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Photodegradation of the antibiotics nitroimidazoles in aqueous solution by ultraviolet radiation

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ABSTRACT

The objective of this study was to analyze the efficacy of ultraviolet (UV) radiation in the direct photodegradation of nitroimidazoles. For this purpose, i) a kinetic study was performed, determining the quantum yield of the process; and ii) the influence of the different operational variables was analyzed (initial concentration of antibiotic, pH, presence of natural organic matter compounds, and chemical composition of water), and the time course of total organic carbon (TOC) concentration and toxicity during nitroimidazole photodegradation was studied. The very low quantum yields obtained for the four nitroimidazoles are responsible for the low efficacy of the quantum process during direct photon absorption in nitroimidazole phototransformation. The R_{254} values obtained show that the dose habitually used for water disinfection is not sufficient to remove this type of pharmaceutical; therefore, higher doses of UV irradiation or longer exposure times are required for their removal. The time course of TOC and toxicity during direct photodegradation (in both ultrapure and real water) shows that oxidation by-products are not oxidized to CO_2 to the desired extent, generating oxidation by-products that are more toxic than the initial product. The concentration of nitroimidazoles has a major effect on their photodegradation rate. The study of the influence of pH on the values of parameters ε (molar absorption coefficient) and k'_E (photodegradation rate constant) showed no general trend in the behavior of nitroimidazoles as a function of the solution pH. The components of natural organic matter, gallic acid (GAL), tannic acid (TAN) and humic acid (HUM), may act as promoters and/or inhibitors of OH· radicals *via* photoproduction of H_2O_2. The effect of GAL on the metronidazole (MNZ) degradation rate markedly differed from that of TAN or HUM, with a higher rate at low GAL concentrations. Differences in MNZ degradation rate among waters with different chemical composition are not very marked, although the rate is slightly lower in wastewaters, mainly due to the UV radiation filter effect of this type of water.

1. Introduction

Ultraviolet (UV) radiation is frequently applied to disinfect water intended for human consumption and wastewater. Due to the greater chemical contamination of water, UV radiation (Hijnen et al., 2006) is increasingly proposed as a technology to remove organic micropollutants, underlining its high efficacy to eliminate certain pesticides and pharmaceuticals from water (Kang et al., 2004; Lazarova and Savoye, 2004).

Significant advances have recently been made in our understanding of the photochemical processes undergone by organic contaminants and pharmaceuticals in aqueous

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medium (Boreen et al., 2004; Latch et al., 2003; Packer et al., 2003). However, fewer data are available on their photochemical transformation (Boreen et al., 2003). The majority of pharmaceuticals are photo-active, i.e. able to absorb light. This is because their structures generally contain aromatic rings, heteroatoms, and other functional groups that make them prone to absorb UV–vis radiation (direct photolysis) or to react with photosensitizing species capable of inducing pharmaceutical photodegradation in natural water (indirect photolysis).

During direct photolysis, photon absorption gives rise to compounds in excited electronic states that are susceptible to chemical transformation. However, indirect or sensitized photolysis leads to the transformation of contaminants by energy transference or by chemical reactions with transitory species formed by the presence of light, such as hydroxyl radicals (HO•), singlet oxygen ($^1O_2$), and triplet excited states of natural organic matter (^{3}NOM*) (Schwarzenbach et al., 2003; Canonica et al., 1995; Canonica and Tratnyek, 2003; Gerecke et al., 2001; Zepp et al., 1985). Hence, the efficacy of direct photooxidation is governed by the contaminant absorption spectrum and the quantum yield of the process (Φ), whereas the dominant mechanism in indirect photolysis is the reaction between OH• radicals and the micropollutant. Hence, addition of H_2O_2 during the photooxidation process accelerates the micropollutant removal rate, reducing the UV radiation required in comparison to direct photooxidation (Rosenfeldt and Linden, 2004); this is due to the generation of highly reactive radicals in H_2O_2 decomposition (Glaze et al., 1987).

Nitroimidazole antibiotics were recently detected in waters at concentrations of 0.1–90.2 μg/L (Lindberg et al., 2004). They are widely used to treat infections caused by anaerobic and protozoan bacteria (e.g., *Trichomonas vaginalis* and *Giardia lamblia*) in humans and animals and are added to chow for fish and fowl, leading to their accumulation in animals, fish-farm waters and, especially, meat industry effluents. Little is yet known about the capacity of current water treatment systems to remove nitroimidazoles (Wennmalm and Gunnarsson, 2005) but it is not expected to be very high given the complex chemical structure of these compounds.

The objective of the present study was to analyze the efficacy of UV radiation in the direct photooxidation of nitroimidazoles. For this purpose, i) a kinetic study was conducted to determine the quantum yield of the process; and ii) the influence of the different operational variables (initial concentration of antibiotic, pH, presence of NOM components and chemical composition of water) was analyzed, and the time course of total organic carbon (TOC) concentration and toxicity during nitroimidazole photodegradation was studied.

2. Experimental

2.1. Reagents

All chemical reagents used (phosphoric acid, sodium hydroxide, hydrogen peroxide, atrazine, gallic acid, tannic acid, humic acid, acetonitrile, ammonium acetate, and nitroimidazoles) were high purity analytical grade reagents supplied by Sigma–Aldrich. Ultrapure water was obtained using Milli-Q® equipment (Millipore). Fig. 1 depicts the chemical structure and the acidity constant values of the nitroimidazoles selected for this study: Metronidazole (MNZ), Dimetridazole (DMZ), Tinidazole (TNZ) and Ronidazole (RNZ).

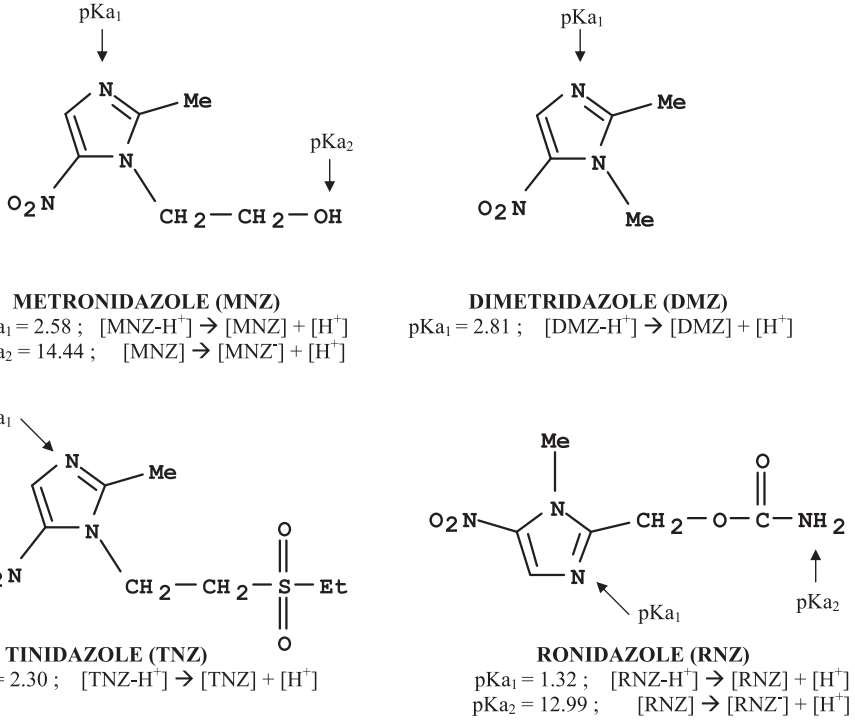

Fig. 1 – Chemical structure of the nitroimidazoles studied.