



## Modeling of photocatalytic degradation of organic components in water by nanoparticle suspension



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### HIGHLIGHTS

- Development of a model for the kinetic processes in photocatalytic water purification.
- Experiments with ciprofloxacin and methylene blue in TiO<sub>2</sub> and ZnO nanosuspensions.
- Estimation of model parameters from comparison with experimental findings.
- Calculated concentration evolution of degradation intermediates.
- Simulated TOC curves for different model assumptions.

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### ABSTRACT

Photocatalytic degradation of organic components in water by means of TiO<sub>2</sub> nanosuspensions under ultraviolet (UV) irradiation represents an efficient method for water purification. In the present paper, a modeling approach is proposed to simulate the involved kinetic processes based on the Langmuir–Hinshelwood mechanism. The extended model also includes the formation of intermediate organic components either by an incremental degradation mechanism or by a fragmentation mechanism. Model parameters were estimated from comparison with experimental findings. To demonstrate these models, adsorption and degradation experiments were performed using the antibiotic ciprofloxacin and the dye methylene blue as organic compounds and TiO<sub>2</sub> and ZnO as photocatalytic materials. By comparing our simulations with concentration measurements, we found that the adsorption of organic molecules on the surface of the photocatalyst was rate determining at an irradiation intensity of about 20 W m<sup>-2</sup>. The derived adsorption rates for ZnO were considerably higher than those for TiO<sub>2</sub>. The calculated concentration evolution of intermediates as well as the TOC evolution are discussed for different model assumptions with respect to their desorption rates from the photocatalyst surface.

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## 1. Introduction

Many pollutants, such as heavy metals, dyes, and pharmaceuticals are discharged into the water cycle at many stages in our daily lives. In particular, antibiotics represent a serious problem because of their toxicity to microflora and -fauna, and of the possible development of antibiotic-resistant microorganisms [1–3]. Global over- and abuse of antibiotics has resulted in their concentrations steadily increasing in wastewater [4]. Another common pollutants

are dyes, which are widely used in various industries and which are often released into the wastewater. Some dyes are toxic, mutagenic [5] or carcinogenic [6] and should therefore be removed from wastewater.

Photocatalytic oxidation is a promising approach in the purification of water, which is contaminated with organic pollutants [7–11]. Successful degradation experiments have been reported [7] for various organic molecules, such as azo dyes [12], furfural [13], sulfamethoxazole [14], and acetylene [15]. An efficient way to study the photocatalytic oxidation process is the application of suspensions of photocatalytic nanoparticles, since these suspensions exhibit a large specific surface area. For example, the anatase phase of TiO<sub>2</sub> is known for its good photocatalytic properties [16,17].

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## Nomenclature

$a$	particle spacing (m)	$j_{\text{reac}}$	reaction flux ( $\text{m}^{-2} \text{s}^{-1}$ )
$A(\text{ad})$	adsorbed organic molecule	$k_{\text{ads}}$	adsorption rate constant ( $\text{m s}^{-1}$ )
$A(\text{aq})$	organic molecule in solution	$k_{\text{app}}$	apparent rate constant ( $\text{s}^{-1}$ )
$a_s$	specific surface area ( $\text{m}^{-1}$ )	$k_B$	Boltzmann constant ( $\text{J K}^{-1}$ )
$A_m$	surface area covered per molecule ( $\text{m}^2$ )	$k_{\text{des}}$	desorption rate constant ( $\text{s}^{-1}$ )
$C_{A(\text{ad})}$	concentration of adsorbed organic molecules ( $\text{m}^{-2}$ )	$k_{\text{reac}}$	reaction rate constant ( $\text{s}^{-1}$ )
$C_{A(\text{aq})}$	concentration of organic molecules in solution ( $\text{m}^{-3}$ )	$M$	mineralized components
$C_{A(\text{aq}),0}$	initial concentration of organic molecules in solution ( $\text{m}^{-3}$ )	$n$	molecule size index
$C_{A(\text{aq}),\infty}$	equilibrium concentration of organic molecules in solution ( $\text{m}^{-3}$ )	$T$	temperature (K)
$C_{M(\text{aq})}$	concentration of mineralized components in solution ( $\text{m}^{-3}$ )	$t$	time (s)
$C_p$	particle concentration ( $\text{m}^{-3}$ )	$t_D$	characteristic diffusion time (s)
$D$	diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )	$\alpha_{0/1}$	parameters for $v_0$
$E_{0/1}$	fit parameters for $k_{\text{des}}$	$\beta_{0/1}$	parameters for $E_{\text{des}}$
$E_{\text{des}}$	desorption energy (J)	$\eta$	viscosity
$I_0$	photon flux ( $\text{m}^{-2} \text{s}^{-1}$ )	$\kappa$	adsorption prefactor (m)
$j_{\text{ads}}$	adsorption flux ( $\text{m}^{-2} \text{s}^{-1}$ )	$v_0$	pre-exponential factor ( $\text{s}^{-1}$ )
$J_{\text{des}}$	desorption flux ( $\text{m}^{-2} \text{s}^{-1}$ )	$\phi$	quantum yield
		$\Theta$	surface coverage

The simulation of the kinetic processes, which are involved in the photocatalytic oxidation of organic pollutants, are expected to lead to a deeper quantitative understanding of the whole mineralization process. This could also help in optimizing the design of reactors for photocatalytic water purification. A very important issue of reactor design is the radiation transport in the reaction volume, investigated for example in [18–20]. The degradation kinetics of organic pollutants has often been described within the framework of the Langmuir–Hinshelwood (LH) model (see e.g. [10] and references therein). For example, Minero [21] discussed several kinetic models of the photocatalytic process with the aim to obtain equations with physical meaning and reduced complexity. An experimental validation of reported kinetic models has been performed by Andreozzi et al. [22] for the photocatalytic degradation of 4-nitrophenol. The LH model combined with a Lambert–Beer type model for the radiation transport has been applied to describe the degradation of methylene blue by Sannino et al. [23].

Generally, the photocatalytic mineralization of organic molecules is a complex process, where parts of the initial molecules are oxidized step by step on the catalyst surface in the presence of photo-generated radicals. These radicals may also destroy the molecules' bonds thereby breaking them into smaller molecules. These molecules may then desorb from the surface of the photocatalyst. Consequently, various intermediate molecules of different sizes emerge in the solution. In the present study, we propose two model approaches of photocatalytic degradation which extend models with only one molecule species [10,23,24] by including the evolution of intermediates. In a first limiting case, we study degradation by successive oxidation of the elements of the initial molecules, excluding the possibility of molecule fragmentation. Within a second complementary model, random fragmentation of organic molecules into smaller intermediates and oxidation of the smallest fragments is considered. Investigations of the concentration evolution of intermediates have been presented for example in [25–27]. A comprehensive experimental analysis and theoretical modeling of the degradation of phenol has been reported in [26,27]. The kinetic model was based on a 'series-parallel' reaction network which included several intermediate species. The model parameters were fitted from measured concentration profiles of intermediates in the solution. In the present paper, we propose a model approach where, besides the concentrations in the solution, we

explicitly include also the dynamics of the surface concentrations of adsorbed intermediates. In particular, we demonstrate the effect of different desorption properties of intermediates on their concentration evolution.

Our theoretical analysis was compared with degradation experiments performed on the antibiotic ciprofloxacin [28–30] and on the dye methylene blue [23,24,31] in a photocatalytic slurry. Nanoparticles of  $\text{TiO}_2$  and  $\text{ZnO}$  were used as photocatalysts. This way, we attempted to obtain characteristic values for kinetic model parameters. Additionally, we compared also with literature data on the degradation of methylene blue [31].

This paper is organized as follows. After a brief presentation of the experimental investigations, different mathematical models to describe the degradation process of the organic compounds in the solution are presented. Thereafter, our degradation experiments are presented and rate constants in our model are determined by fitting to these measurements. Finally, simulations of the concentration evolution of the initial and intermediate organic molecules, and of the total organic carbon (TOC) in the solution, are discussed.

## 2. Materials and methods

### 2.1. Experimental investigations

For performing adsorption experiments in the dark and degradation experiments under UVA, aqueous solutions of  $12.5 \mu\text{M}$  ciprofloxacin and  $11.0 \mu\text{M}$  methylene blue were prepared. To those solutions,  $1 \text{ g L}^{-1}$  of  $\text{TiO}_2$  P25 (Evonik) or  $\text{ZnO}$  (IOLITEC Ionic Liquids Technologies GmbH) was added under constant stirring. The textural properties of the photocatalyst nanoparticles were analyzed at 77 K by nitrogen adsorption–desorption in a Micromeritics TriStar analyzer (Micromeritics, Norcross GA). Before performing adsorption experiments, samples (0.5 g) were outgassed at 26.7 Pa and 350 °C for 6 h. The specific surface area of the particles was determined by the Brunauer–Emmett–Teller (BET) method.

In all experiments, the samples were analyzed using a Varian CARY-100 UV–VIS spectrophotometer. The concentrations were calculated by comparing the measured absorption spectra to the calibration curves.

For the absorption experiments in the dark, a sample was taken using a syringe and then pressed through a filter (Rotilabo nylon,

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