

Kinetic and mechanistic studies of the photolysis of metronidazole in simulated aqueous environmental matrices using a mass spectrometric approach

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Abstract Metronidazole is a nitroimidazole antibiotic derivative used in humans against anaerobic bacteria and protozoa. In light of the recent detection of metronidazole in hospital wastes, sewage treatment plants, and surface waters, along with its known sensitivity toward photolytical degradation, this study aimed to model the photolysis in environmental waters by sunlight as a natural attenuation process. To this end, the degradation of metronidazole in a

photoreactor simulating solar radiation (Suntest CPS) was compared in five different aqueous matrices: deionized water, artificial freshwater (AFW), AFW supplemented with nitrate (5 mg/L), AFW containing humic acids, and AFW with both nitrate and humic acids. Irrespective of the test medium, the degradation of the metronidazole solutions (10 and 0.02 mg/L) was found to follow pseudo-first-order kinetics. Degradation rates were dependant on the matrix, with humic acids causing a two to threefold decrease in the rate constants while the presence of nitrate had no marked effect on the kinetics. Therefore, the direct photolysis of metronidazole was apparently attenuated through a filter effect of humic acids. Screening of the irradiated water samples by ultra performance liquid chromatography/quadrupole time-of-flight mass spectrometry allowed separation and characterisation of four principal phototransformation products of the antibiotic. The high-resolution MS data pointed to the formation of two rearrangement products ($C_6H_{10}N_3O_3$) isobaric with metronidazole, a third product deriving from the elimination of NO from the nitro group ($C_6H_{11}N_2O_2$), and a fourth unidentified degradate with a likely elemental composition of $C_5H_{10}N_3O$.

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Introduction

In recent years, the detection of a large number of pharmaceutical substances in wastewater, freshwater, and groundwater resources has raised worldwide concerns about potential environmental risks [1–3]. Most drugs are