

ABSTRACT

Yang He, M.S., Purdue University, June, 2013. Photochemical reactions of Ibuprofen, Naproxen and Tylosin. Major Professor: Inez Hua.

Pharmaceuticals and personal care products (PPCPs) include a wide range of compounds that are used extensively and sometimes daily by people. Some PPCPs have been detected in surface water (streams, rivers, lakes) due to incomplete removal in wastewater treatment plants. The water contaminated by PPCPs is harmful to aquatic organisms and human. Naproxen (NXP), ibuprofen (IBP) and tylosin (TYL) are chosen as representative PPCPs in the current research, because they are consumed in large quantities throughout the world and there is limited data about photodegradation of these compounds in aqueous solution at the wavelength of 254 nm.

The combination of ultraviolet light (UV_{254nm}) and hydrogen peroxide (H_2O_2) (UV/H_2O_2) degraded greater than 90% of the initial concentration of NXP and IBP within 3 min ($k = 0.018\text{ sec}^{-1}$, $k = 0.023\text{ sec}^{-1}$ for NXP and IBP, respectively). Under direct photolysis (UV_{254nm}) and at pH = 7, 20 min of treatment was required to obtain 90% degradation ($k = 0.0028\text{ sec}^{-1}$ for NXP, $k = 0.0023\text{ sec}^{-1}$ for IBP). Under the same conditions, molar absorptivity (ϵ) and quantum yield (ϕ) of each compound were determined (for NXP, $\epsilon = 4240\text{ M}^{-1}\text{cm}^{-1}$ and $\phi = 0.008$; for IBP, $\epsilon = 299\text{ M}^{-1}\text{cm}^{-1}$ and $\phi = 0.098$). Overall, degradation rate constants increased with increasing initial H_2O_2 level (0 mM, 1mM and 3 mM) and increasing pH values (at pH =3, $k = 0.0016\text{ sec}^{-1}$ for NXP and $k = 0.0015\text{ sec}^{-1}$ for IBP; at pH =9, $k = 0.0036\text{ sec}^{-1}$ for NXP and $k = 0.0029\text{ sec}^{-1}$ for IBP). The presence of nitrate increased the photolysis rate constants of both NXP and IBP slightly due to hydroxyl radical formation from irradiation of nitrate. The rate constants were decreased because of screening light effect from the addition of natural organic matter (NOM): the rate constants were reduced by 18% and 36% for NXP and by 30% and 46% for IBP degradation with fulvic acid (FA) and humic acid (HA), respectively. To understand the mechanism of degradation under the

UV_{254nm}/H₂O₂ with NOM, a model was constructed to predict the phototransformation rate constants of NXP and IBP. From the model results, it could be seen that there was a concentration of H₂O₂ corresponding to the maximum enhancement of photolysis of select PPCPs. The mineralization of NXP and IBP was 30% and 32%, respectively.

The degradation behaviors of TYL under UV_{254 nm} and UV_{254nm}/H₂O₂ were quite different from the degradation of NXP and IBP. TYL was present as a mixture of two compounds: TYL A and TYL B. Photoisomerization and photodegradation proceeded at the same time, and photoisomerization reactions predominated. A kinetic model was constructed for determining the kinetic data. Under UV_{254nm} condition and at pH = 7, for TYLB, rate constant for forward reaction $k_f = 0.069 \text{ sec}^{-1}$, rate constant for backward reaction $k_r = 0.023 \text{ sec}^{-1}$ and degradation rate constant $k_d = 0.00068 \text{ sec}^{-1}$, and for TYLA, $k_f = 0.075 \text{ sec}^{-1}$ $k_r = 0.019 \text{ sec}^{-1}$ $k_d = 0.00093 \text{ sec}^{-1}$. Solution pH values and the presence of nitrate and NOM did not have any significant influences on the direct photolysis (UV_{254nm}) of TYL. Also at pH =7, the addition of H₂O₂ did not dramatically affect the photoisomerization reaction, but accelerated the photodegradation of TYL (for TYLB, k_d was increased to 0.0016 sec^{-1} ; for TYLA, $k_d = 0.0013 \text{ sec}^{-1}$).

Selected major photochemical reaction by-products were identified by Gas Chromatography/Mass Spectroscopy (GC/MS) and Liquid Chromatography/Mass Spectroscopy (LC/MS). For both UV_{254nm} and UV_{254nm}/H₂O₂ conditions, the first step of NXP and IBP photodegradation is decarboxylation, then the intermediates were oxidized to ketone and other products. Possible pathways of NXP and IBP degradation are proposed. For TYL, photoisomerization results from the γ/δ rotation of bond of the ketodiene on the TYL ring.