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Batch Microreactor for Photocatalytic Reactions Monitoring

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Photocatalytic oxidation of organic contaminants is a hot topic in environmental research. However, an effective purification process needs an effective photoreactor. Typical light sources such as mercury and halogen lamps are replaced with more energy efficient Light Emitting Diodes. In the current work, a miniature photoreactor with low catalyst consumption was presented. The work of the micro-photoreactor is investigated using anatase and P25 industrial titania as model catalysts. The key element of the microreactor is replaceable UV-LED. The used 365 nm emission wavelength is optimal for the model pollutant Rhodamine B dye. The micro-photoreactor is able almost completely to mineralize the Rhodamine B dye.

Key words: micro-photoreactor, rhodamine B, photocatalyst, LED, photodegradation.

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Introduction

In the last years, much attention is paid to “green” methods of wastewater remediation [1-4]. Photocatalysis is considered as a promising method of organic pollutant degradation. Photocatalytic oxidation leads to complete degradation of organic pollutants. The final products are non-toxic substances CO₂ and H₂O. Sunlight-activated photocatalyst leads to splitting of water molecules and formation of hydroxyl radicals. The highly aggressive radicals destroy the pollutant molecules [5-7]. It is known that the most active photocatalysts are TiO₂ [8-10] and ZnO [11,12]. Both the substances are inexpensive, non-toxic and chemically stable. However, the drawback is that these oxides absorb ultraviolet photons only. The UV part of the Sun energy is known to be 5 % only. For that reason, the key characteristics of photocatalyst is energy band gap, related strongly with crystalline structure. For example, the band gap for anatase, rutile, and brookite polymorphs of TiO₂ are 3.23 eV, 3.1 eV and 3.4 eV, respectively [13]. This is due to the difference in crystal lattice parameters and spatial locations of TiO₆ octahedra, in which Ti⁴⁺ ions are coupled with six O²⁻ ions. The anatase and rutile have tetragonal structure with different spatial arrangement of TiO₆ octahedra (Fig. 1) [13]. The crystal lattice distances are: a = b = 3.78 Å, c = 9.50 Å for anatase and a = b = 4.58 Å, c = 2.95 Å for rutile. Instead, brookite

polymorph has an orthorhombic crystalline structure with lattice parameters a = 5.43 Å, b = 9.16 Å, and c = 5.13 Å [13]. The differences in crystalline structure cause different photocatalytic activities of the three titania polymorphs. The most active is rutile [14]. This is why extensive research are focused on simple and environment friendly methods of rutile production [15-19].

Titania photocatalytic activity may be improved via doping with heavy elements such as Fe, Co, Ga, W, Bi, Mo, V and Ni [20]. The dopants reduce rate of electron-holes recombination and extend the photocatalyst lifetime. Dopant amount should be chosen correctly. Too high modifier amount may distort crystal lattice and reduce photocatalytic activity. Optimal dopant amount is below 3 % [20]. On the other hand, heavy metal dopants are hazardous pollutants. Thus gradual photocatalyst destruction can lead to heavy metal dissemination. Surface properties of titania may be modified via grafting phosphate [21], arsenate [22], and carbonate [23] groups.

An important step in developing water purification method is optimization of experimental conditions. The photocatalyst efficiency is usually evaluated measuring rate of model pollutant decomposition. Common model pollutants are organic dyes [24-29]. Among them the Rhodamine B dye (RhB) is very sensitive to hydroxyl radicals [6, 7, 30-32]. The RhB dye is photooxidized to colorless products, so its decomposition rate may be

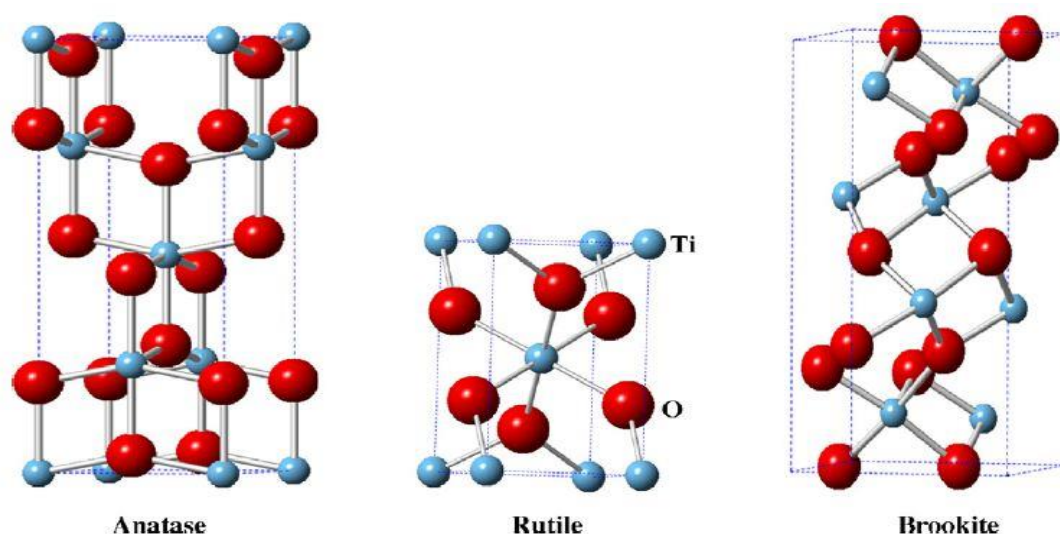


Fig. 1. Crystal structure of anatase, rutile and brookite [10].

easily monitored by photometry. The main factors affecting the rate and degree of RhB photodegradation are UV radiation power and photocatalyst activity. Oxygen vacancies on titania surface are active centers for superoxide radical formation. Superoxide and hydroxyl radicals are highly reactive to degrade organic pollutants. For example, Zhang and others [32] completely discolored RhB solution (10^{-5} M) for 120 min under 20 W UV irradiation using Fe-CNT/TiO₂ catalyst. Guo et

al. [6] described effect of H₂O₂ on RhB decomposition. Addition of H₂O₂ results in formation of large amount of hydroxyl radicals that destroy RhB molecules. However, excess of H₂O₂ may act as electron capture agent and cause recombination of electron-hole pairs. Phutanon et al. [5] used copper oxide for photocatalytic degradation of the RhB dye. Active centers in formation of superoxide radicals are oxygen vacancies in CuO structure.

Table 1

Features of laboratory photocatalytic reactors

Reactor and solution volume	Model pollutant	Light source	Catalyst	Ref.
Photoreactor, 250 ml	textile dyes	UV-LED 11 mW, 200 mW (λ_{\max} = 385 nm)	TiO ₂	[35]
LED photoreactor, 1.5 L	[Co(CN) ₆] ³⁻	UV-LED 30 W (λ_{\max} = 365 nm)	TiO ₂ (P25, Aeroxide)	[41]
Multistage rotating mesh support photoreactor	p-nitrophenol	11 W UV-C lamps (λ_{\max} = 253.7 nm)	TiO ₂ P-25	[42]
Batch photocatalytic reactor	phenol	LED (20 mA - 25 mA) (λ_{\max} = 375 nm)	Degussa P-25	[43]
Mini-photoreactor, 23 ml	n-decane	9 UVA LEDs 270 mW (λ_{\max} = 365 nm)	TiO ₂ - P25	[44]
Batch monolith photoreactor	CO ₂ reduction with H ₂	200W Hg (λ_{\max} = 252 nm)	TiO ₂ monolithic catalyst	[45]
Photo-microfluidic chip reactor, 0.0095 ml	propene oxidation	UV-LED light (0.55 W/cm ²)	TiO ₂	[36]
UV-LEDs floating-bed photoreactor, 200 ml	caffeine, paracetamol	LED 14 W*m ⁻¹ (λ_{\max} = 365 nm)	ZnO- Polystyrene	[11]
Continuous photoreactor, 1500 ml	Direct Red 23	LED 3.6 W	UV-LED/S ₂ O ₈ ²⁻	[26]
Flat-panel photoreactor, 3.4 L	Methylene Blue	solar illumination	TiO ₂	[37]
Stream reactor, 600 ml	phenol	5W Hg lamp (λ_{\max} = 253.7 nm)	TiO ₂ film	[46]
Flow-through reactor, 1.5 L	phenol, Reactive blue	15W Hg lamp (λ_{\max} = 355 nm)	fiber glass strips coated with TiO ₂	[47]

Continuation of Table 1

LED photoreactor	Reactive blue	6 UV-LED 1 W ($\lambda_{\max} = 365 \text{ nm}$)	ZnO	[48]
Flat-plate photoreactor, 250 ml	urea	S-VD LED 25-78 W ($\lambda_{\max} = 550 \text{ nm}$)	nitrogen-doped TiO ₂	[49]
Mini-photoreactor, 3 ml	salicylic acid, methylene blue	UV-LED 5W ($\lambda_{\max} = 370 \text{ nm}$)	ZnO	[34]
Micro-photoreactor, 30 ml	RhB	UV-LED 3W ($\lambda_{\max} = 365 \text{ nm}$)	TiO ₂ - P25	This article

Photoreactor design is crucial in developing an effective purification process. Typical limitation is low lighting efficiency. Table 1 describes features of laboratory photocatalytic reactors. Mini- and micro-photoreactors are very convenient to study photocatalyst performance [11, 33-39]. The microreactors have several advantages such as: (i) low amount of photocatalyst needed; (ii) high light permeability throughout the reactor; (iii) uniform light distribution in the reactor space [40].

The light source plays an important role in photocatalytic processes. The very promising light sources are power UV LEDs. LEDs are environment friendly and are superior to mercury and halogen lamps [11, 26, 34, 41, 43, 48, 50]. With using LEDs, photoreactors are miniaturized in line with the basic principles of green chemistry. To be energy efficient, LED light sources should be optimized in terms of both power and emission spectrum. In the work [33] a LED-driven reactor with variable light intensity was presented. The surfactant sodium dodecylbenzenesulfonate (SDBS) was used as a model solution. The most effective removal (approximately 94 %) was observed with electric power consumption of $27.5 \text{ mW}\cdot\text{cm}^{-2}$. In terms of energy efficiency, the best result has been obtained with energy consumption of $3.22 \text{ mW}\cdot\text{cm}^{-2}$ and SDBS degradation of 90 %. Removal of SDBS was far less effective under mercury lamp illumination. With degradation of RhB dye, energy consumption was several times higher than that with using modernized LED reactor. These data suggest that mercury lamps should be replaced by LEDs. Bukman et al. [34] proposed a new approach to evaluation of photoreaction performance. UV LED was combined with a

spectrophotometer cuvette in order to perform measurements *in situ*. Such approach allows to calculate accurately rate constants of the photoreactions studied. Working volume of the mini-reactor is as small as 3.0 ml.

In this study, new photocatalytic micro-photoreactor is presented. The mini-reactor has volume of 30 ml. The small working volume allows all the catalyst particles to receive necessary illumination. In the same time, this reactor volume is enough to take several aliquots for analysis. To prevent the change in the total catalyst mass, the precipitate after centrifugation was returned back to the reactor. The mini-reactor is environmentally friendly due to small amount of catalyst and reagents used.

I. Experimental

Mixed anatase-rutile titania P25 come from Degussa (Germany). Reagent-grade titanium dioxide (anatase 99.7 %) and Rhodamine B dye ($\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$) were obtained from Sigma (now Merck). Structural formula of the Rhodamine B dye is presented in Fig. 2.

Spectra in the range 350 - 700 nm were registered with spectrophotometer ULAB 102-UV using 5 mm quartz cuvettes. Calibration line was plotted using absorbance at 558 nm against RhB concentration in the range from 1 to 20 mg/L. The calibration plot is quite straight line with determination coefficient $R^2 = 0.999$ (Fig. 3-b).

Photodegradation experiments were carried out using 30 mL of 5 mg/L aqueous solution of the RhB dye and 30 mg of titania photocatalyst. Before the experiment, the reaction solution was stirred for 30 min in order to

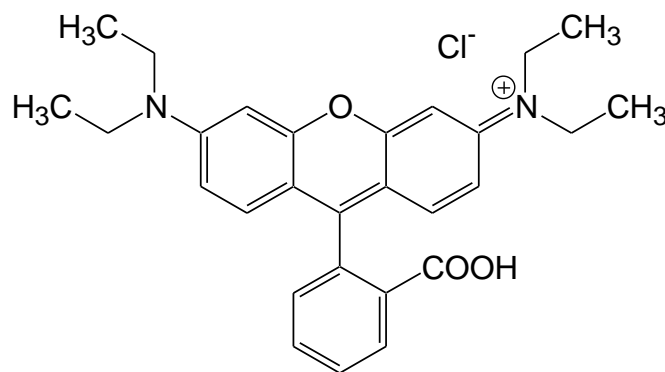


Fig 2. Rhodamine B dye structure.

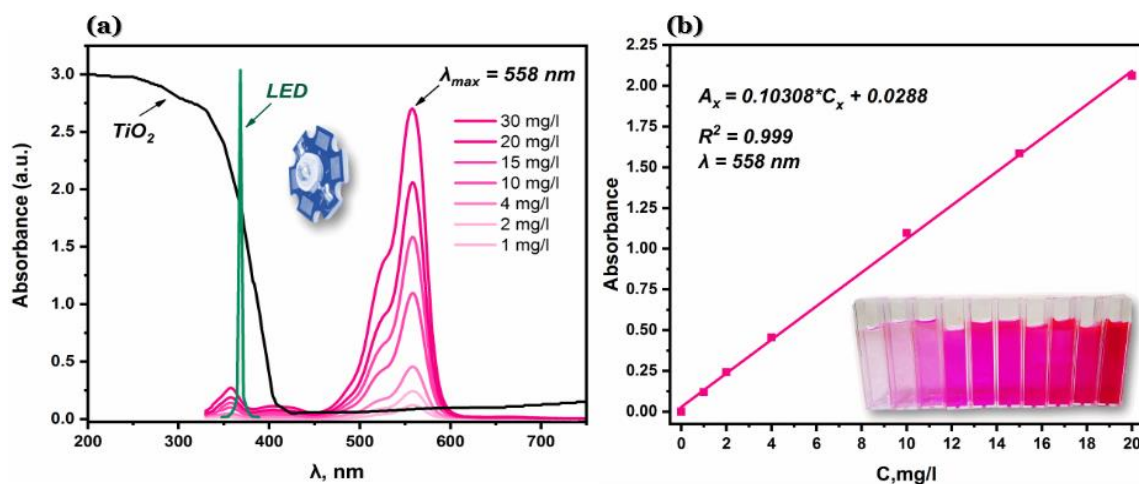


Fig. 3. (a) UV-vis spectrum of RhB solutions at indicated concentrations. (b) Absorbance at 558 nm (the spectral peak wavelength) versus RhB concentration.

equilibrate adsorption of the dye on titania surface. The solution pH was in the range from 6 to 7. Samples were collected at 0, 180, and 300 minutes. Fig. 4 shows images of RhB solution before and after photo-degradation. The sample of 5 mL was centrifuged for 5 min at 3500 rpm. Supernatant was analyzed for the rest dye concentration while precipitate was returned back to the micro-reactor. Degradation extent was calculated as follows:

$$K = \frac{A_0 - A_t}{A_0} \times 100\%, \quad (1)$$

with K is degradation extent (%), A_0 is initial absorbance and A_t is absorbance at time t.

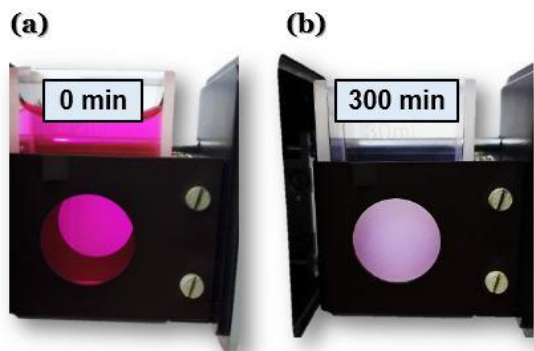


Fig. 4. Images of RhB solution before (a) and after (b) photo-degradation.

II. Results

3.1. Design of the micro-photoreactor.

Principal scheme of the micro-photoreactor is presented in Fig. 5. The main element is rectangle glass cuvette with 20 mm optical path. The cuvette volume is 30 mL. Magnetic stirrer ensures even distribution of photocatalyst. The light source is a LED supplied with 700 mA current at 3.4 - 3.8 V. The power LED is placed in a cooler designed to allow quick replacement. The cooler maintains temperature of the LED not exceeding 25°C. General view of the cuvette housing is shown in

Fig. 6. The cuvette holder is moved to collect samples of the solution.

3.2. Photocatalytic experiments.

The microreactor was designed for rapid testing of photocatalysts. The exemplary study presents photocatalytic degradation of the RhB dye. The RhB dye is typical contaminant in textile and paper industrial waste waters [51-53]. The RhB dye is known to irritate skin, eyes and respiratory tract [54]. Due to strong absorbance, extent of the dye degradation can be easily monitored via spectrophotometric measurements. The dye molecule contains aromatic rings, sulfonate and amino groups typical for organic contaminants (Fig. 2). For that reason, the RhB dye is often used as model compound to study photocatalyst efficiency (Table 2).

Replaceable light source allows to choose wavelength optimal to absorbance spectrum of the substance studied. If the goal of a study is stability test of a substance, the wave length should match peak of the substance absorption spectrum. On contrary, a study on a catalyst efficiency requires minimal light absorption by a model substance. In the present study, wave length of the LED light source was 365 nm. This wavelength corresponds to the range of minimal light absorption of the RhB dye (Fig. 3a). Thus, photodegradation of RhB dye is minimalized. On the other hand, the LED emission spectrum corresponds to the absorption range of the titania photocatalyst used (Fig. 3a). The TiO_2 photocatalyst is usually activated with irradiation of short wavelengths less than 400 nm. Optical power of the light source should be optimal for a studied catalyst [58]. In the present study, the luminous power was 15 lumen.

Efficiencies of the studied photocatalysts were evaluated using extent of the dye degradation. The numerical data are presented in Table 3. The data indicate clearly that the P25 catalyst has higher activity than anatase.

Spectra of the degraded RhB samples are presented in Fig. 7. There was no new spectral band registered. Decrease of the main absorption peak indicate degradation of the dye chromophore structure. In the case of the anatase catalyst, spectra of the samples are shifted

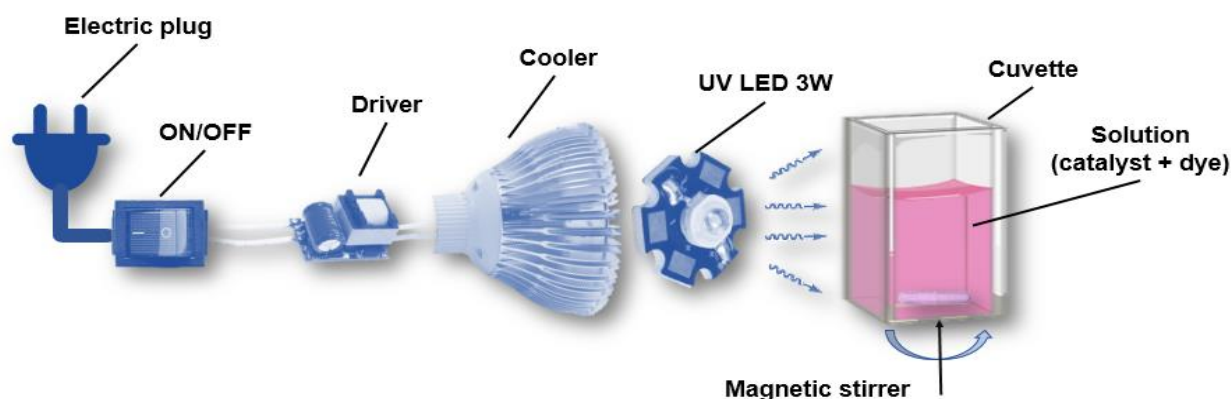


Fig. 5. Principal scheme of the micro-photoreactor.

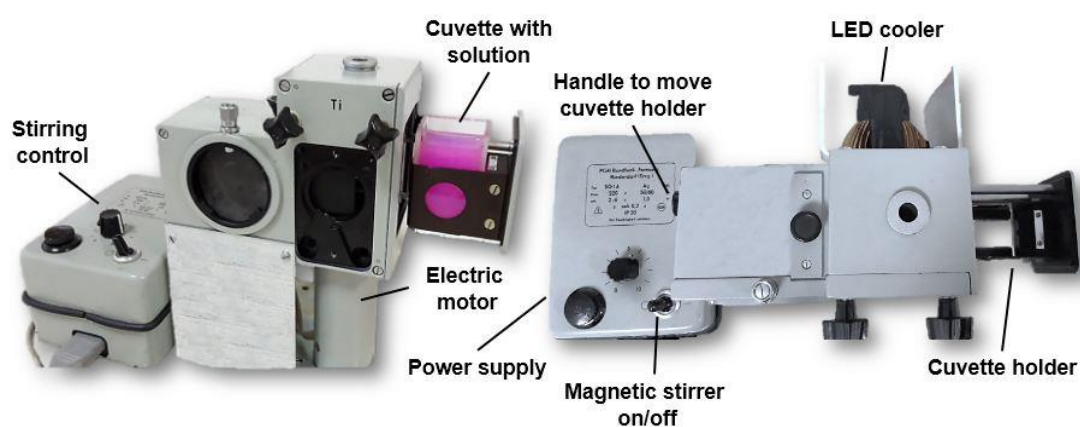


Fig. 6. General view of the micro-reactor for photocatalytic studies.

Table 2

The photocatalysts tested with using RhB dye

Photocatalyst	Concentration	Dye concentration	Conditions	Degradation extent, %	Time, min	Ref.
PVP/AS/6%BiOBr	25mg/ 50mL	10 mg/L		75	120	[7]
Fe ₃ O ₄ NPs	4g/L	0.025 mM	30% H ₂ O ₂ , 0.5 mL/L	99.5	60	[24]
Fe ₂ O ₃ + 10% In ₂ O ₃	30mg/ 100mL	100 mg/L	30% H ₂ O ₂ 50 µl/100mL pH = 4	94	20	[6]
ZnO	100mg/100 mL	50 mg/L		96	180	[55]
CR-ZnONPs	20mg/ 100mL	10 µM		98	200	[30]
g-C ₃ N ₄ /TiO ₂ (TC3)	0.04g/ 30mL	10 ⁻⁵ M		95.2	80	[56]
Sn _{0.05} Ti _{0.95} O ₂ -SBA-15	100mg/100mL	50 µM	pH = 4.5	99	180	[57]
CuO	25mg/ 100mL	1 ppm	30% H ₂ O ₂ 0.1mL/ 100mL	*	240	[5]
KNbO ₃	0.5g/ 200mL	10 mg/L		-	180	[31]
Fe-CNTs/TiO ₂	50mg/ 50mL	10 ⁻⁵ M		100	120	[32]
TiO ₂ P25 (Degussa)	30mg/ 30mL	5 mg/L		97.3	300	this article
anatase (99.7%)	30mg/ 30mL	5 mg/L		59.6	300	this article

* rate constant = 0.002 - 0.007 min⁻¹

Table 3
Extent of RhB dye degradation using P25 and anatase photocatalysts

Catalyst	Degradation (%)	
	180 min	300 min
P25	67.5	97.3
anatase	39.7	59.6

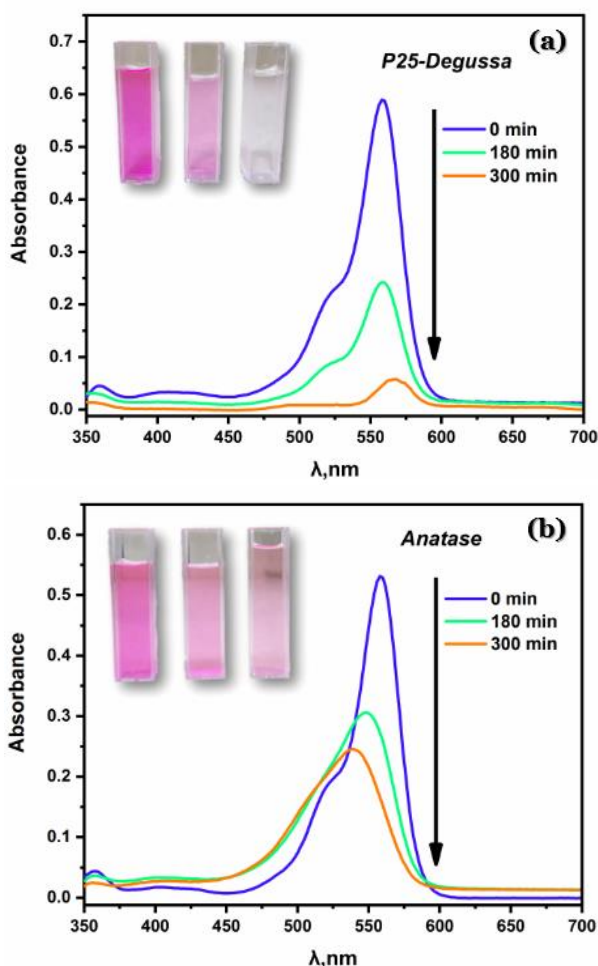


Fig. 7. Spectra of Rhodamine B samples degraded for 0, 180 and 300 min using (a) P25 and (b) anatase photocatalysts.

markedly to shorter wavelength (Fig. 7b). In the case of the P25 catalyst, spectra of the samples are slightly shifted to longer wavelengths (Fig. 7a). Probable mechanism of RhB photodegradation comprises three stages [6, 57]. At first, auxochrome ethyl groups are detached from amino groups. Second, the deethylated products lose carboxyle group. Third stage is decomposition of chromophore core and formation of low molecular acidic compounds. Finally, carbon dioxide and water are formed.

The comparison of photocatalytic micro-reactors aimed to degradation of dyes are presented in Table 4. The advantages of the presented micro-reactor are low operating costs, simple experimental design, high energy efficiency and very narrow emission spectrum.

Conclusions

LED photocatalytic reactors can be successfully used to study degradation of organic pollutants. The important features of the LED UV sources are the following: (i) high energy efficiency; (ii) small size and low toxicity (Hg-free); (iii) high durability leading to long service life; (iv) very narrow emission spectrum. This paper presents new LED micro-photoreactor. The LED source is optimized for photocatalytic degradation of RhB dye. The main advantages of this microphotoreactor are: (i) low cost; (ii) low amount of photocatalyst used; (iii) rapid replacement of the light source to adjust wavelength range to absorption spectrum of model compound. The commercial LEDs with different characteristics (wavelength, radiation power) are widely available. The proposed microreactor may be used to select optimal reaction conditions, to evaluate efficiency of photocatalytic degradation and reactor energy consumption. Further development of such microreactors requires implementation of automatic systems to control light source when the sample reaches the desired percentage of degradation. In situ measurement can be used to monitor degradation of pollutants.

Table 4
Comparison of photocatalytic micro-reactors aimed to dye degradation

Contaminant	λ_{\max} , nm	λ_{LED} , nm	ref.
Congo red	500	365	[59]
Methyl orange	464	UV light	[60]
Direct red 23	500	365	[61]
Reactive Red 120	522	315 - 400	[62]
Reactive Red 231	545	385	[35]
Reactive Orange 13	487		
Reactive Black 5	598		
Reactive Blue 198	624		
Direct red 80	528	UV light	[63]
Methylene blue	655	370	[34]
Rhodamine B	558	365	this work

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- [1] I. Anastopoulos, I. Pashalidis, A.G. Orfanos, I.D. Manariotis, T. Tatarchuk, L. Sellaoui, A. Bonilla-Petriciolet, A. Mittal, A. Núñez-Delgado, J. Environ. Manage. 261 (2020) (<https://doi.org/10.1016/j.jenvman.2020.110236>).
- [2] M. Naushad, A.A. Alqadami, A.A. Al-Kahtani, T. Ahamad, M.R. Awual, T. Tatarchuk, J. Mol. Liq. 296, 112075 (2019) (<https://doi.org/10.1016/J.MOLLIQ.2019.112075>).
- [3] T. Tatarchuk, A. Shyichuk, I. Mironyuk, M. Naushad, J. Mol. Liq. 293, 111563 (2019) (<https://doi.org/10.1016/j.molliq.2019.111563>).
- [4] M. Naushad, Z.A. ALOthman, Desalin. Water Treat. 53, 2158 (2015) (<https://doi.org/10.1080/19443994.2013.862744>).
- [5] N. Phutanon, P. Pisitsak, H. Manuspiya, S. Ummartyotin, J. Sci. Adv. Mater. Devices. 3, 310 (2018) (<https://doi.org/10.1016/j.jsamd.2018.05.001>).
- [6] N. Guo, H. Liu, Y. Fu, J. Hu, Optik (Stuttg) 201, 163537 (2019) (<https://doi.org/10.1016/j.ijleo.2019.163537>).
- [7] Y. Wang, Q. Yang, X. Wang, J. Yang, Y. Dai, Y. He, W. Chen, W. Zhang, Mater. Sci. Eng. B Solid-State Mater. Adv. Technol. 244, 12 (2019) (<https://doi.org/10.1016/j.mseb.2019.04.005>).
- [8] M.A. Lazar, S. Varghese, S.S. Nair, Catalysts 2, 572 (2012) (<https://doi.org/10.3390/catal2040572>).
- [9] K. Karthik, S. Vijayalakshmi, A. Phuruangrat, V. Revathi, U. Verma, J. Clust. Sci. 30 (2019) (<https://doi.org/10.1007/s10876-019-01556-1>).
- [10] R. Aswini, S. Murugesan, K. Kannan, Int. J. Environ. Anal. Chem. 00 (2020) (<https://doi.org/10.1080/03067319.2020.1718668>).
- [11] V. Vaiano, M. Matarangolo, O. Sacco, Chem. Eng. J. 350, 703 (2018) (<https://doi.org/10.1016/j.cej.2018.06.011>).
- [12] S. Sa-nguanprang, A. Phuruangrat, K. Karthik, S. Thongtem, T. Thongtem, J. Aust. Ceram. Soc. (2020) (<https://doi.org/10.1007/s41779-019-00447-y>).
- [13] V. Etacheri, C. Di Valentin, J. Schneider, D. Bahnemann, S.C. Pillai, J. Photochem. Photobiol. C Photochem. Rev. 25, 1 (2015) (<https://doi.org/10.1016/j.jphotochemrev.2015.08.003>).
- [14] M. Buchalska, M. Kobielski, A. Matuszek, M. Pacia, S. Wojtyła, W. Macyk, ACS Catal. 5, 7424 (2015) (<https://doi.org/10.1021/acscatal.5b01562>).
- [15] S. Zhang, C.Y. Liu, Y. Liu, Z.Y. Zhang, L.J. Mao, Mater. Lett. 63, 127 (2009) (<https://doi.org/10.1016/j.matlet.2008.09.032>).
- [16] L. Li, J. Yan, T. Wang, Z.J. Zhao, J. Zhang, J. Gong, N. Guan, Nat. Commun. 6, 1 (2015) (<https://doi.org/10.1038/ncomms6881>).
- [17] J. Kang, L. Gao, M. Zhang, J. Pu, L. He, R. Ruan, M. Omran, J. Peng, G. Chen, Adv. Powder Technol. 6 (2020) (<https://doi.org/10.1016/j.appt.2019.12.042>).
- [18] M. Nag, P. Basak, S.V. Manorama, Mater. Res. Bull. 42, 1691 (2007) (<https://doi.org/10.1016/j.materresbull.2006.11.032>).
- [19] G. Nabi, Qurat-ul-Aain, N.R. Khalid, M.B. Tahir, M. Rafique, M. Rizwan, S. Hussain, T. Iqbal, A. Majid, J. Inorg. Organomet. Polym. Mater. 28, 1552 (2018) (<https://doi.org/10.1007/s10904-018-0812-0>).
- [20] M. Surówka, M. Kobielski, M. Trochowski, M. Buchalska, K. Kruczała, P. Broś, W. Macyk, Appl. Catal. B Environ. 247, 173 (2019) (<https://doi.org/10.1016/j.apcatb.2019.01.074>).
- [21] I. Mironyuk, T. Tatarchuk, H. Vasylyeva, M. Naushad, I. Mykytyn, J. Environ. Chem. Eng. 7, 103430 (2019) (<https://doi.org/10.1016/j.jece.2019.103430>).
- [22] I. Mironyuk, T. Tatarchuk, H. Vasylyeva, V.M. Gun'ko, I. Mykytyn, J. Mol. Liq. 282, 587 (2019) (<https://doi.org/10.1016/j.molliq.2019.03.026>).
- [23] I. Mironyuk, T. Tatarchuk, M. Naushad, H. Vasylyeva, I. Mykytyn, J. Mol. Liq. 285, 742 (2019) (<https://doi.org/10.1016/j.molliq.2019.04.111>).
- [24] A. Radoń, S. Łoński, T. Warski, R. Babilas, T. Tański, M. Dudziak, D. Łukowiec, Appl. Surf. Sci. 487, 1018 (2019) (<https://doi.org/10.1016/j.apsusc.2019.05.091>).
- [25] J.C. Espíndola, V.J.P. Vilar, Chem. Eng. J. 394, 124865 (2020) (<https://doi.org/10.1016/j.cej.2020.124865>).
- [26] M.H. Rasoulifard, M. Fazli, M.R. Eskandarian, J. Ind. Eng. Chem. 24, 121 (2015) (<https://doi.org/10.1016/j.jiec.2014.09.018>).
- [27] N. Danyliuk, J. Tomaszewska, T. Tatarchuk, J. Mol. Liq. 309, (2020). (<https://doi.org/10.1016/j.molliq.2020.113077>).

- [28] K. Karthik, V. Revathi, T. Tatarchuk, *Mol. Cryst. Liq. Cryst.* 671, 17 (2018) (<https://doi.org/10.1080/15421406.2018.1542080>).
- [29] M. Naushad, A.A. Alqadami, Z.A. AlOthman, I.H. Alshohaimi, M.S. Algamdi, A.M. Aldawsari, *J. Mol. Liq.* 293, 111442 (2019) (<https://doi.org/10.1016/j.molliq.2019.111442>).
- [30] T. Varadavenkatesan, E. Lyubchik, S. Pai, A. Pugazhendhi, R. Vinayagam, R. Selvaraj, *J. Photochem. Photobiol. B Biol.* 199, 111621 (2019) (<https://doi.org/10.1016/j.jphotobiol.2019.111621>).
- [31] T.B. Wermuth, S. Arcaro, J. Venturini, T.M. Hubert Ribeiro, A. de Assis Lawisch Rodriguez, E.L. Machado, T. Franco de Oliveira, S.E. Franco de Oliveira, M.N. Baibich, C.P. Bergmann, *Ceram. Int.* 45, 24137 (2019) (<https://doi.org/10.1016/j.ceramint.2019.08.122>).
- [32] K. Zhang, Z. Meng, W. Oh, Cuihua Xuebao/Chinese J. Catal. 31, 751 (2010) ([https://doi.org/10.1016/S1872-2067\(09\)60084-X](https://doi.org/10.1016/S1872-2067(09)60084-X)).
- [33] S. Dominguez, M.J. Rivero, P. Gomez, R. Ibañez, I. Ortiz, *J. Ind. Eng. Chem.* 37, 237 (2016) (<https://doi.org/10.1016/j.jiec.2016.03.031>).
- [34] L. Bukman, C.F. de Freitas, W. Caetano, N.R.C. Fernandes, N. Hioka, V.R. Batistela, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* 211, 330 (2019) (<https://doi.org/10.1016/j.saa.2018.12.033>).
- [35] T. Tapia-Tlatelpa, J. Trull, L. Romeral, 9, 1 (2019) (<https://doi.org/10.3390/catal9080669>).
- [36] J. Fernández-Catalá, G. Garrigós-Pastor, Berenguer-Murcia, D. Cazorla-Amorós, *J. Environ. Chem. Eng.* 7, 103408 (2019) (<https://doi.org/10.1016/j.jece.2019.103408>).
- [37] Sutisna, M. Rokhmat, E. Wibowo, Khairurrijal, M. Abdullah, *Sustain. Environ. Res.* 27, 172 (2017) (<https://doi.org/10.1016/j.serj.2017.04.002>).
- [38] V.J.P. Vilar, P. Alfonso-Muniozguren, J.P. Monteiro, J. Lee, S.M. Miranda, R.A.R. Boaventura, *Chem. Eng. J.* 379, 122341 (2020) (<https://doi.org/10.1016/j.cej.2019.122341>).
- [39] D. Heggo, S. Ookawara, *Chem. Eng. Sci.* 169 67 (2017) (<https://doi.org/10.1016/j.ces.2017.01.019>).
- [40] K.P. Sundar, S. Kanmani, *Chem. Eng. Res. Des.* 154, 135 (2020) (<https://doi.org/10.1016/j.cherd.2019.11.035>).
- [41] S.A. Joven-Quintero, S.F. Castilla-Acevedo, L.A. Betancourt-Buitrago, R. Acosta-Herazo, F. Machuca-Martinez, *Mater. Sci. Semicond. Process.* 110, (2020) (<https://doi.org/10.1016/j.mssp.2020.104972>).
- [42] S. Moeini Najafabadi, F. Rashidi, M. rezaei, *Chem. Eng. Process. - Process Intensif.* 146, 107668 (2019) (<https://doi.org/10.1016/j.cep.2019.107668>).
- [43] A. Jamali, R. Vanraes, P. Hanselaer, T. Van Gerven, *Chem. Eng. Process. Process Intensif.* 71, 43 (2013) (<https://doi.org/10.1016/j.cep.2013.03.010>).
- [44] B.M. da Costa Filho, A.L.P. Araujo, S.P. Padrão, R.A.R. Boaventura, M.M. Dias, J.C.B. Lopes, V.J.P. Vilar, *Chem. Eng. J.* 366, 560 (2019) (<https://doi.org/10.1016/j.cej.2019.02.122>).
- [45] B. Tahir, M. Tahir, N.S. Amin, *Energy Convers. Manag.* 90, 272 (2015) (<https://doi.org/10.1016/j.enconman.2014.11.018>).
- [46] M. Jafarikojour, B. Dabir, M. Sohrabi, S.J. Royae, *J. Photochem. Photobiol. A Chem.* 364, 613 (2018) (<https://doi.org/10.1016/j.jphotochem.2018.03.043>).
- [47] R. Oblak, M. Kete, U.L. Štangar, M. Tasbihi, *J. Water Process Eng.* 23, 142 (2018) (<https://doi.org/10.1016/j.jwpe.2018.03.015>).
- [48] M. Khademalrasool, M. Farbod, M.D. Talebzadeh, *J. Sci. Adv. Mater. Devices.* 1, 382 (2016) (<https://doi.org/10.1016/j.jsamd.2016.06.012>).
- [49] V. Vaiano, O. Sacco, G. Di Capua, N. Femia, D. Sannino, *Water (Switzerland)*. 11, (2019) (<https://doi.org/10.3390/w11081642>).
- [50] Z. Wang, J. Liu, Y. Dai, W. Dong, S. Zhang, J. Chen, *Ind. Eng. Chem. Res.* 50, 7977 (2011) (<https://doi.org/10.1021/ie200297x>).
- [51] A. Phuruangrat, P.O. Keereesaensuk, K. Karthik, P. Dumrongrojthanath, N. Ekthammathat, S. Thongtem, T. Thongtem, *J. Inorg. Organomet. Polym. Mater.* 30 (2020) (<https://doi.org/10.1007/s10904-019-01190-4>).
- [52] P. Intaphong, A. Phuruangrat, K. Karthik, T. Thongtem, S. Thongtem, *Dig. J. Nanomater. Biostructures.* 14 (2019).
- [53] P. Intaphong, A. Phuruangrat, K. Karthik, P. Dumrongrojthanath, T. Thongtem, S. Thongtem, *J. Inorg. Organomet. Polym. Mater.* 30 (2020) (<https://doi.org/10.1007/s10904-019-01259-0>).
- [54] R. Jain, M. Mathur, S. Sikarwar, A. Mittal, *J. Environ. Manage.* 85, 956 (2007) (<https://doi.org/10.1016/j.jenvman.2006.11.002>).
- [55] J. Duraimurugan, S.K. G., S. Shanavas, R. Ramesh, R. Acevedo, P.M. Anbarasan, P. Maadeswaran, *Optik (Stuttg)* 202, 163607 (2020) (<https://doi.org/10.1016/j.ijleo.2019.163607>).
- [56] R. Hao, G. Wang, C. Jiang, H. Tang, Q. Xu, *Appl. Surf. Sci.* 411, 400 (2017) (<https://doi.org/10.1016/j.apsusc.2017.03.197>).
- [57] D.C. Khandekar, A.R. Bhattacharyya, R. Bandyopadhyaya, *J. Environ. Chem. Eng.* 7, 103433 (2019) (<https://doi.org/10.1016/j.jece.2019.103433>).
- [58] C. Casado, R. Timmers, A. Sergejevs, C.T. Clarke, D.W.E. Allsopp, C.R. Bowen, R. van Grieken, J. Marugán, *Chem. Eng. J.* 327, 1043 (2017) (<https://doi.org/10.1016/j.cej.2017.06.167>).

- [59] J. Fowsiya, G. Madhumitha, N.A. Al-Dhabi, M.V. Arasu, J. Photochem. Photobiol. B Biol. 162, 395 (2016) (<https://doi.org/10.1016/j.jphotobiol.2016.07.011>).
- [60] X. Zheng, D. Zhang, Y. Gao, Y. Wu, Q. Liu, X. Zhu, Inorg. Chem. Commun. 110, 107589 (2019) (<https://doi.org/10.1016/j.inoche.2019.107589>).
- [61] M. Torkaman, R. Moradi, B. Keyvani, Rev. Roum. Chim. 61, 763 (2016).
- [62] Y.P. Ong, L.N. Ho, S.A. Ong, J. Banjuraizah, A.H. Ibrahim, S.L. Lee, N. Nordin, Chemosphere 219, 277 (2019) (<https://doi.org/10.1016/j.chemosphere.2018.12.004>).
- [63] M. Nawaz, W. Miran, J. Jang, D.S. Lee, Catal. Today 282, 38 (2017) (<https://doi.org/10.1016/j.cattod.2016.02.017>).

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Мікрореактор періодичної дії для моніторингу фотокаталітичних реакцій

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Фотокаталітичне окислення органічних забруднень є актуальною темою екологічних досліджень. Однак для ефективного процесу очищення потрібен ефективний фотореактор. При цьому типові джерела світла, такі як ртутна та галогенні лампи, повинні бути замінені на енергоефективні світлодіоди. У цій роботі представлено мініатюрний фотореактор, який для досліджень потребує малу кількість фотокаталізатора. Робота мікрофотореактора досліджувалася з використанням анатазу та титан (IV) оксиду (P25), як модельних фотокаталізаторів, та родаміну В, як модельного забруднювача. Ключовим елементом мікрореактора є змінний УФ-світлодіод. Довжина хвилі його випромінювання становить 365 нм і є оптимальною для модельного забруднювача барвника родаміну В. Представлений мікрореактор здатний майже повністю мінералізувати забруднюючий барвник і його можна використовувати для різних фотокаталітичних досліджень

Ключові слова: мікрофотореактор, родамін В, фотокаталізатор, світлодіод, фотодеградація.