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TiO_2 photocatalysis of naproxen: Effect of the water matrix, anions and diclofenac on degradation rates

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HIGHLIGHTS

- TiO_2 photocatalytic oxidation of naproxen was studied in the presence of anions and diclofenac.
- Addition of a dual anion system had a greater effect on the degradation rate.
- Degradation rates of diclofenac were greater than naproxen in mixtures.
- High photocatalytic oxidation of naproxen did not correlate with a significant decrease in the dissolved organic carbon removal.
- Degradation products, were identified using liquid chromatography and mass spectrometry.

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ABSTRACT

The TiO_2 photocatalytic degradation of the active pharmaceutical ingredient (API) naproxen (NPX) has been studied using a laboratory-scale photoreactor equipped with a medium pressure mercury lamp. UV/TiO_2 photocatalysis proved highly efficient in the elimination of NPX from a variety of water matrices, including distilled water, unfiltered river water and drinking water, although the rate of reaction was not always proportional to TiO_2 concentration. However, the NPX degradation rate, which follows first-order kinetics, was appreciably reduced in river water spiked with phosphate and chloride ions, a dual anion system. Addition of chloride into drinking water enhanced the TiO_2-photocatalysed degradation rate. Competitive degradation studies also revealed that the NPX degradation was greatly reduced in the presence of increased concentrations of another API, diclofenac (DCF). This was established by (i) the extent of mineralization, as determined by dissolved organic carbon (DOC) content, and (ii) the formation of intermediate NPX by-products, identified using liquid chromatography and electrospray ionization (positive and negative mode) mass spectrometry techniques. This study demonstrates that competition for active sites (anions or DCF) and formation of multiple photoproducts resulting from synergistic interactions (between both APIs) are key to the TiO_2-photocatalysed NPX degradation.

1. Introduction

Naproxen (NPX), a 2-arylpropionic acid derivative, is commonly used as a non-steroidal anti-inflammatory drug (NSAIDs) for pain relief and the treatment of both osteoarthritis and rheumatoid arthritis (Grenni et al., 2013). Active pharmaceutical ingredients (APIs), such as NPX, are frequently detected in sewage treatment plant influents and effluents as well as environmental matrices such as surface water (Heberer, 2002; Fatta-Kassinos et al., 2011; Ziylan and Ince, 2011). The concentrations of NPX in wastewater treatment plant (WWTP) effluents are reported to range from 25 ng L^{-1} to 33.9 μg L^{-1} (Marotta et al., 2013). Its occurrence in the environment has been highlighted in several monitoring studies (Andreozzi et al., 2003; Jelic et al., 2011; Vidal-Dorsch et al., 2012) and so has its presence in drinking water (Benotti et al., 2009). Furthermore, bioassays of NPX, and of mixtures of NPX and other anti-inflammatory drugs including diclofenac (DCF), have demonstrated high chronic toxicity (Cleuvers, 2004; Feng et al., 2013). Thus, the potential ecotoxic risks and long term

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