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Photocatalytic Decomposition of Metoprolol and Its Intermediate Organic Reaction Products: Kinetics and Degradation Pathway

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Abstract: High purity metoprolol prepared by neutralization of an aqueous solution of metoprolol tartrate is efficiently mineralized to CO_2 and water by photocatalysis with TiO_2, UV light and a constant flow rate of oxygen. Since the tartrate anions were eliminated, all the HO• generated by photocatalysis reacted efficiently with the aromatic part of the medication. The reaction pathway includes two routes of degradation. The first one includes the transformation of metoprolol to hydroquinone via formation of 4-(2-methoxyethyl)phenol, 2-(4-hydroxyphenyl)ethanol and 4-hydroxybenzaldehyde. Metoprolol is also degraded directly to hydroquinone. Then, this aromatic compound is oxidized to 1,2,4-benzenetriol, which is rapidly oxidized to low molecular weight organic acids before being completely mineralized to CO_2 and water. Kinetic studies indicated that the initial reaction rate of the degradation of metoprolol, 4-(2-methoxyethyl)phenol, 2-(4-hydroxyphenyl)ethanol and 4-hydroxybenzaldehyde is described by the LH-HW model.

Keywords: metoprolol, pharmaceuticals, photocatalytic degradation, reaction pathway

1 Introduction

Large amounts of different chemical compounds, classified as hazardous waste, (Loganathan and Lam, 2011) are discarded worldwide. These include household waste, industrial waste, mining tails, and pathological materials from hospitals and laboratories. Industrial, domestic and hospital wastewaters containing a variety of surfactants, solvents, disinfectants, and other chemical compounds that are classified as persistent micro pollutants (Oliveira et al. 2015; Verlicchi et al. 2012). Residues of fragrances, personal care products, medications and their metabolites (Félix–Cañedo, Durán–Álvarez, and Jiménez–Cisneros 2013; Verlicchi et al. 2010) are also discharged into urban wastewater.

Most of the macro pollutants can be eliminated in conventional wastewater treatment plants by chemical and biological processes that are very efficient to remove carbon, nitrogen and phosphorous compounds (Oliveira et al. 2015). However, these methods are not efficient to completely remove the organic compounds present in low concentrations and constantly injected to wastewater streams, as in the case of recalcitrant micro pollutants (Simazaki et al. 2015; Basha et al. 2015; Yan and Song 2014). Therefore, a large number of organic micro pollutants has been detected in sewage lines, rivers, lakes, damps, groundwater and even in tap water in Europe (Gros et al. 2008; Samaras et al. 2013; Lopez et al. 2015), Asia (Simazaki et al. 2015; Sun et al. 2015), USA (Zenobio et al. 2015; Oliveira et al. 2015) and other countries around the world (Félix–Cañedo, Durán–Álvarez, and Jiménez–Cisneros 2013). Literature reports have confirmed the presence of analgesics, antibiotics, antidiabetics, antiepileptics, barbiturates, beta-blockers, diuretics and other pharmaceuticals compounds in the different water sources sampled (Ternes et al. 2001; Ratola et al. 2012).

Contamination of water bodies with traces of prescription drugs and their metabolites is of great concern because they may cause adverse effects on living organisms including humans (Félix–Cañedo, Durán–Álvarez, and Jiménez–Cisneros 2013; Oliveira et al. 2015; Simazaki et al. 2015). For these reasons, every wastewater treatment plant should include an advance oxidation process (AOP) to completely mineralize all the organic contaminants (Cavalcante et al. 2015). Photocatalysis is an important AOP based in the use of a semiconductor

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