Development of a computational tool to predict the degradation fate of organic contaminants in aqueous phase advanced oxidation processes

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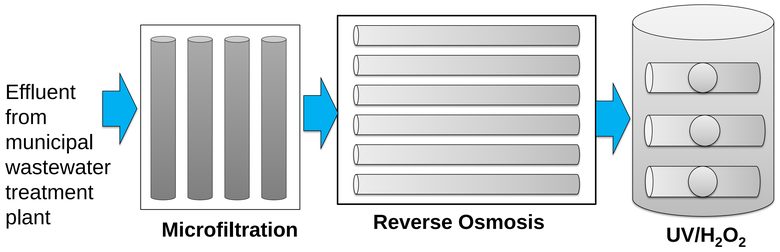
Significance of study

- Detection of EMERGING CONTAMINANTS in drinking water sources

Contaminants such as pharmaceuticals and personal care products detected in drinking water sources (Picture source: Emerging contaminant threats and the Great Lakes, 2011)

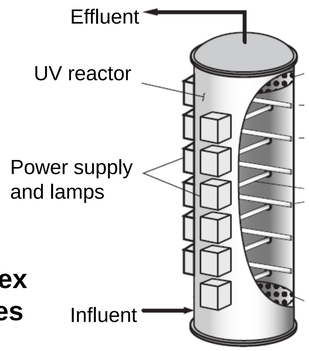
- WATER REUSE and RECLAMATION becoming a prominent Water Treatment and supply option

Indirect potable reuse schematic in Fountain Valley, CA



Advanced Oxidation Process (AOP)

- An oxidation technology that mineralizes complex organic compounds when attacked by a highly reactive species called Hydroxyl Radical (HO•)
- Rational design of AOP requires:
  (a) Chemical kinetics
  (b) Reactor flow conditions
- Chemical kinetic modeling is the focus of this research
- Modeling kinetics of AOPs is complex because of the radical-initiated series of chain reactions



Target + HO• → R-CH_2• → ROO•(Peroxyl radical) → byproducts (Carboxylic acids, aldehydes, etc.)

Challenges and Research Scope

- DIFFICULT AND EXPENSIVE TO EXPERIMENTALLY STUDY the fate of the parent compound and stable byproducts
- Uncertainty about the QUANTITY and the nature of stable BYPRODUCTS
- The complexity and diversity of structures of a number of known and emerging chemical CONTAMINANTS

GOAL

We need a computational kinetic model that will "predict" the degradation of target organic contaminants, intermediates and stable byproducts

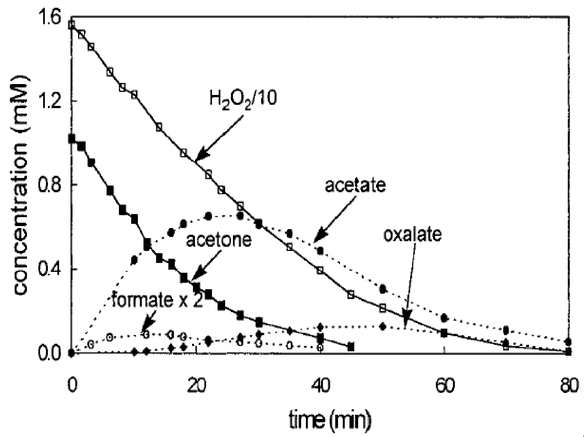
Preliminary Results

- ULTIMATE GOAL OF A KINETIC MODEL: Obtain a concentration-time profile of the most important compounds

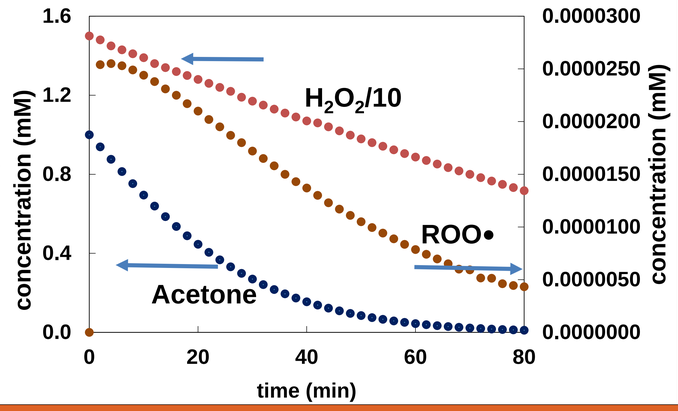
EXPERIMENTAL/ SIMULATED CONDITIONS

1) Test compound: ACETONE (0.001 M)
2) UV Lamp: Medium pressure (9 kW)
3) Wavelength: 200-295 nm
4) pH: 7
5) $[H2O2]_o$: 0.015 M
6) Reactor Volume: 214 L

Concentration-time profile from experimental results (Stefan *et al.*, 1996)



Concentration-time profile from dynamic non-steady state model (AdOx™)



- VALIDATION of pseudo-first order rate constant (k_R) for test compound, Acetone

Model	[HO•]ss (in M)	$k_R = k'_{HO} * [HO•]ss$ (in s^{-1})
Simplified pseudo steady state	4.95×10^{-11}	5.44×10^{-3}
Dynamic non-steady state (AdOx)	1.11×10^{-11}	1.22×10^{-3}

[HO•]ss=steady state concentration of HO• (M)
k'_{HO} = Second order Hydroxyl rate constant of Acetone ($M^{-1}s^{-1}$)

Objectives of the project

1) Experimental data on kinetics and byproduct measurement

Pulse photolysis experiments will be conducted for kinetics and measuring the resulting byproducts using mass spectrometry

2) Theoretical investigations on thermodynamics and kinetics

Theoretical calculations using principles of quantum chemistry will be done to arrive at reaction barriers and reaction rate constants of multi-channel overall reactions

3) A predictive computational model capable of predicting the probable fate of degradation pathways

Design will be based on (a) factors that account for interaction between different species (b) Rate of the interactions (c) Orientation of the resulting molecule

References and Acknowledgements

1) Minakata, Mezyk, Jones, Daws, and Crittenden. ES&T 2014, 48 (23), 13925-13932

2) Stefan, Hoy, and Bolton. ES&T, 1996, 30, 2382-2390

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