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Research Paper

Photolysis and TiO_2-catalysed degradation of diclofenac in surface and drinking water using circulating batch photoreactors

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Environmental context. Diclofenac, a common non-steroidal anti-inflammatory drug, is not completely removed from surface and drinking water by conventional treatment methods. Consequently, this drug is present in the aquatic environment and has been subsequently linked to toxic effects on organisms. We show that photolysis and TiO_2-catalysed degradation in circulating batch reactors efficiently results in diclofenac removal under a variety of conditions. These photochemical methods thus may lead to more effective water treatment processes.

Abstract. The occurrence of diclofenac (DCF) as an emerging pollutant in surface waters and drinking water has been attributed to elevated global consumption and the inability of sewage treatment plants to remove DCF. In this study, DCF spiked drinking water and river water was subjected to photolysis and TiO_2 photocatalytic treatments in a circulating laboratory-scale (immersion-well) and a demonstration-scale loop reactor (Laboclean). The operational parameters for the immersion-well reactor were optimised as follows: TiO_2 P25 loading, 0.1 g L^{-1}; natural pH, 6.2; initial concentration, 30 mg L^{-1}; water type, distilled water. Complete DCF removal was realised within 15 min under the optimised conditions using the immersion-well reactor. Sunlight-mediated photochemical degradation required a prolonged exposure period of up to 360 min for complete DCF removal. DCF in distilled and drinking water was efficiently degraded in the larger Laboclean reactor. Differences were, however, observed based on their pseudo-first-order rate constants, which implies that the water matrix has an effect on the degradation rate. Six major photoproducts, 2-(8-chloro-9*H*-carbazol-1-yl)acetic acid, 2-(8-hydroxy-9*H*-carbazol-1-yl)acetic acid, 2,6-dichloro-*N*-*o*-tolylbenzenamine, 2-(phenylamino)benzaldehyde, 1-chloromethyl-9*H*-carbazole and 1-methyl-9*H*-carbazole, generated from TiO_2 photocatalysis of DCF were identified by liquid chromatography–mass spectrometry (LCMS) and Fourier transform–ion cyclotron resonance–mass spectrometry (FT-ICR-MS). This work has shown that photocatalytic degradation kinetics of DCF are dependent on both the geometry of the photoreactor and the nature of the water matrices.

Additional keywords: advanced oxidation processes, pharmaceuticals, photocatalysis, titanium dioxide.

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Introduction

Pharmaceuticals and personal care products have been frequently detected in waterways in trace levels ranging from parts per trillion (ppt, ng L^{-1}) to parts per billion (ppb, μg L^{-1}).[1,2] The presence of pharmaceuticals in the water cycle largely arises from their excretion either as metabolites or in their unmetabolised form. Pharmaceuticals and their active pharmaceutical ingredients (APIs) are generally designed to be both highly active and stable to efficiently execute a specific physiological action in humans and animals.[3] Their incomplete removal by wastewater treatment plants (WWTPs) thus represents an important urban source of these pharmaceuticals and their APIs in the aquatic environment.[4,5] In view of this, pharmaceutical abatement requires innovative technologies to combat their continued presence in the environment.[6] Advanced oxidation processes (AOPs) have been proposed as a superior technology over that of conventional water treatment methodologies for the removal of recalcitrant pharmaceuticals and other endocrine-disrupting chemicals.[7–9] All AOPs are based on the in situ generation of highly reactive and short-lived reactive oxygen species such as $HO^{\bullet}$, H_2O_2, O_3 and $O_2^{\bullet-}$ for the mineralisation of organic compounds.[10] Among various AOPs, TiO_2 photocatalysis has been extensively studied for the photodecomposition of a variety of pharmaceuticals used for different therapeutic effects.[11–14] One of the most widely consumed class of drugs globally are non-steroidal anti-inflammatory drugs (NSAIDs), which are primarily used to reduce inflammation.[15] DCF (2-[(2,6-dichlorophenyl)-amino] phenylacetic acid, diclofenac) a commonly used NSAID, is important environmentally because of its frequent detection in