

Original Research

PROCESS OPTIMIZATION OF ZnO–ASSISTED PHOTOCATALYTIC
DEGRADATION OF METHYL ORANGE USING RESPONSE SURFACE
METHODOLOGY

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Sonja Stanković^{1,a*}, Milan Radovanović^{1,b}, Ana Simonović^{1,c}, Žaklina Tasić^{1,d},
Aleksandar Cvetković^{1,e}, Vladan Nedelkovski^{1,f}, Dragana Medic^{1,g}

¹ University of Belgrade, Technical Faculty in Bor, Vojske Jugoslavije 12, 19210 Bor, SERBIA

^a <https://orcid.org/0000-0003-0745-5422> ^b <https://orcid.org/0000-0002-5175-6022>

^c <https://orcid.org/0000-0003-2392-0048> ^d <https://orcid.org/0000-0001-6544-1980>

^e <https://orcid.org/0009-0003-5184-6874> ^f <https://orcid.org/0000-0001-7724-1118>

^g <https://orcid.org/0000-0001-9980-5949>

Abstract

This study examines the photocatalytic degradation of methyl orange (MO) using ZnO nanoparticles, focusing on the effects of key operational parameters and process optimization through Response Surface Methodology (RSM). A Box–Behnken design was used to assess the impact of initial MO concentration, UV irradiation time, and catalyst dosage on degradation efficiency. Based on the experimental results, a quadratic regression model was developed and validated. The model showed a high coefficient of determination ($R^2 = 0.9361$), indicating good agreement between experimental and predicted values. Analysis of variance (ANOVA) identified the initial MO concentration as the most influential factor among the linear, interaction, and quadratic terms evaluated. Numerical optimization identified an initial MO concentration of 1 ppm, a UV irradiation time of 60 min, and a ZnO catalyst dosage of 0.2 g.

Keywords: ZnO, photocatalysis, methyl orange, optimization, RSM.

INTRODUCTION

Water pollution by organic pollutants is a significant environmental problem due to their adverse effects on aquatic ecosystems and human health. Synthetic azo dyes are particularly notable among these pollutants, as their widespread use in the textile, pharmaceutical, and other industries often leads to their presence in wastewater. Methyl orange (MO) is one of the most commonly used azo dyes. Because of its chemical stability and resistance to biodegradation, removing this compound by conventional methods can be difficult [1,2]. Therefore, photocatalysis is considered one of the most promising advanced oxidation processes for removing organic pollutants from water [1]. This process enables the decomposition of organic compounds under light in the presence of a semiconductor photocatalyst. Among various photocatalytic materials, ZnO has attracted considerable attention for its low cost, nontoxicity, chemical stability, and high exciton binding energy

* sstankovic@tfbor.bg.ac.rs

[3,4]. The efficiency of photocatalytic degradation depends on several process parameters, including the initial contaminant concentration, catalyst amount, and irradiation time [5].

This work aims to investigate the influence of process parameters (initial MO concentration, catalyst dosage, and UV irradiation time) on the efficiency of photocatalytic degradation of MO in the presence of ZnO as a catalyst, with particular emphasis on process optimization using response surface methodology (RSM).

MATERIALS AND METHODS

Synthesis of ZnO Nanoparticles

ZnO nanoparticles (ZnO NPs) were synthesized by a mechanochemical method using an agate mortar and subsequent calcination at 700°C. For the synthesis, zinc acetate dihydrate (NRK Inženjering, Belgrade, Serbia) and oxalic acid dihydrate (NRK Inženjering, Belgrade, Serbia) were used in analytical grade without further purification.

Photocatalytic measurements

Methyl orange was used to evaluate the photocatalytic activity of ZnO nanoparticles. The photocatalytic reaction was conducted in a homemade photoreactor under UV radiation (92 W). For laboratory tests, 30 mL of methyl orange solution was used. After the photocatalytic reaction, the solution was centrifuged and then analyzed with a UV–Vis spectrophotometer (Merck Spectroquant Pharo 300, Rahway, NJ, USA) at a wavelength of 502 nm.

Optimization process

Design–Expert software with the Box–Behnken design was used to examine the influence of process parameters on the efficiency of photocatalytic degradation of methyl orange and to optimize the process. The effects of three factors at three levels were studied: initial concentration of methyl orange (1, 50, and 100 ppm), UV irradiation time (30, 60, and 180 min), and catalyst dosage (0.05, 0.1, and 0.2 g). The Table 1 shows the range and levels of the three independent variables investigated.

Table 1 Experimental factors and range levels in the experimental design

Factors	Range level		
	-1	0	1
Initial concentration of methyl orange, C_0 (ppm)	1	50	100
Irradiation time, t (min)	30	60	180
Catalyst dosage, m (g)	0.05	0.1	0.2

RESULTS AND DISCUSSION

Response Surface Methodology is a statistical and mathematical tool widely used to evaluate the relationship between process variables and the corresponding response. Unlike conventional optimization approaches, which vary one parameter while keeping all other conditions constant, RSM allows simultaneous examination of several independent variables. This approach enables more efficient interpretation of experimental results while significantly reducing the number of required experiments, experimental time, and reagent consumption. Among the various experimental designs used in RSM, the Box–Behnken design has received considerable attention in photocatalytic studies due to its efficient experimental arrangement,

satisfactory predictive capability, and good agreement between predicted and experimental values [6]. The effects of initial concentration of MO, UV irradiation time, and catalyst dosage on the efficiency of photocatalytic degradation of methyl orange were studied. Seventeen experiments were performed in random order. The center point was repeated several times to estimate errors. The Box–Behnken matrix with experimental and model–predicted methyl orange degradation efficiencies is shown in Table 2.

Table 2 The Box–Behnken matrix with experimental and predicted degradation efficiencies of MO

Run	Coded factor values			Actual factor values			E (%)	
	C_0	t	m	C_0	t	m	Experimental	Predicted
1	0	1	-1	50	180	0.05	63.67	56.5988
2	0	0	0	50	60	0.1	80.43	80.43
3	-1	1	0	1	180	0.1	100	100
4	1	-1	0	100	30	0.1	21.33	11.1613
5	1	0	-1	100	60	0.05	28.45	25.285
6	0	0	0	50	60	0.1	80.43	80.43
7	-1	0	-1	1	60	0.05	100	96.9025
8	0	1	1	50	180	0.2	94.64	81.3063
9	-1	-1	0	1	30	0.1	95.83	85.5937
10	0	0	0	50	60	0.1	80.43	80.43
11	1	0	1	100	60	0.2	35.11	38.2075
12	0	0	0	50	60	0.1	80.43	80.43
13	-1	0	1	1	60	0.2	100	100
14	0	-1	1	50	30	0.2	28.4	35.4712
15	0	-1	-1	50	30	0.05	27.66	40.9937
16	0	0	0	50	60	0.1	80.43	80.43
17	1	1	0	100	180	0.1	37.79	48.0262

Figure 1 shows a comparison of the experimentally obtained and model–predicted efficiency of photocatalytic decomposition of MO. All points are closely distributed around the regression line, indicating good agreement between the experimentally determined and model–predicted values [6,7].

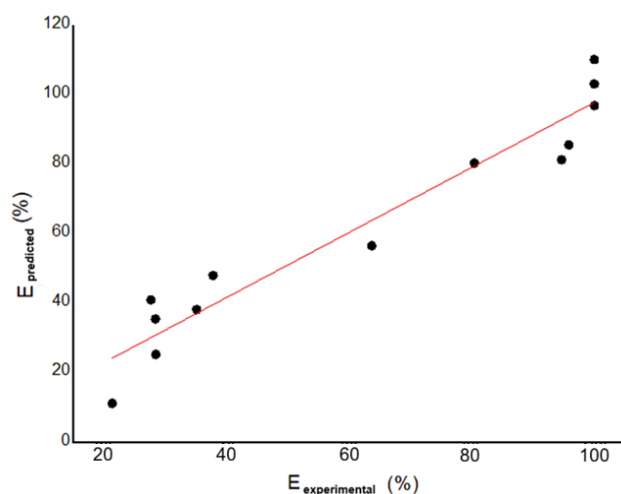


Figure 1 Comparison of experimental and model–predicted methyl orange degradation efficiency

To evaluate the adequacy and significance of the developed model, the experimental results were statistically analyzed using analysis of variance (ANOVA) [7]. The ANOVA results confirmed that the proposed quadratic model is statistically significant (Table 3).

Table 3 Analysis of variance (ANOVA) for methyl orange removal with ZnO–NP

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	13342.59	9	1482.51	11.39	0.0021	significant
Co	9326.37	1	9326.37	71.65	< 0.0001	
t	1887.44	1	1887.44	14.50	0.0066	
m	184.03	1	184.03	1.41	0.2732	
$C_0 \cdot t$	37.76	1	37.76	0.2901	0.6069	
$C_0 \cdot m$	11.09	1	11.09	0.0852	0.7788	
$t \cdot m$	228.46	1	228.46	1.76	0.2268	
C_0^2	20.33	1	20.33	0.1562	0.7044	
t^2	884.65	1	884.65	6.80	0.0351	
m^2	641.42	1	641.42	4.93	0.0619	
Residual	911.17	7	130.17			
Lack of Fit	911.17	3	303.72			
Pure Error	0.0000	4	0.0000			
Cor Total	14253.77	16				
R^2	0.9361					
R^2_{Adjusted}	0.8539					
Std. Dev.	11.41					
Adeq Precision	11.3146					

Based on the obtained F-values, the initial concentration of methyl orange had the strongest influence on photocatalytic degradation efficiency, followed by UV irradiation time and the quadratic effect of irradiation time. The interaction between the initial concentration of MO and catalyst dosage had the least impact on photocatalytic degradation efficiency. Additionally, probability values (p-values) lower than 0.05 for the investigated factors C_0 , t , and t^2 indicate that these factors significantly influence MO degradation efficiency.

Model validation is an important step in assessing the ability to reliably predict responses from experimental data. The robustness of the developed model was evaluated by the experimentally determined coefficient of determination (R^2) and the adjusted coefficient of determination (R^2_{adjusted}) [8]. Both coefficients, with values greater than 0.80, indicate good agreement between the experimental and predicted values, confirming the model's satisfactory predictive ability and adequacy. Additionally, the adequate precision was 11.3146, well above the recommended value of 4. This result confirms an appropriate signal-to-noise ratio and indicates the reliability, applicability, and suitability of the model for predicting responses within the examined experimental domain [6].

Design Expert software was used to create 3D response surface plots (Figure 2), which show the influence of interactions among the investigated parameters on MO degradation efficiency. During the examination of the interaction of process parameters on the efficiency of photocatalytic decomposition of MO, one independent variable was kept constant while the

influence of the interaction between the other two independent variables on the efficiency of photocatalytic decomposition was examined.

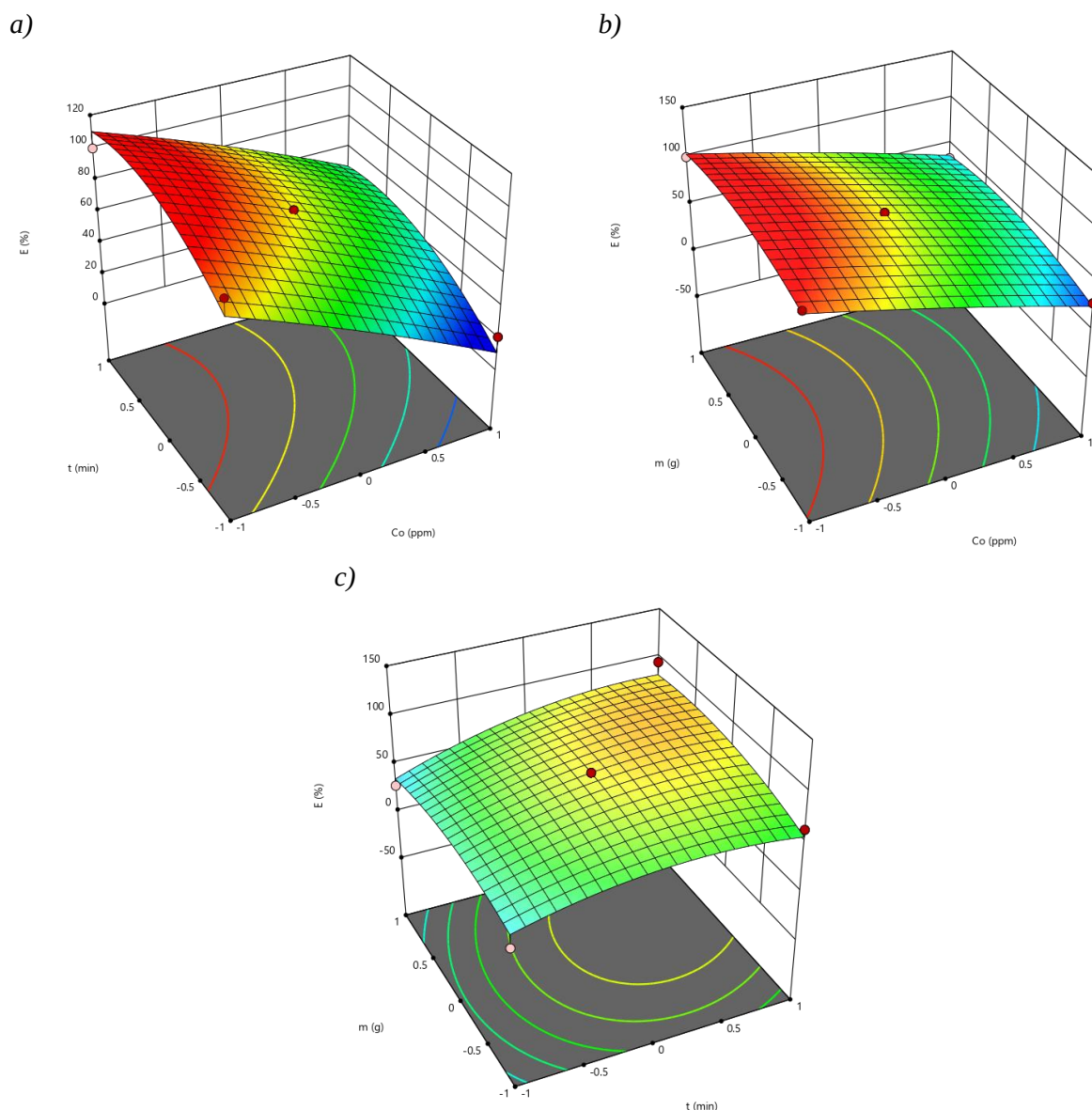


Figure 2 3D response surface plots showing the effects of (a) initial MO concentration and UV irradiation time; (b) initial MO concentration and catalyst dosage; and (c) catalyst dosage and UV irradiation time on the photocatalytic degradation efficiency of methyl orange

The effect of the interaction between the initial concentration of MO and UV irradiation time on the efficiency of photocatalytic degradation at a constant catalyst dosage (0.1 g) is shown in Figure 2a. Increasing the UV irradiation time and decreasing the initial MO concentration both lead to higher degradation efficiency. This can be attributed to the greater availability of hydroxyl radicals ($OH^\bullet$) relative to the number of pollutant molecules, enabling more efficient degradation of MO. In contrast, at higher initial MO concentrations, more reactive species are required. However, with a constant catalyst dosage, the amount of generated $OH^\bullet$ radicals is limited, resulting in lower degradation efficiency [9].

Figure 2b shows the effect of the initial concentration of MO and the catalyst dosage on the efficiency of MO photocatalytic degradation. Increasing the catalyst dosage while simultaneously decreasing the initial MO concentration leads to higher degradation efficiency. A larger catalyst dosage provides more active sites and excited charge carriers, promoting the formation of reactive radicals and enhancing the photocatalytic degradation process. Similar results were reported by Assimeddine et al. [10].

The effect of the interaction between catalyst dosage and UV irradiation time is shown in Figure 2c. The results indicate that increasing both factors positively affects MO degradation efficiency. Extending the irradiation time and increasing the catalyst dosage generate more $\text{OH}\cdot$ radicals, which accelerate the decomposition of methyl orange molecules and increase the efficiency of the photocatalytic process.

Numerical optimization determined the optimal process conditions: an initial MO concentration of 1 ppm, a UV irradiation time of 60 minutes, and a catalyst dosage of 0.2 g. Under these conditions, 100% photocatalytic degradation efficiency was achieved within the tested experimental range.

CONCLUSION

In this study, Response Surface Methodology was used to investigate the effects of initial MO concentration, UV irradiation time, and catalyst dosage on MO photocatalytic degradation efficiency and to determine the optimal operating conditions. The quadratic model showed good agreement with the experimental results, as indicated by high coefficients of determination and satisfactory adequacy of precision values, demonstrating its reliability for predicting photocatalytic degradation efficiency within the studied experimental domain. According to the ANOVA results, the initial MO concentration was the most influential factor affecting degradation efficiency. Numerical optimization identified the optimal conditions as an initial MO concentration of 1 ppm, a UV irradiation time of 60 min, and a ZnO catalyst dosage of 0.2 g. Under these conditions, 100% degradation of methyl orange was achieved, confirming the suitability of ZnO nanoparticles as an effective photocatalyst for dye removal.

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REFERENCES

- [1] Alhussain, H., Ferjani, H., Ozewo, O.A., *et al.* Inorg. Chem. Commun. 2024, 162, 112272.
- [2] Aldama–Huerta, O.A., Medellin–Castillo, N.A., Marin, F.C., *et al.* Appl. Sci. 2025, 15 (22) 12084.
- [3] Shaba, E.Y., Jacob, J.O., Tijani, J.O., *et al.* Appl. Water Sci. 2021, 11, 48.
- [4] Al–Rawashdeh, N.A.F., Allabadi, O., Aljarrah, M.T. ACS Omega 2020, 5, 28046–82055.
- [5] Tan, S.N., Zuen, M.L., Ramli, R.A., GAC 2025, 12, 100230.

- [6] Stanković, S., Radovanović, M., Đorđievski, S. *et al.* Metals 2026, 16 (1) 71.
- [7] Al, C., Zhou, D., Wang, Q., *et al.* Sol. Energy 2015, 13, 34–42.
- [8] Moussa, S.B. J. Photochem. Photobiol. A. Chem. 2024, 447, 115284.
- [9] Parida, K.M., Parija, S. Sol. Energy. 2006, 80, 1048–1054.
- [10] Assimeddine, M., Farid, Z., Abdennouri, M., *et al.* Environ. Sci. Pollut. Res. 2023, 30, 62494–62507.