SCCWRP #1224

Photolysis of the nonsteroidal anti-inflammatory drug sulindac: elucidation of kinetic behaviour and photodegradation pathways in water

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Abstract

Non-steroidal anti-inflammatory drugs are recognized widely as emerging contaminants. Sulindac has received additional attention as a prodrug in cancer treatment and because of its detection in drinking water and wastewaters. Nevertheless, there is limited knowledge about its kinetic behaviour and fate in the aquatic environment. In this work, the direct photolysis of sulindac, in which photochemical reactions were monitored and phototransformation products identified, was investigated under prolonged periods using UV-A and UV-B radiation and pH conditions (2 and 7) to evaluate the effect of the protonation state and the efficiency of the photolytic process. A novel kinetic mechanism has been proposed in which sulindac exhibits a consecutive reaction pathway, with pseudo-first order kinetics for rapid and reversible Z to E isomerization. Once photoequilibrium was reached, second-order degradation of the isomers in the presence of the new photodegradation products was observed. Photochemical transformation was faster under UV-B irradiation and lower pH, which suggests greater persistence of sulindac at more relevant environmental conditions of UV-A and pH 7. Two novel and major byproducts were identified, corresponding to the oxidative cleavage of the alkene exo to the indene system. The degradation pathway is mainly photoinduced, enhanced by acidic conditions and presumes the double bond as the most reactive site for the parent compound. This research demonstrates an approach for determining kinetics of compounds under challenging conditions, including, absorption from multiple electronic transitions, photoinduced products with unknown extinction coefficients, concentration dependence, photoinduced sensitizing intermediates, and speciation effects. Our work greatly improves our understanding of the degradation process of sulindac and will contribute to exposure assessments and treatment methodologies for this compound in impacted waters.