The Photocatalytic Degradation of 17α-ethynylestradiol (EE2) and Related Estrogens

Kevin Fleshman '23

Endocrine disrupting chemicals (EDCs) are a group of chemicals that interfere with the function of the endocrine system of humans and wildlife by inhibiting hormonal synthesis and metabolism (L. Barreiros et al. 2016). EDCs are becoming an even more imminent issue to the environment because they are introduced to water systems via human excretion and are incompletely removed by wastewater treatment plants (WWTPs) causing their bioaccumulation in aquatic environments and subsequent entrance into the food chain.

Estrogens of synthetic and natural origin contribute to the EDCs that enter water systems. 17β-estradiol (E2) and 17α-ethynylestradiol (EE2) are two EDCs with higher endocrine disruption potency (L. Barreiros et al. 2016). EE2 is a synthetic estrogen derived from the natural estrogen E2 and mostly used as birth control (Diamanti-Kandarakis et al. 2009). The presence of E2 and EE2 in the environment has been associated with fish feminization, reduction in reproductive fitness, and an increase of breast and testicular cancer in humans (L. Barreiros et al. 2016). These estrogens have the potential to bioaccumulate and enter the food chain, hence the European Union adding E2 and EE2 to their list of emerging aquatic pollutants included in their Water Framework Directive. To alleviate the bioaccumulation of estrogens such as EE2 and E2, their removal from water and wastewater, is crucial. Photocatalytic degradation is a promising technique for estrogen removal from water systems.

Photocatalysts are solid particles that degrade organic contaminants in water when irradiated with light. Ideally, the degradation products, or photoproducts, are less harmful forms, with full degradation producing carbon dioxide and water. Most work has been directed at titanium dioxide (TiO_2) as an environmental contaminant photocatalyst, but other photocatalysts are being explored with the goal of more rapidly or more completely degrading contaminants. A newer photocatalyst is bismuth oxychloride (BiOCl). Recent work has provided evidence that BiOCl uses a different degradation mechanism, which can result in the generation of different degradation products (Arthur et al. 2018; Speller 2021; Price 2022).

The goal of my proposed research was to study the photocatalytic degradation of E2 and EE2 as representatives of natural and synthetic estrogens using BiOCl and to compare photodegradation via BiOCl and TiO_2. Titanium dioxide and BiOCl may degrade the model estrogens at different rates and may also produce different degradation products. I hypothesized that BiOCl, using a different degradation mechanism, will be able to degrade these compounds more effectively. My project focused on determining which photocatalysts is the most effective for breaking down these representative models of natural and synthetic estrogenic compounds.

Bismuth oxychloride and TiO_2 exhibit different reaction kinetics upon photocatalytic degradation of EE2 and E2 under the same experimental conditions (Figure 1A-B). Bismuth oxychloride exhibits pseudo-first order kinetics hence the exponential decay of the estrogens, while TiO_2 exhibits zero-order kinetics as seen from its linear decay of both estrogens (Figure 1A-B). The zero-order kinetics that TiO_2 exhibits is indicative of a constant amount of estrogen degradation per unit time, while the pseudo-first order kinetics BiOCl exhibits, is indicative of a constant percentage of estrogen degradation per time and more effectively degrades the estrogens. To determine which photocatalyst is most effective at eliminating estrogens in wastewater influent, future photocatalytic experiments should be run using spiked wastewater influent. This is a pertinent experiment to test the photocatalyst applicability because the presence of organic matter and carbonate species in WWTP influent can quench hydroxyl radicals, the predominant pathway by which TiO_2 functions as a catalyst, while BiOCl can directly oxidize contaminants via direct hole oxidation.

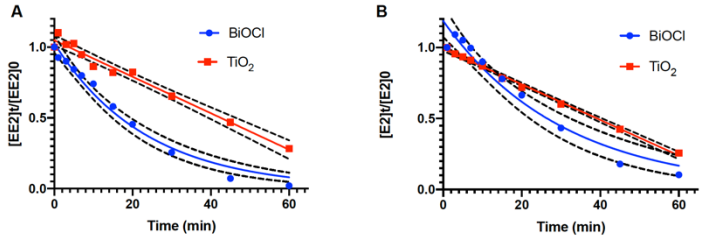

Figure 1A-B. Photocatalytic degradation of 50 μM (A) EE2 and (B) E2 by 0.25g/L BiOCl and TiO_2, irradiated with 254 nm light. Data was fit to a one phase decay model (BiOCl) and a simple linear regression model (TiO_2) with 95% confidence intervals represented by dotted lines.

17α-ethynylestradiol and E2 are estrogens tagged as potent EDCs with toxic effects on the environment due to their continued bioaccumulation. These environmentally destructive estrogens are not effectively degraded by WWTPs, so new technology is needed to remediate this issue. Photocatalysts such as BiOCl and TiO_2 are promising for estrogen removal from aquatic environments, as both degrade these model compounds when excited with UV light.

Faculty Mentor: Dr. Elizabeth Stemmler; Funded by the Surdna Foundation Undergraduate Research Fellowship

References

Arthur, R. B.; Bonin, J. L.; Ardill, L. P.; Rourk, E. J.; Patterson, H. H.; Stemmler, E. A., Photocatalytic Degradation of Ibuprofen over BiOCl Nanosheets with Identification of Intermediates. Journal of Hazardous Materials **2018**, 358, 1-9.

Barreiros, Luísa et al. "Analysis of 17-β-estradiol and 17-α-ethinylestradiol in biological and environmental matrices — A review." Microchemical Journal 126, **2016**, 243-262.

Diamanti-Kandarakis, Jean-Pierre Bourguignon, Linda C. Giudice, Russ Hauser, Gail S. Prins, Ana M. Soto, R. Thomas Zoeller, Andrea C. Gore, Endocrine-Disrupting Chemicals: An Endocrine Society Scientific Statement, Endocrine Reviews, Volume 30, Issue 4, **2009**, 293–342

Price, J. The Photocatalytic Degradation of Atenolol and Ibuprofen with BiOCl: An Investigation into the Mechanisms Responsible for Photocatalytic Activity. Honors Project, Bowdoin College, **2021-22**.

Speller, K. The Photocatalytic Degradation of Ibuprofen and Atenolol Using Bismuth Oxychloride and Titanium Dioxide. Honors Thesis, Bowdoin College, Bowdoin Digital Commons, **2021**.