phosphate buffer pH~7, H_2O_2 dosages: 0 mM to 10 mM]

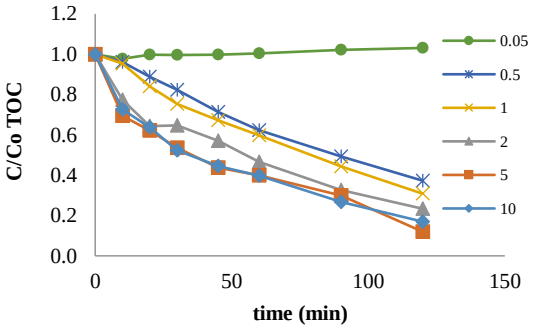

Figure 6. Effect of different $Na_2S_2O_8$ concentration on TOC concentration [[Ceftriaxone] =22.7 μmol L^{-1}, phosphate buffer pH~7, $Na_2S_2O_8$ dosages: 0 mM to 10 mM]

4. Conclusions

UV-C irradiation can be very efficient for the removal of the studied cephalosporin, under the present experimental conditions and the degradation can be faster with the addition of H_2O_2 and $Na_2S_2O_8$. The concentration of TOC remained unchanged with direct UV-C irradiation but decreased under the effect of UV-C/H_2O_2 and more efficiently under the effect of UV-C/ $Na_2S_2O_8$ photochemical degradation.

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