Catalytic Treatment of Pharmaceutical Contaminants for Wastewater Reclamation and Reuse

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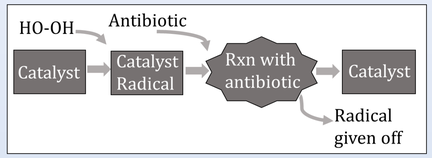
Background

What is a catalyst?

A catalyst is a compound that helps start or speed up a reaction but does not get consumed in the reaction (scheme 1). The tetraazomacrocyclic catalysts in this study have been recently synthesized and are unique because of their ethylene cross-bridged structure, which enhance their stability in wastewater.



***Scheme 1**: Showing general mechanism of catalytic degradation*

How can catalysts improve water quality?

A majority of antibiotics ingested by humans and animals are excreted unmetabolized, and are detected in wastewater. However, wastewater treatment plants are not designed to eliminate antibiotics, and then these contaminants persist in the effluent, rendering it unfit for reuse without additional treatment. The **overall goal** of this work was to study the effectiveness of catalytic degradation for removal of antibiotics in advanced water reuse systems. Due to their prevalence in wastewater, ciprofloxacin (CIP) and azithromycin (AZI) were selected as test compounds [1].

Methodology

Experimental Setup: A 25 mL solution contained 10 µM of antibiotic, 4 µM of catalyst, and 1 mM of hydrogen peroxide (acting as the source of radical species) and deionized water (DI) that was buffered at pH 7 with 1mM of phosphate buffer (figure 1). Samples were taken at 0, 5, 10, 20, 30, 60, 120, and 180 minutes. Antibiotic concentrations were measured using liquid chromatography-tandem mass spectrometry.

To confirm that degradation rate of antibiotics was catalyst driven, dose of catalyst MRK97A was varied between 2 to 20 µM.

To test the impact of real water samples, CIP degradation was tested at 4 µM of MRK97A in tap water and lake water from Boomer Lake. Additional water quality variables tested include carbonate concentration (0 to 10 µM), pH (3 to 11) and free chlorine concentration (0 to 4 mg/L) [2].

***Figure 1**: Experimental Setup. All experiments were conducted in duplicate.*

How do different antibiotics react to crossed bridged catalysts?

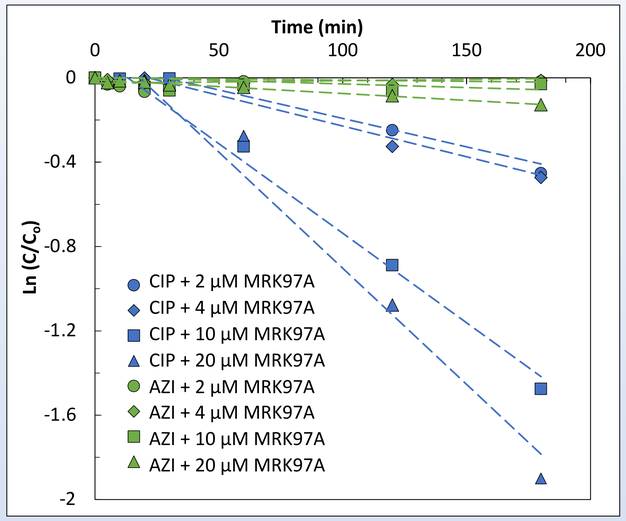
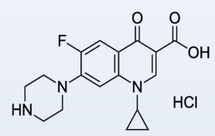


***Figure 2**: Pseudo first-order degradation of CIP and AZI over 3 hours with varying dose of catalyst MRK97A.*

a. Ciprofloxacin



b. Azithromycin

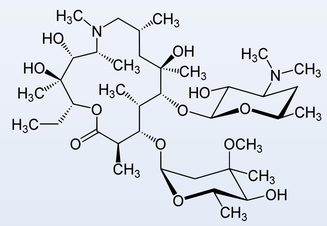


***Figure 3**: Chemical structures of antibiotics tested in this study*

As the dose of MRK97A increased from 4 µM to 20 µM, rate constant of CIP degradation increased from 0.47 min^{-1} to 1.90 min^{-1} (figure 2), *i.e.*, highest degradation of CIP after 3 hours being 85%, when MRK97A was dosed at 20µM, compared to 37% at 4µM.

In contrast to CIP, AZI was more resistant to catalyst degradation, with a rate constant of 0.13 min^{-1}, when MRK97A was dosed at 20 µM. The lowered reactivity of AZI is likely due to the lower degree of aromaticity (i.e. fewer unsaturated rings) or because of larger size (steric hindrance) compared to CIP, as seen in figure 3.

Does water quality affect rate of antibiotic degradation?

Our initial hypothesis was that the catalyst-driven antibiotic degradation would be faster in lab-grade DI water, and slower in tap water and lake water due to the presence of organic matter and other inorganics present in environmental water. However, preliminary testing of **CIP displayed consistently high degradation rates in tap water compared to DI water (figure 4).** For example, when tested with 4 µM MRK97A, the observed rate constant for CIP increased by a factor of 2.52, *i.e.*, from 5.37×10^{-3} min^{-1} in DI to 1.89×10^{-2} min^{-1} in tap water. As a result, we hypothesized that residual chlorine in tap water (typically ranging from 0 - 4 mg/L)[2] served as a source of additional reactive species during catalyst degradation.

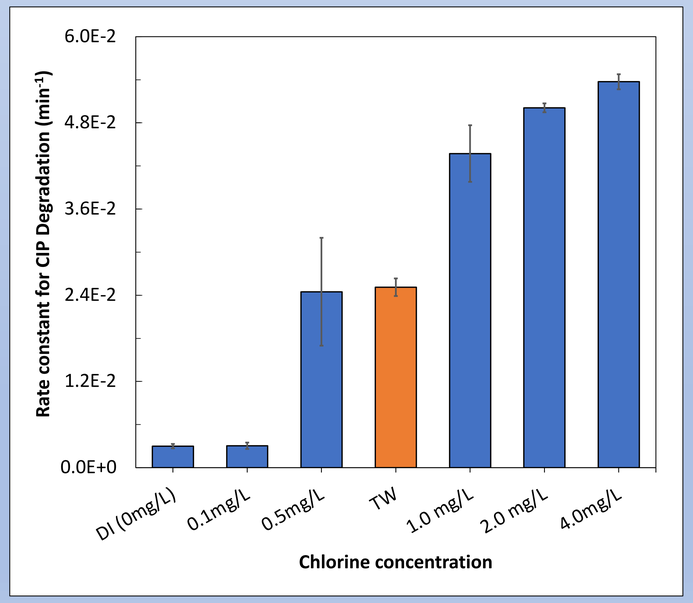


***Figure 5**: Comparing rate of ciprofloxacin degradation over 2 hours for different concentrations of free chlorine.*

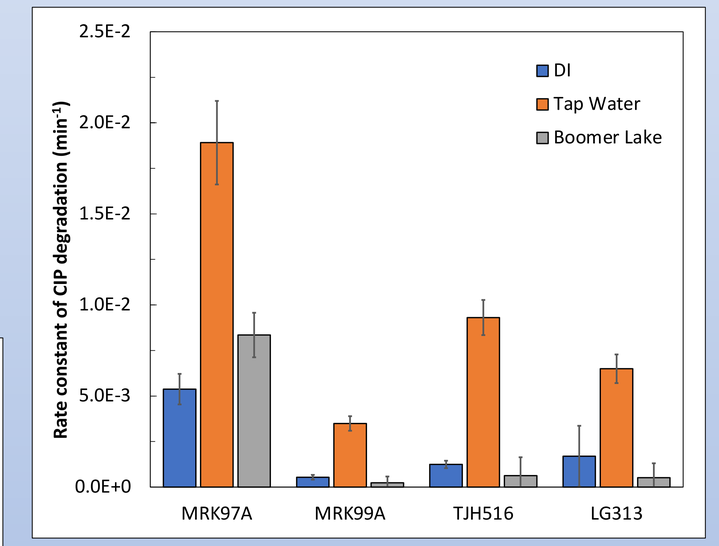


***Figure 4**: Comparing rate constant of CIP degradation with different catalysts under varying water conditions.*

When free chlorine (as sodium hypochlorite) was added to DI containing 4 µM of MRK97A at doses of 0, 0.1, 0.5, 1, 2, and 4 mg/L of Cl_2, CIP degradation rate constant increased significantly between 0 mg/L (0.30×10^{-2} min^{-1}) to 0.5 mg/L (2.44×10^{-2} min^{-1}) and 1 mg/L (4.37×10^{-2} min^{-1}). This increase was consistent with typical concentrations of free chlorine expected in tap water (~0.5 mg/L) with observed rate constant of 2.51×10^{-2} min^{-1}, as seen in figure 5. For these conditions, the percent degradation of CIP at 60 minutes increased from 64.5% in DI to 99.0% in tap water.

In the case of MRK97A, addition of lake water instead of DI caused 56% faster degradation of CIP when compared to DI (figure 4). Future tests can be performed to determine what components of lake water sped up this degradation reaction.

How does catalyst structure affect degradation?

Different catalyst structures and stabilizing ligands proved to have different effectivity for antibiotic degradation. For example, CIP degradation in DI for the same dose of catalyst varied from 0.54 to 5.37×10^{-3} min^{-1} (figure 4). Moreover, the ratio of the rate constant in tap water compared to that of DI water (figure 6) showed that the iron based catalyst (LG313) was an order of magnitude lower (0.47) compared to the manganese based complexes (2.7 – 4.7). Future research will determine the relationship between antibiotic degradation and catalyst structure. In addition, future research will explore identification of reaction mechanisms and byproduct formation.

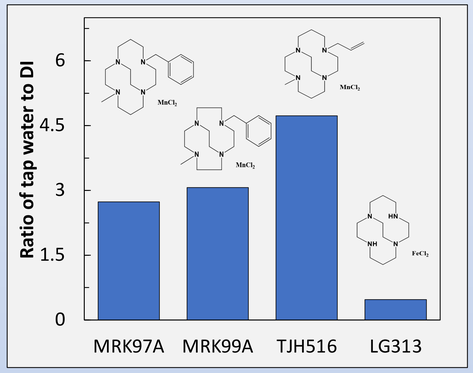


***Figure 6:** Ratio of rate constant of CIP degradation in tap water to DI water rate constant for four catalysts.*

Conclusion

How could this research help Oklahoma?

Crossed bridged catalysts could be a viable option in large scale water treatment systems to help deteriorate contaminants in water. Findings from this work allow for safe reuse of wastewater that can provide Oklahomans with supplemental water for drinking, as well as irrigation. These findings can also address growing concerns of antibiotic resistance, a major public health threat.

References

1. Niang, Mamadou et al. "Ciprofloxacin- and azithromycin-resistant bacteria in a wastewater treatment plant." *Journal of occupational and environmental hygiene* vol. 20,5-6 (2023): 219-225. doi:10.1080/15459624.2023.2205485
2. "Stillwater Municipal Water System 2017 Annual Water Quality Report ..." *The City of Stillwater Oklahoma*, 2017, stillwater.org/files/water-quality-reports/FINAL-2017-Annual-Water-Quality-Report---Stillwater.pdf.

Acknowledgements

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