# A reaction engineering approach to kinetic analysis of photocatalytic reactions in slurry systems

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## ABSTRACT

The knowledge of the rate equation is fundamental for the assessment of the activity of the photocatalytic material and for the study, design and optimization of photocatalytic reactors. In the case of photocatalytic reactions, the local volumetric rate of photon absorption (LVRPA) affects the reaction rate and its inherently uneven distribution within a "slurry" reactor makes complex a correct kinetic analysis. In the present work it is shown which are the critical aspects of the kinetic analysis in slurry reactors and how to carry out photocatalytic experiments to minimize the misinterpretations of the experimental results. In particular, the influence of the type of illumination and of the operating conditions (recirculation flow rate, optical thickness) are studied. For instance, it is shown that the average values of the reaction rate and of the rate of photon absorption give no direct insight on the intrinsic kinetic if the reactor is not uniformly illuminated and the optical thickness is beyond a given value, which is significantly higher than the one usually suggested in literature for a "safe" kinetic analysis. Furthermore, the estimation of the average rate of photon absorption must take into account the backscattering of radiation from the reactor. In any case, the utilization of a proper mathematical model allows carrying out a sound kinetic analysis also in critical situations as those which can arise with an illumination by LEDs.

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## 1. Introduction

The design and operation of chemical reactors require the knowledge of the "rate equation". In catalysis and particularly in photocatalysis, the assessment of the "intrinsic kinetics" of the reaction is fundamental also to evaluate and compare the performances of the catalyst. Therefore, a correct "kinetic analysis" is absolutely necessary for the study of any reacting system. Rigorous kinetic analysis are usually carried out in reactors which are as close as possible to ideal systems to get rid of all the bias that could affect the interpretation of the experimental results. For instance, particular care is deserved to mixing with the aim to guarantee uniform reactant concentration and temperature in all the volume (batch reactors and CSTR) or in the cross sections (PFR) of the reactor. In heterogeneous catalysis, the possible limitation of mass transfer inside the catalyst particle must be eliminated or precisely evaluated to obtain reliable results. In photocatalysis an "ideal" system

with a "perfect" distribution of all the parameters, which affect the reaction rate is impossible to attain. In particular, the radiation field is intrinsically not uniform, since the absorption of the radiation and, consequently, its attenuation are necessary to activate the reaction. On the other hand, photons, unlike reactants, cannot be "mixed". The apparent paradox is that the ideal reactor for kinetic analysis seems to be the "isoactinic" reactor, i.e. a reactor where reaction does not take place. One of the objective of the present work is to understand if it is really so.

These problems are well known in photocatalysis. It is emblematic that in photocatalysis the volumetric rate of photon absorption (or of the correlated radiant energy absorption), which appears in the constitutive equation of the rate of a photocatalytic reaction [1–3], is explicitly called "local" (usually Local Volumetric Rate of Photon Absorption, LVRPA). Conversely, the concentrations of the reagents in any kinetic equation are implicitly assumed to be "local". Nonetheless, kinetic analysis is sometimes carried out without the necessary consciousness on the best choice for the type of reactor and for the operative conditions or on the acceptable assumptions and simplifications. The aim of the present work is to present a rational for the kinetic analysis in photocatalytic slurry

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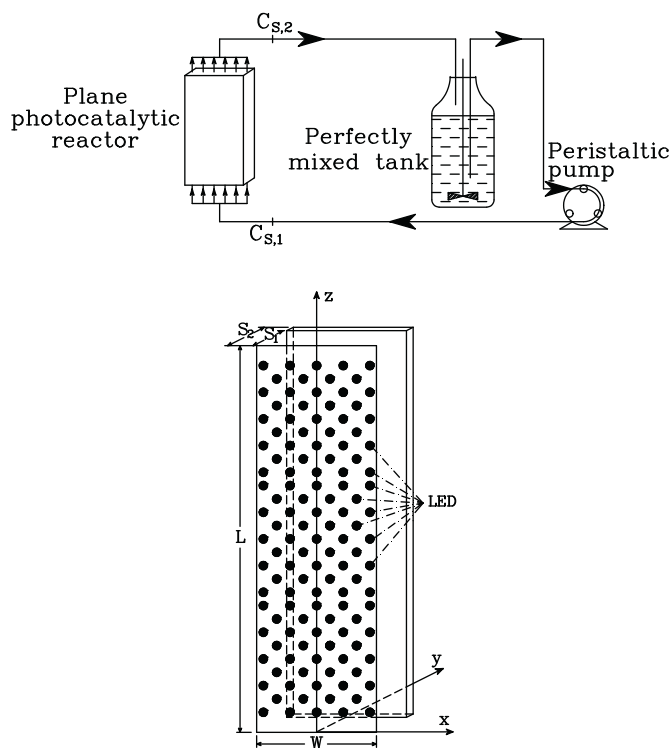E-mail address: giovanni.cameraroda@unibo.it (G. Camera-Roda).

**Fig. 1.** Schematic representation of the system (top) and geometry of the reactor and of the LED disposition (bottom). The LEDs on the $x,z$ plane at $y = 0$ are represented by black circles.

systems. Other works have been published on the subject [4–15], but some points still merit in-depth consideration and on some issues the present study draws new conclusions.

## 2. Experimental apparatus

The possibilities of carrying out a correct kinetic analysis also in conditions far from the ideality, has been tested with the adopted experimental apparatus. The utilization of LEDs with a narrow emission angle makes the radiant field highly irregular inside the reactor, thus generating a critical situation for the kinetic analysis. Furthermore, the modeling and the study of a photocatalytic system adopting this type of light source may be of interest in view of the increasing utilization of LEDs in photocatalytic applications [16–21].

A plane reactor with total recycle was used for the photocatalytic oxidation of formic acid in aqueous slurry of irradiated TiO$_2$ (Evonik Degussa P25) powders. Fig. 1 shows the scheme of the system and the geometry of the reactor. The slurry flows from $z = 0$ to $z = L$ in the space between the borosilicate glass wall at $y = S_1$ (illuminated front window) and the one at $y = S_2$ (rear window). At the entrance of the reactor the slurry enters a duct with 9 side parallel channels (3 mm diameter) evenly spaced along it to obtain a uniform distribution of the flow at the reactor entrance. The same configuration is used at the exit.

UVA LEDs (total number = 123) are positioned on the $x,z$ plane at $y = 0$ with the disposition illustrated in Fig. 1. The angle of emission of the LEDs is $20°$ (see Fig. S2 in the supplementary material) and their emission spectrum presents a narrow peak at 378.5 nm (see Fig. S3 in the supplementary material). A dimmer controls the intensity of emission with the possibility of varying the average radiative flux $\langle q_{in} \rangle$ entering the reactor from 0 to 9.4 W/m$^2$ as it was measured by a Delta Ohm photo quantum meter (model HD 9021) with a LP 9021 UVA sensor probe.

The fluid, which exits the reactor, is continuously recycled back by a peristaltic pump to the reactor after passing through a perfectly mixed tank (a 1 L bottle, partially filled), whose task is to aerate the solution, to increase the volume of the solution and to stir the reactants and the photocatalyst. In the system, the slurry is in contact with inert materials: stainless steel and borosilicate glass in the reactor, glass in the tank, tetrafluoroethylene in the tubing and Chem-Durance Bio tubing in the peristaltic pump. The flow rate was set at 2.38 L/min and the operating temperature was maintained at about 25 °C.

The solution was prepared by stirring overnight at room temperature 156 mg of formic acid (Fluka) in 1 L of demineralized water to obtain a 3.4 mM solution. Formic acid has been chosen as substrate of the photocatalytic reaction because it undergoes photocatalytic direct mineralization without the formation of intermediates [22–24] and therefore the interpretation of the experimental data for a kinetic study is simpler.

A weighted amount of photocatalytic powders (Evonik Degussa P25) was added to the solution to obtain the desired concentration of photocatalyst (from 0.125 to 1 g/L). The slurry was then ultrasonicated for 15 min before pouring 600 mL of it in the tank. In every experimental run the slurry recirculated in the system for 30 min at the dark before switching on the LEDs, then the reactor was illuminated for about 3 h.

Samples (3 mL each) were withdrawn from the tank every 30 min, were filtered with a 0.2 μm Whatman PTFE microfilter to remove the photocatalyst and analyzed by a Shimadzu TOC-5000A analyzer to measure the acid formic concentration.

The pH of the solution was measured by a Hanna HI 3220 pH meter equipped with a HI 1131B electrode. The initial value of the pH is 3.5 and slightly increases as formic acid mineralizes. The highest value (pH ≈3.8) is not much higher than the initial one and was measured only at the end of the experiment with the highest degradation of formic acid ($C_{cat} = 1$ g/L and $\langle q_{in} \rangle = 9.4$ W/m$^2$). The agglomeration of the photocatalytic particles appears to be negligible. In fact, the efficient mixing in the tank and the acidic pH (the pH is much lower than 6.25, the P25 pH value of zero charge point [25], which represents the pH value at which agglomeration is favored [26]) prevent a progression of this phenomenon in the relatively short experimental times (0.5 h at dark plus 3 h of illumination). Actually, the optical properties of the suspension, which are highly affected by agglomeration, did not change during an experimental run as the constancy of the measured values of the transmitted radiant power demonstrated. In the present experimental system, it was observed that only at longer times or at catalyst concentrations higher than 1 g/L, agglomeration might become of concern.

The values of the dimensional and dimensionless parameters for the investigated system are listed in Table 1. These values will be adopted throughout the current work.

## 3. Kinetic equation

Photocatalytic powders suspended in water solutions containing the target substrate are widely utilized in photocatalysis. Several constitutive equations have been proposed from different researchers to describe the reaction rate dependence on the intervening parameters in this system. Usually the parameters are the concentrations of the substrate, of the oxygen and of the catalyst together with the local volumetric rate of photon absorption. The kinetic equation must be able to reproduce some typical behaviors, which are experimentally observed in these photocatalytic systems, such as Langmuir–Hinshelwood behavior for the substrate concentration (which does not necessarily imply a Langmuir–Hinshelwood mechanism) and a decrease of the quantum yield with the intensity of the radiation or, more precisely, with