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Reaction Rates and Mechanisms of AOP Technologies for Water Reuse

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Objectives:

The main objective of this study was to develop a better understanding of the water-based free radical chemistry in the destruction of organic microconstituents by

- Determining reaction rates of 30 - 50 target chemicals with hydroxyl radicals, $^{\bullet}OH$, and hydrated electrons, $\mathbf{e^{-}_{aq}}$.
- Elucidating destruction mechanisms for five (5) selected target compounds representative of broader classes of organic microconstituents.
- Determining the efficiency of the hydroxyl radical-mediated destruction of bisphenol A and three other model organic contaminants, in pure water, laboratory solutions containing bicarbonate ion and/or DOM and treated wastewaters of different quality.

Project Conclusions:

- Measured reaction rate constants with the hydroxyl radical for the 51 compounds studied were in the range of 1×10^{9} – 10×10^{9} M^{-1} s^{-1}, with few exceptions (See Table E.1). A reaction rate constant in this range suggests that the compound of concern has a high probability of being effectively destroyed by an advanced oxidation process radical.
- The absolute reaction rate constants with the solvated electron (e^{-}_{aq}), with few exceptions, fall in the range of 10^{8} – 10^{10} M^{-1} s^{-1}. Although this range was larger than that for the hydroxyl radical, these results also suggest that advanced reduction processes that produce reducing radicals are similarly capable of organic contaminant destruction.
- Radical reaction efficiency is also a critically important parameter when considering the application of advanced oxidation free radical processes to water reuse. This efficiency parameter evaluates the effectiveness of the reactive species in the destruction of chemical contaminants, which varies according to water quality. In pure water, the hydroxyl radical reacts with most organic contaminants with less than 100% efficiency. A decrease in the $^{\bullet}OH$ and contaminant reaction occurs in the presence of radical scavengers, which is dependent on many factors including the: nature/concentration of dissolved species, efficiency of $^{\bullet}OH$ reaction with contaminants in pure water, and other effects potentially present with additional dissolved species.
- Studies that were based on liquid chromatography/mass spectrometry (LC/MS) measurements were conducted to elucidate reaction by-products of the free radical-induced contaminant degradation reactions. In many cases, several reaction by-products potentially fit the measured mass spec values. This has led to many proposed destruction mechanisms for the compounds studied. With the exception of the sulfa drugs listed in Table 1, destruction mechanisms for all of these compounds were outlined. Reaction by-products were not chemically synthesized or isolated for further study.