



# Performance of different advanced oxidation technologies for the abatement of the beta-blocker metoprolol



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## ABSTRACT

In this study UV/H<sub>2</sub>O<sub>2</sub>, photo-Fenton and photocatalysis (TiO<sub>2</sub>) were used to degrade metoprolol tartrate salt (MET) in aqueous solution. This study investigates the variation of different parameters such as MET concentration, total organic carbon (TOC), chemical oxygen demand (COD) per accumulated energy (determined by actinometries), analyzing the performance of the different set-ups tested. First order apparent rate constants were calculated for the systems. Nearly total MET removal was achieved through the three technologies tested, the UV/H<sub>2</sub>O<sub>2</sub> system being more efficient for MET degradation. On the other hand, the kinetic study indicated that TiO<sub>2</sub> photocatalysis seems to be one step ahead of the others when assessing the mineralization and the overall oxidation of the solution for a specific amount of accumulated energy (18 kJ/L). The acute toxicity measured by the inhibition percentage of bioluminescence from *Vibrio fischeri* indicates that all the processes tested promote the toxicity reduction for this target compound. The major reaction intermediates in the three processes were identified by ionization/mass spectrometry.

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## 1. Introduction

Pharmaceutical and personal care products (PPCPs) are extensively consumed annually in the world [1]. As a result, these PPCPs may be found in waste effluents [2,3], in ranges varying from the value of an industrial discharge (10–100 mg/L) to the very small value founded in the aquatic environment (far less from 1 mg/L) [4]. These micropollutants are not completely eliminated by the conventional activated sludge treatment [5] and have been found at concentrations up to µg/L in the effluent of the municipal wastewater treatment plants (MWTP) [6,7]. This fact is in contrast to the Water Framework Directive which requires a 'good chemical and biological status' of all water bodies until 2015 [8]. Therefore, it is necessary to apply adequate technologies to definitively eliminate these contaminants from water. In this sense Advanced Oxidation Processes (AOPs) have been described as a useful tool for their completely degradation, increasing biodegradability and detoxifying effluents. A large number of studies have shown the potential for using single AOPs (UV radiation, ozone, photo-Fenton, photocatalysis, etc.) as well as different combinations of UV radiation and ozone with H<sub>2</sub>O<sub>2</sub>, TiO<sub>2</sub>,

Fe(III), etc. [9]. All these processes are characterized by the production of hydroxyl radicals, which are extraordinarily reactive and present low selectivity, oxidizing most of the persistent pollutants in water.

Among these pharmaceuticals, β-blockers are frequently detected in the environment [10]. Metoprolol is one of the most commonly used β-blockers for the treatment of cardiovascular diseases [11]. According to the pharmacokinetics study [12], about 5% of metoprolol is excreted unchanged after oral administration and spilled into wastewaters. In addition, an important contribution to the occurrence of these drugs in the aquatic environment is the discharge of effluents from pharmaceutical industries, because discharge regulations are not focused on the concentration of these particular pollutants but on more general parameters such as COD or TOC [5]. In this framework, MET removal has been studied using many different AOPs, including UV/H<sub>2</sub>O<sub>2</sub> [13], photocatalysis [14,15], photo and Fenton based technologies [9,13,16], in which the efficiency of MET degradation depends strongly on the particular technology and conditions used.

According to the state of the art, the objective of the present work was to compare H<sub>2</sub>O<sub>2</sub>/UV<sub>254</sub>, TiO<sub>2</sub> photocatalysis and photo-Fenton, for the removal of MET. The efficiency of these three technologies in MET degradation was compared in terms of accumulated energy. Moreover, the pharmaceutical degradation kinetics at each process was modeled and compared.

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## 2. Materials and experimental set-ups

### 2.1. Chemicals and reagents

Solutions of 50 mg/L of metoprolol tartrate salt (MET) (CAS: 56392-17-7, Sigma-Aldrich) were prepared using deionized water. TiO<sub>2</sub> Degussa P-25 was used as catalyst in heterogeneous photocatalysis. Acetonitrile (analytical reagent grade from Fischer Chemical) and orthophosphoric acid (85% from Panreac Quimica) were used for HPLC analysis. H<sub>2</sub>O<sub>2</sub> (30%, w/w, from Merck), FeSO<sub>4</sub>·7H<sub>2</sub>O (Panreac PA), liver bovine catalase (Sigma-Aldrich), NaHSO<sub>3</sub> and MeOH (Panreac PAI) reagents were used without further purification.

### 2.2. Analysis

All samples were previously filtered with a polyethersulfone membrane (0.45 μm, Chmlab group) to remove the catalyst before analytical procedures. MET concentrations were monitored by HPLC Waters with a SEA18 column (5 μm, 25 × 0.46 cm, Teknokroma–Spain) and a Waters 996 photodiode array detector. The mobile phase was composed of water (pH 3 adjusted by orthophosphoric acid) and acetonitrile (80:20), injected with a flow-rate of 0.85 mL/min and detected at its maximum UV absorbance of 221.9 nm. TOC was analyzed with a Shimadzu TOC-V CNS analyzer. To analyze COD, the Standard Methods (5220D) procedure was followed, using a spectrophotometer (Hach Lange DR 2500) at 420 nm. Biochemical oxygen demand (BOD<sub>5</sub>) was determined according to Standard Methods (5210) by respirometric process using OxiTop equipment, during five days, under constant stirring and controlled temperature (20 °C ± 1 °C). H<sub>2</sub>O<sub>2</sub> consumption was followed using the metavanadate spectrophotometric procedure [17]. H<sub>2</sub>O<sub>2</sub> containing samples were quenched with sodium hydrogen sulfite, liver bovine catalase or the same volume of methanol to avoid further reactions depending on the analysis to be done. The ecotoxicity of the samples were measured by the acute toxicity using Microtox tests, where the inhibition of *Vibrio fischeri* bioluminescence at 15 min of incubation was determined. For the intermediates identification, samples were analyzed by the electrospray ionization/mass spectrometry using an electrospray (ion spray) ESI–MS, and a LCMSD–TOF (2006) mass spectrometer.

### 2.3. Solarbox: Artificial solar irradiation

Photocatalysis and photo-Fenton experiments were carried out in a solarbox (CO.FO.ME.GRA 220V 50Hz) with a Xenon lamp (Phillips XOP 1 kW), located at the top of the Solarbox [14,18]. The tubular photoreactor (24 cm length × 2.11 cm diameter) was placed at the bottom of the solarbox in the axis of a parabolic mirror. The radiation arriving at the photoreactor (2.68 μEinstein/s) was measured by *o*-Nitrobenzaldehyde (*o*-NB) actinometry 290–400 nm [19]. The procedure was as follows: batch tank (total volume 1 L) was fed with MET solution (50 mg/L) following the addition of TiO<sub>2</sub> (0.4 g/L) or Fe<sup>2+</sup> (2.5, 10 mg/L) and/or H<sub>2</sub>O<sub>2</sub> (25, 150 mg/L). In order to keep the solution at 25 °C or 14 °C, the jacket temperature of the stirred tank was controlled with an ultra-thermostat bath (Haake K10).

Samples were collected from the batch tank every 60 min during 360 min for the photocatalytic process. Photo-Fenton process was considered as complete when all H<sub>2</sub>O<sub>2</sub> was consumed. Most experiments in solarbox were performed twice in order to ensure the system reproducibility and the error was calculated based on the standard deviations.

Radiation between 300 and 400 nm was considered for the TiO<sub>2</sub> experiments and between 300 and 500 nm for the photo-Fenton

technology since the photolysis of Fe(III) complexes with organic ligands is efficient up to 500 nm.

### 2.4. Double jacket reactor

All experiments for UV/H<sub>2</sub>O<sub>2</sub> were performed in a thermostated Pyrex-jacketed 2 L vessel, equipped with three fluorescent low pressure mercury lamps (Phillips TUV 8W, G8T5), emitting monochromatic radiation with a maximum at 254 nm. The light inside the photoreactor was assessed with actinometric experiments [20] and the obtained value was 1.70 μEinstein/s at 254 nm. The solution was fully stirred with a magnetic stirrer to ensure sufficient mixing. The reaction temperature was kept constant at 25 °C. UV/H<sub>2</sub>O<sub>2</sub> experiments were considered finished once H<sub>2</sub>O<sub>2</sub> reached a value of 10 mg/L due to the marked kinetic slowing down.

## 3. Results and discussion

### 3.1. Direct photolysis of MET

MET (initial concentration 50 mg/L) direct irradiation was carried out. MET removal achieved was 94%, using monochromatic radiation at 254 nm, and 18.0%, using solarbox, both after 300 min of irradiation. Moreover, mineralization accomplished resulted to be negligible for both processes (6% at 300 min). Experimental data were fitted to first order kinetics and the values obtained for the apparent rate constants were calculated from the slopes of the regression curves representing  $-\ln(C/C_0)$  vs time. Thus, the apparent rate constants obtained were 0.00067 min<sup>-1</sup> ( $R^2 = 0.994$ ) and 0.0101 min<sup>-1</sup> ( $R^2 = 0.991$ ), for Xe and UV-C lamps, respectively. This behavior could be explained from MET absorption spectrum presented in Fig. 1, showing that MET has main UV absorption peaks centered on 221 and 273 nm. This means that UV-C spectrum covers much better than Xe lamp the zone where MET absorbs, and for this reason the photolysis of MET is faster with UV-C radiation.

### 3.2. Photocatalysis of MET

Four different catalyst loads were assessed for 0.05, 0.1, 0.4 and 0.5 g/L TiO<sub>2</sub> to choose the optimum catalyst concentration for further comparison with other processes.

Working with 0.5 g/L TiO<sub>2</sub>, catalyst sedimentation at the bottom of the reactor was observed, therefore this catalyst concentration was not considered for the experiments. Figs. 2 and 3 show the effect of TiO<sub>2</sub> concentration on MET degradation and mineralization, and both improve when titania concentration increases.

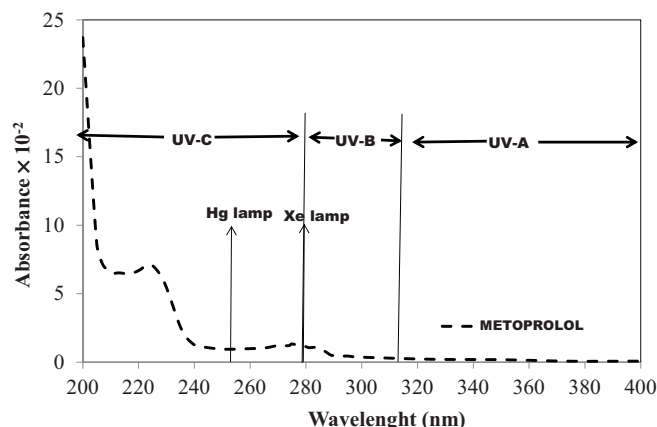


Fig. 1. MET absorption spectrum.

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