

## The Photocatalytic Degradation of Beta-Blockers: A Structure-Activity Study

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Environmental contamination by organic wastes poses a looming threat to aquatic ecosystems and sources of drinking water all over the world. In just the US, organic waste contaminants, including veterinary and human antibiotics, prescription and non-prescription drugs, and steroids, were found in 80% of surveyed streams (1). Among the general classes of organic wastes, pharmaceutical and personal care products (PPCPs) present a unique challenge. PPCPs, including general classes of drugs such as hormones, antibiotics, and antimicrobials, and personal care products such as toothpastes, soaps, perfumes, and sunscreens, play significant roles in the daily routines of many consumers and are widely available over the counter (2). Due to their beneficial properties, low risk of abuse, and high demand, these products have received very little regulatory attention with regard not only to consumption, but also to disposal, either indirectly through excretion or directly through dumping down the drain. Furthermore, as there are not strict guidelines concerning environmental concentrations of PPCPs, sewage treatment plants and wastewater treatment plants are not wholly effective at removing them before discharging waste, allowing these contaminants to accumulate in ecosystems.

Though most are not currently present at harmful levels, PPCP concentrations are projected to increase, and the effects of consistent and heightened exposure are not currently known. To combat this, photocatalysis provides an eco-friendly alternate pathway that can be implemented before the discharging of effluent. With photocatalysis, photocatalytic materials can utilize ultraviolet or visible light to break down analytes such as PPCPs into simpler products. To do this, most photocatalysts produce reactive oxygen species such as hydroxyl or superoxide radicals to facilitate degradation, though some photocatalysts can directly oxidize analytes through oxidation via an electron hole.

In this study, I compared the efficacy of two photocatalysts,  $\text{TiO}_2$  and  $\text{BiOCl}$ . While  $\text{TiO}_2$  has been heavily studied and is known to produce reactive hydroxyl radicals,  $\text{BiOCl}$  is a more recently introduced photocatalyst with enhanced activity but whose mechanism is not well understood, though it has been hypothesized to primarily use direct hole oxidation. In order to determine which mechanism  $\text{BiOCl}$  employs, I used scavenging compounds to shut down specific reaction pathways and then monitored to determine how the addition of scavengers affected the rate constant and products formed. I chose ibuprofen and atenolol as my target pharmaceuticals, as both are available over the counter and atenolol (a beta-blocker) has been detected in sewage effluent in Brunswick.

Ibuprofen ( $50 \mu\text{M}$ ) was photolyzed using 254 nm light in the presence of  $\text{BiOCl}$ . In some experiments, quenchers (oxalate, t-butyl alcohol, or 1,4-benzoquinone) were added to the solution. Rate constants for photodegradation of ibuprofen in the presence  $\text{BiOCl}$  were determined using HPLC to monitor the decrease in ibuprofen concentration and fitting the data to a pseudo-first order kinetics model. Photodegradation products were determined using chip-based nanoLC analysis with a 6530 Q-TOF instrument.

Preliminary work using quenchers in experiments with  $\text{BiOCl}$  has supported the hypotheses that  $\text{BiOCl}$  reacts via direct hole oxidation as its primary mechanism. While trials with a hydroxyl radical quencher and superoxide radical quencher did not significantly affect the rate constant, the addition of a hole quencher caused the rate constant to become ~18x slower.

## References

1. Kolpin, D.W.; Furlong, E.T.; Meyer, M.T.; Thurman, E.M.; Zaugg, S.D.; Barber, L.B.; Buxton, H.T. Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999-2000: A National Reconnaissance. *Environ. Sci. Technol.* **2002**, *36*, 1202-1211.
2. Wong, M.; Liu, J.; Pharmaceuticals and personal care products (PPCPs): A review on environmental contamination in China. *Environ. Int.* **2013**, *59*, 208-224.