Removal Of Macrolide Antibiotics In Wastewater By Solar Photo-Fenton Processes At Neutral pH

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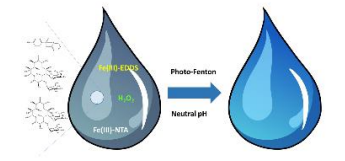

In this work, the behaviour of erythromycin (ERY) and clarithromycin (CLR) and their main TPs generated in wastewater during photo-Fenton processes at neutral pH using two ferric iron complexes, with ethylenediamine-N,N-disuccinic acid (EDDS) and nitrilotriacetic acid (NTA), as chelating agents, was studied. An analytical methodology based on a green sample treatment procedure and liquid chromatography with mass spectrometry (LC-MS) using triple quadrupole (QqQ) analyzer has been used for determination and identification of these pollutants and their main transformation products. Comparison of these chelating agents showed that NTA is the most efficient for the removal of studied pollutants. The results confirm the efficacy of the treatment to remove pollutants from wastewater using natural sunlight as renewable source.

Introduction

Several chemical compounds which are not commonly regulated have been detected in wastewater treatment plant effluents. This broad and growing group of chemicals is termed Compounds of Emerging Concern, Emerging Pollutants or Emerging Contaminants (ECs,), and include pharmaceuticals and personal care products, surfactants, plasticizers, pesticides, fire retardants, and nanomaterials. Conventional processes in WWTPs are unable to degrade these compounds. Therefore, many treatment methods, such as advanced oxidation processes (AOPs) have recently been investigated for the degradation of ECs from the aqueous phase. Among them, photo-Fenton process under UV-visible (UV–vis) radiation exhibits its highest efficiency at pH 3 [1,2]. The use of chelating agents, as ethylenediamine-N,N-disuccinic acid (EDDS) and nitrilotriacetic acid (NTA), at neutral pH have been proposed to avoid the disadvantage associated with the pH 3 [3]. Erythromycin and clarithromycin (CLR) are macrolide antibiotics with bacteriostatic activity against a broad-spectrum of organisms. The aims of this work is to study the behaviour of these ECs (erythromycin and clarithromycin) and their main transformation products (TPs) generated in water during solar photo-Fenton processes at neutral pH using EDDS and NTA as chelating agents.

Material and Methods

Standard of ERY and CLR were acquired from Dr. Ehrenstorfer (Augsburg, Germany). Ferric sulphate monohydrate ($Fe_2(SO_4)_3{\cdot}H_2O$, 75% w/w) and hydrogen peroxide (33% w/v) were supplied by Scharlab (Barcelona, Spain). Nitrilotriacetic acid (NTA, >99% w/w, Sigma Aldrich, Steinheim, Germany) and ethylenediamine-N,N'-disuccinic acid (EDDS, 35% w/v, Sigma Aldrich) were used, as complexing agents, for photo-Fenton experiments. WWTP effluent (pH 7.7; conductivity 1.1 dS m^{-1}; dissolved organic carbon (DOC) 2.6 mg L^{-1}; total nitrogen 1.8 mg L^{-1}; Ca^{2+} 67 mg L^{-1}; Mg^{2+} 46 mg L^{-1}; Na^{+} 99 mg L^{-1}; K^{+} 6.0 mg L^{-1}; SO_4^{2-} 263 mg L^{-1}; Cl^{-} 150 mg L^{-1}; HCO_3^{-} 122 mg L^{-1}; NO_3^{-} 1.9 mg L^{-1}; NO_2^{-} < 0.01 mg L^{-1}; PO_4^{3-} < 0.2 mg L^{-1}) was taken from a modular AT-8 WWTP supplied by AugustSpain (Alicante, Spain). Five hundred mL of water spiked at 200 µg L^{-1} were introduced in pyrex glass vessels and maintained in continuous agitation. Each trial was initiated with the addition of the corresponding complex (Fe^{3+}:EDDS (1:1) and Fe^{3+}:NTA (1:1)) and H_2O_2. Samples were exposed to solar irradiation for 360 min. A photolytic assay, without ferric ion complexes and H_2O_2 was also carried out. For this purpose, a suitable analytical method based on a green sample treatment procedure and liquid chromatography (LC) coupled to triple quadrupole tandem mass spectrometry (QqQ-MS/MS) or high resolution mass spectrometry (HRMS) using quadrupole time of flight (QTOF), was developed to determine ERY, CLR and their main TPs in wastewater. The analytical column was a Zorbax Eclipse XDB-C8.

Results and Discussion

Figure 1 shows the degradation curves of ERY and CLR in wastewater during the different treatments under sunlight exposure. In consonance with other studies [4], the comparison of both chelating agents showed a higher efficiency for NTA in the removal of these macrolide antibiotics. Thus, around 22% for ERY and 11% for CLR of degradation was achieved after 360 min of irradiation when the complex Fe^{3+}:NTA was used in comparison with 46% for ERY and 37% for CLR observed for Fe^{3+}:EDDS. This higher rate of degradation of ECs can be explained by the higher efficiency observed for the kinetic reaction between EDDS and $HO^{\bullet}$[5]. Figure 1 also shows the residual level of ECs after 360 min in the absence of ferric ion complexes and H_2O_2. The photolytic decomposition of ECs took place at a lower rate than that provided by the photocatalysis process. Finally, the kinetic evolution of

the main TPs was also studied during the solar experiment. In general, 7, 11 and 3 TPs were found during the photocatalytic treatments for ERY and CLR, respectively. The differences detected in number and concentration of TPs for the different treatments could be due to the relationship between mineralization and transformation processes.

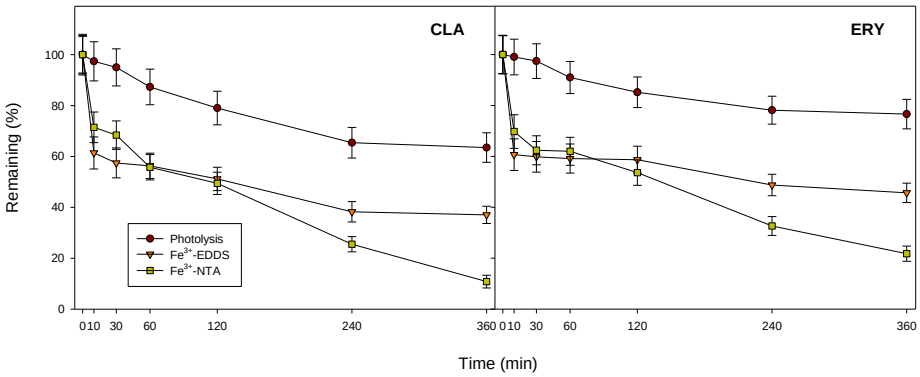

Figure 1. Degradation decay of clarithromycin (CLR) and erythromycin (ERY) in the different treatments under solar irradiation.

Conclusions

In summary, the kinetic photodegradation of erythromycin and clarithromycin by photo-Fenton processes using two ferric iron complexes (Fe^{3+}-EDDS and Fe^{3+}-NTA) at neutral pH has been investigated in a WWTP effluent, demonstrating that NTA is the most efficient for the removal of these pollutants and their TPs.

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