Remediation of Estrogenic Contamination for Runoff with Sustainable Green Chemistry

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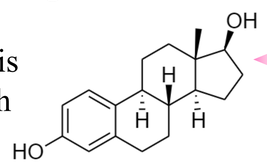
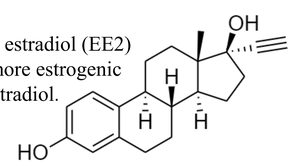
Environmental Background

- Agrochemicals, including the growth hormone estrogen, are used in animal production to increase yield.
- These chemicals are excreted and carried downstream in runoff water where they act as endocrine disrupting compounds (EDCs), disrupting ecosystems.
- Hormone imbalance due to EDCs cause population collapse and ecosystem disruption, most evidently in fish biomass.
- Concentrations as low as 1ng/L can disrupt male fish development and higher concentrations can cause male feminization and sterilization.
- Aquatic food webs are disrupted when fish populations collapse and organisms are released from fish predation.
- Ethinyl estradiol (EE2) is a synthetic estrogen with bioactivity about 2X greater than naturally occurring estrogens. EE2 is used in birth control and other commercial products.



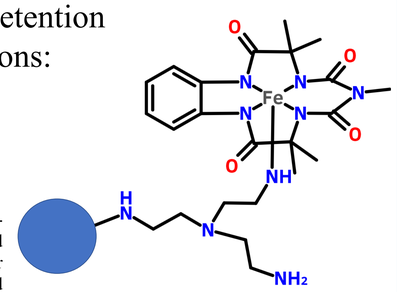
Estradiol (E2) is the major form of estrogen found in humans



Ethinyl estradiol (EE2) is 2X more estrogenic than Estradiol.

Chemical Background

- There are multiple chemical, mechanical, and biological methods (RBCs, Electro-Fenton, etc) for remediation of estrogenic contamination. Each has unique challenges that limit their commercial uses.
- Fe-TAML, a green catalyst, oxidizes organic compounds in the presence of H_2O_2. This remediation strategy has implications and uses for a wide variety of contaminants.
- Fe-TAML (Iron Tetra-amido Macrocyclic Ligand) is a biomimetic catalyst that coordinates with H_2O_2 to oxidize compounds in a non-radical dependent mechanism.
- A solid phase support structure would allow Fe-TAML to remain in a flowing water system and be reused. This promotes sustainability and ease of use for a final product.
- Three solid-phase support structures have been investigated for suitability of Fe-TAML uptake and retention under variable pH conditions:
  1) 2-aminoethyl amine
  2) 2-diethyl triamine
  3) Chelex



Fe-TAML coordinated to a 2-aminoethyl amine covalently linked to a styrene divinylbenzene polymer bead

Methods

- H2O2 is generated *in situ* via redox reaction using a Titanium MMO anode and a Carbon cathode. $TiSO_4$ indicates presence of H_2O_2 through a color change.
- Methylene blue (MB), a model indicator, is broken down in the presence of Fe-TAML and H_2O_2, seen as a decrease in absorbance at 660 nm.
- Fe-TAML is incubated with solid phase resin, seen as a decrease in absorbance at 400 nm. Large batch prep ensures standard Fe-TAML molarity in each test.

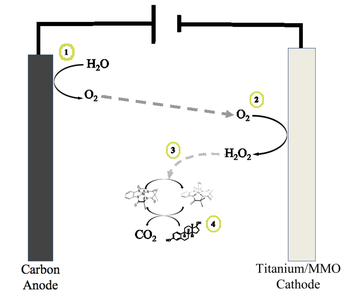
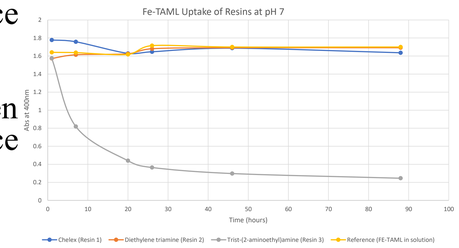


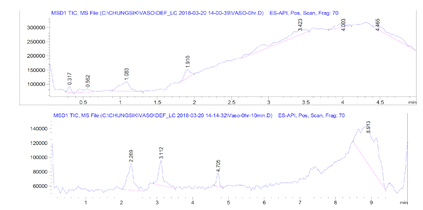
Diagram of H_2O_2 generation and activation of Fe-TAML. Batteries currently power the redox reaction that generated H_2O_2.



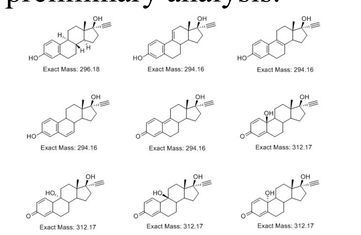
Decline of absorbance at 400 nm showing uptake of Fe-TAML by various resins.

Findings

- LCMS analysis shows degradation of EE2 under experimental conditions. Reaction products have been proposed based on preliminary analysis.

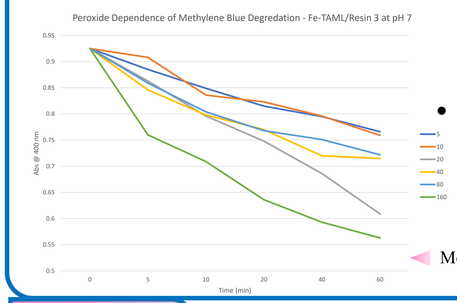


Mass spectroscopy of estrogen samples treated with Fe-TAML show dramatic estrogen degradation, as can be seen by the drop in magnitude of the peaks between the top and bottom figures.



Proposed degradative products of EE2 oxidation

- Fe-TAML catalyzed breakdown of EE2 and MB in an $[H_2O_2]$ dependent reaction.
- H_2O_2 generation requires more study, optimal levels for degradation haven't been achieved *in situ*
- Fe-TAML/R2 appears most suitable for continued investigation



Methylene blue degradation under variable $[H_2O_2]$.

Interpretation

- Our system is designed to tackle the issue of estrogenic contamination in runoff and groundwater in a sustainable way.
- Fe-TAML demonstrates superior catalytic potential. Rendering it stable in a heterogenous solid phase system shows promise as a means for increasing its superior catalytic ability further.

Next Steps

- Testing a heterogeneous polymeric system. Investigating if the addition of Cys-residues to polymers will make Fe-TAML a more effective catalyst.
- Moving from a battery powered to a solar powered method for H_2O_2 generation.
- Coordinate components into one fluid system.
- Test degradative products for estrogenic activity.

Citations

Brown, V. J. (2006). Fe-TAML: Catalyst for Cleanup. *Environmental Health Perspectives*, *114*(11), A656–A659
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