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Semi-empirical study of *ortho*-cresol photo degradation in manganese-doped zinc oxide nanoparticles suspensions

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Abstract

The optimization processes of photo degradation are complicated and expensive when it is performed with traditional methods such as one variable at a time. In this research, the condition of *ortho*-cresol (o-cresol) photo degradation was optimized by using a semi empirical method. First of all, the experiments were designed with four effective factors including irradiation time, pH, photo catalyst's amount, o-cresol concentration and photo degradation % as response by response surface methodology (RSM). The RSM used central composite design (CCD) method consists of 30 runs to obtain the actual responses. The actual responses were fitted with the second order algebraic polynomial equation to select a model (suggested model). The suggested model was validated by a few numbers of excellent statistical evidences in analysis of variance (ANOVA). The used evidences include high F-value (143.12), very low P-value (<0.0001), non-significant lack of fit, the determination coefficient ($R^2 = 0.99$) and the adequate precision (47.067). To visualize the optimum, the validated model simulated the condition of variables and response (photo degradation %) be using a few number of three dimensional plots (3D). To confirm the model, the optimums were performed in laboratory. The results of performed experiments were quite close to the predicted values. In conclusion, the study indicated that the model is successful to simulate the optimum condition of o-cresol photo degradation under visible-light irradiation by manganese doped ZnO nanoparticles.

Keywords: Photo degradation, Mn-doped ZnO nanoparticles, Optimization, Modeling, RSM, Simulation, ANOVA, Semi-empirical, Photo catalyst

Background

Advanced oxidation processes (AOPs) are physicochemical procedures, which are designed to remove environmental organic and inorganic pollutions. Photo catalysis, the current interest of AOPs, is applied for decontamination of environmental organic pollutions [1-4]. The photo catalysis, under suitable light illumination, produces hydroxyl radical ($^\bullet$OH) and hole (h[+]) which are powerful and non-selective oxidants to degrade a variety of organic compounds [5-7]. Zinc oxide (ZnO) with great advantage in absorption a larger fractions of the solar spectrum, is one of the photo catalyst that removed

several environmental contaminants under visible-light irradiation [8-11]. To enhance the visible-photo activity of ZnO, doping the transition metals such as manganese (Mn) has been prepared [12]. In the most cases, the evaluation of the photo degradation was carried out by a traditional method (one variable at a time), which is not only costly and time consuming but also often leads to misinterpretation of Experimental results [13-19]. Since the photo degradation is dependent on several effective parameters such as irradiation time, pH value, photo catalyst loading and substrate concentration [11,20], it needs to preform too many experiments for finding the optimum condition. While the managing of these experiments is difficult, the real world of photo degradation's experiments is very expensive because of chemicals, instruments, time of the researchers and etc. Therefore, prediction of the optimal condition seems necessary.

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Table 1 Experimental-Design of *o*-cresol photo degradation

Std	Run	X_1	X_2	X_3	X_4	Y (%)
12	1	1	1	-1	1	
3	2	-1	1	-1	-1	
28	3	0	0	0	0	
11	4	-1	1	-1	1	
18	5	2	0	0	0	
29	6	0	0	0	0	
19	7	0	-2	0	0	
6	8	1	-1	1	-1	
21	9	0	0	-2	0	
13	10	-1	-1	1	1	
24	11	0	0	0	2	
4	12	1	1	-1	-1	
25	13	0	0	0	0	
23	14	0	0	0	-2	
14	15	1	-1	1	1	
5	16	-1	-1	1	-1	
8	17	1	1	1	-1	
22	18	0	0	2	0	
9	19	-1	-1	-1	1	
2	20	1	-1	-1	-1	
20	21	0	2	0	0	
15	22	-1	1	1	1	
17	23	-2	0	0	0	
7	24	-1	1	1	-1	
27	25	0	0	0	0	
1	26	-1	-1	-1	-1	
26	27	0	0	0	0	
30	28	0	0	0	0	
10	29	1	-1	-1	1	
16	30	1	1	1	1	

Recently the response surface methodology (RSM) was used as an efficient technique for these purposes (simulation the condition) [21-26]. In the methodology, central composite design (CCD) was used for experimental-design and fitting the performed (actual) results with a polynomial equation in vicinity region of the optimum condition to make a model [27]. The model relates the responses (sometimes yield) and the variables of the photo degradation process [28]. However, no study has been conducted on application of the RSM that have been reported on the photo degradation of *ortho*-cresol (*o*-cresol) by manganese-doped zinc oxide (Mn-doped ZnO) nanoparticles as photo catalyst. In this work, the optimum condition was simulated by the RSM and

then visualized by 3D plots in vicinity region of reported optimum condition [29]. The predicted optimum of the responses and the variables were confirmed by the actual responses of the laboratories experiments.

Experiment
Empirical methodology
O-cresol (99%, Fluka), NaOH (99% Merck), H_2SO_4 (95%-97%) are of reagent grade, obtained from Merck which used without further purification. Mn-doped ZnO nanoparticles (photo catalyst) were synthesized according to procedures that is previously described [12]. Photocatalic degradation of *o*-cresol was performed in a designed batch photo reactor with Philips lamp (23 watt) as visible light source [30]. Throughout the study, a desired concentration of *o*-cresol solution was mixed with an appropriate amount of photo catalyst in the photo reactor. At specific time intervals, aliquot samples were withdrawn from the bulk solution and filtered through 0.2 μm polytetrafluoro ethylene (PTFE) filters. The concentration of *o*-cresol was measured using UV-visible spectrophotometer (shimadzu, uv-1650pc).

Statistical methods
To find the optimum conditions of the photo degradation, the experiments were designed by RSM and CCD (Table 1 the design is in code). The design with four effective variables (Table 2) was run by the design-expert version 8.0.7.1. The plan was included 16 factor points (2^n), 8 axial points (2n), and 6 center points (replications) the total numbers of performed runs were 30 experiments. The designed actual responses were fitted to the linear, 2FI, quadratic and cubic models by CCD. The fitting was based on a second order polynomial model (Eq. 1) by a multiple regression analysis [27],

$$Y = \beta_0 + \sum_{i=1}^{4}\beta_i\chi_i + \sum_{i=1}^{4}\beta_{ii}\chi_i^2 \sum_{i=1}^{3}\sum_{j=i+1}^{4}\beta_{ij}\chi_i\chi_j + \varepsilon \quad (1)$$

where Y (photo degradation %) represents the response variable, β_0 is the constant term, β_i represents the coefficients of the linear parameters, x_i represents

Table 2 Independent variables and their levels employed in the central composite design

	Variables	Units	Level of variables	
			Low	High
X_1	Irradiation time	minute	120	360
X_2	pH	-	6.6	9.8
X_3	Photo catalyst amount	g/L	0.5	2.5
X_4	Concentration of *o*-cresol	mg/L	15	55

the variables, β_{ii} represents the coefficients of the quadratic parameter, β_{ij} represents the coefficients of the interaction parameters and ε is the residual associated to the experiments. The significance and adequacy of the model was determined by a few numbers of statistical evidences that appear in analysis of variance (ANOVA) as output of the CCD method. These evidences include Fisher variation ratio (F-value), probability value (P-value), Lack of Fit, coefficient of determination R-squared (R_d^2), adjusted R-squared (R_{Adj}^2), predicted R-squared (R_{Pred}^2) and adequate precision of Predicted Residual Error of Sum of Squares (PRESS). Most of these parameters are clearly defined in the experimental design texts. PRESS is a signal-to-noise ratio, which compares the range of the predicted values at the design points to the average prediction error. The ratios greater than 4 indicate adequate model discrimination [30]. R_{Adj}^2 and the R_{Pred}^2 are the measurement of the amount of variation around the mean and the new explained data, respectively. The very significant is the Fisher test where P-value is compared with F-value. F-value is a statistically valid measure of how well the factors described the variation in the data about its meaning while P-value represents the degree of significance of each variable. Mathematically, F-value is given by the ratio of mean square due to model variation by that due to error variance (Eq. 2). The high value of F-value indicates significance and adequacy of the model,

$$\text{F} - \text{value} = S_r^2/S_e^2 \qquad (2)$$

where S_r^2 and S_e^2 are mean of the model and residuals square respectively, obtained by dividing the sum of squares of each of the two sources of variation, the model, and the error variance, by the respective degrees of freedom (DF) [27]. For a variable having a P-value smaller than 0.05, response would be influenced at a confidence level of 0.95.

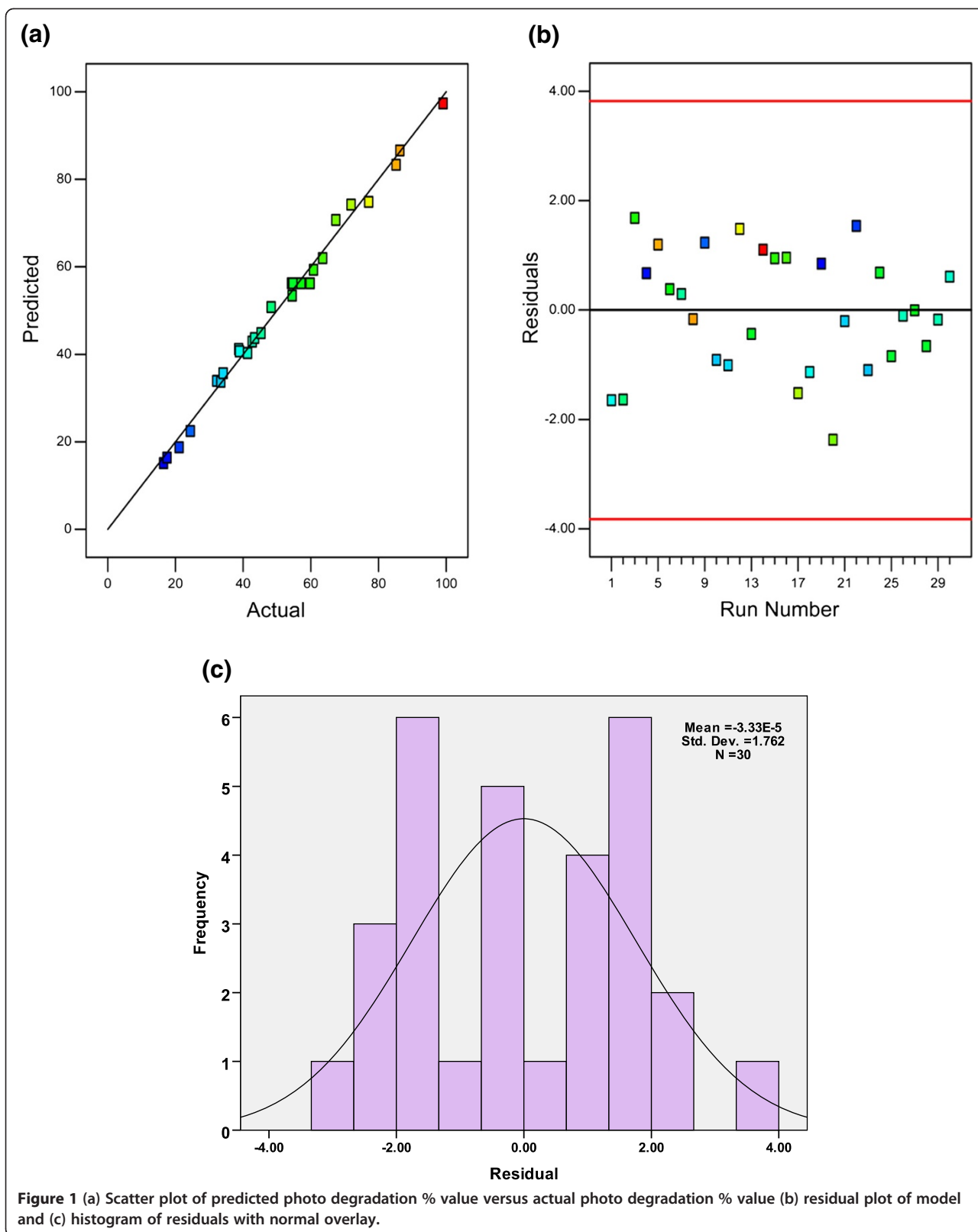## Analysis of the results
Satisfactory adjustment of the model
Table 3 shows the ANOVA of the quadratic model for the photo degradation. A high F-value (F_{model} = 143.12) was obtained while there is only 0.01% chance of occurrence of noise, indicating substantial significance of the model. The Prob > F (<0.0001) of model is much smaller than 0.05 which indicates the most terms of the model including (X_1, X_2, X_3, X_4, $X_2 X_3$, $X_2 X_4$, X_2^2, X_3^2, X_4^2) are significant (reckoning that the values greater than 0.1 are indication of the model terms are not significant). Pure errors such as experimental errors are minimal as the Lack of Fit is not significant ((=1.72).

R_d^2 provide a measure of how much variability in the observed response values can be explained by the experimental factors and their interactions. In this

Table 3 Analysis of the variance for photo catalytic degradation of *o*-cresol parameters

Source	Sum of squares	Degree of freedom	Mean square	F Value	Prob > F
Model	12227.40	14	873.39	143.12	< 0.0001
X_1	3658.07	1	3658.07	599.43	< 0.0001
X_2	184.26	1	184.26	30.19	< 0.0001
X_3	497.77	1	497.77	81.57	< 0.0001
X_4	5701.08	1	5701.08	934.20	< 0.0001
X_1^2	14.25	1	14.25	2.34	0.1473
X_2^2	10.40	1	10.40	1.70	0.2114
X_3^2	0.53	1	0.53	0.09	0.7732
X_4^2	271.43	1	271.43	44.48	< 0.0001
$X_1 X_2$	43.89	1	43.89	7.19	0.0171
$X_1 X_3$	0.076	1	0.076	0.01	0.9128
$X_1 X_4$	9.98	1	9.98	1.63	0.2205
$X_2 X_3$	491.79	1	491.79	80.59	< 0.0001
$X_2 X_4$	1040.58	1	1040.58	170.51	< 0.0001
$X_3 X_4$	182.31	1	182.31	29.87	< 0.0001
Residual	91.54	15	6.10		-
Lack of Fit	70.91	10	7.09	1.72	-
Pure Error	20.63	5	4.13	-	-
Corrected Total	12318.93	29	-	-	-
R-Squared		0.9926	Standard Deviation		2.47
Adjusted R^2		0.9856	Coefficient of variation %		4.90
Adequate Precision		47.067	PRESS		438.15

study, as obtained R_d^2 (0.9926) indicates that the model is capable of accounting for more than 99.26% of the variability in the responses. In addition, the R_{Adj}^2 (0.9856) is in reasonable agreement with (<0.20) with the R_{Pred}^2 (0.9644) which confirms the aptness of the model. Moreover, the adequate precision (47.067) shows remarkable signal (>> 4). These observations can be corroborated by regression plots. Further, Figure 1a shows the actual values versus predicted values of the photo degradation %, which indicated an excellent agreement between actual and predicted responses. A residual plot allowed visual assessment of the distance of each observation from the fitted line (Figure 1b). The residuals randomly scattered in a constant width band about the zero line. Figure 1 (c) shows the histogram of the residuals in allowed visual assessment of the assumption. As observed, the measurement errors in the response variable were normally distributed. This ensured model (quadratic) was suitable to navigate the design space and a satisfactory adjustment of the polynomial model to the experimental data.

Figure 1 (a) Scatter plot of predicted photo degradation % value versus actual photo degradation % value (b) residual plot of model and (c) histogram of residuals with normal overlay.

The quadratic expression model for the photo degradation

The quadratic model displayed in Eq. (3) expresses the relationship between responses of actual variables and the variables themselves.

$$
\begin{aligned}
Y = {}& -616.18340 + 0.31631 X_1 \\
& + 132.45247 X_2 - 174.38646 X_3 \\
& - 1.70016 X_4 - 0.019661 X_1 X_2 \\
& - 0.026875\, X_1 X_3 + 3.02083 E \\
& - 004\, X_1 X_4 - 10.29688 X_2 X_3 \\
& - 20703\, X_2 X_4 - 0,013750 X_3 X_4 \\
& + 1.67535 E - 004 X_1{}^2 - 6.61621 X_2{}^2 \\
& - 24.63750 X_3{}^2 + 0.025781 X_4{}^2
\end{aligned}
\tag{3}
$$

Where X_1, X_2, X_3 and X_4 are demonstrated in Table 2. The positive sign in front of the terms indicates synergistic effect while negative sign indicates antagonistic effect. From the equation, the photo degradation % has been linear and quadratic effects by the four process variables (X_1, X_2, X_3 and X_4). The linear effects are irradiation time (X_1), pH (X_2), photo catalyst amount (X_3), concentration of o-cresol (X_4) and the second order effects are square of the variable (X_1^2, X_2^2, X_3^2 and X_4^2). In addition, the interactions effects of ($X_1 X_2$, $X_1 X_3$, $X_1 X_4$, $X_2 X_3$, $X_2 X_4$) were observed in the model. The local optimums in terms of the actual variables can be determined by differentiating Eq. 3 for irradiation time (Eq. 4), pH (Eq. 5), amount of photo catalyst (Eq. 6), and o-cresol concentration (Eq. 7).

$$
[\partial Y / \partial X_1]_{X_2, X_3, X_4} = 0 \tag{4}
$$

$$
[\partial Y / \partial X_2]_{X_1, X_3, X_4} = 0 \tag{5}
$$

$$
[\partial Y / \partial X_3]_{X_1, X_2, X_4} = 0 \tag{6}
$$

$$
[\partial Y / \partial X_4]_{X_1, X_2, X_3} = 0 \tag{7}
$$

Response surface 3D plots

Simulation is used when the real system cannot be engaged, because it may be inaccessible, dangerous, unacceptable, and expensive to perform. In photo degradation of o-cresol, the main limitations are expensive chemicals and instruments, time of experiments and numerous errors in the multiple experiments. Based on the validated model, the 3D plots presented the numerous predicted (simulated) responses with the four variables and one response (Table 2) of the photo degradation (Figure 2). As a preliminary study, the effect of pH, photo catalyst amount and o-cresol concentration on photo degradation was investigated during the irradiation time while two variables in each case held constant (e.g. Figure 2a). As observed, the photo degradation illustrated a peak at particular amount of pH, photo catalyst and o-cresol during the irradiation time. Therefore, a

large numbers of experiments were simulated by end of 240 minutes of irradiation time while it was only one variable kept constant in each case (Figure b, c, d). Figure 2(b) shows the interaction between photo catalyst amount (1.0 – 2.0 g/L) and o-cresol concentration (25 – 45 mg/L) simultaneously with constant pH 8.2. As shown, the photo degradation % was decreased with increasing the o-cresol concentration for all the range of photo catalyst concentration. The reduction may be due to this reasons that o-cresol can be degraded directly by the generated holes (h^+) over photo catalyst surface. In a high o-cresol concentrate solution, o-cresol molecules can compete with H_2O to attract the h^+ which is a limited agent [31]. On the other hand, the photo degradation % was increased with increasing photo catalyst amount up 1.6 g/L for all the concentration of o-cresol. This can be attributed to the fact that the increase in the effective surface area of the photo catalyst, which in turn leads to enhanced production of $^\bullet OH$ radicals. However, when the amount of photo catalyst was increased in excess of the optimum (1.6 g/L), the photo degradation % decreased. The decreased efficiency observed above the optimum photo catalyst loading may be attributed to the interception of light by the excess of photo catalyst particles in solution as known screen effect [8].

Figure 2(c) shows the interaction between pH (6-10) and photo catalyst amount (1.0 – 2.0 g/L) with constant o-cresol concentration 35 mg/L. As it is shown, the photo degradation % increased slightly with increasing pH from pH 7 to 9 in the range of photo catalyst amount. The increase in the photo degradation % may be due to increasing adsorption of o-cresol on the photo catalyst surface [32]. Moreover, It has been reported that, in slightly alkaline solution (pH=8), $^\bullet OH$ radicals are more easily generated by oxidizing the available OH^- on the photo catalyst surface [33]. Thus, generally, the photo degradation % is expected for becoming enhanced with increasing pH owing to the availability of $^\bullet OH$ radicals for the reaction. However, a decrease in photo degradation % was observed above the optimum. This can be attributed to the reduction for o-cresol adsorbed on the photo catalyst surface in the region of pH [31]. It should be noted as well that the radicals are rapidly scavenged in the presence of excess concentrations of OH^- and therefore would not have the opportunity to react with the substrates [33].

Figure 2(d) shows the interaction between pH (6-10) and o-cresol concentration (25 – 45 mg/L) with constant photo catalyst amount 1.5 g/L. As observed, the acceptable photo degradation % was obtained at 35 mg/L of o-cresol concentration. Any increase in the concentration resulted in diminishing photo degradation %. The decrease in photo degradation % may be due to the reason that the o-cresol concentration increased while the active sites of photo catalyst remained constant [34]. As a result, the optimum
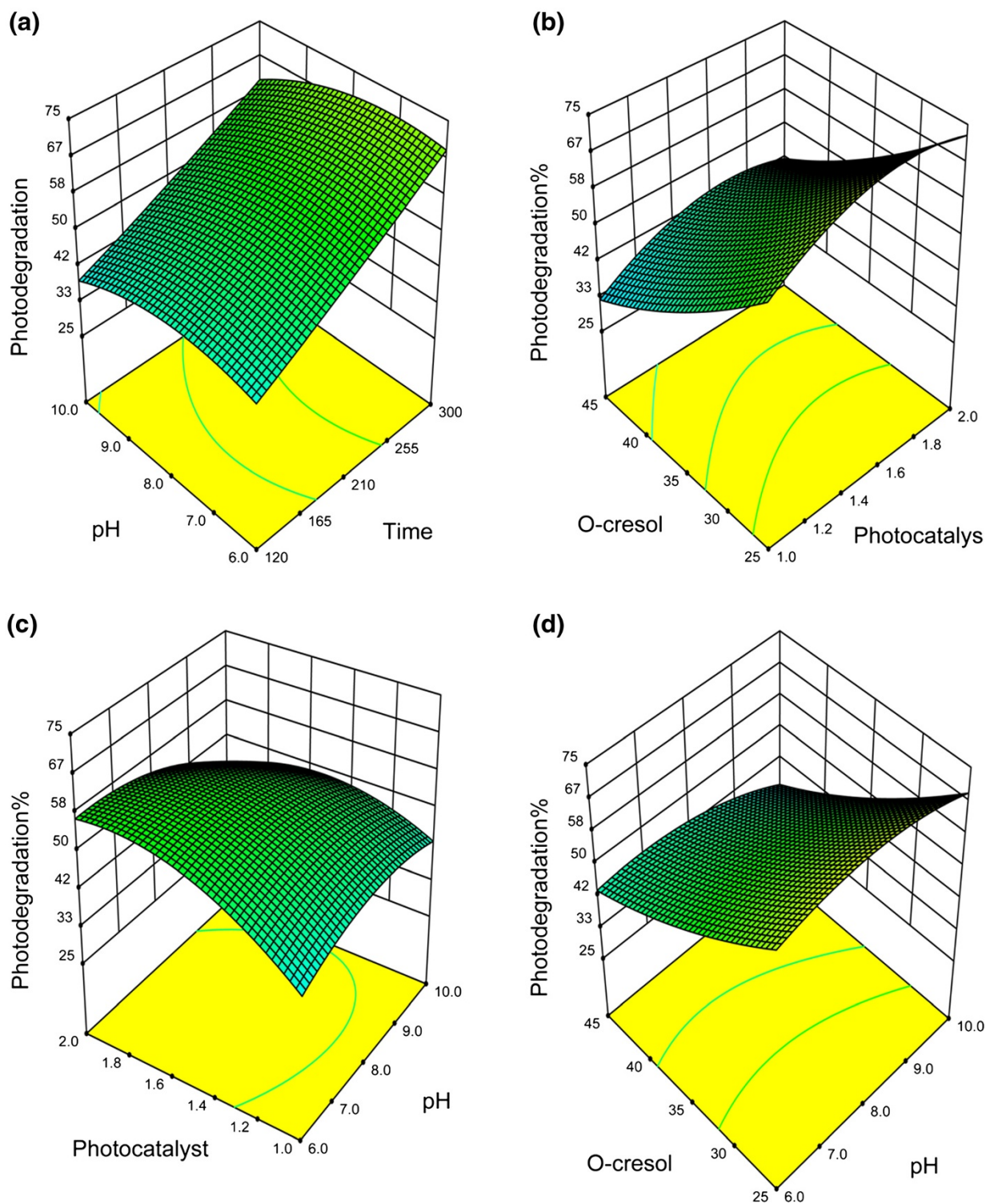
Figure 2 Response surface 3D plots indicating the effect of interaction between process variables on photo degradation of *o*-cresol (a) Interaction between irradiation time and pH while holding the photo catalyst amount at 1.5 g/L and *o*-cresol concentration at 35 mg/L (b) Interaction between photo catalyst amount and *o*-cresol concentration while holding pH at 8.2 at end of 240 minutes of reaction time (c) Interaction between photo catalyst amount and pH while holding *o*-cresol concentration at 35 mg/L at end of 240 minutes of reaction time (d) Interaction between *o*-cresol concentration and pH while holding photo catalyst at1.5 g/L at end of 240 minutes of reaction time.

photo degradation was 60% (average) in the condition (pH 8.2, photo catalyst amount 1.6 g/L and o-cresol concentration 35 mg/L at 240 minutes of irradiation time). The optimum was validated by performing the similar experimental methodology [20]. As observed, the experimental values were reasonably close to the simulated values that indicated the high validity and adequacy of the model.

Conclusion

The optimization and modeling of o-cresol photo degradation was studied by RSM. The experiments were designed with four effective factors including irradiation time, pH, photo catalyst's amount and o-cresol concentration by the CCD. The CCD considered 30 runs to obtain actual responses. To suggest a model for the photo degradation process, the responses were fitted with a quadratic model. The ANOVA confirmed the high validity of the model by using excellent evidences such as high F-value (143.12), very low P-value (<0.0001), non-significant lack of fit, the R^2 (0.99), and the adequate precision (47.067). The results of simulated 3D plots for the photo degradation (60%) were agreed with experimental results (63%). This study indicates the success of RSM to simulate the optimum condition of o-cresol photo degradation % under visible-light by Mn-doped ZnO nanoparticles as photo catalyst.

Authors' contributions
Yadollah Abdollahi (AB, JY, MT); Azmi Zakaria(FG); Abdul Halim Abdullah (FG); Hamid Reza Fard Masoumi (MT); Hossein Jahangirian (JY); Kamyar Shameli (JY); Majid Rezayi (JY); Santo Banerjee (MT); Tahereh Abdollahi (JY, MT). AB carried out the catalyst design and ligand screening studies. JY carried out the synthesis, purification and characterization of the compounds. MT carried out the computational experiments. FG conceived of the study, and participated in its design and coordination and helped to draft the manuscript. All authors read and approved the final manuscript.

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