How to correctly determine the kinetics of a photocatalytic degradation reaction?
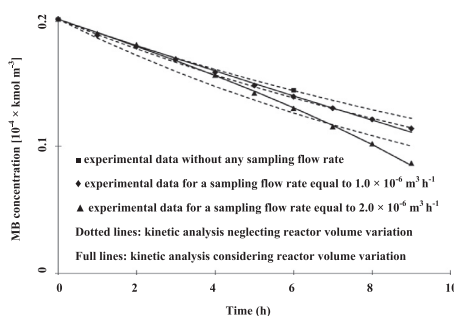
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HIGHLIGHTS

- Regular samplings allows following the degradation of a pollutant in photocatalysis.
- The volume variation due to sampling influences the kinetic rate constant.
- The error on the reaction rate constant depends on the relative volume variation.
- Researchers performing a kinetic study on photocatalytic film have to be careful.

GRAPHICAL ABSTRACT

- ■ experimental data without any sampling flow rate
- ◆ experimental data for a sampling flow rate equal to 1.0×10^{-6} m^3 h^{-1}
- ▲ experimental data for a sampling flow rate equal to 2.0×10^{-6} m^3 h^{-1}

Dotted lines: kinetic analysis neglecting reactor volume variation
Full lines: kinetic analysis considering reactor volume variation

ARTICLE INFO

ABSTRACT

This study deals with the kinetics of photocatalytic degradation of a pollutant. The variation of the volume of the reactor necessary to monitor the pollutant degradation might change the ratio between the amount of pollutant and of catalyst involved in the photocatalytic reaction and thus might falsify the modelling of the photocatalytic activity. However, kinetic studies published up to now in the literature do not take the volume variation into account. In this study, the influence of the experimental sampling procedure on the determination of kinetic parameters is highlighted and it is explained how to correctly determine the kinetics of a photocatalytic degradation reaction in the case of powders and films. Mass balances are developed and the particular case of a first order reaction is treated. Furthermore, the error on the reaction rate constant induced by neglecting the volume variation is quantified. Experimental measurements with powders and films have been performed and validate theoretical statements developed in this study.

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1. Introduction

Heterogeneous semiconductor photocatalysis is an advanced oxidation processes (AOP) which was proven to be a promising technology for the total mineralization of most of the organic pollutants present in water by using natural or artificial light [1]. The most frequently used photocatalyst is titanium oxide, TiO_2, in the form of powder or thin film [2]. Two model molecules are generally used: methylene blue under artificial UV light [3–7] or 4-nitrophenol under UV–visible light [8]. During the photocatalytic experiments, pollutant solution aliquots are sampled at regular time intervals over a period of several hours to measure the absorbance of the solution before and after illumination using a UV–Vis spectrophotometer at a given wavelength depending on the pollutant.

In most of published studies, an apparent first-order kinetic model is adjusted on the experimental data to determine the reaction rate constant, without taking into account the variation of the volume in the reactor due to the sampling of the pollutant solution [9–16].

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The aim of this paper is to highlight the influence of the operating variables as well as the experimental sampling procedure on the determination of the kinetic parameters. In order to model the system, the sampling procedure is approximated by a continuous sampling of the solution with a given flow rate $\overline{V_S}$.

2. Photocatalytic powders

2.1. Theoretical development

In the case of a photocatalytic powder homogeneously dispersed in a perfectly mixed solution, the mass balance for the pollutant in a semi-continuous reactor is [17]:

$$\frac{dn}{dt} = -r_V m_{catalyst} - \overline{V_S} C \tag{1}$$

with

$$V = V_0 - \overline{V_S} t \tag{2}$$

$$m_{catalyst} = m_{catalyst,0} \frac{V_0 - \overline{V_S} t}{V_0} \tag{3}$$

$$n = CV \tag{4}$$

In Eqs. (1)–(4), n is the number of moles of the pollutant (kmol), r_V is the specific reaction rate (kmol h^{-1} kg$_{catalyst}$$^{-1}$), V is the volume of the solution (m^3), V_0 is the initial volume of the solution (m^3), t is the time (h), $m_{catalyst}$ is the mass of catalyst homogeneously dispersed in the solution (kg$_{catalyst}$), $m_{catalyst,0}$ is the initial mass of catalyst homogeneously dispersed in the solution (kg$_{catalyst}$), C is the pollutant concentration (kmol m^{-3}) and $\overline{V_S}$ is the pollutant sampling flow rate (m^3 h^{-1}).

So Eq. (1) becomes:

$$\frac{d\left(C(V_0 - \overline{V_S} t)\right)}{dt} = -r_V m_{catalyst,0} \frac{V_0 - \overline{V_S} t}{V_0} - \overline{V_S} C \tag{5}$$

After derivation, Eq. (5) becomes:

$$\frac{dC}{dt} = -r_V \frac{m_{catalyst,0}}{V_0} \tag{6}$$

Eq. (6) is the general equation describing the evolution of the concentration of the pollutant for a photocatalytic powder homogeneously dispersed and this equation is independent on the expression of the reaction rate r_V.

As an example, if the kinetics of the reaction is of the first order, meaning $r_V = kC$ where k is the reaction rate constant (m^3 h^{-1} kg$_{catalyst}$$^{-1}$), Eqs. (2)–(6) becomes:

$$\frac{dC}{dt} = -kC \frac{m_{catalyst,0}}{V_0} \tag{7}$$

and after integration:

$$C = C_0 e^{\left(-k \frac{m_{catalyst,0}}{V_0} t\right)} \tag{8}$$

Because the sampling flow rate, $\overline{V_S}$ does not appear in Eq. (8) we can conclude that the variation of the volume due to the sampling with a constant flow rate does not modify the kinetic equation. The conclusion is the same for a periodic sampling of a given volume of the solution.

Concretely, in the case of a photocatalytic powder homogeneously dispersed in a perfectly mixed solution for a first order reaction, the following expression has to be adjusted on experimental data:

$$C = A e^{(-Bt)} \tag{9}$$

The reaction rate constant k is obtained by:

$$k = \frac{BV_0}{m_{catalyst,0}} \tag{10}$$

When the fitting between the exponential law and experimental data is not satisfying, it can be suggested that the reaction is not a first order reaction. Hence, another reaction rate expression corresponding to a different order has to be considered and another mathematical development of Eq. (6) has to be performed in order to obtain new expressions for Eqs. (7) and (8).

2.2. Experimental validation

In order to validate the mathematical model developed in the previous section, the photocatalytic activity of a Zn^{2+} doped TiO$_2$ powder (TiO$_2$–Zn–D), synthetized according to the aqueous sol–gel process reported in [18], has been evaluated by measuring the degradation of 4-nitrophenol (4-NP) over a 9 h period using a custom-designed multisample photoreactor described in Fig. 1. A jacketed glass vessel was covered by an aluminum foil and filled with water to control the reactor temperature. An halogen lamp (300 W, 220 V, $\lambda \geqslant 400$ nm, a 20 mL glass reactor equipped with a magnetic bar and a thermometer dedicated to the measure of the water bath temperature which is considered as the reaction temperature) were immersed in a jacketed quartz vessel system.

A stock solution of 4-NP with a concentration of 1.0×10^{-4} kmol m^{-3} was prepared by dissolving 4-NP in reagent-grade water. In this case, the pH is equal to 4.1 and only the protonated form of 4-NP is present in the solution. Two batch reactors ($V_0 = 10 \times 10^{-6}$ m^3 each) containing an initial mass of catalyst homogeneously dispersed in the 4-NP solution equal to $m_{catalyst,0} = 10 \times 10^{-6}$ kg$_{catalyst}$ were placed at equal distances from cylindrical halogen lamp (Philips, 200 W) inside a black box and continuously mixed using vigorous magnetic stirring. The spectrum of the lamp was measured with a spectrophotometer (mini-spectrophotometer Hamamatsu TG) and it was found that the light source yielded a continuous spectrum from 330 nm to 800 nm. Both batch reactors were hermetically closed to avoid evaporation and the internal temperature was maintained at 30 °C.

As revealed during preliminary tests, blank measurements have highlighted that no spontaneous 4-NP breakdown occurs under illumination in the absence of catalyst. Hence, the actual degradation of 4-NP has been determined by measuring the absorbance of the solution at regular time intervals using a Genesys 10S UV–Vis
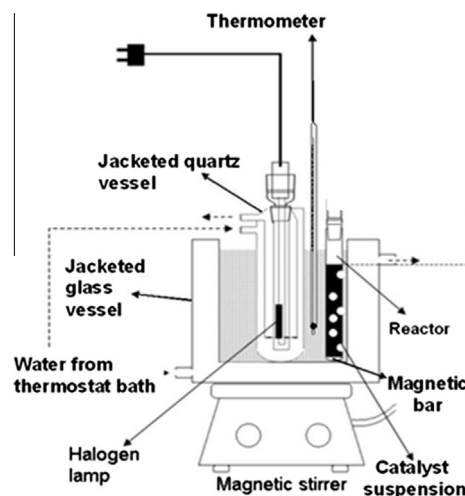

Fig. 1. Experimental device for measuring photocatalytic activity under halogen-lamp illumination [19,20].