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RESEARCH ARTICLE

Solar photolysis versus TiO_2-mediated solar photocatalysis: a kinetic study of the degradation of naproxen and diclofenac in various water matrices

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Abstract Given that drugs and their degradation products are likely to occur as concoctions in wastewater, the degradation of a mixture of two nonsteroidal anti-inflammatory drugs (NSAIDs), diclofenac (DCF) and naproxen (NPX), was investigated by solar photolysis and titanium dioxide (TiO_2)-mediated solar photocatalysis using an immersion-well photoreactor. An equimolar ratio (1:1) of both NSAIDs in distilled water, drinking water, and river water was subjected to solar degradation. Solar photolysis of the DCF and NPX mixture was competitive particularly in drinking water and river water, as both drugs have the ability to undergo photolysis. However, the addition of TiO_2 in the mixture significantly enhanced the degradation rate of both APIs compared to solar photolysis alone. Mineralization, as measured by chemical oxygen demand (COD), was incomplete under all conditions investigated. TiO_2-mediated solar photocatalytic degradation of DCF and NPX mixtures produced 15 identifiable degradants corresponding to degradation of the individual NSAIDs, while two degradation products with much higher molecular weight than the parent NSAIDs were identified by liquid chromatography mass spectrometry (LC-MS) and Fourier transform-ion cyclotron resonance-mass spectrometry (FT-ICR-MS). This study showed that the solar light intensity and the water matrix appear to be the main factors influencing the overall performance of the solar photolysis and TiO_2-mediated solar photocatalysis for degradation of DCF and NPX mixtures.

Keywords Pharmaceuticals · Sunlight · Photocatalysis · Photolysis · Active pharmaceutical ingredients · Degradation

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Introduction

Drug products (pharmaceuticals) containing active pharmaceutical ingredients (APIs), despite being originally designed to treat a variety of ailments in humans and animals, have in fact turned out to adversely impact the environment due to their excessive use and subsequent occurrence or accumulation in surface water, groundwater, urban wastewater, and also drinking water (Santos et al. 2010; Ziylan and Ince 2011). The nonbiodegradable nature and relatively high solubility of the APIs render conventional biological and chemical treatments ineffective (Mompelat et al. 2009) as a result of a reduced likelihood of sorption, electrostatic interactions, and chemical bonding with particulates. This leads to an increased presence and persistence of the parent drugs and their metabolites (and their inherent biological activities) in both aquatic and terrestrial environments (Klavarioti et al. 2009).

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