Degradation of erythromycin by photoelectrochemical process using a metal mixed oxide anode

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Abstract

The macrolide antibiotic erythromycin (ERY) was included in the watch list by European Union in the decision number 2015/495. In view of this problem, the photoelectrochemical (PEC) process, using (70-30%) TiO_2RuO_2-Ti as electrode, was applied aiming the ERY degradation. The PEC process was evaluated in terms of total organic carbon (TOC), chemical oxygen demand (COD) and pH. The electric consumption (E_{EO}) and degradation kinetic (k') were also calculated. Voltammetry study demonstrated that the direct oxidation between the work electrode and ERY did not occur. Furthermore, the UV irradiation results demonstrated that direct photolysis is not an important ERY degradation pathway. This means that ERY degradation will occur meanly by radicals, by photocatalytic and electrocatalytic processes at the electrode/catalysis surface. TOC and COD removal are parallel, which means that the portion of ERY that is being oxidized is also mineralized. At the treatment time of 240 minutes, ERY degradation by PEC process shows a TOC abatement of 56%. Also, a first-order kinetics with $k' = 0.0034$ min^{-1} and an electric consumption of 666351 kWh m^{-3} order^{-1} was found.

Keywords: Photoelectrochemical process; Metal mixed oxide anode; Erythromycin; Total organic carbon abatement.

1. Introduction

The degradation of natural environments have been one of the main problems faced by modern society. The production of several chemical products become more and more present, many times without knowledge of the long-term effects on the environment, which can cause negative and unexpected impacts (1). Due to the lack of data and research, parameters or legal limits do not exist for these types of chemical products, such as pharmacy, hygiene products, hormones, among others. These substances are denominated contaminants of emerging concern (CEC) (2). Among the pharmaceutical products, the antibiotics, particularly the macrolides group, are included in the European Union surveillance list as priority for monitoring (3). The antibiotics are developed to act on structures and specific cellular systems and they are used in the treatment and prevention of human and veterinary infections. However, they can lead to adverse and poisonous effects to various species, including species that should not be reached.

Substances as CEC are not efficiently removed in conventional water/wastewater treatments, being discharged and accumulated in the environment (4). In view of the removal inefficiency, it is necessary the application of an advanced oxidation processes (AOP) (5). AOP are systems that promote the degradation of organic structures, mainly through the generation and interaction of hydroxyl radicals (HO•). AOP have been investigated in the elimination of CEC using ozone (6), chemical oxidants (7), sonolysis (8), Photo-Fenton (9) and electrochemical oxidation (10). Some studies have pointed out the use of UV radiation in the degradation of some pharmaceutical active compouds (PhACs) but concluded that UV radiation alone was not effective enough to the degradation of macrolide contaminants (11–14). Aiming the improvement of the CEC degradation, the photoelectrochemical (PEC) process using a metal mixed oxide anode can be an alternative; the PEC makes use of the advantages of different process and their synergistic effects, combining electrooxidation, direct photolysis and heterogeneous photocatalysis. In a PEC process a UV radiation source illuminates the electrodes surface and a potential or current density is applied between the electrodes, avoiding the recombination between the electron/hole pair and improving the HO• formation. The HO• will interact with the pollutants promoting degradation (15,16). At this work, the PEC process using a metal mixed oxide anode was applied aiming the ERY degradation. The samples were collected and characterized by total organic carbon (TOC), Chemical Demand of Oxygen (COD) and pH. The degradation kinetic (k') and electric consumption were also evaluated.

2. Experimental

Before starting the PEC process to the degradation of the ERY, cyclic voltammetry (CV) experiments and UV radiation analysis were performed.

2.1. Solution

The work solutions were prepared diluting ERY (Sigma-Aldrich, $\geq$ 99%) in distilled and deionized water to a final volume of 4 L and a final ERY concentration of 50 mg L^{-1}. Due to the low electrical conductivity of the working solutions, 2 g L^{-1} of sodium sulfate (Na_2SO_4) was added as supporting electrolyte.

2.2. UV irradiation

A Spectrometer Princeton Acton Spectra Pro 2300, equipped with a photomultiplier, was used to analyze the emission of the 250 W high-pressure commercial mercury vapor lamp (HPL-N) in UV-C spectra.

For the 250W HPL-N lamp, in UV-C spectra, the radiation intensity (E, in mW cm^{-2}) was measured on the anode/catalyst surface, when ultrapure water or the working solution containing ERY fulfill the reactor, by an Instrutherm MRUR-203 UV light meter.

The E value can be converted to photon flux using Planck's equation. (1):

$$E_p = h \times c / \lambda \qquad (1)$$

where E_p (J) is the photon energy, h is the Planck's constant (6.626 x 10^{-34} J s), c is the speed of light (2,998 x 10^{8} m s^{-1}) and λ the wavelength (m).

The number of photons (N_p) can then be calculated by the equation 2:

$$N_p = E / E_p \qquad (2)$$

Finally, the photon flux (E_{qf}) in mol m^{-2}s^{-1} can be represented by the equation 3.

$$E_{qf} = N_p / N_A \qquad (3)$$

where N_A is the Avogadro number (6.02 x 10^{23} mol^{-1}).

2.3. Cyclic voltammetry experiments

Cyclic voltammetry (CV) experiments with the work solution were accomplish in order to evaluate the influence of the direct and/or mediated electrochemical oxidation in the PEC process. The electrochemical measurements were obtained using a conventional three-electrode cell, where metal mixed oxide composed by $(70\%)TiO_2(30\%)RuO_2$-Ti with geometric area of 1.5 cm^2 was used as work electrode, platinum (Pt) was used as counter electrode and Ag/AgCl (saturated) was applied as a reference electrode. The CV experiment was carried out between 0 and 1.5 V starting and finishing at the 0 V at a scan rate of 50 mV s^{-1}. The potentiostat used was the Autolab PGSTAT302 potentiostat/galvanostat.

2.4. Experimental System

The reactor used in the PEC assays was a jacket borosilicate glass reactor with a capacity of 2 L, operated in batch mode connected to a 5 L reservoir. An ultra-thermostatic bath was used to control the temperature (~25 ºC). The anode was a metal mixed oxide composed of $(70\%)TiO_2(30\%)RuO_2$-Ti with geometric area of 475.2

cm^2 and the cathode was composed of TiO_2-Ti with geometric area of 118 cm^2. The electrodes were placed concentrically with a gap between electrodes of 0.3 cm around the lamp (250W HPL-N), without the glass bulb and inside a quartz tube, remaining under UV radiation. A current density of 10 mA cm^{-2} was applied on the electrodes by a CEL P-6000. 5 L of the working solution were placed in the reservoir that feeds the reactor at an average flow rate of 1 L min^{-1} with the aid of a peristaltic pump (figure 1). The experiments were conducted in triplicate.

To evaluate the effect of the catalyst on the oxidation of ERY, one assay with the same experimental conditions used on PEC but without applied current was carried out (Heterogeneous Photocatalysis, HP).
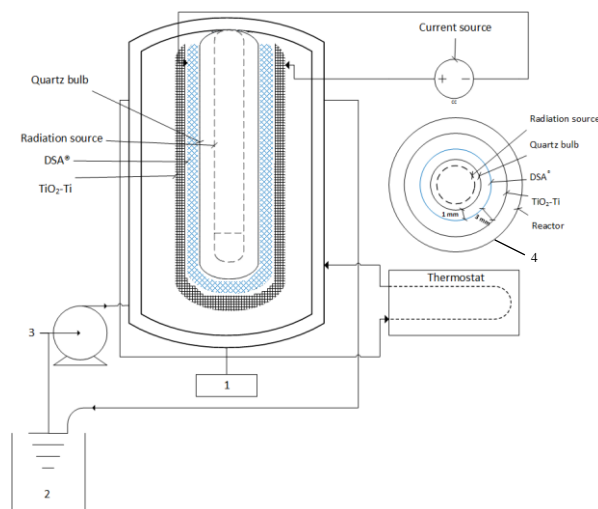

Figure 1. PEC reactor operated in batch mode with recirculation, where 1 is a jacket borosilicate glass reactor with capacity of 3 L, 2 is a 5 L reservoir, 3 is a peristaltic pump and 4 is the top view of the reactor.

2.5. Analysis

Samples were collected at the treatment times of 0, 60, 120, 180 and 240 minutes and characterized by pH, COD and TOC.

The pH was determined by the potentiometric method using a DM-22 Digimed.

Chemical oxygen demand COD was determined by closed reflux colorimetric method according to Standard Methods (17).

The total organic carbon (TOC) abatement was determined on a Shimadzu TOC-LCPH analyzer according to the thermal catalytic oxidation principle using the Non-Purgeable Organic Carbon (NPOC).

Kinetics (k') were calculated based on the Langmuir-Hinshelwood equation (18).

$$-k' \times t = \ln(TOC/TOC_0)$$
(4)

where TOC_0 is the initial TOC value and TOC is the TOC value at any treatment time (t, min) and t is the treatment time in min.

The electric energy in order of magnitude (E_{E0}, in kWh m^{-3} order^{-1}) was calculated from equation 5 (19).

$$E_{EO} = P \times t \times 1000/V \times 60 \times \log_{10}\left(\frac{TOC_0}{TOC}\right) \qquad (5)$$

where U is the cell voltage (V), I is the applied current (A) and V is the treated volume (L).

3. Results and discussion

3.1 UV radiation

The characterization of the 250 W HPL-N lamp in UV-C spectra shows a peak in 254 nm. Based in this result and with equations 1 to 3 the UV photon flux can be calculated.

The results of UV photon flux arriving at the anode surface when the liquid media are distilled and deionized water or working solution is 1.45 x 10^{-4} mol m^{-2} s^{-1} and 1.40 x 10^{-4} mol m^{-2} s^{-1}, respectively, meaning that the working solution containing ERY absorbs UV photon (5 x 10^{-6} mol m^{-2} s^{-1}) and, therefore, undergo photo-transformation. Notwithstanding, the UV photon that reaches the anode surface through the working solution is much higher than the one absorbed by the ERY, in other words, the photocatalytic process should be favored.

3.2 Cyclic voltammetry

Cyclic voltammetry experiments were performed in order to analyze the influence of the electrochemical oxidation process, the direct and/or the mediated oxidation, in the degradation of ERY. Figure 2 shows no anodic neither cathodic peaks for the support electrolyte Na_2SO_4 and the solution containing ERY, indicating that this antibiotics are not electro-active in the potential window used for this electrode. This effect can cause difficulties by the competition with the oxygen evolution reaction and because various organic compounds have oxidation potential in this region, leading to a decreased efficiency of the direct electrochemical degradation. In fact, with these results, only mediated electrochemical degradation by generation of radical species in the anode surface would be expected.

3.3 Photoelectrochemical degradation of ERY

The COD reduction represents the amount of organic substances which was oxidized under defined conditions. On the other hand, the TOC abatement represents the mineralization of the organic compound, that is, the portion that was oxidized to CO_2, water and inorganic ions.

Figure 3 shows for both, PEC and HP process a COD reduction and a TOC abatement with the time. In addition, it is possible to observe that the reduction of COD and TOC are parallel, which means that the portion of ERY that is being oxidized is also mineralized. Furthermore, when a current is applied between the catalysts/electrodes an improvement in the COD and TOC abatement is observed. It means that the applied current is able to avoid

the electron/gap recombination in the photocatalysis process leading to higher hydroxyl radical generation and as consequence more ERY degradation.

3.4 Kinetics

In general, when the absorption of the organic contaminants occurs onto a surface where the TOC abatement will occur, the model of Langmuir-Hinshelwood
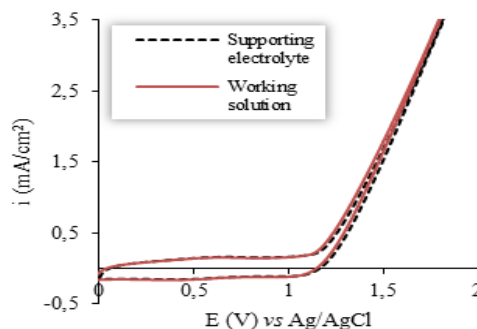

Figure 2. Cyclic voltammogram response of mixed metal oxide for the electrolyte solution containing 2 g L^{-1} of Na_2SO_4 and working solution containing 50 mg L^{-1} of the antibiotic ERY.

can describe the reaction kinetics (18). Figure 4 shows that the ln (TOC/TOC$_0$) is linear (R^2 = 0.99), thus following a first order kinetics, and can be explained by the quasi-steady content achieved for hydroxyl radicals, since these species cannot be accumulated in the anode surface or in the bulk solution because they have a very short lifetime (20). The constant k' for the ERY is calculated and resulting in 0.0034 min^{-1}.
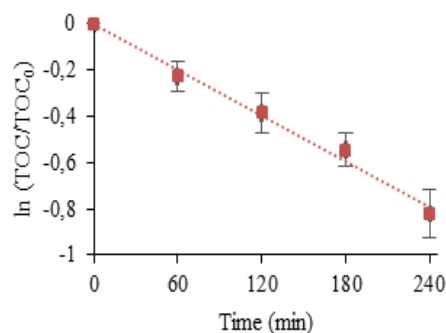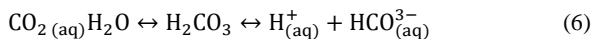

Figure 4. Behavior of the natural logarithm (ln) of TOC/TOC$_0$ as function of the treatment time.
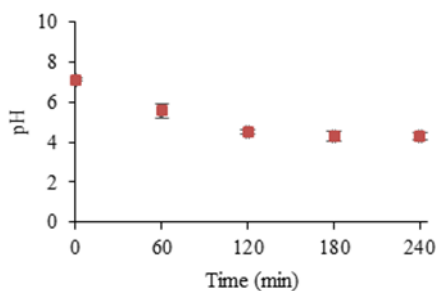
3.5 pH changes

A decrease in pH is expected since H$^+$ ions are released into the solution, resulting from water oxidation, either by the gap photogenerated in the catalyst as also by the anodic discharge on the electrocatalytic process. Furthermore, there is a decrease in the concentration of OH$^-$ ions consumed for HO• generation (21). Another explanation for pH reduction can be related to the ERY mineralization. With CO_2 released in the solution by the ERY mineralization and dissolved in water, carbonic acid can

form from equation 6 and can be dissociated (equation 7) contributing to a pH decrease.

$$CO_{2\,(aq)}H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+_{(aq)} + HCO^{3-}_{(aq)} \qquad (6)$$

$$HCO^{3-}_{(aq)} \leftrightarrow H^+_{(aq)} + CO^{2-}_{3(aq)} \qquad (7)$$

Another possible explanation for the decrease in pH is that the ERY degradation leads to byproducts formation that can be short chain organic acids (16,21) and this found must be more investigated.

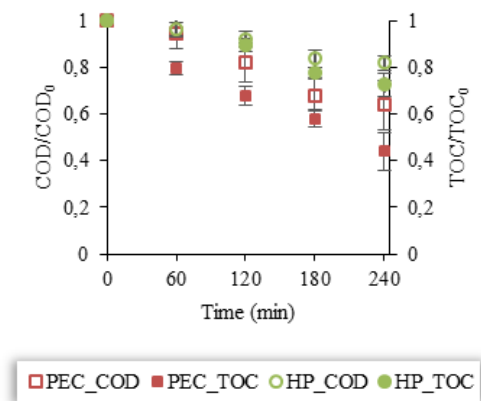**Figure 5.** pH changes as function of treatment time.

Figure 3. COD reduction and TOC abatement of solutions containing ERY untreated and treated by PEC and HP process.

3.6 Electric energy consumption

Scaling-up the process for an industrial use, it will be necessary the calculation of the energy consumption to treat the contaminated water/wastewater, as this is an important parameter for the overall cost of the process. The energy consumption was calculated according to equation 5 and the results are showed in figure 6.

It is possible to observe that the energetic consumption is almost constant during the PEC process, indicating that no electric potential increase occurred during the process, with no extra resistance augmentation in the system. This results means that no significant deterioration or passivation phenomena occurs in the electrodes/catalysts.

Furthermore, the values obtained is not low because the incorporation of the HPL-N lamp may considerably increase the energy consumption of water/wastewater treatment.
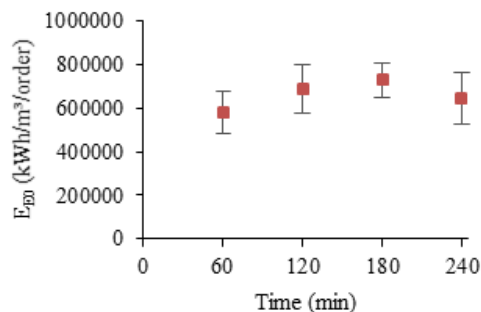
Figure 6. Energetic consumption by PEC process to treat 1 m³ of solution containing ERY

4. Conclusions

The present study analyzed the use of PEC process in Erythromycin degradation. Studies like this are important to contribute to the progress of the knowledge in the area of removal of CPEs in water / wastewater, collaborating for the reduction of the environmental contamination. Results shows that COD removal is parallel to TOC abatement, i.e. the majority ERY oxidized are mineralized. Results from UV radiation and cyclic voltammetry shows that the mineralization is more linked to the fotocatalyisis and electrocatalyisis than to direct phototransformations or oxidation at the anode surface. It also showed a pH reduction that may be indicative of the by-products or carbonic acid formation from CO_2 mineralization product. Moreover, it is necessary to investigate the byproducts by liquid chromatography couple to mass spectroscopy.

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