On the Kinetics of Photo-degradation of Organic Pollutants

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Generally, the kinetics of photocatalytic degradation of organic pollutants and dyes by semiconductors has most often treated as first order kinetics.   This is most common in literature and as an example one of the recent references [1] is provided. The purpose of this short presentation is to analyze some of the consequences of treating the kinetic data on the removal of pollutants and other organic species especially under photo-catalytic conditions generally under first order kinetic equation.   The first order kinetic equation generally employed in such circumstances can be written as $- \ln (C/C_0) = kt$; where C is the concentration at any time t seconds and C_0 is the value of concentration of the species that is undergoing degradation at time – 0 (initial concentration taken).and k is the value of the rate constant, this may be a lumped parameter including the value of the intrinsic rate constant. Typical data analyzed by first order kinetic data from ref 1 is given for information.
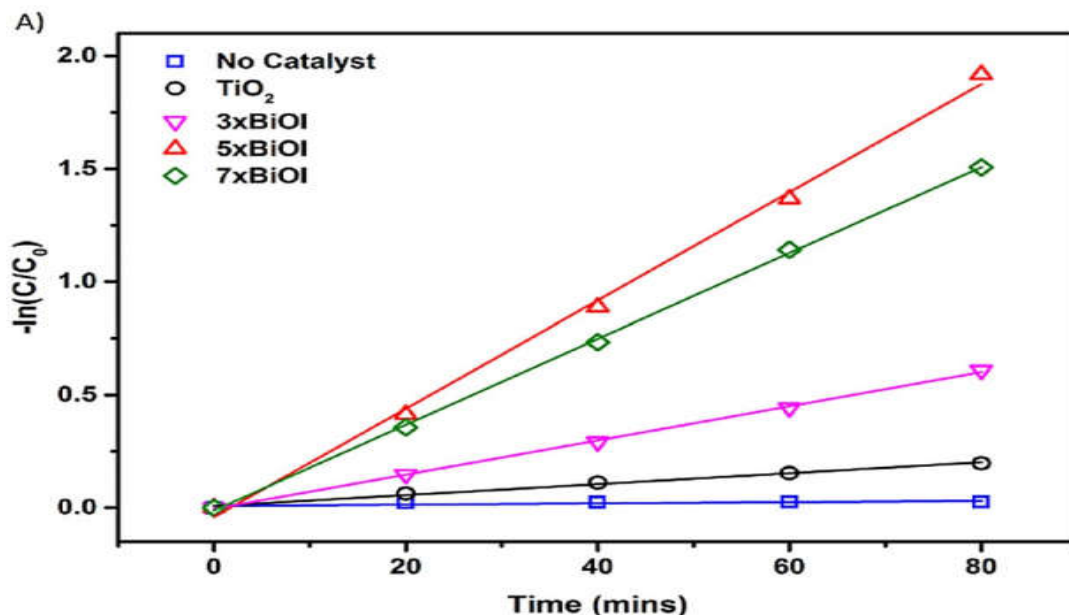

Fig 1 Photocatalytic degradation kinetics of Rhodamine B on various photo-catalysts [data reproduced from ref.1.] as an example.

The main conclusion of this study is that the inherent rate consists of the photo-catalytic and also photo-induced self-degradation of the dye. If this argument were to be accepted then the treatment of kinetic data according to first order is only grossly approximate and the apparent rate constant in the equation is only a lumped parameter consisting of mostly the value of the intrinsic rate constant and the rates of other parallel reactions that would have taken place on the surface of the catalyst and many other accompanying non-elucidated rates of degradation. Possibly, the value of

the apparent rate constant cannot be taken as a measure of the activity of the catalyst for comparison since the process taking place on the two or more catalysts are not identical or not even similar.   This will have serious misconceptions for comparison purposes.

In the example given, the authors report the apparent rate constant on the most active catalyst as 23.9 min^{-1} while the value of the apparent rate constant for the degradation of chlorophenol (where the photon induced degradation is assumed to be nearly negligible) is 3.47 min^{-1} which can be assumed in this case as the value of the intrinsic rate constant.   May be caution has to be exercised while comparing two or more catalytic systems on the basis of the rate constant values of the kinetic data treated as first order since on all catalyst systems the reaction may not follow the same kinetics though the treatment according to first order kinetics may apparently satisfy the first order kinetics.

The statements given may be applicable to all general reactions which can involve multiple steps like surface reactions which are more often treated with first order kinetics.   However, it is not our intention to make a general treatment. In a subsequent presentation, this concept will be further developed.

Reference

[1] Gylen Odling and Neil Robertson, ChemPhysChem, 18, 728 – 735 (2017); DOI: 10.1002/cphc.201601417.