

DISTINGUISHED SPEAKER

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Unscrambling the Photochemical and Photocatalytic Kinetics of Multi-Reaction Liquid Phase Systems: Dye Degradation by Direct and Indirect Photochemistry

Both dyes and semiconductor photocatalysts are strong absorbers of near UV (365) and UV (254) nm wavelengths. Dye degradation may initiate via direct photolysis (254 nm), photocatalysis (254 or 365 nm), and photosensitized conversions (visible). When reactant and photocatalyst compete for photons, kinetic disguises may easily arise and must be recognized to properly interpret kinetic data from these multi-reaction systems.

We published a 1990 simple kinetic analysis for liquid phase reactors involving simultaneous heterogeneous and homogeneous photochemical reactions. This circumstance applies to many of the approximately 6,000 papers published to date on dye photo-degradation. While these reaction models may become complex in large reactors, the lab scale photoreactor provides simple lamp immersion geometries which allow for a clean separation of the relative weights carried by each available reaction path for dye degradation. In multiple cases, the proper consideration of the relative optical density of the dye solution and the photocatalyst suspension is not appreciated, leading to incomplete or incorrect kinetic interpretations.

We analyze literature examples of dye conversions and demonstrate examples of the following situations: (a.) Kinetic disguises when dye conversion appears to be zero order from initial rate data, but first order due to linear $\ln(C)$ vs time plots. (b.) Photo-catalyst addition to a photolysis system which can either increase or decrease the overall photochemical reaction rate. (c.) Dye addition to a photocatalyst system which may increase or decrease the overall rate of photochemical conversions. (d.) Simultaneous homogeneous and heterogeneous reactions occurring due to use of a multi-wavelength light source, such as one providing both 254 and 365 nm photons.

These results may be followed in time qualitatively through use of a simple graph from our 1990 paper showing the regimes for the [relative absorbance x quantum yields] for heterogeneous vs. homogeneous reactions.

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2:00 - 3:00 PM
Winston Chung Hall
Room 205/206