THE ROLE OF REACTIVE SPECIES IN THE TRANSFORMATION OF TRIMETHOPRIM DURING THE UV-LED/CHLORINE PROCESS

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The WHO defined safe drinking water as "water that does not represent any significant risk to health over a lifetime of consumption, including different sensitivities that may occur between life stages". The production of adequate quality drinking water is a universal problem today, partly due to the biologically active and persistent organic pollutants that cannot be removed by conventional water treatment processes. Among pharmaceuticals, antibiotics have a high ecological, and health risk, because of the development of antibiotic-resistant bacterial strains. Over 30,000 deaths are caused annually by the infections of these strains of bacteria. Consequently, the elimination of antibiotics requires additional or quaternary water treatment processes, such as UV/chlorine method.

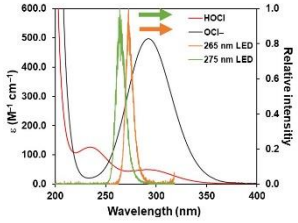

Fig.1: Molar absorbance of HOCl and OCl^- and LEDs emission spectra

For the UV/FAC (FAC: freely available chlorine, i.e. the sum of HOCl and OCl^-) process, considering the UV-Vis absorption spectrum of HOCl and OCl^-, the LEDs emitting at 265 and 275 nm are a good alternative to traditional low-pressure mercury vapor lamps emitting 254 nm photons. In this study, two types of LEDs (with emission maxima at 265 nm and 275 nm) were used for the photolysis of HOCl/OCl^- solutions. The ratio of protonated and deprotonated forms (pK_a = 7.4) determines the absorption properties of the treated solution and the steady-state concentration of the formed radicals, such as $^{\bullet}OH$, $Cl^{\bullet}$, $Cl_2^{\bullet-}$ and $ClO^{\bullet}$.

The UV photolysis of HOCl and OCl^-, the role of the various reactive species in trimethoprim (a widely used antibiotic) transformation were studied under different conditions. The quantum yield of the HOCl photolysis was determined and found to be 0.74 and 0.94 at 265 and 275 nm, respectively. These values for OCl^- photolysis were 0.64 and 0.58. HOCl reacts fast with trimethoprim, while there is no reaction with OCl^-. Thus, the pH affects strongly the relative contribution of radical-initiated reactions to the trimethoprim transformation. The trimethoprim reacts fast with $^{\bullet}OH$ and Cl-containing radicals ($Cl^{\bullet}$, $ClO^{\bullet}$, $Cl_2^{\bullet-}$) so the transformation rate increased with increasing oxidant concentration, even at high pH. The contribution of $^{\bullet}OH$-based reaction depends on pH; at acidic and neutral pH the $^{\bullet}OH$ originated from the HOCl photolysis and has a significant role ($[^{\bullet}OH]_{ss} \approx 4.5\times10^{-13}$ M), while at basic pH the importance of $^{\bullet}OH$ is moderated ($[^{\bullet}OH]_{ss} \approx 3.2\times10^{-14}$ M), mainly chlorine-containing radicals ($Cl^{\bullet}$, $ClO^{\bullet}$, $ClO_2^{\bullet}$) are formed and responsible for the transformation.

Special attention was paid to the chlorinated products and matrix effect, using biologically treated wastewater as a matrix. The transformation rate of trimethoprim was only slightly affected by this matrix, while the formation of chlorinated compounds was suppressed, due to the reaction of $Cl^{\bullet}$ and HCO_3^-.

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