A new approach to heterogeneous kinetics of photosensitized oxidation

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ABSTRACT

This work focus on modelling of the photosensitized oxidation in heterogeneous and its experimental verification. The experiments of heterogeneous degradation of butyl- and benzylparaben in aqueous solutions using photochemically excited meso-tetraphenylporphyrin (TPP) immobilized in polyurethane nanofabrics were used to validate the proposed model. The major role of the singlet oxygen was proven. The kinetics study showed that the heterogeneous photodegradation of parabens could be described using the Langmuir–Hinshelwood model. However, this model does not fully reflect the reaction that occurs during the photosensitized oxidation process. The aim of this study was to develop a kinetic model of photosensitized oxidation processes in a heterogeneous system, which will expand the knowledge of this process as well as the photochemical reactions occurring in the environment.

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1. Introduction

Photosensitized oxidation may occur in both homogeneous and heterogeneous systems. The disadvantage of the homogenous process is the necessity of removing the photosensitizer from the solution after the reaction has been completed [1]. However, water-insoluble chromophores used in suspension form have weak activity and often undergo aggregation at specific concentrations, resulting in a decrease of activity [2]. The reduction in the yield of singlet oxygen generation by multiparticle aggregates is attributed to the dispersion of excitation energies by relaxation oscillation [2,3]. This problem can be overcome by the use of immobilized photosensitizers, which exhibit the advantage of easy operation but sometimes demonstrate a reduced rate of reaction because of mass transfer limitations [1,3,4]. In this situation, the photosensitizer can be easily separated from the reaction mixture, e.g., by filtration, and prepared for reuse. The immobilization of a photosensitizer reduces its photobleaching, allowing for it to be used many times [1,3]. Immobilization of a photosensitizer is associated with a decrease of the singlet oxygen quantum yield, which may be attributed to limitations in oxygen diffusion into and from the carrier material [1,3,4]. These disadvantages can be

overcome by reusing the immobilized photosensitizers in water treatment, which has many environmental and economic benefits.

The idea of anchoring the photosensitizer into an insoluble carrier was first proposed by Kautsky in 1939 [5] and then by Merrifield in 1963 [6]. Immobilization was obtained on a solid carrier, such as silica gel, alumina, celite, cellulose, polysiloxane, copolymers, polydimethylsiloxane, chitosan, or more recently, Nafion [7–11]. Photosensitizers can also be immobilized on the reactor walls directly or indirectly through an additional binder [12]. Immobilization of chromophores also leads to the maintenance of their molecular dispersion [13]. However, the process of chemical or physical bonding of the photosensitizer with the carrier causes a partial loss of activity. The first commercially available immobilized photosensitizer, rose bengal immobilized on Merrifield's polymer [14], showed a 100-fold decrease in the efficiency of singlet oxygen generation [15]. The study on meso-tetraphenylporphyrin embedded in polyurethane nanofabric showed that the activity of the photosensitizer is likely dependent on the sensitizer–carrier configuration [16]. The lifetime of singlet oxygen generated by the modified fabric is nearly double that of a homogeneous system [16]. Moreover the immobilization of zinc both tetraphenylporphyrin (ZnTPP) and zinc phthalocyanine (ZnPc) onto polyurethane nanofabrics increased the singlet oxygen

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Nomenclature

$^1O_2$	Singlet oxygen
$^3O_2$	Molecular triplet oxygen
BeP	Benzylparaben
BuP	Butylparaben
EDCs	Endocrine disrupting compounds
E_a	Flux of absorbed photons per unit of the reaction volume
e	Photosensitized oxidation process of organic compounds in a heterogeneous system on the carrier surface
K	The dynamic equilibrium constant of parabens adsorption onto nanofibers material
$K_{BuP/BeP}$	Langmuir equilibrium constant
k	Rate constant
k_d	Rate constant of singlet oxygen decay in water
k_D	Rate constant for triplet photosensitizer decay
k_{LH}	The apparent reaction rate constant,
k_r	Rate constant for chemical reaction of singlet oxygen
k_r^{EDCs}	Rate constant for chemical reaction of singlet oxygen with EDCs
k_t	Rate constant for physical and chemical decay of singlet oxygen
k_q	Rate constant for physical quenching of singlet oxygen
$k_\Delta^{O_2}$	Rate constant for triplet photosensitizer reaction with oxygen which gives $^1O_2$
$k_Q^{O_2}$	Rate constant for triplet photosensitizer quenching by oxygen
k_q^{EDCs}	Rate constant for triplet photosensitizer quenching by endocrine disrupting compounds
l	Photosensitized oxidation process of organic compounds in a heterogeneous system in reaction solution in close proximity to the carrier
L-H	Langmuir-Hinshelwood model
r	Reaction rate
t	Time
TPP	Meso-tetraphenylporphyrin
ϕ	Quantum yield
ϕ_T	Quantum yield of triplet formation
$\phi\Delta$	Quantum yield of singlet oxygen formation
λ	Wavelength
*	Excited state
0	Initial conditions

lifetime compared with individual immobilization [17]. However, nanofabric containing TPP was more effective photosensitizing material than those with zinc tetraphenylporphyrin (ZnTPP) or zinc phthalocyanine (ZnPc) [17].

As mentioned previously, in most cases, the quantum yield of singlet oxygen generation by immobilized photosensitizers decreases in comparison to homogenous processes. However, the singlet oxygen quantum yield of the polymer with covalently bound rose bengal is 0.73, which is comparable to the value obtained in homogeneous solution ($\Phi_D = 0.76$) [18]. Thus, generation of singlet oxygen is possible by using an immobilized photosensitizer without the loss of its properties, making it a novel and innovative way to remove impurities from a water environment.

In a homogenous system, photosensitized oxidation can proceed by two pathways of reactions, while in a heterogeneous system, the adsorption of a substrate on the selected carrier should be taken into account. The rates of photocatalytic processes in the heterogeneous system are typically expressed by the Langmuir-Hinshelwood kinetics model (L-H) [19]. The kinetics of water pollutant degradation in the presence of TiO_2 are commonly characterized according to this approach [20–22]. However, the L-H kinetics application for the photocatalytic process allows for the kinetic parameters to be obtained, which are not directly related to the chemical reaction constants or even the Langmuir adsorption isotherm [23,24]. This observation leads to the conclusion that the L-H kinetic constants have no physical meaning but are merely experimental constants used to describe the degradation under chosen experimental conditions, including a specific range of substrate concentrations [23–25]. Therefore, it is reasonable to search for a new kinetic model that allows for the determination of kinetic constants that describe the chemical reactions in the heterogeneous process. Thus far, the L-H constants have been known to be dependent on the intensity of the incident photon flux [22,26,21].

To date, photosensitized oxidation in a heterogeneous system has not been analyzed in terms of a kinetic description. Thus, the aim of this study was to develop a kinetic model of photosensitized oxidation processes in a heterogeneous system, which will expand the knowledge of this process as well as photochemical reactions occurring in the environment.

2. Methods

Butylparaben (>99%) (BuP) and Benzylparaben (>99%) (BeP) were obtained from Fluka (Buch, Switzerland) and Sigma-Aldrich Chemie GmbH (Steinheim, Germany), respectively. Meso-tetra-phenylporphyrin (TPP) was purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). The polymer nanofabrics with immobilized photosensitizer were prepared by the electrospinning technique according to [17]. The study was conducted in a semi-continuous system in flat reactors (6×10 cm) with a volume of 0.01 dm^3. Five reactors were symmetrically positioned around a xenon lamp (100 W), simulating solar radiation. The 1%wt. of TPP onto PUR nanofabric with 2.1 g/m^2 area weight was applied. The reactions were carried out in pH 10.8 at 25 °C. The photon flux entering to the reactors was determined using Reinecke salt actinometer as equal to $E_0 = 5.54 \times 10^{-4}$ einstein s^{-1} dm^{-3}. The reaction mixture was agitated by gentle air or oxygen stream. The inner walls of the reactors were covered by the nanofabrics with immobilized photosensitizer. The BuP and BeP decay were monitored by an High-Performance Liquid Chromatography (HPLC, Waters instrument equipped with 600E Controller, photo diode array 996 detector ($\lambda_{det} = 255$ nm), Waters 717 Autosampler; Waters, Milford, USA). The chromatograph was equipped with a Nova-Pak 150/C18 column (Waters, Milford, USA). A detailed detection procedure as well as the sample preparation were previously published in [23,24].

3. Results and discussion

At the first step of experiments the mechanism of photo-degradation has been investigated. Several reactions were carried out in order to exclude the decomposition of parabens as a result of: adsorption, hydrolysis or action of hydroxyl radicals. Furthermore, the experiments with singlet oxygen quencher were performed. The results are shown in Fig. 1.

As can be seen only about 5% of photodegradation was observed in the dark as well as upon irradiation in the absence of photosensitizer, what confirm that adsorption takes small participation in degradation, However, experiments with hydroxyl radicals scavenger and singlet oxygen quencher proved that singlet