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Combined effect of temperature and dissolved oxygen on degradation of 4-chlorophenol in photo microreactor

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ABSTRACT

Microreactors receive a lot of interest in photochemical application, however, the fundamental effects of micro flow on the photochemical reactions have not been fully understood so far. We report on the investigation of the combined effect of temperature and concentration of dissolved oxygen on degradation of 4-chlorophenol in photo microreactor. Sulfonated zinc phthalocyanine was used as a photosensitizer to generate singlet oxygen. Temperature and dissolved oxygen affect the overall reaction, however, the effect is not straightforward. To investigate their combined effect, the experiments were carried out in the advanced opto-chemical apparatus with a thin-gap photo microreactor. To obtain accurate information on actual process conditions, temperature of the reaction zone was measured by an integrated temperature sensor and the concentration of dissolved oxygen was measured by the in-line oxygen probe. As results, the reaction rate constant of the model reaction was evaluated and the apparent activation energy was calculated.

1. Introduction

Application of photo catalyzed reactions in the continuous microreactors successfully combines the advantages of microreactor technology with the light as the clean and traceless reagent. A comprehensive review of photochemical reactions carried out in different types of photo microreactors is given by Oelgemoller [1]. Continuous flow photochemical reactions in microreactors have several advantages. Thanks to their relevant characteristic dimension the microreactors provide a homogeneous and effective irradiation of the reaction mixture. Flow regime enables to remove products and avoid undesired reactions. The literature shows several types of arrangement of photo microreactors. One of these is based on capillary, which is tightly wrapped around a glass cylinder with a light source [2–5]. Multi micro capillary flow reactor can be simply used for sensitizer screening, process optimization, validation and library synthesis [6]. Another type of arrangement is photo microreactor with embedded meander reaction channel with the light source positioned above the reaction channel [3,7–10], or falling film photo microreactor [11], which was used for synthesis of juglone [12]. A thin-gap photo microreactor was proven to be an efficient tool for light induced oxidation reactions [13]. From the brief literature review presented above it is clearly evident that the microreactors are interesting alternative for the research of photochemical processes providing. However, the fundamental effects of micro flow on the photochemical reactions have not been fully understood so far.

Photochemical reactions are initiated by the electron-excited molecules after the absorption of suitable radiation. Among these molecules, phthalocyanines (PhC) are macrocyclic organic compounds with metal ion in the central position. Selected phthalocyanines (e.g., AlPhC, SiPhC, ZnPhC [2]) after the light irradiation produce the highly reactive singlet oxygen.

In this article we focus on the model photo oxidation of 4-chlorophenol (4-CP) with a photosensitizer in a thin-gap photo microreactor. Based on the previous studies [10–12], sulfonated zinc phthalocyanine ($ZnPcS_{mix}$) was chosen as suitable homogeneous photosensitizer. According to the literature there are two possible ways how 4-chlorophenol can be oxidized using

$$ZnPcS_{mix} \xrightarrow{h\nu^1} ZnPcS_{mix}{}^{*} \xrightarrow{ISC^3} ZnPcS_{mix}{}^{*} \quad (1)$$

$$^3ZnPcS_{mix}{}^{*} + {}^3O_2 \rightarrow {}^1O_2 \quad (2)$$

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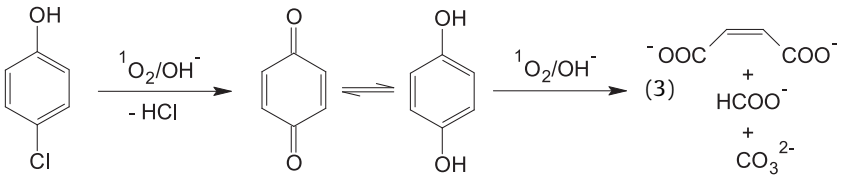

$ZnPcS_{mix}$ as sensitizer [14–16]. Type I mechanism is based on the characteristic electron or hydrogen transfer and radical formation. Type II mechanism is characterized by the $ZnPcS_{mix}$ excitation to the singlet state followed by the intersystem crossing (ISC) to the triplet state (Eq. (1). The next mechanism step is the energy transfer from the sensitizer in the triplet state and formation of the singlet oxygen $^1O_2$ from ground-state molecular oxygen $^3O_2$ Eq. (2). Singlet oxygen then participates in the chemical reaction with 4-CP to form the oxidation products Eq. (3). Generally, it is assumed that the dominant mechanism is Type II.

The photochemical generation of singlet oxygen is initially ruled by the light absorption by the photosensitizer, which is not affected by temperature. In aqueous solution, the temperature has only the minor effect on the lifetime of singlet oxygen [17]. Therefore, the reaction steps leading to the formation of singlet oxygen can be considered as temperature independent from the chemical-engineering point of view. The oxidation reaction Eq. (3), on the other hand, can be described by the first order kinetics and its kinetic constant depends on temperature according to the Arrhenius equation.

Concentration of dissolved oxygen directly influences the generation of singlet oxygen Eq. (1) and thus the 4-CP oxidation, even if oxidation reaction Eq. (3) is supposed to be a zero order reaction in relation to the singlet oxygen. Concentration of dissolved oxygen in water depends also on temperature [18]. This work is focused on the investigation of the combined effect of temperature and concentration of dissolved oxygen on the photochemical oxidation of 4-CP in photo microreactor.

2. Materials and methods

2.1. Chemicals

Reaction mixture components were 4-CP (Sigma–Aldrich, >99%), $ZnPcS_{mix}$ (prepared according to the routine published previously [19]). Constant reaction pH was maintained by addition of NaOH (Sigma–Aldrich, 98%). For HPLC analysis methanol (Lachner, 99.8%) was used as a mobile phase.

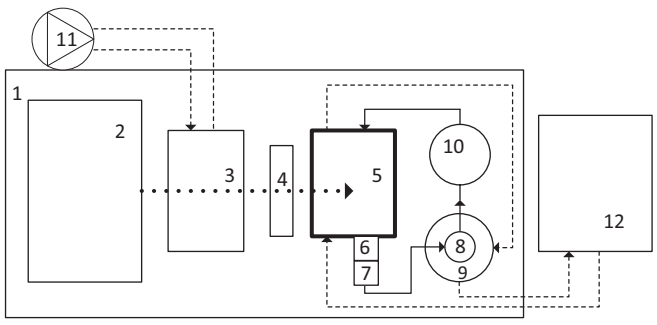

Fig. 1. Scheme of experimental setup: (1) optical bench, (2) UV lamp witch cooling, (3) IR water filter, (4) light filter, (5) photo microreactor, (6) in-line oxygen sensor, (7) in-line pH sensor, (8) reservoir solution, (9) cooling jacket, (10) micro annular gear pump, (11) peristaltic pump for thermostating medium, (12) thermostatic bath; Full line – process flow, dashed line – thermostating medium.

2.2. Experimental set-up

The experimental setup consisted of a light source, calibrated optical bench and microreactor system. The arrangement is schematically depicted in Fig. 1. The optical setup comprised a 201-1 K Air collimated beam arc lamp housing (Sciencetech Inc.) with DUV-500 (Advanced Radiation Corporation) with light filter and the IR water coolers. The oxygen was introduced into the solution by bubbling the air through the solution reservoir.

The main part of the experimental set-up was a photo microreactor (PMR) and supporting modules of modular micro reaction system (Ehrfeld Mikrotechnik BTS). The PMR has operating range 15–50 °C and maximum allowable fluid pressure 2 bar at 24 °C. The body of the microreactor was of stainless steel (A4 1.4404), the reaction space was located between the exchangeable 270 μm PFA (perfluoroalkoxy) spacer and the quartz cover window (Fig. 2). The irradiated volume and area were 432 μl and 1600 mm^2, respectively. Reaction mixture was circulated with flow rate 10 ml min^{-1} through PMR using a micro annular gear pump MRZ-7205 (HNP Microsysteme). The PMR was fixed on a base plate together with the liquid connector modules and the oxygen and pH probes. The reaction temperature was controlled by the integrated heat exchanger with an internal PT100 sensor. The construction of photochemical microreactor had the advantage of relatively high ratio of "thermal mass" of the reactor body and the volume of the reaction mixture enclosed inside the microreactor. The enclosed liquid volume was small (only 432 μl in a thin liquid film) compared to the body of microreactor so that the liquid temperature was equalized with the temperature of the micro-reactor body before the liquid reached the irradiation zone. The sufficient capacity of the IR filter and the microreactor internal heat exchanger was sufficient to keep the reaction volume temperature within ±0.35 °C during the whole experiment.

The PMR and reservoir solution were thermostated with a circulating water-bath Ministat 125 (Huber). Multi meter M3850D (Metex) with Si photodiode Hamamatsu S1337-BQ was used for measuring the light intensity. Dissolved oxygen concentration was

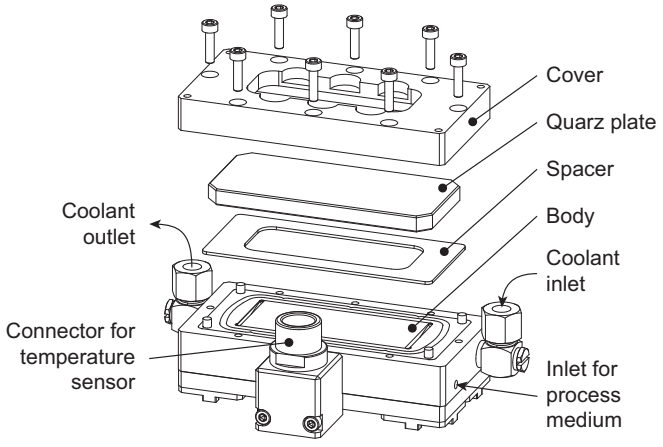

Fig. 2. Exploded view of the thin-gap photo microreactor.