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Degradation of Metoprolol by means of Advanced Oxidation Processes

ABSTRACT

Nowadays, there is worldwide concern about environmental problems such as water scarcity, droughts and water quality. The water pollution has been increasing along the time, being this big problem that threatens the environment. In order to avoid this situation and increase the water quality, the treatment of different pollutants present in water plays an important role. In this way, the emerging pollutants imply a new challenge. Pharmaceuticals are considered as emerging pollutants and they present peculiar problems.

Pharmaceuticals in waters come from hospitals, pharmaceutical industry or from domestic waters, by rejected drugs not used or by human excretions, because they are partially metabolized by the body and excreted. In addition, the amount of these compounds is continuously increasing and they can be ecotoxicological important, because of their biological activity, causing potential environmental impact. Once in the sewage treatment plants, the complete removal of these pharmaceuticals cannot be assured by conventional water treatment methods because of the recalcitrant nature of many of these compounds. Thereby, it is necessary to use alternative treatments such as "Advanced Oxidation Processes" (AOPS) which are based on the production of very reactive species (especially hydroxyl radicals, HO·). The reactive species produced are able to degrade or transform chemical pollutants producing ultimately total mineralization.

For this study the emerging contaminant β -blocker Metoprolol has been selected due that it is a highly prescribed pharmaceutical to treat hypertension, tachycardia, and heart failure and it has been detected in waste water treatment plants influents, thus, in natural waters. Several studies, focused on the toxicological potential of Metoprolol, indicate its potential environmental relevance and its recalcitrant nature. To remove MET from water, different AOPs were used. The Total Organic Carbon (TOC) is monitored to observe the organic matter removal, HPLC is used to determine the concentration of this pharmaceutical along the experiments. The BOD₅ and COD are analyzed, and its ratio BOD₅/COD is used as a biodegradability index. Furthermore, toxicity bioassays were carried out with the marine bacterium *vibrio fischeri*.

MET removal was studied, in different reactors with natural and artificial light, by photolysis, UVC/H₂O₂, photocatalysis, Fenton, photo-Fenton, Bicarbonate-activated hydrogen peroxide and Cobalt or iron/bicarbonate/hydrogen peroxide processes. After that, the different set-ups and technologies tested have been compared in order to establish the efficiency of the processes.

An actinometric method was used to measure the photon flow entering a photocatalytic reactor. In addition, it was studied the influence of suspended TiO₂ particles, inside the photoreactor, on the actinometry.

Photolysis experiments were carried out with 50 mg/L of initial MET in Milli-Q water, free pH, and 25 ± 5 °C in solarbox (SB), Compound Parabolic Collector (CPC), Black light blue lamps (BLB) and UVC254 nm (UVC) reactors. The results show that after 240 minutes of irradiation MET removal was too low in all reactors except in reactor UVC where 93.5% of MET removal was achieved. However, photolysis did not promote relevant mineralization in all set-ups.

UVC/H₂O₂ experiments were carried out with 50 mg/L of initial MET in Milli-Q water, free pH, and 25 °C in UVC reactor. Different hydrogen peroxide concentrations and pH solution were tested. An initial dose of 125 mg H₂O₂/L exhibited the best performance regarding to MET (98% in 7.5 minutes) and TOC degradations (70.7% in 230 minutes). Biodegradability was improved and the final toxicity decreases.

Photocatalysis experiments were carried out with 50 mg/L of initial MET in Milli-Q water, free pH, and 25 ± 5 °C in solarbox (SB) and Compound Parabolic Collector (CPC). Different TiO₂ concentrations (0.05, 0.10 and 0.40 g /L) were studied in both reactors and the best concentration for MET and TOC removal was 0.4 g TiO₂/L. After 300 minutes of irradiation in SB, a complete MET removal and 45.7% of mineralization were observed. Photocatalytic experiments were also carried out varying the initial MET concentration (25, 50 and 100 mg/L), pH and the water matrix with 0.4 g TiO₂/L in SB. It is observed that at lower MET initial concentration there is higher MET and TOC removal. Complete MET elimination was achieved at pH 9 (240 min). Changing the water matrix to effluent from WWTP just 20.8 % of MET elimination was achieved. Additionally, 25 and 150 mg/L of H₂O₂ were added to 50 mg/L MET solution directly in the batch tank with catalyst. A complete depletion of MET is reached within 180 and 120 min by use of 25 and 150 mg/L of H₂O₂, respectively. Photocatalytic treatment in CPC reactor was also a good alternative in MET degradation (81.5% at 2.6 kJ/L for 0.4 g/L of TiO₂) and 29.2% of mineralization. In CPC reactor 70% (Q= 3.1 kJ/L) and 96% (Q= 6.0 kJ/L) of MET removal is observed with 25 and 150 mg/L of H₂O₂, respectively, and 0.4 g/L of TiO₂. After 270 minutes the biodegradability increases and toxicity decreases.

From the intermediates identified using SB and CPC reactors, a possible MET fragmentation was proposed for photocatalysis/TiO₂ and UV-Vis/H₂O₂/TiO₂ processes, where, mainly oxidative attacks were detected and the binding of HO· radicals in the aromatic ring.

The dark-Fenton experiments were carried out with 50 mg/L of initial MET in Milli-Q water at pH 3 and 25°C temperature in a reactor of 2 L. Two different amounts of Fe (II) (2.5 mg/L or 10 mg/L) and two different H₂O₂ concentrations (25 mg/L or 150 mg/L) were used. With the highest values of Fe (II) and H₂O₂, the highest MET and TOC conversions were reached (degradation: 67.0%, TOC: 8%, COD: 7.63%). To improve the Fenton process, the total Iron (II) concentration was divided in equal parts (5) and added at constant periods of time (12 minutes) during 1 hour. With the highest concentrations of iron and H₂O₂ the maximum MET conversion was 87.0% and mineralization 15.6%. From the intermediates identified a possible MET fragmentation was proposed.

Photo-Fenton experiments were carried out with 50 mg/L of initial MET in Milli-Q water, pH 3, and temperature of 14 or 25 °C in BLB, SB, CPC and UVC reactors. Two different amounts of Fe (II) were used (2.5 mg/L or 10 mg/L) and two different H₂O₂ concentrations (25 mg/L or 150

mg/L). In all reactors with the highest iron and H₂O₂ concentrations, the best results in MET degradation were observed (BLB: 100% in 7 min; SB: 97.3% in 7 min; CPC: 98.3% in 3 min); however, in UVC the lowest iron and H₂O₂ concentrations were used and 97.0% of MET conversion was achieved in 20 min. Similar behavior was observed for TOC removal, biodegradability and toxicity.

From the intermediates identified, a possible MET fragmentation was proposed, where mainly oxidative attacks were detected.

The dark- Bicarbonate/hydrogen peroxide experiments were carried out with 5 mg/L of initial MET in drinking water, pH 6.2, and room temperature in a reactor of 0.5 L. The highest conversion of MET within 120 minutes was almost 20% when 600 mg/L of NaHCO₃ and 600 mg/L of H₂O₂ were used. This process does not show as a good alternative for MET degradation. To improve the process, Cobalt (II) as catalyzer was added in the batch reactor. When 1 mg/L of cobalt were used an improvement of 10 times was observed. The highest MET conversion was reached when 600 mg/L of NaHCO₃, 2400 mg/L of H₂O₂ and 1 mg/L of cobalt were used (47.2%).

For the following series of experiments, cobalt was changed for iron as catalyst, the pH was 3.0 and the initial concentration of MET was 25 mg/L. Three different amounts of Fe (II) were used: 2.5 mg/L, 5.0 mg/L and 10 mg/L, and H₂O₂ concentration was constant (25 mg/L). When the process was carried out without HCO₃³⁻, lowest MET conversion was reached (25.5%). When HCO₃³⁻ was added the process improves ~1.3 times. The addition of TBA as scavenger showed a decrease of MET conversion in ~3.5 times. To improve the process, the total Iron (II) concentration was divided in equal parts (5) and added at constant periods of time (12 minutes) during 1 hour. With the highest iron concentrations (10 mg/L) a complete MET conversion in 40 minutes was achieved.

The efficiency of different AOPs tested and reactors used was compared from the ratio between accumulated energy and MET eliminated. The efficiency is higher for UVC reactor (0.07 kJ/mg) than SB (0.25 kJ/mg), possibly due to the high MET absorbance centered on 221 and 273 nm.

Concerning the efficiency ratio for MET removal by photocatalysis, the energy is better used in CPC (0.065 kJ/mg) than in SB (0.275 kJ/mg). A possible explanation can be related to the fact that the CPC are able to concentrate on the receiver, practically, all the radiation arriving at the collectors.

Finally, the ratio energy/MET removal is compared in four different installations for photo-Fenton process: 0.04 kJ/mg in UVC, 0.05 kJ/mg in BLB, 0.26 kJ/mg in CPC and 0.30 kJ/mg in SB reactor. UVC and BLB reactor exhibit a much better performance than SB reactor and CPC reactor.

On the other hand, the irradiation in the photocatalytic reactor (SB) was measured by o-NB actinometry in two different ways, based on pH or o-NB concentration, giving photon flows of 2.81×10^{-10} Einstein/s and 2.68×10^{-10} Einstein/s, respectively. In addition, this work has demonstrated that the o-NB actinometry, followed by o-NB concentration consumption, could be used in the presence of the catalyst TiO₂.