Journal of Advances in Environmental Health Research

Photocatalytic degradation of methylene blue dye over immobilized ZnO nanoparticles: Optimization of calcination conditions

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Original Article

Abstract

In the present study, calcination conditions during the synthesis of zinc oxide nanoparticles were optimized using response surface methodology (RSM) based on central composite design (CCD). After that, the effect of the type of UV irradiation on the photocatalysis of methylene blue (MB) dye was studied based on the kinetic model obtained at optimum conditions. Analysis of variance (ANOVA) exhibited a reasonable high correlation coefficient between the predicted and experimental values (R^2 = 0.95). For a decolorization efficiency of 90%, the optimum calcination temperature and calcination time were identified to be 459 °C and 3.65 h, respectively. According to the reaction rate constant (k), the time required for the removal of MB using UVC lamps (0.027 1/min) was shorter than that of UVA lamps (0.0098 1/min), indicating higher exciting potential of the UVC irradiation for the generation of hydroxyl radicals through photocatalysis.

KEYWORDS: Nanoparticles, Methylene Blue, Zinc oxide, Hydroxyl Radical, Kinetics

Date of submission: 28 Sep 2014, ***Date of acceptance:*** 12 Dec 2014

Citation: Darvishi Cheshmeh Soltani R, Rezaee A, Rezaee R, Safari M, Hashemi H. **Photocatalytic degradation of methylene blue dye over immobilized ZnO nanoparticles: Optimization of calcination conditions.** J Adv Environ Health Res 2015; 3(1): 8-14.

Introduction

In recent decades, advanced oxidation processes (AOPs) have been proposed as efficient techniques for the degradation of organic pollutants such as dyes.[1,2] The most widely investigated AOPs for the treatment of wastewater containing dye are photocatalytic processes.[2] Among the various photocatalysts employed in photocatalytic processes, TiO_2 and ZnO are known to be efficient photocatalysts for the degradation of various environmental contaminants.[3-5] Compared to TiO_2, ZnO nanoparticles have a large area-to-volume ratio, high UV absorption capacity and long life-span. When ZnO nanoparticles are irradiated with UV light, highly reactive hydroxyl radicals (OH) are produced, which promote the degradation of target pollutants.[6,7] To mitigate the toxicity of ZnO nanoparticles for aqueous ecosystems and to make their use more economical, in the present study, ZnO nanoparticles were immobilized onto glass plates.[8] One of the most important parameters influencing the structure and activity of the photocatalyst is calcination conditions.[9,10] Therefore, a photocatalytic process consisting of low-pressure UV lamps and

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immobilized ZnO nanoparticles was used to characterize the photocatalytic activity of ZnO nanoparticles toward the degradation of methylene blue (MB) dye under different calcination conditions. To better evaluate the effect of calcination conditions, response surface methodology based on central composite design was used due to its advantages compared to the "one-factor-at-a-time" statistical approach.[11-14] In the following, the effect of the type of UV irradiation on photocatalytic decolorization of MB was evaluated at optimum calcination conditions.

Materials and Methods

The ZnO nanoparticles were prepared via co-precipitation method. First, 3.6 g ammonium nitrate was dissolved in 40 mL deionized water. Then, 0.9 mL aqueous ammonia was added to the abovementioned solution. Subsequently, 10 mL zinc nitrate was added dropwise to a stirred solution for 3 h at room temperature. After that, nitric acid was added to adjust the pH of the solution to 6.0. After aging for 24 h, 40 ml hydrogen peroxide (10 wt%) was added the stirred solution for 1 h. The precipitate was filtered and washed with deionized water, then, was dried in an oven at 80 °C. The resulted powder was immobilized on the glass plates via the heat attachment method.[15] To functionalize the surfaces of the glass plates (3 × 20 cm in size) with hydroxyl groups, concentrated industrial grade NaOH (50%) was used.[16] The functionalization with hydroxyl groups would be beneficial to achieve a stronger attachment of the ZnO nanoparticles to the plates. A 5% suspension of amorphous ZnO powder was prepared. After sonication in an ultrasonic bath (Starsonic 18-35, Liarre, Italy) at a frequency of 30 kHz for 90 min, the sonicated suspension was coated on the surface of the glass plates. Next, it was dried in an oven at 90 °C for 1 h. Finally, ZnO nanoparticle-coated glass plates were calcined in an electric furnace at different exposure times and temperatures based on the experimental design obtained using central composite design (CCD).

The photocatalytic process was carried out in a 600 ml rectangular reactor. Then, 5 low-pressure mercury vapor lamps (6 W) (Philips, Holland) were placed in the reactor top of the 3 glass plates containing immobilized ZnO nanoparticles. Recirculation of the solution was carried out via a peristaltic pump (Heidolph 5001, Germany). All the experiments were carried out with the solutions containing 5 mg/l MB at neutral pH.

Residual MB in the solution was measured with a UV-Vis spectrophotometer (Unico 2100) at 663 nm. Furthermore, the X-ray diffraction (XRD) patterns of the samples were obtained using a diffractometer (XRD, X'Pert MPD, Philips, Netherlands).

To evaluate the effect of calcination conditions on decolorization efficiency, two main variables regarding calcination conditions were selected; the calcination temperature and time. The number of required experimental runs was calculated via equation (Eq). 1:[12,13]

$$N = 2^k + 2k + x_o \quad (1)$$

where N is the number of required experimental runs (fact), k is the number of variables, and x_o (axial) is the number of central points. Thus, according to Eq. 1, the total number of required experimental runs is 13 (k = 2, x_o = 5). Design-Expert software (Stat-Ease, Inc., Minneapolis, MN, USA) was used for the analyses of the obtained data. The variables X_i were coded as x_i for statistical analysis according to Eq. 2:[14]

$$x_i = \frac{X_i - X_o}{\delta X} \quad (2)$$

where X_o and δX are the values of X_i at the center point and step change, respectively. The experimental ranges of the variables concerning MB removal are summarized in table 1.

Due to low melting point of the glass plates and the high energy required, the immobilized ZnO nanoparticles could not be calcined at above 500 °C. The catalyst was prepared

according to the calcination conditions described in the experimental runs, then, the photocatalytic MB removal (%) was measured at constant MB concentration of 5 mg/l, reaction time of 120 min, and neutral pH. The process can be described by means of a second-order model as represented in Eq. 3:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + (\sum_{i=1}^{n} b_{ii} x_i)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \quad (3)$$

where Y is the dependent variable [decolorization efficiency (%)], b_o is a coefficient constant, b_i are linear coefficients, b_{ij} are interaction coefficients, and b_{ii} are quadratic coefficients. Moreover, x_i and x_j are the coded values for the experimental variables.[12-14]

Results and Discussion

CCD model results

Using the CCD model, an empirical mutual relationship was established between the response [decolorization efficiency (%)] and independent variables based on the coded variables according to Eq. 4:

$$Y = 86.74 + 5.92x_1 - 0.68\,x_2 - 2.37\,x_1x_2 - 4.12x_1^2 - 1.83x_2^2 \quad (4)$$

where Y is the decolorization efficiency (%). The CCD matrix, experimental results, and predicted values for the photocatalytic decolorization are summarized in table 2. The statistical significance of the quadratic model was assessed through analysis of variance (ANOVA). The ANOVA results are presented in table 3. Table 3 demonstrates that the regression model has a high coefficient of determination (R^2 = 0.95), indicating that 95% of the variations of decolorization can be explained by the independent parameters. In fact, the model fails to explain only 5% of the variation. The low P-values obtained in the ANOVA indicate the significance of the results.[11]

Table 1. Ranges of the experimental parameters

Parameters	Ranges and levels				
	-2	-1	0	+1	+2
Calcination temperature (°C)	250	287.00	375.0	463.00	500
Calcination time (h)	3	3.44	4.5	5.56	6

Table 2. Experimental and predicted results of applied central composite design (CCD)

Run	Calcination temperature (°C)	Calcination time (h)	Decolorization efficiency (%)		
			Experimental	Predicted	Residual
1	375	4.50	85.12	86.74	-1.62
2	375	4.50	86.60	86.74	-0.14
3	463	3.44	91.56	89.77	1.79
4	375	4.50	88.21	86.74	1.47
5	463	5.56	86.23	83.68	2.55
6	375	6.00	80.35	82.13	-1.78
7	287	5.56	77.24	76.56	0.68
8	500	4.50	84.32	86.88	-2.56
9	375	4.50	86.56	86.74	-0.18
10	375	3.00	83.36	84.05	-0.69
11	250	4.50	70.23	70.13	0.10
12	287	3.44	73.10	73.19	-0.09
13	375	4.50	87.23	86.74	0.49

Table 3. Analysis of variance (ANOVA) for the photocatalytic methylene blue (MB) removal

Source of variations	Sum of squares	Degree of freedom	Mean square	F-value	P (Probe > F)
Regression	436.43	5	87.29	23.96	0.0003
Residuals	25.51	7	5.10		
Total	461.93	12			

R^2: 0.95; adjusted R^2: 0.91; adequate precision: 15.14; C.V: 2.30%

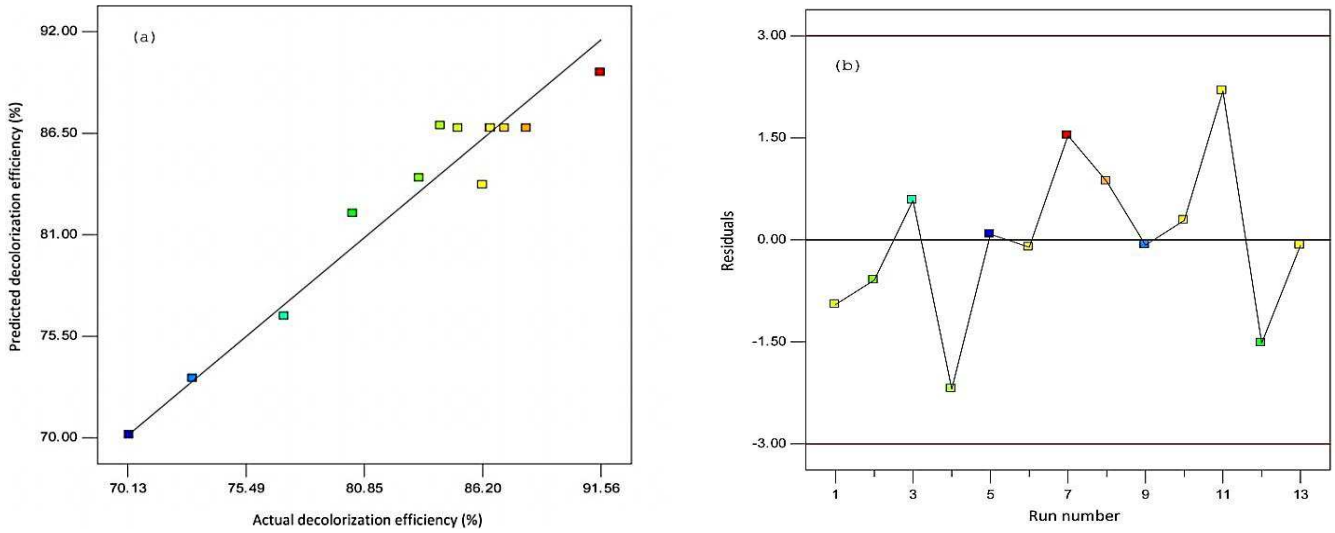

Figure 1. (a) Predicted versus actual decolorization efficiency and (b) residual versus run number for the photocatalytic methylene blue (MB) removal

It is important to note that "Adequate precision" measures the difference between the signal and noise (signal-to-noise ratio), and a ratio of greater than 4 is favorable.[13] As shown in table 3, the obtained ratio of 15.14 indicated an adequate signal. In addition, the low value of the coefficient of variation (CV = 2.30%) exhibited the relatively high reliability of the model for describing the removal of MB dye via the photocatalytic process.

In order to evaluate the adequacy of the model, experimental and predicted data were compared [Figure 1 (a)]. Figure 1 (a) demonstrates a good agreement between the predicted decolorization efficiency (%) and the experimental values (R^2 = 0.95). Residuals (Table 2) indicate how well the model satisfies the assumptions of ANOVA.[11,13] The plot of residuals versus run number is depicted in figure 1 (b). Figure 1 (b) shows no apparent dispersal of residuals for each experimental run, indicating suitability of the model for satisfying the assumptions of ANOVA.

Interactive effects of the independent parameters

Response surface and corresponding contour plot were applied for interaction of any two parameters. The effects of calcination temperature and calcination time on photocatalytic MB removal are shown in figure 2. These plots visualize how high and low values of calcination temperature affect MB removal during the photocatalytic process. At low calcination temperature, the synthesized nanoparticles have a wide range of particle size, while with increasing calcination temperature, the average particle size of aggregated particles increases as a result of increasing primary size of the nanoparticles during heat aggregation.[10] In agreement with our study, another investigation has demonstrated that increasing calcination temperature results in the increasing of average crystallite size.[17] Moreover, Yu and Wang[9], and

Yu et al.[18] showed that calcination temperature has a great effect on the structure and photocatalytic activity of TiO_2 nanotube arrays and TiO_2 film prepared by liquid phase deposition.

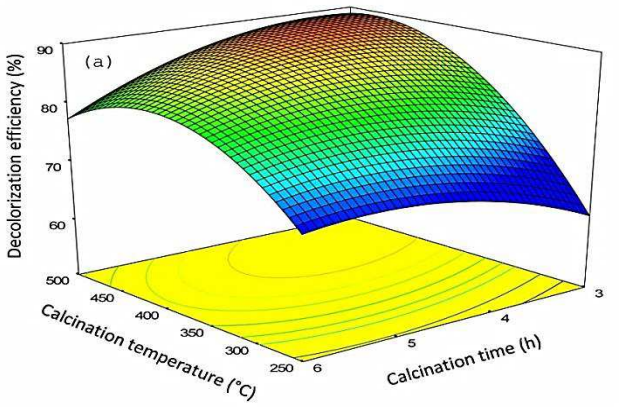

Figure 2. a) Response surface plot of photocatalytic methylene blue (MB) removal (%) as the function of calcination temperature and calcination time

As can be seen in figure 2, at low calcination temperature, decolorization efficiency (%) increased with increasing calcination time from the lowest value of 3 h to the moderate values. Then, it became constant as the calcination time increased from the moderate values to the highest value of 6 h. At high calcination temperature, increasing calcination time led to an evident drop in decolorization efficiency (%). A desirable value for each independent variable and response can be selected by using numerical optimization. Using this approach, the maximum decolorization efficiency (%) by the photocatalytic process was 90% at a calcination temperature of 459 °C and a calcination time of 3.65 h. In accordance with our study, Lai et al., in their study, showed that photocatalytic activity depends on calcination temperature.[19] According to their finding, the calcination temperature of 450 °C had the highest photocatalytic activity for degradation of methyl orange.[19] In a comparative photocatalytic study carried out using TiO_2 film, it was exhibited that the photocatalytic activity of TiO_2 film calcined at 700 °C was 2.5 times higher than that of the thin film calcined at 500 °C.[18]

Characteristics of synthesized ZnO nanoparticles

To determine the actual crystallite size of ZnO nanoparticles, XRD analysis was performed and the result is depicted in figure 3. Figure 3 displays the excellent crystal structure of synthesized ZnO nanoparticles. The crystallite size of ZnO nanoparticles was determined using the Debye–Scherrer's equation.[7] Accordingly, the average crystallite size of the ZnO nanoparticles was about 47.4 nm.

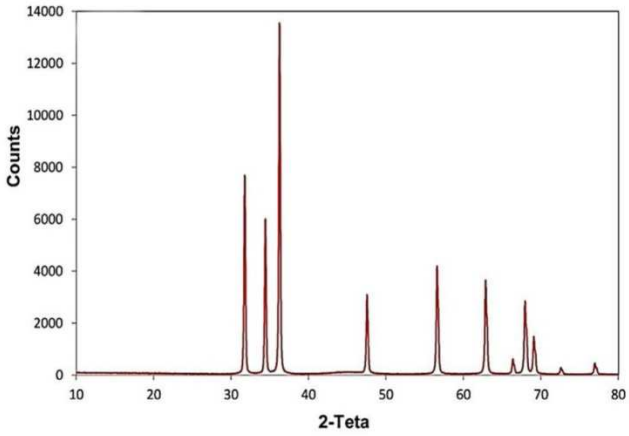

Figure 3. X-ray diffraction (XRD) spectrum of as-synthesized ZnO nanoparticles in optimal calcination conditions (Calcination temperature = 459 °C, calcination time = 3.65 h)

Kinetics for photocatalytic MB removal

The rate of a reaction is of principal concern. The rate at which a reaction occurs is usually determined by the concentration of the reactant as the reaction proceeds. To evaluate the reaction rate of photocatalytic MB removal using different types of UV lights, an integrated form of pseudo-first-order kinetic model was used (Figure 4).

The obtained correlation coefficients for both UVA and UVC ($R^2 > 0.99$) indicated that the amount of MB removal is directly proportional to the concentration of MB in the solution. Nishio et al., in their study, showed that

photocatalytic azo dye removal with ZnO powder followed pseudo-first-order kinetic model.[20] This finding is in agreement with our findings. As is evident from figure 4, the reaction rate constant (k) of MB removal for the UVC and UVA lamps was found to be 0.027 1/min and 0.0098 1/min, respectively, implying that the time required for MB removal by UVC lamps is shorter than that of UVA light. As reason, the application of UVC lamps produces more photons to excite more electron-hole pairs for photocatalytic decomposition of MB. Moreover, the application of UVC lamps results in decreasing the electron-hole recombination rate, which is one of the most important reasons for decreasing photocatalytic activity of a photocatalyst.[21]

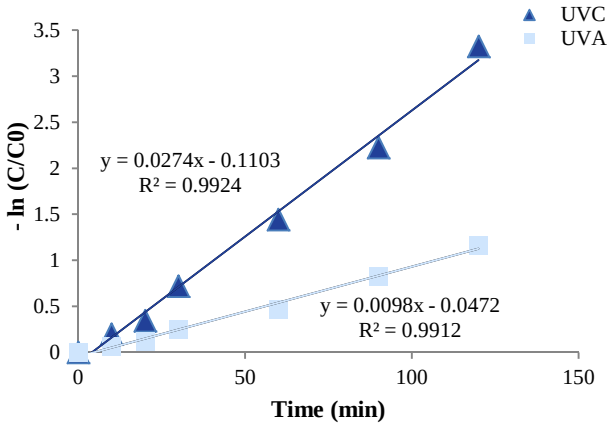

Figure 4. Effect of the type of UV light on decolorization efficiency (%) [Methylene blue (MB) concentration = 5 mg/l, reaction time = 120 min, and pH = neutral]

Conclusion

In the present study, the effect of the calcination conditions on the photocatalytic activity of synthesized nitrogen-doped ZnO nanoparticles has been studied in the context of response surface methodology (RSM). ANOVA analysis indicated a satisfactory fit between the regression model and the experimental results. According to the model, the highest rate of dye removal was attained at a calcination temperature of 459 ^{o}C and a calcination time of 3.65 h. Further experiments in optimum calcination conditions revealed an evident increment in decolorization efficiency (%) using UVC lamps instead of UVA lamps.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

This study was supported by Kurdistan Environmental Health Research Center and Arak University of Medical Sciences.

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