# NOVEL SOLAR LIGHT MEDIATED, REGENERATIVE, PHOTOCHEMICAL IRON REDOX CYCLE BASED TREATMENT PROCESS FOR ORGANIC CONTAMINANTS

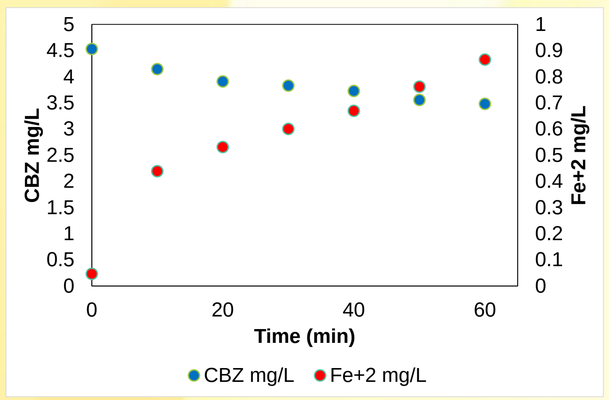
John Albino Dominic, Purnima Somathilake, Cooper H Langford, Gopal Achari & Joo-Hwa Tay

University of Calgary, AB, Canada

## Background and Objectives

- Photochemical iron reduction in natural waters under sunlight has shown bleaching of natural organics and organic contaminants[1]
- In classical Fenton's process iron is oxidized from $Fe^{2+}$ to $Fe^{3+}$, which is further deemed dysfunctional[2]
- No attempts have been made to combine the above mentioned processes to regenerate iron in the solution to have a continuous potential to degrade organics
- **In this research, for the first time we have demonstrated the possibility of regeneration of iron using a cyclic process that couples photochemical iron reduction and Fenton oxidation for degradation of CBZ**
- **This concept is demonstrated by studying degradation of Carbamazepine (CBZ) and its efficiency is compared with other widely used Advanced Oxidation Processes (AOPs)**
- **The feasibility of this process under sunlight has also been demonstrated**

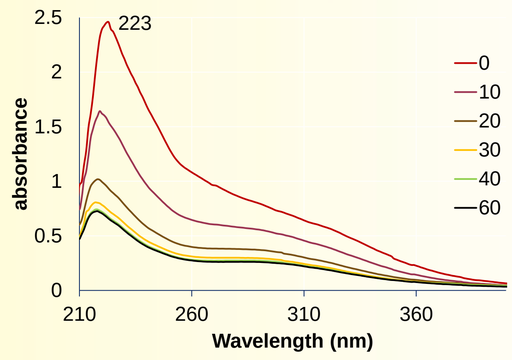
## Photochemical $Fe^{3+}$ Reduction and Degradation of Carbamazepine




**Photochemical degradation of CBZ and simultaneous increase of $Fe^{2+}$ under UV irradiation**

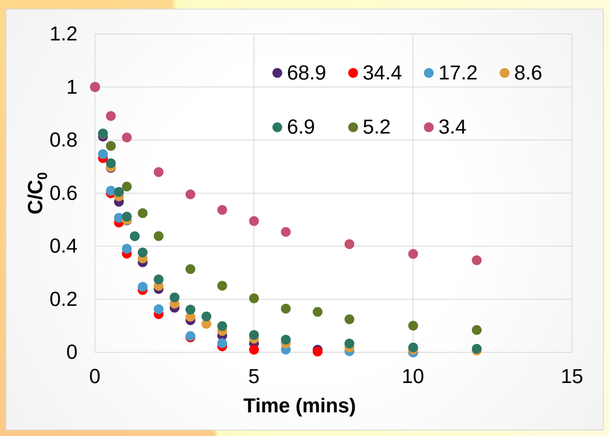
- Degradation of Carbamazepine was proportional to rate of reduction of iron
- Both degradation of CBZ and reduction of Fe followed first order kinetics
- Experiments under longer wavelength UV irradiation in the absence of $Fe^{3+}$ showed no degradation of CBZ

- The $Fe^{3+}$ species showed stronger absorbance in the lower UV region with peak at 223
- Tailing of the absorbance in longer wavelength region shows the feasibility of this reaction in visible light
- UV absorption decreases due to the reduction of $Fe^{3+}$ to $Fe^{2+}$ and its accumulation

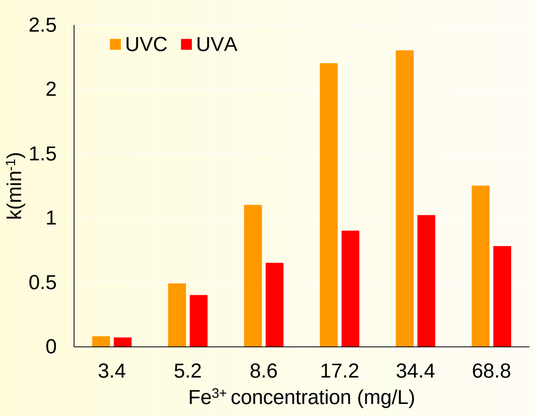



**Change in UV spectrum during the photochemical iron reduction with respect to time**

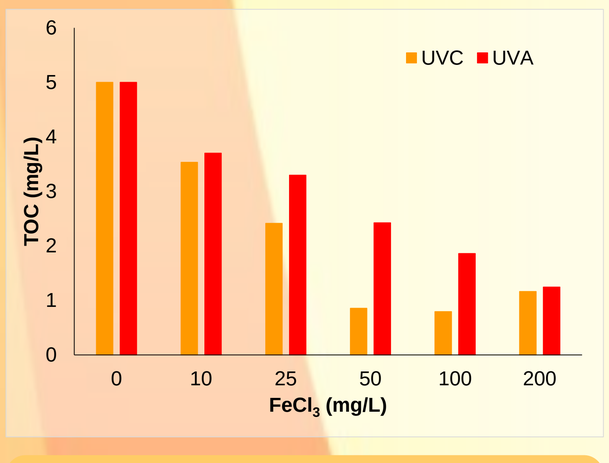
## Influence of Ferric Ion Concentration and Wavelength Dependence




**Effect of $Fe^{3+}$ concentration (mg/L) on the photochemical degradation of CBZ**



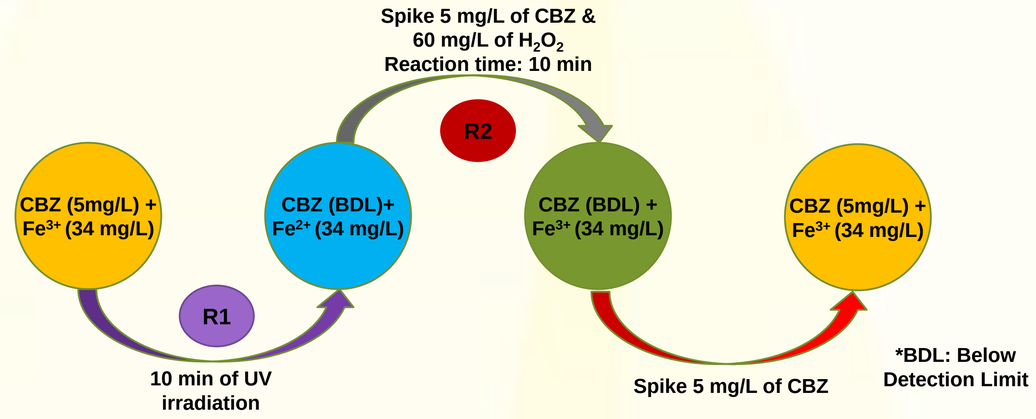

**Kinetic coefficients for various wavelengths and ferric iron doses**




**Reduction in Total Organic Carbon (TOC) for UVA and UVC irradiations for various ferric ion doses**

- Optimal concentration of $Fe^{3+}$ concentration was observed as 17.2 mg/L and 34.4 mg/L for UVC and UVA
- Degradation of CBZ ceased after complete reduction of $Fe^{3+}$ to $Fe^{2+}$
- Rate of degradation reduced in the presence of higher concentration of $Fe^{3+}$ above the optimal concentration
- Reduction in TOC increased with increasing concentration of $Fe^{3+}$ for the same period of irradiation

## Cyclic Regeneration of Photochemically Reduced iron by Fenton's Reaction




**One cycle of photochemical reduction of $Fe^{3+}$ and regeneration by Fenton**

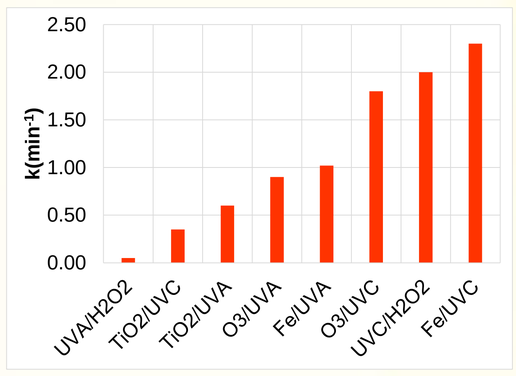
R1 $Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + {\bullet}OH + H^+$

R2 $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {\bullet}OH + OH^-$

- R1 and R2 reactions conducted in succession constitute one cycle of photochemical iron reduction and Fenton reaction

- 5 cycles of the reactions were conducted
- Complete disappearance of CBZ was observed at the end of each reaction
- More than 90% of TOC was degraded by the end of the experiment

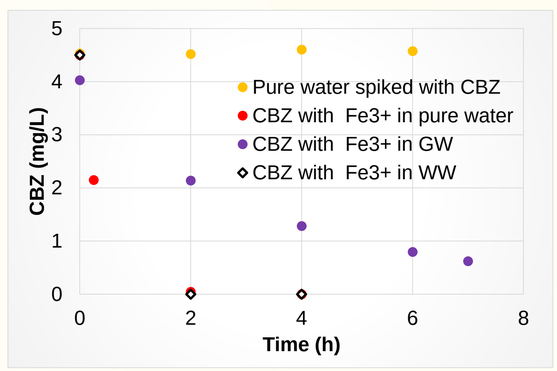
## Comparison of Photochemical Iron reduction with other AOPs




**Comparison of kinetic coefficients for various AOPs with Fe/UVC**

- Photochemical iron reduction demonstrated the fastest kinetics for degradation of CBZ among all the tested AOPs
- Fe/UVC was also superior to other methods as higher degree of mineralization was achieved as compared to other AOPs.
- Highest reduction in TOC was observed in Fe/UVC coupled with Fenton

## Feasibility of the Solar light mediated photochemical iron reduction for organic contaminants




**Degradation of CBZ in various aqueous matrices by Fe/UVC under sunlight irradiation**

- CBZ in wastewater and pure water was completely degraded in the presence of ferric species under sunlight irradiation with in 2 h.
- Kinetics of degradation of CBZ was slower in the case of GW due to the presence of high concentration of other organics.
- More than 50% of TOC was removed by solar irradiation of 7 h for CBZ spiked in WW for an initial concentration of 5mg/L

## Advancing the Technology for Field Applications

- The demonstrated novel treatment method has immense potential for wide applications including drinking water, domestic and industrial wastewater
- Simultaneous degradation of various ESOCs and disinfection of microbial organisms will be further studied at ACWA facility to find the potential of this method as an advanced water treatment.
- The feasibility of applying this process to large stagnant water masses (eg. Storm water ponds) will be further tested

## Conclusions

- Photochemical iron reduction was observed to be superior to other AOPs including $O_3$, $O_3$/UV, UV/$H_2O_2$ and $TiO_2$/UV for degradation of CBZ in terms of faster degradation and mineralization
- Photochemical iron reduction and regeneration by Fenton was successfully demonstrated for 5 cycles along with degradation of contaminant in each cycle
- The demonstrated photochemical iron reduction coupled with Fenton oxidation process also shows promise for solar light mediated water treatment as degradation of CBZ was also observed under sunlight

## References

[1] S. Chiron, C. Minero, D. Vione, 2006, "Photodegradation Processes of the Antiepileptic Drug Carbamazepine, Relevant To Estuarine Waters", Environmental Science & Technology, 40: 5977–5983.

[2] J. J. Pignatello, 1992, "Dark and photoassisted iron (3+)-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide." Environmental Science & Technology, 26(5): 944-951.

## Acknowledgements

The research is conducted as a part of NSERC-IRC project partnered with the City of Calgary chaired by Dr. Tay. Funding received from NSERC and the City of Calgary is gratefully acknowledged. We are thankful for the technical support from the officials of City of Calgary and the help rendered by the operators for collection of wastewater samples.