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Ultrasound Assisted Synthesis of Gadolinium Oxide-Zeolitic Imidazolate Framework-8 Nanocomposites and Their Optimization for Photocatalytic Degradation of Methyl Orange Using Response Surface Methodology

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Abstract: An ultrasound-assisted method was used to prepare gadolinium oxide (Gd₂O₃)-zeolitic imidazolate framework (ZIF)-8 nanocomposites. The surface morphology, particle size, and properties of the Gd₂O₃-ZIF-8 nanocomposites were examined using scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy, and ultraviolet-visible (UV-vis) spectroscopy. The synthesized Gd₂O₃-ZIF-8 nanocomposites were used as a catalyst to degrade methyl orange (MO) under UV light irradiation at 254 nm. The color of the aqueous MO dye solution during photocatalytic degradation was examined using color spectroscopy. Response surface methodology (RSM) using a four-factor Box-Behnken design (BBD) was used to design the experiments and optimize the photocatalytic degradation of MO. The significance of the experimental factors and their interactions were determined using analysis of variance (ANOVA). The efficiency of Gd₂O₃-ZIF-8 nanocomposites for the photocatalytic degradation of MO reached 98.05% within 40 min under UV irradiation at 254 nm under the experimental conditions of pH 3.3, 0.4 g/L catalyst dose, 0.0630 mM MO concentration, and 431.79 mg/L H₂O₂ concentration. The kinetics study showed that the MO photocatalytic degradation followed a pseudo-first-order reaction rate law.

Keywords: ultrasound-assisted method; Gd₂O₃-ZIF-8 nanocomposites; photocatalytic degradation; methyl orange; response surface methodology

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1. Introduction

Azo dyes make up more than half of the dyes produced globally, and anthraquinone dyes can be found abundantly [1]. Organic dyes are commonly released into wastewater. These dyes are hazardous to the environment if they are not destroyed and cause serious pollution [2]. Therefore, it is necessary to degrade such organic dye pollutants [3].

According to their raw materials, process principles, and pollutant characteristics, dye wastewater treatment methods can be classified into various categories, which include physical adsorption, membrane separation, biodegradation, electrochemical treatment, and photocatalysis [3]. The use of advanced oxidation processes (AOPs) is a major pathway for the near-ambient degradation of wastewater pollutants because the waste water pollutants can be degraded almost completely [4].

Photocatalytic degradation of organic dyes employed on metal oxide semiconductors has received a lot of interest in recent years. Owing to its good chemical durability, high thermal stability, and low phonon energy, Gd₂O₃ is a suitable semiconductor material for use as a photocatalyst [4]. It features a high refractive index and a suitable optical band gap, and is a potential candidate material for electronic and optoelectronic devices [4]. Gd₂O₃ is an n-type semiconductor that can be used as a photocatalyst to degrade organic pollutants

in water [5]. However, for a single semiconductor, because the speed of the recombination of electrons and holes is fast, it leads to a decrease in the photocatalytic efficiency [6].

ZIF-8 is a type of metal organic framework (MOF) constructed from imidazolate organic ligands and Zn^{2+} metal ions. It exhibits higher thermal and chemical stability than other MOFs [7]. Owing to its structural features, pore cavities, and large surface area, ZIF-8 is desirable for many potential applications such as gas storage, membrane sieving separation, templating, catalysis, and sensing [7]. Therefore, the coupling of the semiconductor and the metal–organic framework is of great significance due to its porosity and large specific surface area [8]. The formation of hybrid composites between metal oxide semiconductors and MOFs has been shown to result in a synergistic effect in their photocatalytic performance [9,10]. Many studies have shown that metal oxide-ZIF-8 nanocomposites show better photocatalytic efficiency than the metal oxides and ZIF-8 alone [11]. TiO_2 /ZIF-8 composites have been used to enhance the photocatalytic degradation of rhodamine B [12], while ZIF-8 and ZnO composites have been used to degrade MO under visible light [13]. The combined SnO_2 and ZIF-8 nanocomposites showed higher photocatalytic activity compared to a single-compound catalyst [14]. Herein, a composite photocatalyst was obtained by coupling Gd_2O_3 and ZIF-8 via a simple method.

An ideal photocatalyst for dye degradation should have high light absorption efficiency, efficient electron-hole separation, and large surface area. The absorbed photons are used for degrading MO while a larger surface area of the photocatalyst provides more contact points between the photocatalyst and the MO dye and thereby leads to faster photocatalytic degradation.

Response surface methodology (RSM) quantifies the relationships between the controllable parameters and the obtained response surfaces. In RSM, the experimental data is fitted to a polynomial equation using statistical and mathematical analysis [15]. The interactions between the operating parameters can be estimated using a limited number of experiments [15]. The two most popular experimental design methods for RSM are the central composite design (CCD) and Box-Behnken design (BBD) [16–21]. In this study, we carried out both synthesis of hybrid Gd_2O_3 -ZIF-8 nanocomposites using an ultrasound assisted method and an RSM experiment based on BBD to obtain optimum conditions for photocatalytic degradation of MO dye. In addition, a kinetics study was performed to evaluate the photocatalytic degradation rate of MO.

2. Results and Discussion

2.1. Identification of Gd_2O_3 -ZIF-8 Nanocomposites and Color Test of MO Dye Solution

2.1.1. XRD Diffraction

The XRD results of hybrid Gd_2O_3 -ZIF-8 nanocomposites are shown in Figure 1. The characteristic peaks of Gd_2O_3 nanowires and ZIF-8 could be found in Gd_2O_3 -ZIF-8 nanocomposites. The XRD pattern in Figure 1 shows that Gd_2O_3 nanowires were observed at $2\theta = 20.14^\circ$, 28.64° , 33.16° , 47.64° , and 56.53° , which correspond to the (211), (222), (400), (440), and (622) planes of the cubic phases (JCPDS 3-065-3181) [22]. The XRD peak values of ZIF-8 were observed at $2\theta = 7.30^\circ$, 10.37° , 12.70° , 14.60° , 16.43° , 18.08° , and 22.15° , which correspond to the (011), (002), (112), (022), (013), (222), and (114) planes of the sodalite structure (JCPDS 00-062-1030) [23,24]. The crystallite size of the Gd_2O_3 nanowires in the synthesized Gd_2O_3 -ZIF-8 nanocomposites was calculated using the Scherrer formula [25,26].

$$D = K\lambda / \beta \cos\theta \quad (1)$$

where D is the crystallite size, K is the Scherrer constant, λ is the X-ray wavelength ($\text{CuK}\alpha = 0.15406 \text{ nm}$), β is the full width at half maximum intensity of the XRD peak in radians, and θ is the Bragg angle. The average crystallite size of the Gd_2O_3 nanowires at 28.64° in the (222) plane was 22.14 nm.

Figure 1. XRD patterns of synthesized (a) ZIF-8, (b) Gd_2O_3 , and (c) Gd_2O_3 -ZIF-8 nanocomposites.

2.1.2. Raman Spectroscopy

The Raman spectroscopy results of hybrid Gd_2O_3 -ZIF-8 nanocomposites show the prominent mode of Gd_2O_3 and major peaks of ZIF-8 in Figure 2 and the Raman shift ranges from 200 cm^{-1} to 3500 cm^{-1} . A peak corresponding to the $F_g + A_g$ mode of the Gd_2O_3 nanowires was observed at 358.41 cm^{-1} [22,26].

Figure 2. Raman spectra of the synthesized Gd_2O_3 -ZIF-8 nanocomposites.

The major peaks of ZIF-8 were observed at 282 cm^{-1} (Zn–N stretching), 684 cm^{-1} (imidazolium ring puckering), 825 cm^{-1} , 952 cm^{-1} , 1032 cm^{-1} (C–H bending), 1146 cm^{-1} (C–N stretching), 1180 cm^{-1} (C–N stretching + N–H wag), 1186 cm^{-1} (C–N stretching), 1311 cm^{-1} (N–H wag), 1384 cm^{-1} (CH_3 bending), 1460 cm^{-1} (C–H bending), 1509 cm^{-1} (C–C stretching), 2930 cm^{-1} (methyl C–H stretching), 3113 cm^{-1} , and 3135 cm^{-1} (imidazolium ring C–H stretching) [27,28].

2.1.3. Scanning Electron Microscopy

The SEM results of hybrid Gd_2O_3 -ZIF-8 nanocomposites are shown in Figure 3. The SEM image of the Gd_2O_3 shows that it had an aggregated nanowire-like shape (Figure 3a). The nanowire-like shape of Gd_2O_3 was placed on the cubic-shaped ZIF-8 (Figure 3b,c).

Figure 3. SEM images of (a) Gd_2O_3 nanowires, (b) ZIF-8, and (c) Gd_2O_3 -ZIF-8 nanocomposites.

2.2. Investigation of Photocatalytic Activity for Degradation of MO using Gd_2O_3 -ZIF-8 Nanocomposites

The property of light absorption was measured to identify the absorption band of Gd_2O_3 -ZIF-8 nanocomposites that corresponds to the light irradiation at 254 nm in Figure S1. The absorption peak of the Gd_2O_3 -ZIF-8 nanocomposites was observed at 208 nm in UV-vis spectroscopy in Figure S1a. The bandgap energy of Gd_2O_3 -ZIF-8 nanocomposites was evaluated to be 4.85 eV in Figure S1b. Therefore, the photocatalyst of Gd_2O_3 -ZIF-8 nanocomposites could absorb light irradiation at 254 nm.

Figure 4a shows the photocatalytic degradation of MO observed through UV-vis spectrophotometry at constant time intervals. The UV-vis spectrophotometry data confirms that the absorption peaks of the MO solution decreased with time.

Figure 4. (a) UV-vis absorption spectra and (b) kinetics study of MO dye photocatalytic degradation.

Upon UV irradiation, the electrons in the valence band of the photocatalyst moved into the conduction band. This resulted in the continuous generation of holes (h^+) in the valence band and electrons (e^-) in the conduction band. The generation of electron-hole pairs contributed to the activity of the photocatalyst. Holes with high oxidative ability oxidized OH^- ions into $\cdot OH$ radicals in the aqueous MO solution. Valence band holes and conduction band electrons combined with hydroxide ions and oxygen to produce $\cdot OH$ and $\cdot O_2^-$ radicals. The $\cdot OH$ and $\cdot O_2^-$ radicals could act as oxidizing agents to the MO dye molecules [4,5,29]. The role of each component in the Gd_2O_3 -ZIF-8 nanocomposites is as a co-photocatalyst due to the enhanced rate of photocatalytic degradation of MO when Gd_2O_3 and ZIF-8 are combined than when only Gd_2O_3 is alone [6,26].

2.3. Kinetics Study for Photocatalytic Degradation of MO

To determine the photocatalytic kinetic model, the degradation of MO dye is examined with two kinetic models, including the first-order kinetic model and the second-order kinetic model, as expressed in the following equations. First-order kinetic model [30,31]:

$$\ln C_t = -k_1 t + \ln C_0 \quad (2)$$

Second-order kinetic model [32,33]:

$$1/C_t = -k_2 t + 1/C_0 \quad (3)$$

where C_0 (mM) and C_t (mM) are assigned as concentration of MO dyes at time = 0 and time = t (min^{-1}), respectively. k_1 (min^{-1}) and k_2 (min^{-1}) represent the rate constants of first-order and second-order, respectively. Accordingly, the fitting results from experimental investigations into two distinct kinetic models are demonstrated in Figure S2, where higher R^2 (0.9943) among the two examined models appears in the first-order kinetic model, validating the underlying kinetics for MO dye degradation under ultraviolet irradiation at 254 nm.

The linear behavior of the curve confirms that the degradation of MO followed a pseudo-first-order reaction rate law as shown in Figure 4b and the value of R^2 (coefficient of determination) for the pseudo-first-order reaction kinetics was 0.9943.

2.4. Color Test of Photocatalytic Degradation of MO Dye Solution

The changes in ΔL , Δa , Δb , and ΔE are listed in Table 1. The increase in ΔL indicates that the MO solution became whiter because of photocatalytic degradation. The negative values of Δa and Δb indicate that the MO solution tended to become less reddish owing to photocatalytic degradation. The total color change, ΔE , indicates the color difference between two colors under UV light irradiation [34,35]. Before the color of the solution was measured by a color spectrophotometer, the solution was centrifuged for 1 min to remove the photocatalyst from the solution. Then, we measured the color of only liquid solution with a color spectrophotometer. Therefore, the aggregation of photocatalyst did not affect measuring the color of the solution. The color change of the MO photocatalytic degradation was measured within the range of 0 to 100. Figure 5 shows the chromaticity diagram using the calculated x and y coordinates of a given color in the CIE 1931 color space. The color of the MO solution in the CIE1931 color space changed from red to green and from yellow to blue with increasing UV light exposure time because of photocatalytic degradation.

Table 1. Time-dependent color changes of MO solution using Gd_2O_3 -ZIF-8 nanocomposites as photocatalyst.

Times	ΔL	Δa	Δb	ΔE
0 min	0	0	0	0
10 min	8.73	−7.8	−22.68	25.52
20 min	12.78	−12.94	−50.06	54.11
30 min	15.7	−13.06	−67.06	70.10
40 min	16.3	−12.98	−70.15	73.17

Figure 5. The CIE chromaticity diagram for photocatalytic degradation of MO using Gd_2O_3 -ZIF-8 nanocomposites.

2.5. Box-Behnken Design with Response Surface Methodology (RSM)

The photocatalytic degradation of MO using Gd₂O₃-ZIF-8 nanocomposites is optimized by a four-factor and three-level BBD design consisting of 27 sets of experimental data for the optimization reactions, including replication at the center point [25,36]. Four independent variables, namely the initial pH (X_1), catalyst dose (X_2), MO concentration (X_3), and H₂O₂ concentration (X_4), were assessed. The photocatalytic degradation efficiency of MO was used as the response variable (Y). Table 2 shows the low (−1), medium (0), and high (+1) levels and the ranges of the independent variable parameters. The experimental data and response for the photocatalytic degradation of MO are shown in Table 3.

Table 2. Experimental design levels of chosen model parameters.

Independent Variables	Unit	Symbol	Range and Levels		
			Low (−1)	Medium (0)	High (+1)
pH	-	X_1	3	5	7
Dose of catalyst	g/L	X_2	0.1	0.3	0.5
Concentration of methyl orange	mM	X_3	0.0630	0.0840	0.1050
Concentration of H ₂ O ₂	mg /L	X_4	111	333	555

Table 3. Experimental conditions of coded variables for the various runs of Box-Behnken design and the obtained experimental and predicted MO photocatalytic degradation percentages.

Run	X_1	X_2	X_3	X_4	Degradation Percentage		Run	X_1	X_2	X_3	X_4	Degradation Percentage	
					Experimental	Predicted						Experimental	Predicted
1	1	0	1	0	46.93	46.25	15	0	1	1	0	57.62	58.39
2	0	0	0	0	64.76	64.46	16	0	0	−1	−1	52.22	51.45
3	0	0	1	−1	32.12	32.11	17	−1	0	−1	0	94.79	95.74
4	0	0	1	1	48.63	49.06	18	0	−1	0	1	44.80	44.43
5	1	1	0	0	50.35	50.30	19	0	1	0	−1	35.54	36.18
6	0	1	0	1	59.59	58.78	20	0	0	0	0	63.72	64.46
7	0	−1	−1	0	69.74	69.04	21	1	0	−1	0	67.85	68.68
8	0	−1	1	0	43.85	43.89	22	0	1	−1	0	76.03	76.07
9	−1	−1	0	0	67.89	67.60	23	−1	0	1	0	75.89	75.34
10	−1	0	0	1	78.78	79.54	24	1	−1	0	0	45.98	46.24
11	−1	0	0	−1	52.29	52.04	25	−1	1	0	0	85.69	85.09
12	0	0	0	0	64.90	64.46	26	0	−1	0	−1	27.91	28.99
13	1	0	0	1	42.66	42.98	27	0	0	−1	1	72.88	72.55
14	1	0	0	−1	33.12	32.44	-	-	-	-	-	-	-

2.5.1. Effect of pH

In Figure 6a, the effect of pH was investigated by varying only the pH from 3 to 7 while the other conditions remained the same. Under acidic conditions, the MO was negatively charged, and the photocatalyst surface positively charged [29]. Electrostatic attraction occurred between the MO and the photocatalyst. The transformation of the MO dye molecules to CO₂ and H₂O under radical attack in the photocatalytic reaction was attributed to electrostatic attraction [37,38].

Figure 6. The variation of the deviation from the reference point for photocatalytic degradation using Gd_2O_3 -ZIF-8 nanocomposites with (a) X_1 : pH, (b) X_2 : dose of catalyst, (c) X_3 : concentration of MO, and (d) X_4 : concentration of H_2O_2 .

2.5.2. Effect of Photocatalyst Concentration

In Figure 6b, the effect of the photocatalyst concentration was investigated by varying only the photocatalyst dose from 0.1 g/L to 0.3 g/L while the other conditions remained the same. Increasing the concentration of the photocatalyst in the MO solution may decrease the transmission of light [3]. Therefore, excess photocatalyst in solution could interfere with the photocatalytic degradation of the MO solution [36].

2.5.3. Effect of MO Concentration

After 40 min, the MO photocatalytic degradation efficiency decreased when the MO concentration increased from 0.0630 to 0.0105 mM (Figure 6c). Within the experimental range, the pseudo-first-order rate constant k_1 decreased with an increase in the MO concentration based on Equation (10) [3]. These results indicate that the absorption of light on the photocatalyst surface decreased at higher concentrations. Moreover, the photocatalytic degradation of MO occurred on the surface of the active sites of the photocatalyst [39].

2.5.4. Effect of H_2O_2 Concentration

H_2O_2 and metal oxide nanoparticles have been used to increase the photocatalytic degradation rate of MO [40]. The addition of H_2O_2 in the presence of catalyst was studied [41]. Figure 6d shows the effect of the H_2O_2 concentration on the photocatalytic degradation of MO.

2.6. Optimization for Photocatalytic Degradation of MO Using Response Surface Methodology (RSM)

RSM was applied to predict the percentage efficiency (%) of the photocatalytic degradation of MO using the Gd₂O₃-ZIF-8 nanocomposites photocatalyst under the variation of four parameters, namely, the pH, catalyst dose (g/L), MO concentration (mM), and H₂O₂ concentration (mg/L). We obtained the predicted degradation percentage using Design Expert 11 statistical software (Stat-Ease, Minneapolis, MN, USA) in Figure S3.

As shown in Table 3, the resulting photocatalytic degradation efficiency of MO fell in the range of 32.12 to 94.79%. The quadratic polynomial regression model in Equation (4) was used to obtain the degradation percentage of MO:

$$\begin{aligned} \text{Degradation}(\%) = & 64.46 - 14.04 X_1 + 5.39 X_2 - 10.71 X_3 + 9.51 X_4 - 3.36 X_1 X_2 - 0.51 X_1 X_3 - 4.24 X_1 X_4 \\ & + 1.87 X_2 X_3 + 1.79 X_2 X_4 - 1.04 X_3 X_4 + 3.75 X_1^2 - 5.90 X_2^2 + 3.29 X_3^2 - 16.46 X_4^2 \end{aligned} \quad (4)$$

where X_1 , X_2 , X_3 , and X_4 represent the coded values of the pH, photocatalyst dose, initial MO solution concentration, and H₂O₂ concentration, respectively. The accuracy of the model was verified by analysis of variance (ANOVA), and the results are presented in Table 4. The fitness of the BBD model was obtained by applying the suitability equation to the quadratic polynomial model based on the experimental data in Table 4 [15]. The obtained experimental data were scattered very closely to the trend line of the predicted data, as shown in Figure 7 [36]. The statistical parameters evaluated were the value of R^2 , the lack of fit (LOF), the p value, and the F value [42]. A regression model with a R^2 value greater than 0.9 is considered to have a high correlation between the experimental and predicted values [42]. In this study, the R^2 correlation factor obtained was 0.9988, indicating an excellent correlation and a satisfactory model for predicting the best conditions for MO degradation using the Gd₂O₃-ZIF-8 nanocomposites. The p value is an indicator of the statistical significance and interaction ability of each variable, wherein variables with lower p values have greater significance. In the present study, ANOVA for the regression model was highly significant because of the very small p value < 0.0001 , and a correspondingly large F value (710.13) was obtained. The lack of fit value obtained for the F value was 2.02 and had a larger p value (0.3762) > 0.05 , indicating that the lack of fit was not significant [42–45]. Therefore, the regression model is reliable for predicting the effects of variables affecting the photocatalytic degradation of MO by the Gd₂O₃-ZIF-8 nanocomposites and can be used to direct the design space.

Figure 7. Plot of the experimental and predicted response obtained for photocatalytic degradation of MO using Gd₂O₃-ZIF-8 nanocomposites.

Table 4. ANOVA of the BBD quadratic polynomial model for photocatalytic degradation of MO using Gd₂O₃-ZIF-8 nanocomposites.

Source	Sum of Squares	Df	Mean Square	F Value	p Value	
Model	7655.69	14	546.84	710.13	<0.0001	Significant
X ₁	2364.71	1	2364.71	3070.86	<0.0001	-
X ₂	348.02	1	348.02	451.95	<0.0001	-
X ₃	1375.69	1	1375.69	1786.50	<0.0001	-
X ₄	1085.62	1	1085.62	1409.81	<0.0001	-
X ₁ X ₂	45.10	1	45.10	58.56	<0.0001	-
X ₁ X ₃	1.03	1	1.03	1.34	0.2702	-
X ₁ X ₄	71.86	1	71.86	93.32	<0.0001	-
X ₂ X ₃	13.96	1	13.96	18.13	0.0011	-
X ₂ X ₄	12.79	1	12.79	16.61	0.0015	-
X ₃ X ₄	4.31	1	4.31	5.59	0.0357	-
X ₁ ²	75.00	1	75.00	97.40	<0.0001	-
X ₂ ²	185.88	1	185.88	241.38	<0.0001	-
X ₃ ²	57.79	1	57.79	75.05	<0.0001	-
X ₄ ²	1445.08	1	1445.08	1876.62	<0.0001	-
Residual	9.24	12	0.7700	-	-	-
Lack of Fit	8.41	10	0.8408	2.02	0.3762	Insignificant
Pure Error	0.8323	2	0.4162	-	-	-
Total	7664.94	26	-	-	-	-

R² = 0.9988; adequate precision = 102.0570.

The linear and quadratic terms that affect the photocatalytic degradation of MO were highly significant, with $p < 0.0001$. Meanwhile, the interaction terms X_1X_2 and X_1X_4 were significant, with $p < 0.0001$ (Table 4) [16]. However, the interaction term X_1X_3 was not significant within the range assessed in this study. In Figure 6, the influence of a single factor on the degradation of MO was evaluated when all the other factors were maintained at the constant values for which the coded values of these factors are zero and lie between their low and high values. The pH and MO concentration negatively affected the photocatalytic degradation of MO. The efficiency of the photocatalytic degradation of MO decreased as the pH of the solution increased from 3 to 7. (X_2) and (X_4) showed a positive effect on the photocatalytic degradation. The photocatalytic degradation of MO using the Gd₂O₃-ZIF-8 nanocomposites showed an upward trend with an increase in (X_2) and (X_4). This increase is attributed to the increase in the number of active sites on the photocatalyst surface.

Figure 8a,b show the interaction between the pH and photocatalyst dose at constant concentrations of MO and H₂O₂. Figure 8c,d show the interaction between the pH and concentration of H₂O₂ at constant concentrations of MO and the photocatalyst. The results clearly show that the effect of pH was more significant than those of the other factors in the photocatalytic degradation of MO, which could be attributed to the surface charge of the photocatalyst and the structural change of MO under different solution pH values. In runs 1 and 23, the degradation efficiency increased from 46.93% to 75.89% when the solution pH decreased from 7 to 3. The photocatalytic degradation efficiency increased from 43.85 to 57.62% when the catalyst dose increased from 0.1 g/L in run 8 to 0.5 g/L in run 15. In addition, when the concentration of H₂O₂ increased from 111 mg/L to 555 mg/L, the degradation efficiency increased from 32.12% to 48.63%. Meanwhile, the interaction between both factors was highly significant ($p < 0.0001$). This suggests that a high percentage of MO degradation can be achieved with a high H₂O₂ concentration as well as a low pH, which can be seen from the direct proportionality between the H₂O₂ concentration and the pH in Figure 8c,d. In addition, a high concentration of H₂O₂ and photocatalyst at low pH increased the availability of local electrons on the surface of the photocatalyst, thereby increasing the photocatalytic degradation rate. In general, the photocatalytic degradation of MO increased when a larger amount of photocatalyst was

used in the reaction because the number of active sites increased when there was a high surface-to-volume ratio. In addition, the abundant availability of active sites allowed $\cdot\text{OH}$ radicals and MO to be easily adsorbed onto the surface of the photocatalyst followed by the fast exchange of electrons between the reactants. As a result, MO degradation occurred rapidly. However, a slight decline in the photocatalytic degradation percentage was observed when the amount of photocatalyst used exceeded the optimal dosage.

Figure 8. Response surface graphs and plots for photocatalytic degradation (%): (a,b) between pH and catalyst dose with the remaining factors fixed at 0.084 mM MO concentration and 333 mg/L H_2O_2 concentration, and (c,d) between pH and H_2O_2 concentration with the remaining factors fixed at 0.3 g/L catalyst dose and 0.084 mM MO concentration.

2.7. Optimum Condition and Model Verification

Within the experimental conditions of the parameters we used, the RSM method was to determine the optimal condition for the photocatalytic degradation of MO. Therefore, we have limited experimental conditions for the following: The pH ranges from 3 to 7, the dose of catalyst ranges from 0.1 g/L to 0.5 g/L, the concentration of MO ranges from 0.0630 mM to 0.1050 mM, and the concentration of H_2O_2 ranges from 111 mg/L to 555 mg/L.

The optimization function in Design Expert 11.0 was used to obtain the optimum conditions for the photocatalytic degradation of MO under four constraints: (1) The maximum photocatalytic degradation percentage was 97.24% at the initial pH of 3.3, photocatalyst dose of 0.4 g/L, MO concentration of 0.0635 mM, and H_2O_2 concentration of 431 mg/L. The experiment showed a photocatalytic degradation percentage of 98.05% under the optimum conditions compared with the photocatalytic degradation of 97.24% obtained from the regression model. In addition, the conditions for obtaining the highest

MO photocatalytic degradation percentage at (2) the minimum weight of photocatalyst, (3) the minimum volume of H_2O_2 , and (4) neutral pH are also listed in Table 5 [45]. The results show that the experimental design was effectively applied for optimizing the photocatalytic degradation of MO.

Table 5. The obtained optimum conditions for the photocatalytic degradation of MO using Gd_2O_3 -ZIF-8 nanocomposites.

NO.	X_1	X_2	X_3	X_4	Experimental	Predicted	Deviation (%)
1.	3.3	0.40	0.0635	431	98.05	97.24	0.82
2.	3.0	0.10	0.0630	419	85.22	85.53	0.36
3.	3.0	0.40	0.0630	203	83.10	83.63	0.64
4.	7.0	0.39	0.0635	375	68.22	69.29	1.57

3. Materials and Methods

3.1. Materials

Gadolinium nitrate hexahydrate ($\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), ethylamine ($\text{C}_2\text{H}_5\text{NH}_2$), zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), 2-methylimidazole ($\text{CH}_2\text{C}_3\text{H}_3\text{N}_2$), polyvinylpyrrolidone ($(\text{C}_6\text{H}_9\text{NO})_n$, average mol wt. 10,000, PVP), methyl orange ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$, MO), and hydrogen peroxide (H_2O_2 , 30%, *w/w*) were purchased from Yakuri Pure Chemicals (Tokyo, Japan), Sigma-Aldrich (St. Louis, MO, USA), Merck (KGaA, Darmstadt, Germany), and Daejung Chemicals (Siheung, Korea). All the chemicals were used without further purification.

3.2. Measurement Methods

The structure pattern and average crystallite size of Gd_2O_3 -ZIF-8 nanocomposites were investigated using an X-ray diffractometer (Bruker, D8 ADVANCE, Karlsruhe, Germany) with a $\text{Cu K}\alpha$ radiation source (0.1504 nm). The morphology of the synthesized Gd_2O_3 -ZIF-8 nanocomposite photocatalyst was observed at an accelerating voltage of 10–20 kV using scanning electron microscopy (SEM, JEOL Ltd., JSM-6510, Tokyo, Japan). The vibrational states of the synthesized Gd_2O_3 -ZIF-8 nanocomposites were investigated by Raman spectroscopy (532 nm excitation, BWTEK i-Raman Plus, Newark, DE, USA). Photocatalytic degradation of the MO dye was carried out using a UV lamp (Light intensity is 4 W, 254 nm) and was confirmed by UV-vis spectroscopy (Shimadzu UV-1601 PC, Tokyo, Japan). The color of MO dye solution was observed using a color spectrophotometer (Colormate, Scinco, Seoul, Korea).

3.2.1. Preparation of Gd_2O_3 Nanowires

Gd_2O_3 nanowires were synthesized using the following hydrothermal procedure: 0.9 g of $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 25 mL of deionized water. 0.5 mL of $\text{C}_2\text{H}_5\text{NH}_2$ was then added slowly to the $\text{Gd}(\text{NO}_3)_3$ aqueous solution under vigorous stirring. The obtained white precipitate solution was heated for 12 h in an oven at 120 °C. The mixture was centrifuged several times after cooling and washed with deionized water to obtain gadolinium hydroxide. The gadolinium hydroxide was dried at 80 °C in an oven and then annealed in an electric furnace at 700 °C for 4 h in an Ar atmosphere to obtain Gd_2O_3 [22].

3.2.2. Ultrasound Assisted Synthesis of Gd_2O_3 -ZIF-8 Nanocomposites

Gd_2O_3 nanowires (10 mg), PVP (0.1 g), and 2-methylimidazole (0.263 g) were dispersed in 20 mL of methanol with stirring for 30 min. 20 mL of a methanol solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.146 g) was then added to the solution. The solution was sonicated for 30 min at 750 W. The precipitate was washed several times with methanol and collected after centrifugation to obtain the Gd_2O_3 -ZIF-8 nanocomposites [46].

3.2.3. Photocatalytic Activity of MO Degradation using Gd₂O₃-ZIF-8 Nanocomposites

The photocatalytic degradation of MO by the Gd₂O₃-ZIF-8 nanocomposites was performed in an aqueous MO dye solution under UV irradiation at 254 nm.

The initial pH values were adjusted to 3, 5, and 7 using 1 M aqueous HCl solution. The photocatalyst was added to the prepared MO solution and kept under constant stirring in the dark for adsorption. After adsorption-desorption equilibrium was reached between the MO dye and the catalyst in the solution for 30 min, the solution was irradiated under UV light at 254 nm with regular intervals, after which the photocatalytic degradation of MO was observed by UV-vis spectrophotometry. The photocatalytic degradation efficiency was measured using the following equation (Equation (5)) [21,47]:

$$\text{Photocatalytic degradation efficiency (\%)} = (C_0 - C)/C_0 \times 100 \quad (5)$$

where C_0 is the initial MO concentration after adsorption-desorption equilibrium has been reached under dark conditions ($t = 0$), and C is the MO concentration after 40 min. The values for the photocatalytic degradation of MO are shown in Table 2.

3.2.4. Evaluation of Color Change during Photocatalytic Degradation of MO

The CIELAB method was used to determine the color parameters L , a , and b . L indicates the lightness, and a and b are the chromaticity coordinates. The a parameter represents the red (+) to green (−) components. The b parameter represents the yellow (+) to blue (−) components. L can vary from white (100) to black (0) [48]. The colors of the initial and final solutions were measured using a color spectrophotometer. The total color change (ΔE) for each solution was calculated as follows:

$$\Delta a = a_0 - a_t \quad (6)$$

$$\Delta b = b_0 - b_t \quad (7)$$

$$\Delta L = L_0 - L_t \quad (8)$$

$$\Delta E = (\Delta a^2 + \Delta b^2 + \Delta L^2)^{1/2} \quad (9)$$

where a_0 , b_0 , and L_0 are the initial color parameters; a_t , b_t , and L_t the final parameters at the reaction time t (min); and Δa , Δb , and ΔL are the differences between the initial and final parameter values [34,35].

3.2.5. Experimental Design with RSM

The experimental design was based on the Box-Behnken design (BBD) with four factors at three levels. Table 1 shows the independent variables, experimental ranges, and coded levels of the tested variables in the BBD. The initial pH (X_1), dose of catalyst (X_2), concentration of MO (X_3), and concentration of H₂O₂ (X_4) were selected as the independent variables. The predicted photocatalytic degradation efficiency of MO (Y) was used as the dependent variable. A quadratic polynomial equation (Equation (10)) was used to fit the response variables [20,45]:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k \beta_{ij} X_i X_j \quad (10)$$

where β_0 is a constant coefficient, β_i are the linear interaction coefficients, β_{ii} are the quadratic interaction coefficients, β_{ij} are the cross-factor interaction coefficients, k is the number of factors investigated in the experiment, and X_i , and X_j are independent variables [45]. In the analysis of variance (ANOVA), the significance and suitability of the model were assessed using the lack of fit (LOF), F value, p value, and coefficient of determination (R^2). Surface plots (3D) and contour plots (2D) of MO photocatalytic degradation efficiency (%) were employed to demonstrate the effect of two interaction variables on the response (% degradation) based on the model Equation (10).

4. Conclusions

In this study, Gd_2O_3 -ZIF-8 nanocomposites were successfully prepared using an ultrasound-assisted synthesis method and characterized by XRD, Raman spectroscopy, SEM, and UV-vis spectroscopy. The photocatalytic degradation of MO using Gd_2O_3 -ZIF-8 nanocomposites as catalyst under various conditions was studied in detail. The color changes between the initial and final Lab values were confirmed in the coordinate diagram. The optimization of the MO photocatalytic degradation process was studied using response surface methodology based on the Box–Behnken design. The proposed regression model was highly reliable. Under optimal conditions (pH 3.3, 431 mg/L of H_2O_2 , 0.0635 mM of MO, and 0.4 g/L of photocatalyst), the photocatalytic degradation percentage of MO was 98.05% after 40 min. The photocatalytic degradation of MO using Gd_2O_3 -ZIF-8 nanocomposites was found to follow the pseudo-first-order kinetics rate law.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11091022/s1>, Figure S1: (a) UV-vis spectrum and (b) Tauc's plot for the bandgap energy of the Gd_2O_3 -ZIF-8 nanocomposites, Figure S2: Kinetics study for photocatalytic degradation of MO (a) first-order kinetic model and (b) second-order kinetic model, Figure S3: Predicted photocatalytic degradation percentage of MO using Design Expert 11 statistical software (Stat-Ease, Minneapolis, MN, USA).

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