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RESEARCH PAPER

Advance oxidation processes of Rhodamine B under O_3/UV using spent bleaching earth-ZnO composite: Performance in kinetics

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Abstract. Spent bleaching earth and ZnO composite (SBE/ZnO) was prepared as the catalyst for the advanced oxidation processes (AOPs) of rhodamine B (RB) under O3/UV. The photocatalytic ozonation process of RB was conducted at an ozone flow rate of 1 L/min by adjusting the variation of initial RB concentration, catalyst dosage, and reaction time. The RB removal efficiency of 96.7% was reached within 36 min at optimal operational conditions (initial concentration of 100 mg/L and catalyst dosage of 1.5 g). The kinetical analysis at this condition showed that the photocatalytic ozonation process of RB followed a pseudo-first-order reaction with a rate constant of 0.0975 min-1. Meanwhile, the effect of operational variables was evaluated using response surface methodology (RSM) and resulted in an optimized model for RB Removal following equation: RB Removal = 84.95 - 6.24A + 5.81B + 22.45C + 3.07AB + 13.14AC - 6.72BC + 0.1174A^2 + 7.86B^2 - 8.90C^2, where A is the initial concentration of RB, B is catalyst dose and C is reaction time, with a high coefficient of determination R^2 = 0.9432.

Keywords: Advanced oxidation processes; catalytic ozonation; photocatalysis; response surface methodology; Rhodamine B; SBE/ZnO

1. Introduction

In recent years, the textile industry has become a major concern in environmental issues due to the variety of dyes its uses (Kurukutla et al., 2015) that will end up in the environment. Rhodamine B (RB) is one of the most widely used dyes in the textile industry. Rhodamine B is classified as a dye that has high solubility in water, stable under the influence of light and temperature, and non-biodegradable (Saigl, 2021). Even in small concentrations, the effluent wastewater containing rhodamine B will be harmful and require prior treatment to be discharged into water bodies (Sundararajan et al., 2017).

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Advanced oxidation processes (AOPs) are one of the most promising methods to treat various pollutants and produce harmless end products (Chunsun et al., 2020). AOPs such as photocatalytic, ozonation, Fenton, and electrochemical methods have been carried out for the treatment of wastewater containing rhodamine B. However, in recent years, photocatalytic ozonation has become popular to treat rhodamine B due its rapid process and high removal rate (Mohsin & Mohammed, 2021). AOPs can produce several reactive oxygen species that have high oxidizing ability and low selectivity, such as $*O_2^-$, O_3, and *OH that can mineralize almost all organic compounds into CO_2, H_2O, and inorganic ions or acids (Chunsun et al., 2020).

Catalyst composites of porous materials and metal oxides are of interest due to their ability to degrade pollutants, easy to fabricate, and stable under a wide range of conditions compared to other types of catalysts (Wambu et al., 2011). Spent bleaching earth (SBE) is a solid waste from the bleaching of crude oil palm (CPO) and is abundantly available with hundreds of tons per year are produced (Slamet et al., 2021). SBE is a montmorillonite type porous material dominated by SiO_2 and Al_2O_3 with a content of 60-80%, and contains 20-40% of residual oil (Yulikasari et al., 2022). In Indonesia, the oil content must be reduced to below 3% through deoiling process to be legally considered as non-hazardous material. On the other hand, zinc oxide (ZnO) is a metal oxide that has high potential for application in water and wastewater treatment because it has a large surface area, good photocatalytic activity, and low cost (Mohsin & Mohammed, 2021). The photocatalytic activity of the SBE and ZnO composite has been investigated by Slamet et al. (2021) with the maximum capacity of rhodamine B adsorption of 147.06 mg/g under ambient light induction.

The objective of this research is to analyze the performance and kinetic characteristics of photocatalytic ozonation process using SBE/ZnO composite in the degradation of rhodamine B through several variations of operational conditions such as initial concentration, catalyst dosage, and reaction time.

2. Material and method

2.1. Materials

Hydrochloric acid, sodium hydroxide, calcium carbonate, and n-hexane were all purchased from SAP. Meanwhile, ethanol was purchased from Smartlab and zinc acetate was obtained from Merck. Standard solution of rhodamine B (Loba Chemie) was prepared with deionized water. The type of SBE in this study was SBE that had been de-oiled and came from a solvent extraction company in Indonesia.

2.2. Experiments

The composite of spent bleaching earth (SBE) and zinc oxide (ZnO) was carried out based on the results of previous study on Slamet et al., (2021). Photocatalytic activity of SBE/ZnO for the degradation of rhodamine B was evaluated under O_3/UV. Ozone flow rate applied was 1 L/min. The effect of photocatalytic degradation was studied at different RB initial concentration, i.e., 50, 100, 150, and 200 mg/L, also at different catalyst dosage, i.e., 0.5, 1, 1.5, and 2 g. The photocatalytic ozonation process was conducted for 60 min and samples for analysis were collected at 12, 24, 36, 48, and 60 min intervals.

2.3. Analytical Methods

The absorbance of rhodamine B was measured at 554 nm wavelength using UV-Vis spectrophotometer (Thermo Scientific GENESYS 140 Vis/150). The rhodamine B standard solution was measured to develop the calibration curve of absorbance and concentration and use it to calculate the RB removal efficiency.

2.4. Kinetics Studies

The degradation kinetics of rhodamine B under O_3/UV using SBE/ZnO were evaluated using the first order and second order rate equations given in Equation (1) and (2), respectively.

$$\ln\left(\frac{C_t}{C_0}\right) = -k_1 t \quad (1)$$

$$\frac{1}{C_t} = \frac{1}{C_0} + k_2 t \quad (2)$$

where C_0 (mg/L) is the initial concentration of rhodamine B dye solution, C_t (mg/L) is the concentration of rhodamine B solution at time t, k_1(min^{-1}) is the first order rate kinetics, k_2 (g.mg^{-1}.min^{-1}) is the second order rate kinetics, and t (min) is the O_3/UV exposure duration (reaction time).

3. Results and Discussion

3.1. Effect of Initial Concentration

The research was conducted in several different concentrations of rhodamine B from 50 to 200 mg/L to determine the effect of initial concentration of the solution. The results of the study on the effect of initial concentration of rhodamine B are presented in Figure 1. Removal efficiency showed a decrease as the initial concentration of rhodamine B solution increased. However, at a concentration of 50 to 100 mg/L, the removal efficiency at 12 min was slightly greater from 74% to 75% and then decreases again until the removal efficiency reaches 66% at higher initial concentration. These conditions are remained the same until 36 min into the process, then the removal efficiency reached a steady state at the next minute. It can be seen that along with increasing the initial concentration of rhodamine B above 100 mg/L, the removal efficiency was decreased. Due to the increase of rhodamine B initial concentration, the molecular amount of rhodamine B adsorbed by the catalyst surface also increases (Natarajan et al., 2011). The high amount of rhodamine B molecules also leads to an insufficient amount of reactive oxygen species (*OH and *O_2^-) which are required to degrade the rhodamine B molecules (Heidari et al., 2020). Therefore, at higher concentrations of rhodamine B, only limited amount of rhodamine B is able to adsorb and interact with the catalyst surface and the reactive oxygen species.

3.2. Effect of Catalyst Dosage

Rhodamine B removal was studied for photocatalytic ozonation process in several different SBE/ZnO catalyst dosage from 0.5 to 2 g. Figure 2 presents the data from the removal efficiency study due to the effect of catalyst dosage. Overall, the increase in SBE/ZnO catalyst dosage caused the removal efficiency of rhodamine B to increase. During 12 minutes process, the increase in removal efficiency occurred from 40% to 80% as the catalyst dosage increased from 0.5 to 2 g. Removal efficiency became greater up to 90-99% with increasing reaction time from 36 to 60 minutes. At the catalyst dosage of 1.5 g and 2 g, rhodamine B removal efficiency is almost the same at every minute. Therefore, considering the efficient amount of catalyst used in the process, catalyst dosage 1.5 g is considered as the optimal value. The increase in removal efficiency with increasing catalyst dosage is influenced by the catalyst surface area and the active sites provided (Moussavi et al., 2009). The catalyst surface provides active sites that can adsorb and establish oxidation reactions between rhodamine B molecules and reactive oxygen species through the mechanism of the photocatalytic process (Mohsin & Mohammed, 2021). The possible reaction of photolytic ozonation (O_3/UV) is shown in Equation (3) – (6) (Heidari et al., 2020).

O_3 + hv (UV light) → O_2 + O(^{1}D) (O(^{1}D): excited oxygen atom) (3)

$O(^1D) + H_2O) \rightarrow 2^*OH$ (4)

$O_3 + H_2O + hv \rightarrow H_2O_2 + O_2$ (5)

$H_2O_2 + hv \leftrightarrow 2^*OH$ (6)

Due the presence of SBE/ZnO in the O_3/UV process of rhodamine B, another possible reaction is shown in Equation (7) - (18) (Nasseh et al., 2020, Sundararajan et al., 2017).

Direct reaction:

$SBE/ZnO + hv\ (UV\ light) \rightarrow SBE/ZnO\ (h_{vb}^+ + e_{cb}^-)$ (7)

$O_3 + e^- \rightarrow {}^*O_3^-$ (8)

${}^*O_3^- + H^+ \rightarrow {}^*HO_3$ (9)

Inderect reaction:

$SBE/ZnO\ (h^+) + H_2O \rightarrow {}^*OH + H^+ + SBE/ZnO$ (10)

$SBE/ZnO\ (h^+) + OH^- \rightarrow {}^*OH + SBE/ZnO$ (11)

$SBE/ZnO\ (e^-) + O_2 \rightarrow {}^*O_2^- + SBE/ZnO$ (12)

$O_3 + {}^*O_2^- \rightarrow {}^*O_3^- + O_2$ (13)

${}^*O_3^- + H^+ \rightarrow {}^*HO_3$ (14)

${}^*HO_3 \rightarrow O_2 + {}^*OH$ (15)

or ${}^*O_2^-$ can react with H_2O:

${}^*O_2^- + H_2O \rightarrow {}^*HO_2 + OH^+$ (16)

${}^*HO_2 + {}^*HO_2 \rightarrow H_2O_2 + O_2$ (17)

$H_2O_2 + SBE/ZnO\ (e^-) \rightarrow OH^- + {}^*OH + SBE/ZnO$ (18)

Thus, the general process of rhodamine B degradation in photocatalytic ozonation process using SBE/ZnO composite is as follows:

Rhodamine B + (*OH, ${}^*O_2^-$,${}^*O_3^-$, ${}^*HO_2$, ${}^*HO_3$)→ degradation product (19)

3.3. Effect of Reaction Time

Based on Figures 1 and 2, the removal efficiency increased from 75% to 96% as the reaction time increased from 12 minutes to 36 minutes (for a concentration of 100 mg/L and a catalyst dosage of 1.5 g). Removal efficiency reached a stable value from 36 minutes to the end of the process at 60 minutes reaching 99%. This result showed that the rhodamine B degradation time is relatively fast. The degradation of rhodamine B with photocatalytic ozonation process using SBE/ZnO composite in this study provided a good process performance, which was only 36 minutes of the removal process, the efficiency achieved was already 96%. Compared to other studies that do not use catalysts, the reaction time required to achieve 60% removal efficiency was 45 minutes

(Asgari et al., 2019). The results of this study showed the effect of adding catalysts in the process that can accelerate the reaction. The same research results were shown by Nasseh et al., (2020) which required 30 min to achieve a removal efficiency of 76%.

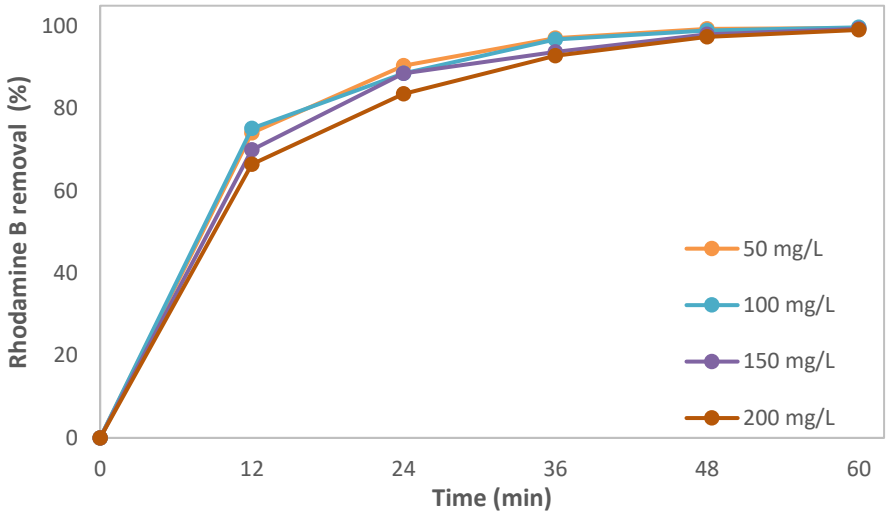

Figure 1. The effect of initial concentration on catalyst dosage of 1.5 g

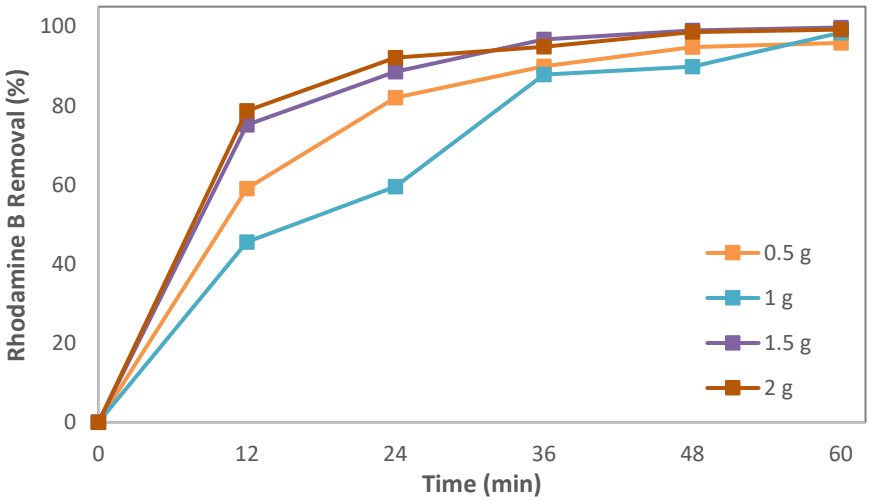

Figure 2. The effect of catalyst dosage on initial concentration of 100 mg/L

3.4. Response Surface Methodology (RSM)

A set of 30 experimental data were used to analyze the optimum operating conditions of photocatalytic ozonation process in variation of rhodamine B initial concentration (50, 100, 150, and 200 mg/L), catalyst dosage (0.5, 1, 1.5, and 2 g), and reaction time (12, 24, 36, 48, 60 min) on rhodamine B removal efficiency. Figure 3 shows the relationship between predicted and actual of the three variables with rhodamine B removal efficiency. Table 1 shows the results of ANOVA analysis of the developed model. The model formed based on ANOVA analysis has a p-value equal to < 0.0001 (<0.0500), which indicates that the model has a significant effect on the response value. The mathematical equation of the model is presented in Equation (11).

$$Rhodamine\ B\ Removal = 84.95 - 6.24A + 5.81B + 22.45C + 3.07AB$$
$$+13.14AC - 6.72BC + 0.1174A^2 + 7.86B^2 - 8.90C^2 \quad (11)$$

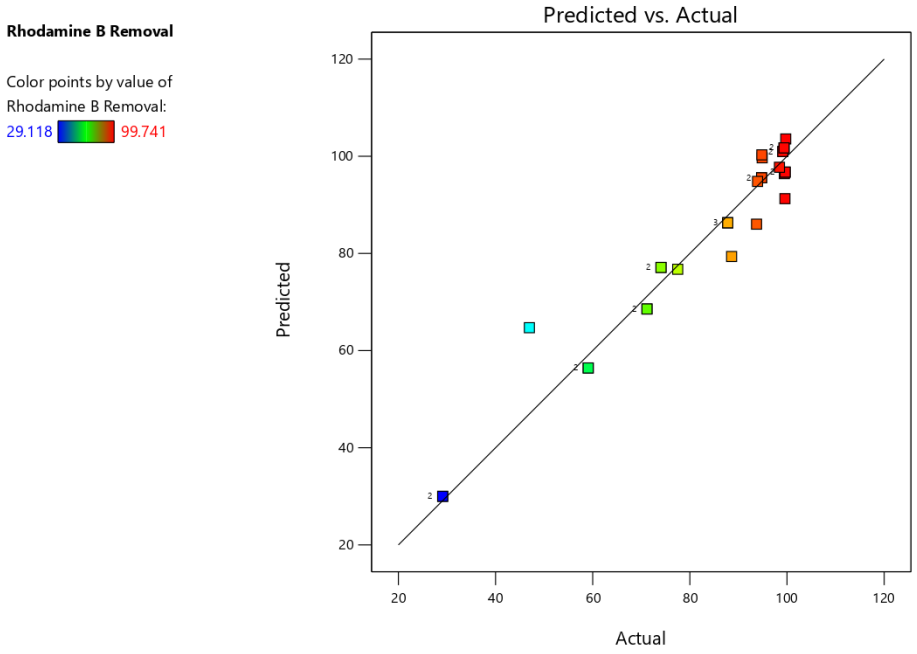

Figure 3. Predicted vs actual removal efficiency

Table 1. ANOVA analysis of response surface model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	11585.34	9	1287.26	36.91	< 0.0001	significant
A-Initial Concentration	611.22	1	611.22	17.53	0.0005	significant
B-Catalyst Dosage	517.78	1	517.78	14.85	0.0010	significant
C-Reaction Time	6464.02	1	6161.02	185.36	< 0.0001	significant
AB	78.34	1	78.34	2.25	0.1495	
AC	1214.73	1	1214.73	34.83	< 0.0001	significant
BC	304.87	1	304.87	8,74	0.0078	significant
A^2	0.0721	1	0.0721	0.0021	0.9642	
B^2	337.44	1	337.44	9.68	0.0055	significant
C^2	426.97	1	426.97	12.24	0.0023	significant
Residual	697.44	20	34.87			
Lack of Fit	697.44	5	69.74			
Pure Error	0.0000	5	0.0000			
Cor Total	12282.78	19				

The model has a correlation coefficient (R^2) of 0.9432 which shows a good relationship between the predicted and actual values (Figure 3). P-values less than 0.05 indicates model is significant. Based on Table 1, the interaction of each variable on rhodamine B removal efficiency shows that initial concentration (A), catalyst dosage (B), and reaction time (C) have a significant

effect. However, in the quadratic coefficient, only catalyst dosage (B^2) and reaction time (C^2) have a significant effect on the removal efficiency. Meanwhile, the interaction between the parameters of initial concentration-reaction time (AC) and catalyst dosage-reaction time (BC) have a significant effect on the removal efficiency.

Figure 4 shows the 3D surface response between the three variables on rhodamine B removal efficiency. The interaction between initial concentration and catalyst dosage shows that the use of catalyst dosage at 0.5 g and 2 g for initial concentration values has the highest value (red color) on the removal efficiency (Figure 4a). The interaction between reaction time and initial concentration shows that the higher the initial concentration of rhodamine B, the longer the reaction time required (Figure 4b). The same thing also applies to the interaction of reaction time with catalyst dosage, that the higher the catalyst used, the shorter the reaction time will be (Figure 4c).

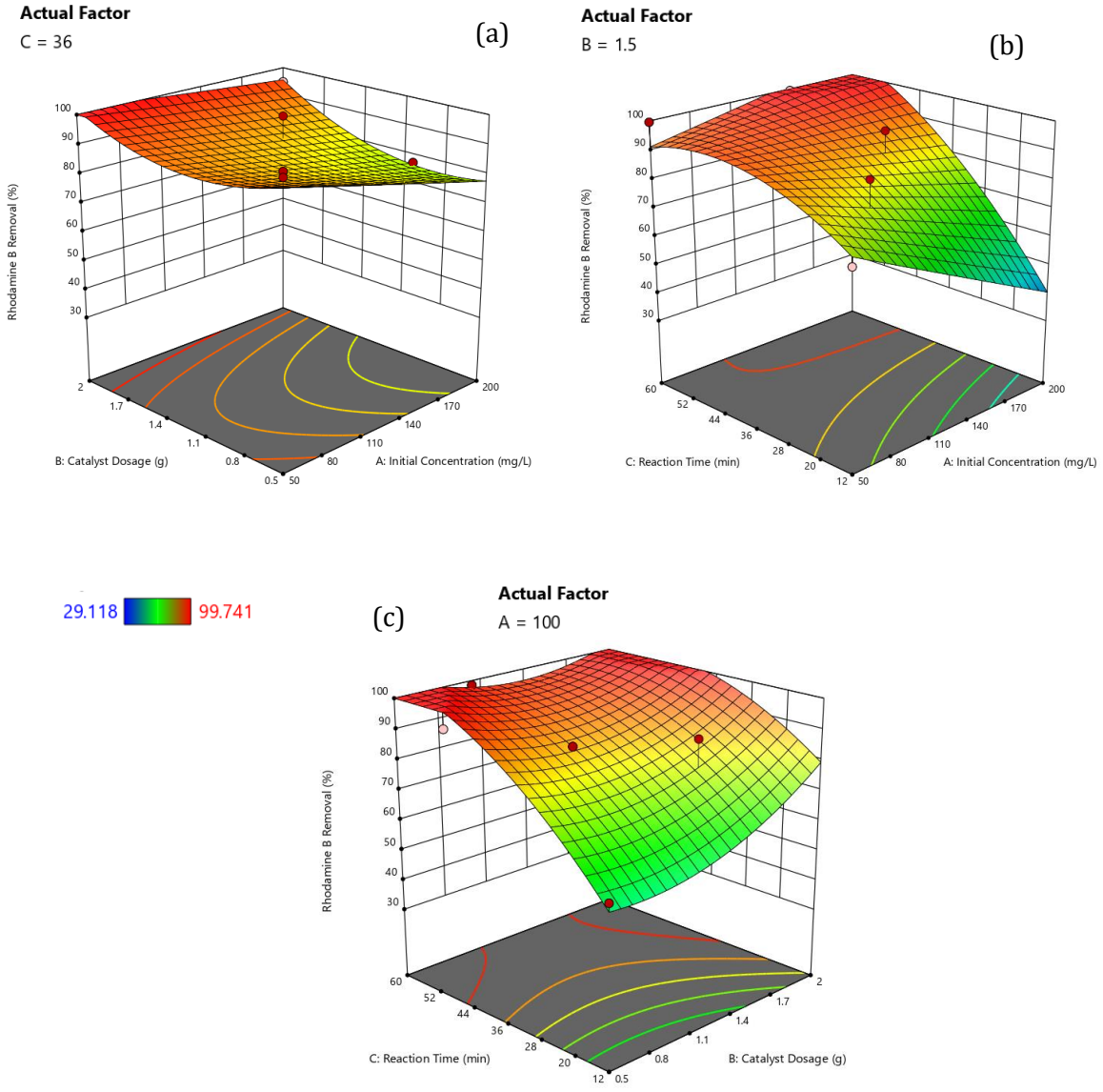

Figure 4. 3D response surface, (a) the interaction between catalyst dosage and initial concentration, (b) the interaction between time and initial concentration, and (c) the interaction between time and catalyst dosage

3.5. Kinetics Analysis

Kinetics analysis can be used to understand the dynamics of photocatalytic ozonation reactions in terms of determining rate constants. Kinetics analysis was performed using two kinetic models namely, pseudo-first order and pseudo-second order. The linear relations [ln(Ct/C0)] and [1/(Ct/C0)] as a function of time (min) are described according to Equation (1) and (2), and the results are presented in Table 2.

Table 2. Kinetic value for the photocatalytic ozonation of rhodamine B

Process		Pseudo First order		Pseudo Second order	
Initial Concentration (mg/L)	Catalyst Dosage (g)	Rate constant, (k1, min^{-1})	R^2	Rate constant, (k2, $g.mg^{-1}.min^{-1}$)	R^2
50	1.5	0.0972	0.9876	0.0793	0.7981
100	1.5	0.0975	0.9957	0.0540	0.6307
150	1.5	0.0836	0.9918	0.0155	0.6661
200	1.5	0.0771	0.9958	0.0080	0.6905
100	0.5	0.0590	0.9604	0.0040	0.9384
100	1	0.0490	0.9503	0.0082	0.5651
100	1.5	0.0975	0.9957	0.0540	0.6307
100	2	0.0862	0.9603	0.0200	0.8016

Based on Table 2, the R^2 value in all process schemes in pseudo-first order is greater than the pseudo-second order. This indicates that the rhodamine B removal efficiency follows pseudo-first order kinetics with R^2 value more than 0.98. Pseudo-first order describes the reaction rate based on the adsorption capacity (physisorption) of SBE/ZnO catalyst (Vargas et al., 2011). The rate constant value, k1, at the initial concentration of 50 to 100 mg/L increased by 0.0003 min^{-1}, then decreased to 0.0204 min^{-1} at the initial concentration of 200 mg/L. This shows that the increasing concentration of rhodamine B, the more rhodamine B molecules that must be degraded so that the reaction rate will be slower in the same amount of catalyst dosage. Another reason is due to the recombination of electron-hole pairs that affect the photocatalytic ozonation process (Sundararajan et al., 2017). On the other hand, after increasing the catalyst dosage from 0.5 to 1.5 g, the rate constant increases from 0.0590 to 0. 0.0975 min^{-1} and then decreases at higher catalyst dosage. According to Zahraei et al., (2023), the increased rate is related to the active sites of the catalyst, while agglomeration and light adsorption effects may lead to reduced reaction rate at higher dosages.

4. Conclusion

This study shows that the performance of SBE/ZnO composite catalyst in photocatalytic ozonation process can achieve removal efficiency of more than 96.7% (C0 = 100 mg/L, catalyst dosage = 1.5 g) in only 36 minutes. The interaction between reaction time and quadratic coefficient of catalyst dosage variables with rhodamine B removal efficiency has a significant impact. The kinetics analysis of photocatalytic ozonation process in this study follows pseudo-first order with R^2 value > 0.98 and rate constant of 0.0975 min^{-1}.

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