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Performance of continuous micro photo reactor – comparison with batch process

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Abstract

Utilization of the flow chemistry as well as microreactors belongs to the latest trends in chemical engineering. Continuous microreactors of various kinds can be found in the literature, for example the micromixers, micro packed beds, or micro photo reactors. In order to evaluate the benefits of microtechnology application for the given process, the performance of a particular microreactor needs to be compared with the conventional setup. This contribution presents the performance of a continuous micro photo reactor in comparison with a batch process. Two model reactions were selected: the catalyzed photooxidation of 4-chlorophenol (4-CP) and the singlet oxygen chemical quencher 9,10-dimethylanthracene (DMA) in dimethylformamide. The tests were carried out using advanced opto-chemical apparatus with a well-defined light filter corresponding to the absorption bands of the used photo catalysts

1. Introduction

Combination of microreactors and photochemistry is interesting and relatively new area in the field of chemistry. Continuous flow microreactors can be used as mixers, meander reactors, capillary reactors, packed-bed reactors and so on. Characteristic feature of these microdevices is at least one of the internal dimensions less than 1 mm. That predisposes the high surface-to-volume ratio. High surface-to-volume

Nomenclature

4-CP	4-chlorophenol
DMA	dimethylanthracene
DMF	dimethylformamide
MPR	micro photo reactor
Pcs	Phtalocyanines
Re	Reynolds number

ratio ensures the better and more accurate control of mass and heat transport [1]. Conventional design of photoreactors is based on a batch or larger-scale continuous reactors used for example in waste water treatment [2]. Recently, however, the micro photo reactors have been developed, exploiting the advantages of thin liquid layer exposed to irradiation. Short residence time in the reaction zone prevents the undesirable side reactions and the process can be easily scaled-up by parallelization.

As an example of successful combination of photochemistry and microtechnology, the synthesis of vitamin D₃ from his provitamin and previtamin can be mentioned. This double step reaction (Chyba: zdroj odkazu nenalezen) consists of photochemical and thermal reaction which was carried out in two quartz microreactors in series. Yields of vitamin D₃ from microreactors are higher (32 %) when compared to the traditional production of vitamin D₃ which leads to yields typically below 20 % .

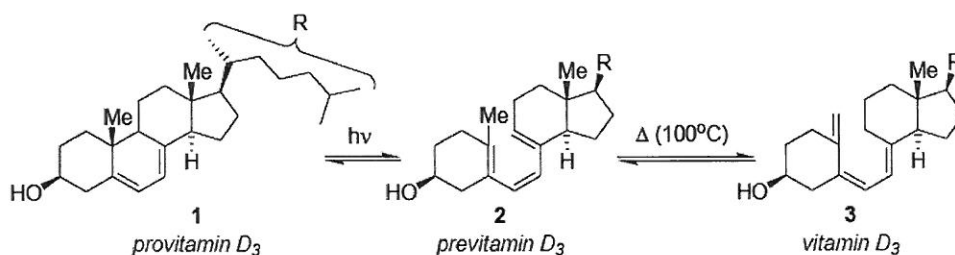


Figure 1. Reaction scheme of vitamin D₃ synthesis

Micro photo reactors can be also used in combination with heterogeneous catalysts immobilized on TiO₂ . Other examples of microreactor utilization in photochemistry include the photoreduction of benzaldehyde to benzyl alcohol and p-nitrotoluene to p-toluidine , photosensitized oxidation , Barton reaction (nitrite photolysis) , asymmetric addition of methanol to (R)-(+)-(Z)-limonene , addition of isopropanol to furanones , photodimerization of maleic anhydride to cyclobutane tetracarboxylic dianhydride , photo-radical chlorination of cykloalkanes or photodecarboxylation of phtaloyl amino acids .

This contribution presents the preliminary comparison of micro photo reactor (MPR) with a conventional lab-scale batch process. The comparison is based on two homogeneously catalyzed photooxidation reactions, which were previously tested and optimized in conventional setup . As catalyst we used the phtalocyanines (Pcs), synthetic structures derived from the structure of porphyrine.

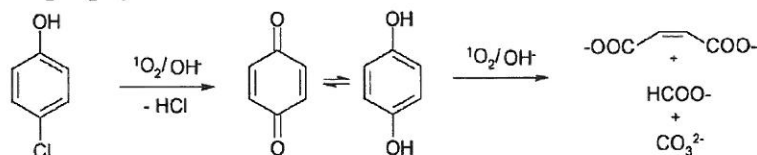


Figure 2. Reaction scheme for 4-chlorophenol oxidation

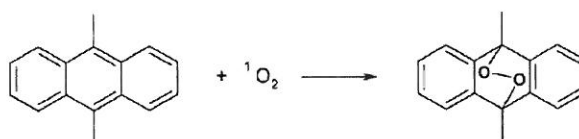


Figure 3. Reaction scheme for DMA oxidation

Pcs are able to produce singlet oxygen ($^1\text{O}_2$), highly reactive and oxidation agent, by excitation of ground-state molecular oxygen ($^3\text{O}_2$) using irradiation of light with suitable wavelength.

The first reference reaction was photooxidation of 4-chlorophenol in deuterated water catalyzed by sulfonated Zn phthalocyanine (Chyba: zdroj odkazu nenalezen). This derivate of Pcs was selected for good solubility in water. Chlorophenols belong among the water pollutants produced by human activities, when used as preservative agents or in pesticides, drugs and dyes. They have bactericidal and phytotoxic effects with the ability of accumulation in organisms.

The second reaction was the internal transformation of singlet oxygen quencher 9,10-dimethylantracene (DMA) in dimethylformamide (DMF) catalyzed by sulfamidic Zn phthalocyanine, which is soluble in DMF (Chyba: zdroj odkazu nenalezen). To the best of our knowledge, the application of micro photo reactor for reaction catalyzed by phthalocyanines was not reported previously.

2. Experimental

2.1. Chemicals

Identical chemicals were used for experiments in micro photo reactor and in conventional batch reactor. Deuterated water (99.8 %) and 9,10-dimethylantracene (97 %) were supplied by Acros Organics, 4-chlorophenol (> 98 %) from Sigma Aldrich, dimethylformamide (> 99.8 %) from Lachner, NaOH (> 98 %) from Penta and methanol (> 99.8 %) from J. T. BAKER. As catalysts were used the sulfonated and sulfamidic Zn phthalocyanine received from VUOS-Pardubice.

2.2. Experimental setup

The experiments were carried out in a continuous-flow micro photo reactor (MPR) fixed onto an optical bench (Chyba: zdroj odkazu nenalezen). The light source was a high-pressure mercury lamp (LOT-LSB610), connected to a monochromatic filter (Melles Griot, 670 nm). Light passed through the cuvette with cooling water towards the MPR. An HPLC pump (ALFA100) supplied the reaction mixture into the MPR. The distance between the lamp and MPR was 120mm. Comparative data were obtained from a similar setup where the continuous microreactor was replaced with a small batch reactor.

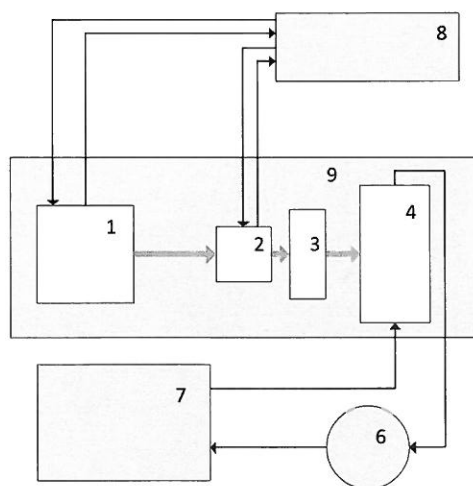


Figure 4. Experimental setup; 1 - UV lamp with cooling, 2 – cuvette with cooling water , 3 - monochromatic light filter, 4 - micro photo reactor setup / batch reactor, 6 - reservoir solution, 7 - HPLC pump, 8 - peristaltic pump, 9 - optical bench.

The microreactor setup consisted of a micro photo reactor (Ehrfeld Mikrotechnik BTS), two pressure transducers (Keller PAA-35XHT), an in-line optical cell (Ehrfeld Mikrotechnik BTS) and the liquid connector modules. All modules were fixed on a base plate with clamping modules. Inside the MPR, the reaction solution was irradiated in a thin film layer with easily adjustable thickness. The layer thickness was defined with an exchangeable PFA spacer. The spacer was pressed between the front quartz glass wall and rear stainless steel wall of the reaction zone.

Temperature of the reaction zone was monitored with a PT100 sensor. The pressure sensors and the MPR temperature sensor were connected to LabVision computer software for data logging. The in-line optical cell was intended for inline analysis of the DMA photooxidation products by spectrophotometry.

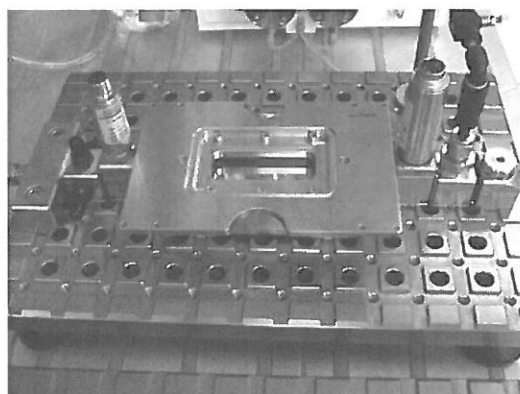


Figure 5. Micro photo reactor setup on the base plate

2.3. Experimental procedure

The reaction mixture for photooxidation of 4-CF in MPR consisted of 4-CF ($1.4 \cdot 10^{-4}$ mol/l), sulfonated ZnPcs catalyst ($7 \cdot 10^{-7}$ mol/l) and 30 ml of D₂O as solvent. Before starting the reaction, the pH was adjusted to 10 and maintained at constant level during the experiments by addition of NaOH. Samples were taken after 0, 40, 80, 120 and 150 minutes of circulation of the reaction mixture through the MPR. Irradiation of MPR started after taking the first sample (at 0 min). All samples were analyzed off-line using HPLC (DIONNEX UltiMate 3000).

The reaction mixture for experiments with DMA in MPR consisted of DMA ($1.4 \cdot 10^{-5}$ mol/l), sulfamidic ZnPcs catalyst ($7 \cdot 10^{-7}$ mol/l) and 30 ml of DMF as solvent. The outlet composition from the MPR was analyzed using the in-line optical cell connected to spectrophotometer and light source (Ocean Optics USB 4000, DT-MINI-2-GS). The spectrum was continuously recorded each 20 s. The total time of circulation of the reaction mixture through the MPR was 150 minutes. Recorded data were evaluated using the calibration curve method.

2.4. Incident light intensity

The incident light intensity was measured in front of and behind the quartz glass with the disassembled microreactor at the light wavelength of 670 nm. The intensity behind the glass corresponded to the light intensity in the reaction zone. Detected decrease in the light intensity due to pass through the glass was below 5 %, and it reached approximately 0.5 mW/cm^2 inside the reaction zone.

2.5. Blind experiments

In order to test the stability of the reaction components we carried out three sets of blind experiments. First, the reaction system was irradiated without the presence of catalyst, only in the solvent. In this case we found that DMA was sufficiently stable; the decrease in concentration was below 2 %. Second, the complete reaction system (DMA, Pcs, solvent) were tested without irradiation. All components were stable and there was no observable degradation. Third, the photo stability of used Pcs was tested at 670 nm wavelength without DMA. Results indicated a concentration decrease between 10 – 13 %. This can be attributed to a self-degradation due to generated ¹O₂.

Similar blind tests were carried out for oxidation of 4-CP with identical results.

3. Results and discussion

Prior to the photochemical experiments, the micro photo reactor hydrodynamics was characterized by the pressure drop measurements at different thicknesses of reaction zone (gap thickness) and different flow rates. Chyba: zdroj odkazu nenalezen summarizes the results of the hydrodynamic experiments. It is evident that by a suitable combination of a given gap thickness and flow rate, the micro photo reactor can provide a wide range of residence time and pressure drop (when relevant) and therefore the operating condition can be optimized for a broad spectrum of chemical reactions. Considering the fact that the gap thickness can be changed very quickly and easily, the micro photo reactor presented a truly modular microreaction system.

For the studied flow rates, the measured pressure drop for 100 μm gap was almost negligible but for the 25 μm gap reached more than 3 bar at 10 ml/min. The studied photochemical reactions took part in liquid phase only, so there was no pressure drop effect on the reaction. If, however, gas would be present inside the reactor, the pressure drop would have been important parameter.

In accordance with our previous experiments, the 100 μm gap was selected as the starting microreactor geometry as it should provide sufficiently long residence times in the tested range of flow rates. The values of Reynolds number indicated that all the experiments were carried out in laminar flow regime.

Table 1. Pressure drop and residence time

gap thickness [μm]	flow rate [ml/min]	pressure drop [bar]	Re in reaction zone [-]	residence time [s]
25	0.1 - 10	0.3 - 3.28	0,86 – 85,9	24 - 0.24
50	2.0 - 100	0.05 - 3.05	17,2 – 859,8	2.5 - 0.05
100	2.0 - 100	0.02 - 0.4	17,2 – 859,8	4.8 - 0.096

3.1. Photooxidation of 4-chlorophenol

Degradation of 4-CP in micro photo reactor was tested at different circulation flow rates of reaction mixture through the system (100, 10 and 1 ml/min), and compared to the batch data (Chyba: zdroj odkazu nenalezen). For MPR, the 4-CP concentration decrease until 80 minutes was practically identical, within the experimental error. However, the final concentration (after 150 minutes of circulation through the MPR) differed for different flow rates. The lower circulation flow rate yielded the higher degradation. The final 4-CP concentration was between 70 and 89 % of the initial concentration.

When compared to batch reactor, the final 4-CP concentrations after 150 minutes achieved with MPR were significantly higher, i.e. the degradation was slower. Possible explanation is that the total residence time (residence time in reaction zone multiplied by the number of passes) is the same for all flow rates. However, there are order-of-magnitude differences in the individual residence time in the reaction zone and the reaction conditions differ. At the short residence times (high flow rates), the reaction can be limited by mass transfer of dissolved oxygen from bulk to catalyst. At this point it has to be noted that the MPR was not optimized for studied reaction system as this was only the preliminary study. More experiments were planned to optimize the microreactor system and to better understand the performance of the MPR.

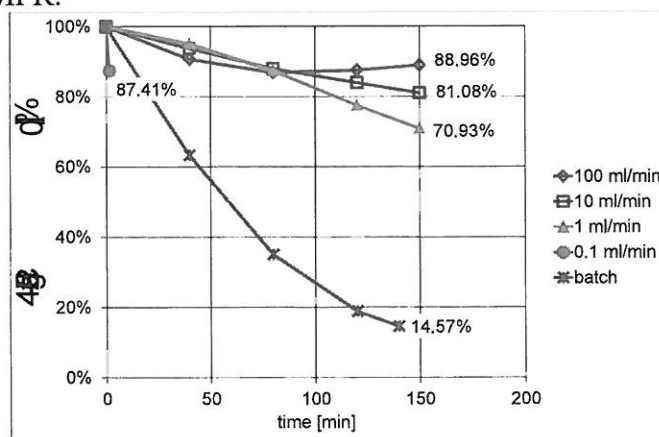


Figure 6. Comparison of the 4-CP degradation in micro photo reactor and batch reactor

Special attention has to be paid to the case of flow rate of 0.1 ml/min. At this flow rate, the reaction products were analyzed after only a single pass through the MPR. After residence time of only 96 s the analysis indicated the 4-CP concentration decrease to about 87 % of the initial concentration. In this case, the degradation was significantly faster than in the batch reactor.

3.2. Photooxidation of 9,10-dimethylantracene

Due to experimental difficulties, the DMA photooxidation was tested only at one circulation flow rate (10 ml/min). Similar to 4-CP results, the final concentration of DMA was significantly higher than in the case of batch reactor. More experiments were planned for optimization of microreactor setup for this system.

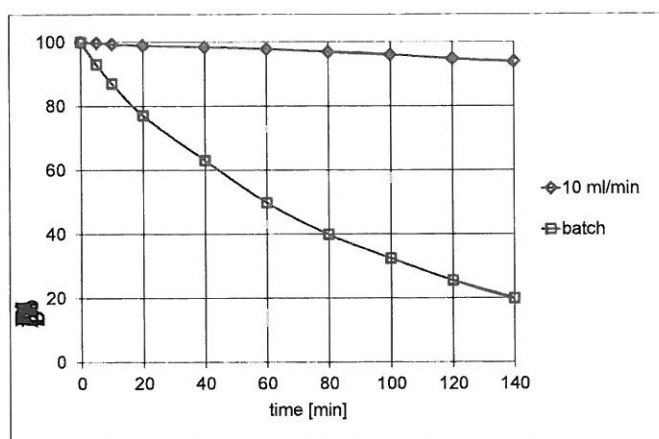


Figure 7. Comparison of the DMA degradation in micro photo reactor and batch reactor

4. Conclusion

Presented contribution described the preliminary results of micro photo reactor (MPR) application for photooxidation catalyzed with phtalocyanines. Two model reactions were tested. The first was the photooxidation of 4-chlorophenol in denudated water catalyzed by sulfonated Zn phtalocyanine; the second was the internal transformation of singlet oxygen quencher 9,10-dimethylantracene (DMA) in dimethylformamide (DMF) catalyzed by sulfamidic Zn phtalocyanine. The MPR performance was compared with previously obtained data from laboratory batch reactor.

Preliminary results indicated that at flow rates between 1 and 100 ml/min, the reactant concentration decrease obtained in MPR were significantly lower than in the case of batch reactor. However, at the flow rate of 0.1 ml/min and residence time of only 96 s, the concentration decrease was significantly faster higher than in the batch reactor.

We can conclude that even if the micro photo reactor was not optimized of the tested reaction systems, the results indicated a possible improvement against the batch reactor at lower flow rates. Further tests were planned for more detailed assessment of microreactor performance and for better understanding of the photo oxidation process carried out in the micro photo reactor.

Acknowledgements

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