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Simultaneous photochemical and photocatalyzed liquid phase reactions: Dye decolorization kinetics

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ABSTRACT

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 6000 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 two detailed literature examples of dye conversions involving simultaneous homogeneous and heterogeneous photochemistries, and demonstrate 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. We show that either light limitations or mass transfer limitations may be responsible for these kinetic disguises. 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 × quantum yields] for heterogeneous vs. homogeneous reactions.

1. Introduction

Earlier papers by two of us [1,2] utilized a lab scale immersion photoreactor to explore photochemical and photocatalyzed, liquid phase decolorization of organic dyes, specificallly Solophenyl Green (SG) BLE 155 [1] and Solophenyl Green, Erionyl Red B(ER), and Chromotrope 2R (C2R) [2]. Extensive kinetic data for reactant concentration vs. reaction time showed apparent first order kinetics for photochemical (photolysis) only (no catalyst) and for simultaneous photocatalysis and photolysis(catalyst slurry) (Fig. 1a and b).

A revised analysis of the original kinetic data is presented here. It shows a zero order (constant) initial rate of reaction for initial dyeconcentration >10–20 mg/L, nearly independent of reactant concentration and presence or absence of photocatalyst.

Thus, we have a kinetic puzzle: "How can a reaction appear to be both first order and zero order at the same time?"

The overall reaction for photolytic, photocatalytic, or photosensitized bleaching of a dye may be written as:

$$\text{Photon} + \text{dye} + (\text{oxygen}) \rightarrow \text{decolorization}$$

We test here the possibility that the constant supply of photons and/or dissolved oxygen could each be rate limiting during initial rate measurements in the high optical density dye solutions and photocatalyst suspensions used in references [1,2]. We show by estimation that liquid phase photoreactors may become either gas transfer or photon absorption rate limited, thereby exhibiting apparent zero order for initial rate data. We also demonstrate that, at the same time, kinetic competition for photons and/or oxidants among reactant and intermediates can lead to apparent first order behavior, i.e., linear ln($C(t)$) vs. time plots, for both homogeneous and heterogeneous photoreactions. This interpretation resolves the kinetic puzzle noted above.

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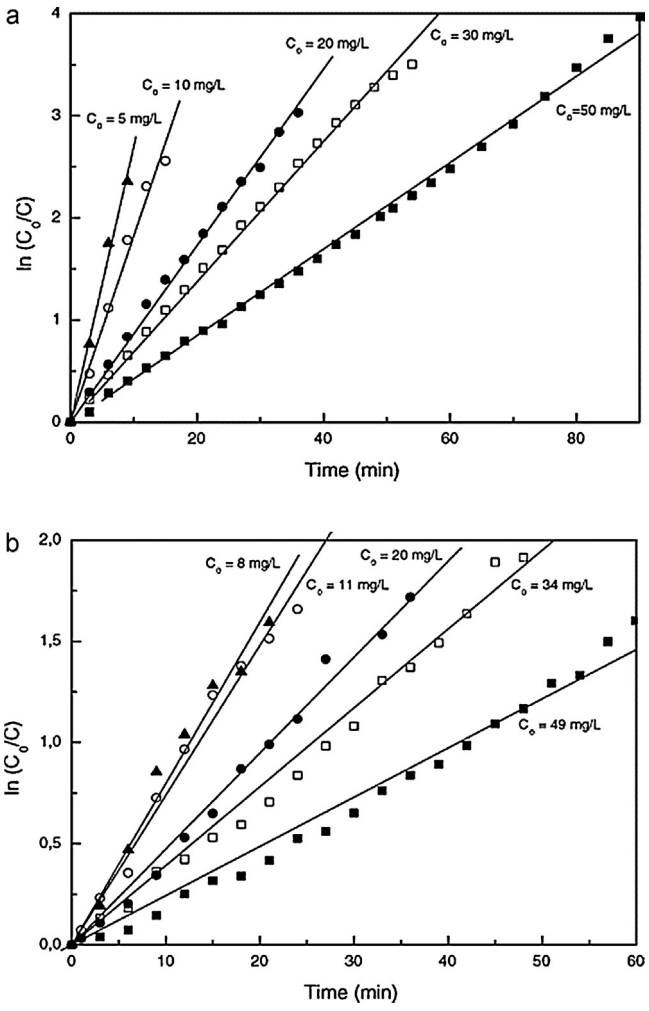

Fig. 1. (a) Kinetics of SG dyestuff degradation (linear transform $\ln C_0/C$ vs. t) in net photochemical experiments for different initial concentrations ((▲) C_0 = 5 mg/L; (○) C_0 = 10 mg/L; (●) C_0 = 20 mg/L; (□) C_0 = 30 mg/L; (■) C_0 = 50 mg/L). (da Silva and Faria [1], reprinted with permission). (b) Kinetics of SG dyestuff degradation (linear transform $\ln(C_0/C)$ vs. t) in photocatalytic experiments using TiO_2 for different initial concentrations of the dyestuff ((▲) C_0 = 8 mg/L; (○) C_0 = 11 mg/L; (●) C_0 = 20 mg/L; (□) C_0 = 34 mg/L; (■) C_0 = 49 mg/L).(da Silva and Faria [1]; reprinted with permission).

2. Experimental

The data for this paper were reported earlier [1,2] and were obtained via photochemical and photocatalyzed degradation of organic dyes Solophenyl Green BLE 155% (SG), Erionyl Red B (ER), and Dye Chromotrope 2R (C2R). A UV (254 nm) 3 W immersion lamp was used in an 800 mL reactor. Intial dye concentrations were 5–50 mg/L. Dye concentrations were determined with UV–visible spectroscopy of samples previously centrifuged to remove photocatalyst (TiO_2) particles. Full details are found in the original references [1,2].

3. Results and discussion

3.1. Initial rate data indicate zero order kinetics

The variation of apparent first order rate constant, k_{app}, with initial dye concentration reported previously [1,2] suggests a kinetic

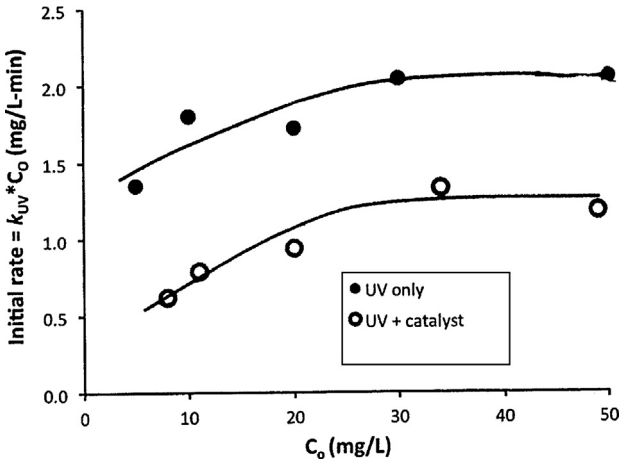

Fig. 2. Calculated initial rates of Solophenyl Green (SG) reaction using equation (initial rate) = $k_{app} \times C_0$, where k_{app} and C_0 are apparent first order rate constant and initial concentration, respectively, taken from Tables 1a and 1a,b of Ref. [1].

disguise, so we first recover the initial rate of reaction, r_0, fron SG dye data of Table 1a–b in Ref. [1]:

$$r_0 = k_{app} C_0 \quad (1)$$

The calculated *initial rate* plots for SG dye only, and (dye + catalyst) circumstances shown in Fig. 2 indicate that above a dye concentration of about 20 mg/L, the initial rate is essentially constant, independent of dye concentration, and thus that the apparent reaction order is zero. Hence, in the concentration range >20 mg/L, some other variable, either photon supply and/or oxygen (if needed) supply, is limiting the initial reaction rate.

3.2. Competitive photochemistries

Fig. 2 shows also that the TiO_2 photocatalyst addition decreases the overall rate of reaction by 45–50%. Several authors have explored before such a phenomenon of rate *decrease* with catalyst addition [3–5].

3.2.1. Model of competitive photochemistries: Solophenyl Green

Ollis and Turc [3] and Turchi [4] used simple kinetic models to consider when heterogeneous photocatalyst addition would augment or decrease a homogeneous photoreaction rate, for example, when photolytic degradation of a pollutant (e.g., dye) would be aided or penalized by addition of a heterogeneous photocatalyst. They calculated the ratio of rate with simultaneous homogeneous and heterogeneous photoreactions divided by the rate for a homogeneous reaction only. They defined this ratio as R,

$$R = \frac{[r_c\,(\text{cat}) + r_{hc}\,(\text{homogeneous})]}{r_0\,(\text{homogeneous})} \quad (2)$$

where during simultaneous photochemistries,

- r_c(cat) is rate contribution by the photocatalyst in the presence of photolysis;
- r_{hc}(homogeneous) = homogeneous photolysis rate in presence of photocatalyst;
- and r_0 (homogeneous) = homogeneous photolysis rate in absence of catalyst.

Their results showed that when photons captured by the photocatalyst were used less efficiently than in the homogeneous reaction, catalyst addition created a rate penalty, not a benefit, when the calculated R value is less than 1.0. A calculated example appears in Fig. 3. Here, for a batch reaction with an initial R

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