Photomicroreactor Efficiency in Flow - [PE]

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1. Introduction

Photochemistry is gaining increasing attention in sustainable and green chemistry, as light can act as a clean reagent to drive chemical transformations under mild conditions, reducing energy consumption and the need for hazardous reagents. An important aspect of photochemical processes is the efficient utilization of light, since the number of photons reaching the reaction medium directly influences the reaction rate. [1]

Photomicroreactors enable photochemical and photocatalytic reactions under well-controlled conditions due to short optical path lengths, high surface-to-volume ratios, and efficient heat transfer. These features can improve light penetration and photon utilization compared to conventional batch photoreactors. [2]

Reactor performance and operating conditions that maximize productivity are evaluated using the photocatalytic degradation of Rhodamine B (RhB) under visible-light irradiation in the presence of a photocatalyst. Reactor performance is quantified using conversion and space–time yield (STY), which describes the amount of RhB degraded per unit reactor volume and time. [3] The obtained results are discussed in relation to data from the batch reactor experiment performed in the laboratory task PD-gCN.

2. Theory

2.1 Photocatalytic degradation

When a semiconductor photocatalyst is irradiated with light of sufficient energy, electrons are excited from the valence band to the conduction band, leaving behind positively charged holes. These photogenerated charge carriers can participate in redox reactions at the catalyst surface, leading to the formation of reactive oxygen species, such as hydroxyl radicals (•OH) and superoxide radicals ($\bullet O_2^-$). These species are responsible for the oxidative degradation of organic dyes, such as Rhodamine B. [4]

Rhodamine B is commonly used as a model compound in photocatalysis because it exhibits a strong absorption peak in the visible region ($\lambda \approx 554$ nm), allowing its concentration to be easily monitored by UV–Vis spectroscopy. A decrease in absorbance at this wavelength directly reflects a decrease in RhB concentration.

In this experiment, graphitic carbon nitride (g-C_3N_4) is used as the photocatalyst. Its photocatalytic properties and mechanism of action were discussed in detail in the previous laboratory task PD-gCN, which should be consulted for additional background information.

2.1 Photomicroreactors versus batch photoreactors

In conventional batch photoreactors, light absorption in the reaction medium follows the Lambert–Beer law:

$$A = \varepsilon l c$$

where *A* is the absorbance, *ε* is the molar absorption coefficient, *l* is the optical path length, and *c* is the concentration of the absorbing species. This relationship shows that absorbance increases linearly with both concentration and optical path length. As a result, light intensity decreases exponentially as it penetrates deeper into the reaction medium. In batch photoreactors with relatively large optical path lengths, this leads to non-uniform irradiation. Regions close to the light source are strongly irradiated, while regions farther away receive significantly fewer photons. This effect limits efficient light utilization and can reduce overall reaction rates.

These limitations are further amplified when heterogeneous photocatalysts are used in batch reactors. Suspended catalyst particles absorb and scatter light, increasing light attenuation and shading effects within the reactor volume. Consequently, a substantial fraction of the catalyst may remain insufficiently irradiated, which lowers the effective photocatalytic activity of the system.

Photomicroreactors address these challenges by operating with small characteristic dimensions and very short optical path lengths. This minimizes light attenuation and enables more uniform irradiation of the reaction medium, even in the presence of heterogeneous photocatalysts. In addition, continuous-flow operation allows precise control of irradiation time through the residence time, which can be adjusted by changing the flow rate. This makes photomicroreactors well suited for studying reactor performance, light utilization, and productivity under well-defined and reproducible conditions. [5]

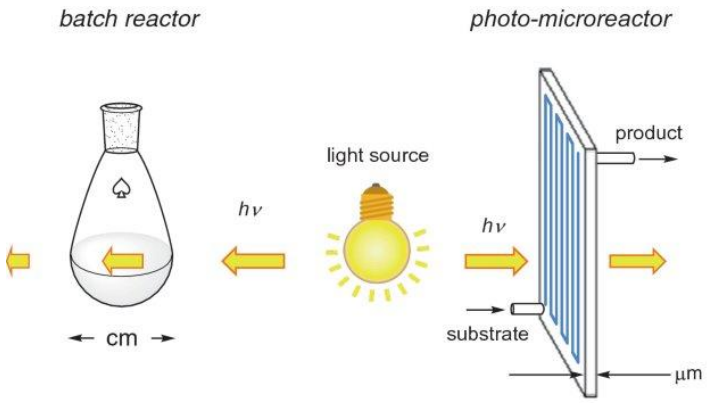

Figure 1: Comparison of microreactor and batch reactor in photochemistry. [cit]

2.1 Residence time, conversion, and reactor productivity

To describe and compare the performance of continuous-flow photomicroreactors, several key variables must be considered, including residence time, conversion, and reactor productivity. These parameters allow quantitative evaluation of how operating conditions influence reactor efficiency.

In a continuous flow reactor, the reaction time is defined by the residence time t, which represents the average time the reaction mixture spends inside the reactor:

$$t = \frac{V}{Q}$$

where V is the internal volume of the reactor and Q is the volumetric flow rate. By changing the flow rate, the residence time can be precisely controlled, enabling systematic investigation of reactor performance under steady-state conditions.

The conversion ς is defined as:

$$\varsigma = \frac{c_{in} - c_{out}}{c_{in}} = \frac{A_{in} - A_{out}}{A_{in}}$$

where c_{in} and c_{out} are the inlet and outlet concentration, respectively. Since absorbance is proportional to concertation, conversion can be calculated directly from UV-Vis absorbance values A_{in} and A_{out}.

The photocatalytic degradation of Rhodamine B under the conditions used in this experiment typically follows pseudo–first-order kinetics, meaning that the reaction rate depends primarily on the Rhodamine B concentration, while other parameters (light intensity, catalyst amount) remain constant. **For a first order reaction, the conversion depends on the residence time and thus on the flow rate of the reaction mixture**. Consequently, increasing the residence time generally leads to higher conversion. The derivation is covered in the Chemical Engineering I course.

To evaluate reactor efficiency, conversion alone is not sufficient, as it does not account for throughput. A key performance metric for continuous flow reactors is the space–time yield (STY), defined as:

$$STY = \frac{(c_{in} - c_{out})Q}{V}$$

Space–time yield expresses the amount of substance degraded per unit reactor volume and time. Increasing residence time generally increases conversion but decreases throughput. As a result, STY often exhibits a maximum at an intermediate residence time, highlighting the trade-off between conversion and productivity in continuous flow photomicroreactors.

3. Aim of the Experiment

The aim of this experiment is to evaluate the performance of a photomicroreactor operated in continuous flow using the photodegradation of Rhodamine B as a model reaction. The reactor is operated at different flow rates Q, corresponding to different residence times t, in order to investigate their influence on reaction performance. Reactor efficiency is quantified by the conversion ς and by the space–time yield STY. This analysis enables the identification of optimal operating conditions and highlights the inherent trade-off between achieving high conversion at long residence times and maximizing productivity at higher flow rates.

4. Material

3.1 Chemicals

- Photocatalyst: g-C_3N_4
- Stock solution of Rhodamine B (with concentration around 70 µM)
- Distilled water

3.2 Equipment and Materials

- LED light source with heatsink and fan
- Photomicroreactor
- Peristaltic pump
- Beaker for reaction mixture with magnetic stirrer
- Disposable plastic cuvettes for UV-Vis measurement
- 2 mL microtubes (Eppendorf tubes) mL
- Microcentrifuge
- Automatic pipettes
- Cuvette for UV-Vis spectrophotometer

5. Analytical instrument: UV-Vis spectrophotometer

In this experiment, a UV–Vis spectrophotometer will be used. It works on the principle of measuring how much ultraviolet and visible light is absorbed by a sample as the light passes through it. The decrease in light intensity at specific wavelengths corresponds to the concentration of the absorbing compound.

6. Plan of Work

6.1 Preparation of the Reaction Mixture

First, prepare the photocatalytic reaction mixture. Weight **25 mg of g-C_3N_4 photocatalyst** and transfer it into **25 mL of an aqueous Rhodamine B** stock solution with a concentration (approximately 70 µM; the exact concentration will be provided by the assistant). **Sonicate** the resulting suspension for **20 minutes** to ensure uniform dispersion of the photocatalyst particles and to allow adsorption–desorption equilibrium of RhB on the catalyst surface. After sonication, transfer the suspension into a beaker equipped with a magnetic stir bar. Cover the beaker with aluminium foil to prevent premature light exposure and place it on a magnetic stirrer. Set the **stirring speed to 1200 rpm** and maintain continuous stirring throughout the experiment.

Meanwhile, proceed with the assembly of the photomicroreactor setup.

6.2 Assembly of the Photomicroreactor Setup

Assemble the photomicroreactor system in the following order:

- Back-end plate with O-rings inserted into the inlet and outlet ports
- Back insulation film (with holes aligned to the inlet and outlet)
- Channel film defining the reactor volume and channel geometry
- Glass plate with the appropriate number of alignment gaskets
- Front rubber insulation
- Front-end plate

Tighten the assembly using the screws and nuts with a torque wrench. Apply the **same torque to all screws and do not change the torque setting** to ensure uniform sealing and reproducible reactor assembly.

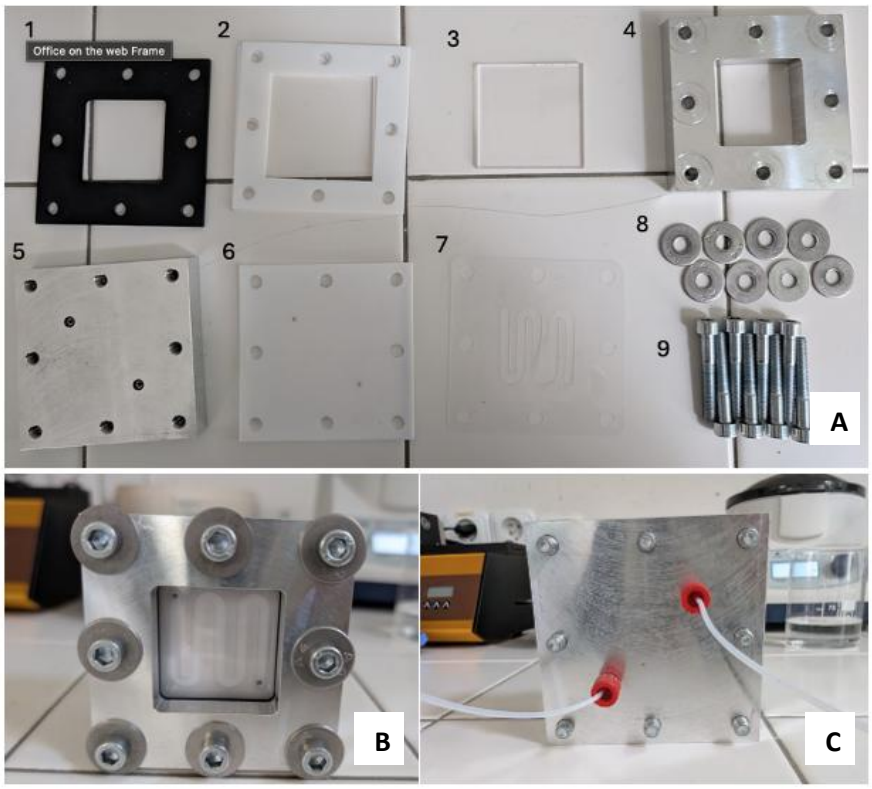

Figure 2: Photomicroreactor: (A) Disassembled reactor components: 1 – front rubber insulation, 2 – alignment gaskets, 3 – glass plate, 4 – front end plate, 5 – back end plate, 6 – back insulation film with inlet and outlet openings, 7 – channel film defining the reactor volume, 8 – nuts, and 9 – screws used for reactor assembly; (B) Assembled photomicroreactor showing the front view and the back view with inlet and outlet connections.

Connect the inlet and outlet tubing of the reactor and check that all connections are leak tight. Position the reactor **10 cm** from the LED light source. Attach the inlet tubing to a peristaltic

pump drawing the reaction mixture from a beaker and place the outlet tubing into an empty waste beaker.

Before illumination, **prime the tubing with the reaction mixture** to remove air bubbles and ensure continuous flow. Set the desired pump flow rate to achieve the required residence time. Switch on the LED light and wait for **at least one residence time** before collecting any sample, to ensure that the collected liquid has been fully irradiated for the intended residence time. Then collect the processed reaction mixture (minimum 1 mL per condition) into a labelled vial. During the final (longest-residence-time) experiment, use the waiting time to prepare the UV-Vis calibration curve.

Calculate the **internal reactor volume** based on the number of channel layers used in the reactor assembly. Using this volume, calculate the **required flow rate** for each target residence time. Record the reactor volume, residence times, and calculated flow rates in the prepared table (see Appendix).

The peristaltic pump does not display the flow rate directly but instead operates using a dimensionless numerical setting. To determine the required pump setting X for a desired flow rate Q [mL/min], use the pump calibration equation provided in Appendix. Calculate the appropriate pump setting and enter this value on the peristaltic pump.

6.3 Calibration curve for UV-VIS

During the final (longest-residence-time) experiment, use the waiting time to prepare the UV–Vis calibration curve for Rhodamine B. A Rhodamine B stock solution of known concentration C_{stock} is provided by the assistant. Prepare five calibration standards by diluting the stock solution with water according to the table. All dilutions should be prepared using automatic pipettes. Measure the absorbance of all calibration standards at the characteristic absorption wavelength of Rhodamine B (λ = 554 nm) using a UV–Vis spectrophotometer. Use the solvent (water) as a blank. Plot absorbance as a function of Rhodamine B concentration and determine the calibration curve by linear regression. This calibration curve will be used to convert absorbance values of collected reactor samples into Rhodamine B concentrations.

Table 1: Dilution to prepare calibration curve

Calibration point	Stock RhB [μL]	Water [μL]	Final Volume [mL]	Final Concentration [mol/L]
Blank	0	2000	2.00	0
1	50	1950	2.00	$0.025C_{stock}$
2	100	1900	2.00	$0.050C_{stock}$
3	150	1850	2.00	$0.075C_{stock}$
4	200	1800	2.00	$0.100C_{stock}$

6.4 Sample Processing

Centrifuge all collected samples for **15 minutes at 3000 rpm** in a microcentrifuge to remove the photocatalyst particles. After centrifugation, carefully transfer **400 µL of the clear supernatant** into a spectrophotometric cuvette and **dilute it to a total volume of 3 mL** with distilled water. Make sure that no catalyst particles are transferred, as suspended photocatalyst would interfere with the UV–Vis absorbance measurements.

7. Data processing and protocol

Prepare an overview table containing all measured and calculated data (see Appendix). Using the UV–Vis measurements of Rhodamine B standard solutions with known concentrations, construct a calibration curve by plotting absorbance versus concentration. Report the calibration equation and the coefficient of determination (R^2). Convert the measured absorbance values of all collected reactor samples into Rhodamine B concentrations using the calibration curve. For each residence time, calculate the conversion and the space–time yield (STY). Present the results graphically by preparing (i) a plot of conversion as a function of residence time and (ii) a plot of space–time yield as a function of residence time

Discuss the observed trends and explain the relationship between residence time, conversion, and reactor productivity. Identify the operating conditions that provide the best trade-off between conversion and STY. Furthermore, discuss possible sources of experimental uncertainty and summarize the key conclusions.

8. Safety instructions

Always **wear protective laboratory dark goggles** when working with the LED light source. Never look directly into the LED. Switch on the LED lamp only when wearing approved dark safety goggles. Ensure that the cooling fan is operating during irradiation. After completing the experiment, switch off the LED lamp and the fan before handling or cleaning the equipment.

9. Control questions

1. What is photochemistry and in which fields is it applied?
2. What are the main limitations of photochemical reactions in conventional batch reactors, and how can these limitations be overcome?
3. How does residence time influence conversion and reactor productivity?
4. Which safety precautions must be followed during this experiment?

10. Literature

1. Beeler, A. B. (2016). Introduction: Photochemistry in organic synthesis. Chemical reviews, 116(17), 9629-9630.

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3. Rehm, T. H. (2020). Reactor technology concepts for flow photochemistry. ChemPhotoChem, 4(4), 235-254.

4. Zheng, M., Guo, M., Ma, F., Li, W., & Shao, Y. (2025). Recent advances in graphitic carbon nitride-based composites for enhanced photocatalytic degradation of rhodamine B: mechanism, properties and environmental applications. Nanoscale Advances, 7(16), 4780-4802.

5. Sambiagio, C., & Noel, T. (2020). Flow photochemistry: shine some light on those tubes!. Trends in chemistry, 2(2), 92-106.

11. List of Symbols

Symbol	Description	Unit
A	absorbance	–
ε	molar absorption coefficient	$L \cdot mol^{-1} \cdot cm^{-1}$
l	optical path length	cm
c	concentration	$mol \cdot L^{-1}$
t	residence time	min
V	volume of reactor	mL
Q	volumetric flow rate	$mL \cdot min^{-1}$
ζ	conversion	_
STY	space-time yield	$mol \cdot L^{-1} \cdot h^{-1}$

12. Appendix

Channel height	**Channel volume**	**Amount of Channels:**	4, 6, 8, 10
h	$V_{channel}$	**Total reactor volume V [mL]**	
[um]	[mL]		
254	0,268	**Pump setting**	X = (Q - 0,0268)/0,0038

Residence time	**Flow rate**	**Pump Values**	**Absorbance before reaction**	**Absorbance after reaction**	**Concentration before reaction**	**Concentration after reaction**	**Conversion**	**STY**
t	Q	X	A0	A	c0	c	ζ	STY
[min]	[mL/min]	[-]	[-]	[-]	[mol/L]	[mol/L]	[-]	[mol/L/h]
2								
5								
10								
20								
30								