Phototransformation of enalapril under natural sunlight radiation and simulated: transformation pathways, environmental and toxicity risk

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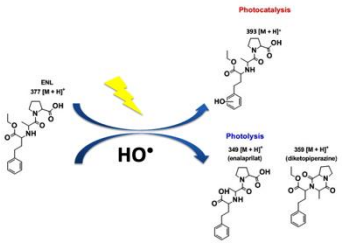
C. G. Aba-Guevara[a], R. Hernández-Tenorio[b*], O. Gaspar-Ramírez[b*], E. González-Juaréz[c], J.L. Guzmán Mar[c], L. Hinojosa-Reyes[c]
[a]Investigador de IIxM CONACYT. Centro de Investigación e Innovación Tecnológica-TecNM/ITNL, Apodaca, N.L., México. [b]Centro de Investigación y Asistencia en Tecnología y Diseño del Estado de Jalisco A.C., Sede Noreste, Apodaca, Nuevo León, México. [c]Universidad Autónoma de Nuevo Léon, UANL, Facultad de Ciencias Químicas, Cd. Universitaria, San Nicolás de los Garza, Nuevo Léon, México.
Corresponding Author: e-mail: rafaelzipoliteumar@gmail.com and ogramirez@ciatej.mx



In the current work, the phototransformation of enalapril (ENL) under photolysis and photocatalysis reactions using natural sunlight radiation and simulated was compared. The semiconductor material chitosan microbeads with C,N(1:10%)-codoped TiO_2 was used as photocatalyst. In photolysis reaction, removal of ENL was incomplete (< 16%) using both radiations. In contrast, total removal of ENL was achieved through the photocatalytic process using both radiations. Proposed transformation pathways during the phototransformation of ENL include hydroxylation and fragmentation reactions. The predicted TPs acute and chronic toxicities corresponding to compounds with *m/z* 409, 363, and 345 may be toxic for aquatic organisms.

Introduction

Pharmaceutical active compounds (PhACs) have been cataloged as "ubiquitous" pollutants detected in wastewater and aquatic environments worldwide [1]. Once in aquatic environments, parent compound of PhACs and its transformation products (TPs) can be naturally attenuated by environmental processes such as biodegradation, sorption, dilution, photolysis, hydrolysis, among other, resulting in an enhanced "mobility" due to polarity increase of the TPs [2]. For this reason, in this work the degradation of enalapril (ENL) under photolysis and heterogeneous photocatalysis processes using chitosan microbeads with C,N-codoped TiO_2 as catalyst and using natural sunlight radiation and simulated in both processes was compared. The main goals of this research were: 1) obtain degradation efficiency of ENL both photolysis and photocatalysis processes; 2) a proposal of transformation pathways of ENL under phototransformation processes; 3) environmental risk assessment and toxicity prediction of ENL and its TPs.

Material and Methods

The chitosan microbeads with C,N-codoped TiO_2 catalyst were synthesized by the sol-gel method under the procedure described by Aba-Guevara et al. 2021 [3]. Photolysis and photocatalysis tests were carried out in a cylindrical quartz batch reactor containing 100 mL at an initial concentration of 5 mg L^{-1} of ENL adjusted at pH 7. ECOSAR software was used as a tool for prediction of the potential toxicological effects such as acute and chronic toxicities of ENL and its TPs against aquatic organisms such as fish, algae and Daphnid.

Results and Discussion

During the photolysis reaction ENL was not completely removed (**Fig. 1**).

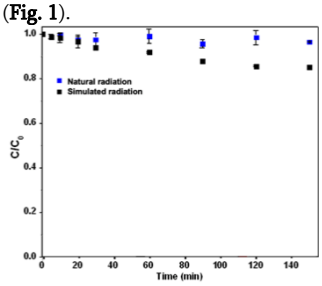


Fig. 1. Photolysis processes of ENL.

During the photocatalytic reaction ENL was entirely removed (**Fig. 2**).

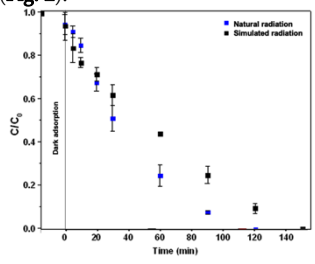


Fig. 2. Photocatalytic processes of ENL.

Several TPs of ENL have been identified under photolysis and photocatalysis reaction [4,5] (**Fig. 3**). In photolysis reaction, the two TPs 359 and 349 seem to be associated with the parent compound of ENL that undergoes processes as cyclization and ester hydrolysis to give diketopiperazine derivative and its main metabolite enalaprilat, respectively [4]. In photocatalysis reaction the major TPs detected are hydroxylated compounds (*m/z* 393), these are generated consequence of HO· radical attack in the parent compound of ENL [5].

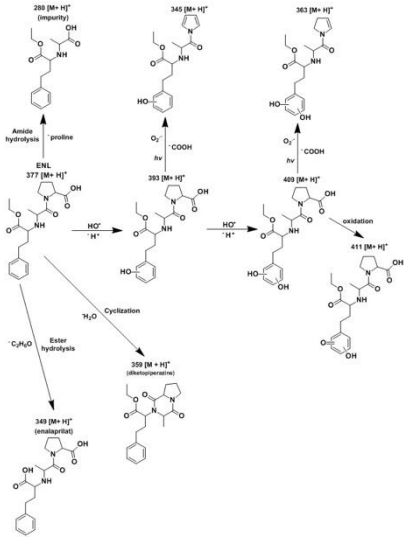


Fig. 3. Proposed phototransformation pathways of ENL [4-5].

Table 3. Prediction of acute and chronic toxicity of ENL and by using ECOSAR (non-toxic > 100 mg L^{-1} (green), harmful 10-100 mg L^{-1} (yellow), toxic 1-10 mg L^{-1}(olive), and very toxic < 1 mg L^{-1} (red).

	Acute toxicity (mg L^{-1})			**Chronic toxicity (mg L^{-1})**		
Compound	Fish (LC50, 96 h)	Daphnid (LC50, 96 h)	Green Algae (EC50, 96 h)	Fish	Daphnid	Green Algae
ENL	1230	728	643	126	79	185
Enalaprilat	1260000	544000	132000	89000	24900	18800
TP 411	259000	121000	404000	20100	6880	6870
TP 409	217	123	92	21	12	24
TP 393	3460	1960	1440	337	189	375
TP 363	62	37	35	6	4	10
TP 359	1480	784	434	133	62	96
TP 345	134	79	67	13	8	19
TP 280	111000	53100	19300	8850	3200	3440

Conclusions

The removal of ENL under photolysis reaction using natural sunlight radiation and simulated was incomplete. However, total removal of ENL was obtained during the photocatalysis reaction using a chitosan microbeads C,N-TiO_2 catalyst under both radiation sources. Hydroxylation and fragmentation reactions can be used as reference for the formation of the main TPs of ENL, thus, hydroxylated TPs (*m/z* 393) and enalaprilat (*m/z* 349) can be main TPs generated in photocatalysis and photolysis reaction, respectively. Using prediction ECOSAR some TPs of ENL, for example, TPs 409, 363, and 345 may be toxic against aquatic organisms.

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