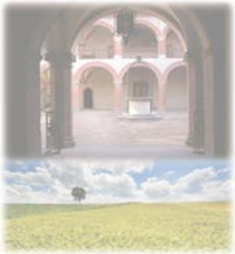
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DİAZEPAM DEGRADATİON USİNG SOLAR PHOTOCATALYSİS

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ABSTRACT: Benzodiazepine drugs are used all over the world for anxiety disorders, as anticonvulsants and anti-epileptics, and for terminally ill people as part of essential medicines list from the World Health Organisation (WHO). The WHO list includes diazepam, which is frequently found as residual pollutant in secondary effluents from wastewater treatment plants (WWTPs). Aiming at the complete removing of this substance from the aqueous environments, two experiments were carried out using Advanced Oxidation Process (AOPs) by simulated solar irradiation with or without TiO_2 as catalyst. Photocatalysis was much efficient (half-life = 6 hours) than photolysis (half-life = 34 hours) giving a series of byproduct that were identified by an LC system coupled to a hybrid linear quadrupole ion trap (LTQ)-Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer.

KEYWORDS: Diazepam; Advanced Oxidation Process; Photolysis; Photo-catalysis; Byproducts.

INTRODUCTION

Pharmaceutical compounds (PhACs), indispensable to cure different diseases, have been detected in surface water, in groundwater and in drinking water in a number of countries since the mid-1990s. These compounds represent a big problem for the environment and life because can alter the endocrine system of humans and wildlife and, at very low concentrations, may accelerate the evolution of antimicrobial resistant bacteria. Among these "emerging organic contaminants", benzodiazepines have recently received high attention for their persistency in the effluents from secondary biological treatment normally performed in municipal Waste Water Treatment Plants (WWTP) (1, 2). Diazepam (7-chloro-l-methyl-5-phenyl-1,4-benzodiazepin-2-one), $C_{16}H_{13}ClN_2O$, MW 284.743 g mol^{-1}, is one of most known member of these pharmaceuticals and is used to relieve anxiety, muscle spasms, and seizures and to control agitation in adults and in children (3). Aiming at the complete removal of this pharmaceutical, Advanced Oxidation Processes (AOPs) were applied by using a solar irradiation simulator (Suntest) and TiO_2 as catalyst.

METHODOLOGY

The secondary effluent (pH 6.2±0.4; BOD 10±5 mg L^{-1}; COD 20±8 mgO_2 L^{-1}; NO_2 50±5 mg L^{-1}) obtained from the Advanced WWTP located at Al-Quds University-Palestine was spiked with the drug (10 mg L^{-1}; 35 μM) and the depletion of diazepam concentration was monitored during photochemical or photocatalytic experiments using a Suntest CPS Solar Simulator (Atlas-Heraeus, Germany) equipped with a xenon lamp, a temperature sensor and a water-cooling circuit. The xenon lamp was filtered by an optically stable borosilicate UV filter (cut-off 290 nm) delivering a light emission spectrum similar to that of the sun. The diazepam residual concentrations were determined, and its degradation products were identified, by using an LC system coupled to a hybrid linear quadrupole ion trap (LTQ)-Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer (Thermo Fisher Scientific, Bremen, Germany).

FINDINGS

Table 1 and figures 2 and 3 show AOPs results. Photocatalysis was the most efficient AOP ($t_{1/2}$=5.19 h). Five byproducts were found during the photolytic degradation of the parent substance, of which three were also detected as photolysis byproducts. The pure standard solution used as a control in the darkness and in presence of TiO_2 shows a slight loss of soluble diazepam during the experiment due to its adsorption on the surface of the catalyst. Hydrolysis products were not found in the solution kept in the dark.

Oxidation Process	n	$t_{1/2}$	k	R^2
Photolysis	1	1853 (min) ÷ 30.89 (h)	3.74E-04 (min^{-1})	0.9993
Photocatalysis	0	311 (min) ÷ 5.19 (h)	0.05280 ($\mu M\ min^{-1}$)	0.9950

Table 1. Kinetic parameters of diazepam photodegradation: n, reaction order; $t_{1/2}$, half-life; k, kinetic constant; R^2, determination coefficient. Values were obtained on the basis of three replicate experiments.

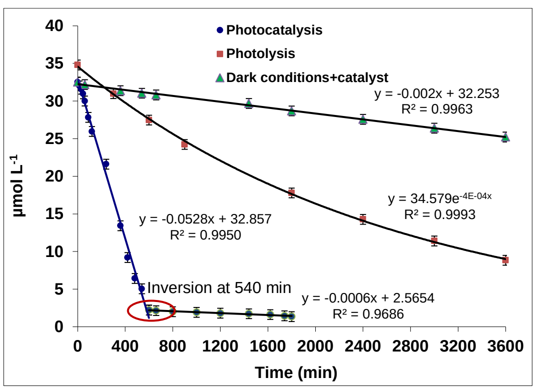

Figure 1. Fraction of diazepam remaining in different conditions.

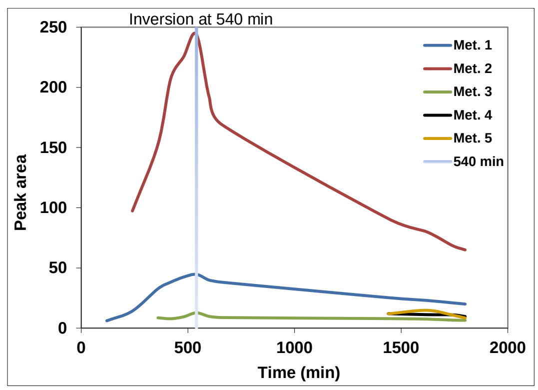

Figure 2. Formation of diazepam byproducts during the photocatalytic process.

CONCLUSIONS

Diazepam underwent degradation both via photolysis and photocatalysis. The TiO_2 catalytic process was able to destroy most of the parent substance and its byproducts confirming as this technique could be conceptually and practically beneficial to remove diazepam from an aquatic environment.

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