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PHOTOCATALYST: A PROMISING SMART MATERIAL IN DEGRADATION OF DYE USING RESPONSE SURFACE METHODOLOGY (RSM)

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ABSTRACT

One of the environmental issues is water Pollution causing serious health related problem not only to human but also seriously affect aquatic life. Dyes are among the pollutants that pollute our water bodies. In the olden days so many methods were applied for the purification of water but recently photocatalysis shown a promising technique where the pollutants (dyes) were degraded to give clean water and carbon dioxide to be liberated as the end product. The specific surface area of the photocatalyst 243.80 m^2g^{-1} and the PZC was found to be 8.10. Only 0.9% of the dye (MG) decolorized in the presence of light (photolysis) while 25% of the MG was adsorbs in the dark with 30 minutes of contact. The ANOVA showed an F-value of 1114.81 which suggests that the model is significant. All model terms i.e. MG initial concentration, photocatalyst dose, irradiation period and pH are all significant with Prob>" values <0.05. The predicted R-squared that has a value 0.995 was in perfect agreement reasonably with Adj R-squared that reached up to 99.8%. Adequate precision more than 4.00 by this model indicates desirable and adequate signal. The influence of MG initial concentration in removing the MG color was higher when compared to other parameters involved and this was indicated by the F-values.

Keywords: Malachite green (MG), Point of Zero charge (PZC), Dye, $ZnFe_2O_4$ / TiO_2 composite, CCD.

INTRODUCTION

Photocatalytic decolorization of dyes using TiO_2 has been studied in the past by various researchers (Behnajady *et al.,* 2007). Various types of dyes were used by textile industries. Malachite green dye (MG) with molecular formula $C_{32}H_{16}N_8S_2O_6CuNa_2$ is among the most persistent compared to acidic dye, disperse dye and reactive dye especially when it was used during photocatalysis with a TiO_2 (Gallo *et al.,* 2008). The values of the optimize parameters vary depending on the water pollutant targeted, photocatalyst nature and of reaction set-up. Advance Oxidation Process means that very reactive species were generated especially hydroxyl radicals and this radical usually oxidizes most of pollutants very fast and it was non-selective. (Uygur, 1997) removed azo dyes using Advance Oxidation Process. (Aplin and Waite, 2000) used this same process in photo- Fenton reaction of hydrogen peroxide, Fe^{2+} /H_2O_2 while (Moraes *et al.,* 2000) applied UV in the photocatalysis of hydrogen peroxide, H_2O_2/UV and (Masten and Davies, 1994) also used TiO_2/UV in decomposing hydrogen peroxide.

In our study, Design expert software v6 compose of Response Surface Methodology was used in carrying out optimization was also used to generate second order model in which the response variables does not require a three-level factorial experiment. Photocatalysis application in the treatment of textile wastewater is long overdue, until today, (Han *et al.,* 2008) reported that there is no photocatalytic system world over that is available commercially with high decolorization efficiency, ease in photocatalyst activity and that can be activate easily in visible light.

Photocatalytic design of experiments by R SM

This approach as implemented in design expert 6.0.6 software (Rezaee *et al.,* 2012), was used to design the photocatalytic experiments. The process variables studied were: initial MG dye concentration (A), photocatalyst dosage (B), irradiation time (C) and the initial pH (D). This method is used in optimizing variables and the variables were considered as independent parameters while decolorization as output response variable. The designed matrix setup was determine using Central Composite Design, consisting 30 experiments as obtained by the equation: $N = 2^n + 2n + C_0$, where total number of experiments required stands for N, number of variables is n, axial runs stands for 2n and center point runs is C_0. These experiments were all obtained from the above variables (n = 4) and at two levels: (−1) stands for low and (+1) for high. Simplifying the above equation the model consist of 2^n (2^4 =16 factor points, + (2n) which gives 2 x 4 = 8: axial points) + 6, points center, i.e. (six replications). The polynomial response equation generated was used to get interaction between dependent and independent parameters. The polynomial model was expressed as:

$$Y = b_0 + \sum_{i=1}^{n} bixi + (\sum_{i=1}^{n} biixi)^2 + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} bijxixj \quad \text{..... i}$$

where, *y* (%) represents predicted response and is the dependent variable, (decolorization rate of MG efficiency), linear coefficients stands for bi, interaction coefficients, (bij) and quadratic coefficients (bii). Moreover, the coded values /

independent parameters studied (initial pH, photocatalyst dosage and initial MG concentration) were xi and xj and affect the response y. The parameters were related by coefficients. The specific weight of the parameters in the model was indicated by coefficients which also show the performance of the variables in the photodecolorization.

METHODOLOGY

photodecolorization experiments were performed in a laboratory scale. Decolorizing malachite green dye in aqueous solution was carried out by the as-synthesized $ZnFe_2O_4$/ TiO_2 composite. The set-up for the experiment consists of a glass beaker (250 cm^3), magnetic stirrer, and a 500 W halogen lamp. Different amounts of the photocatalyst (0.05-1 g/100 cm^3) were added into 100 cm^3 of MG solution of different concentration (5-20 mg/L). 0.01 M HNO_3 was used for pH adjustment to the desired pH (3, 6 and 9). Each of the suspension was magnetically stirred in dark for 30 minutes establishing adsorption/desorption equilibrium before irradiation with 500 W halogen lamps. The suspension was maintained at room temperature and the distance of the lamp from the solution was 20 cm. 10 cm^3 of the suspension was withdrawn at regular time interval of 30 minutes over irradiation period of 90 minutes. The suspension was centrifuged at 6000 rpm for 10 minutes and filtered to remove the photocatalyst particles before measuring absorbance. The absorbance of the dye left was measured at a 624 nm (MG, λ_{max}) using a UV-vis spectrophotometer (T60 PG instrument). All photodecolorization reactions were performed in triplicate to ensure the reproducibility of the experimental results. The Percentage decolorization rate of MG dye was calculated using the formula.

$$\% \text{ Decolorization} = C_0 - C / C_0 \times 100 \quad \text{……} \quad \text{ii}$$

Where C_0 is absorbance before illumination and C is absorbance after visible light illumination, respectively.

For the (PZC), small amount of the sample 0.5 g of $ZnFe_2O_4$/ TiO_2 was added to 40 cm^3 of 0.1 M $NaNO_3$ in seven 50cm^3 beakers. The pH was adjusted to 3, 4, 5, 6, 7, 8 and 9 (±0.1 pH units). 0.1 M HNO_3 acid and 0.1 M NaOH were used. Samples were shaken on a magnetic stirrer over night to reach equilibrium. After this time pH of each sample was measured as final pH. Then the variation between final pH (ΔpH) and initial pH (pH_0) values was plotted. $pHzp^c$ was taken were at zero pH. (Mahmood and Saddique, 2011).

Sear's method was used to estimate Specific surface area (SSA) of the $ZnFe_2O_4$/ TiO_2 (Sear's 1959). In this method 0.5 g of the $ZnFe_2O_4$/ TiO_2 sample was agitated in 100 cm^3 dilute HCl of a pH 3. 20 g NaCl was added with stirring and the volume was made up to 150 cm^3 with deionized water. The solution was titrated with 0.1M NaOH and the volume, (V), needed to raise the pH from 3- 9 was then recorded. The surface area according to this method was calculated from below equation:

$$S\ (m^2g^{-1}) = 32 \times V - 25 \quad \text{……iii}$$

Where V is the volume of the base required to raise the pH of the sample from 3- 9. This volume was measured in replicate and the average value was taken for the surface area calculation.

In the first titration the volume of the base that raised the pH from 3-9 was 8.40 cm^3. For the second titration the volume was 8.38 cm^3 and the third titration the volume of the base was 8.42 cm^3. The average Titre value of the base used was found to be 8.40cm^3.

Therefore the $S\ (m^2g^{-1}) = 32 \times V - 25 = 32 \times 8.40 - 25 = 243.80\ m^2g^{-1}$

Salt addition method: pH of zero Point of charge ($_pHzp^c$)

0.5 g of $ZnFe_2O_4$/ TiO_2 was added to 40 cm^3 of 0.1 M $NaNO_3$ in seven 50 cm^3 beakers to determine pH of zero Point of charge (PZC). The pH was adjusted to 3, 4, 5, 6, 7, 8 and 9 (±0.1 pH units). 0.1 M HNO_3 acid and 0.1 M NaOH were used. Samples were shaken on a magnetic stirrer over night to reach equilibrium. After this time pH of each sample was measured as final pH. Then variation between the final pH (ΔpH) and the initial pH (pH_0) values was plotted. $pHzp^c$ was taken were at zero pH. (Mahmood and Saddique, 2011). The photocatalyst produced was characterized for its specific surface area using sear's Method, Point of zero charge (PZC).

RESULT AND DISCUSSION

Table 1: Characteristics of $ZnFe_2O_4$/ TiO_2 photocatalyst

Parameter (Unit)	Value
Specific surface area (m^2g^{-1})	243.80 m^2g^{-1}
Point of zero charge	8.1

$ZnFe_2O_4$/ TiO_2 have a specific surface area 243.80 m^2g^{-1} and the PZC of the photocatalyst is 8.10. Excellent adsorption of MG molecules onto the surface of $ZnFe_2O_4$/ TiO_2 is expected at basic pH of dye solution since MG is cationic dye.

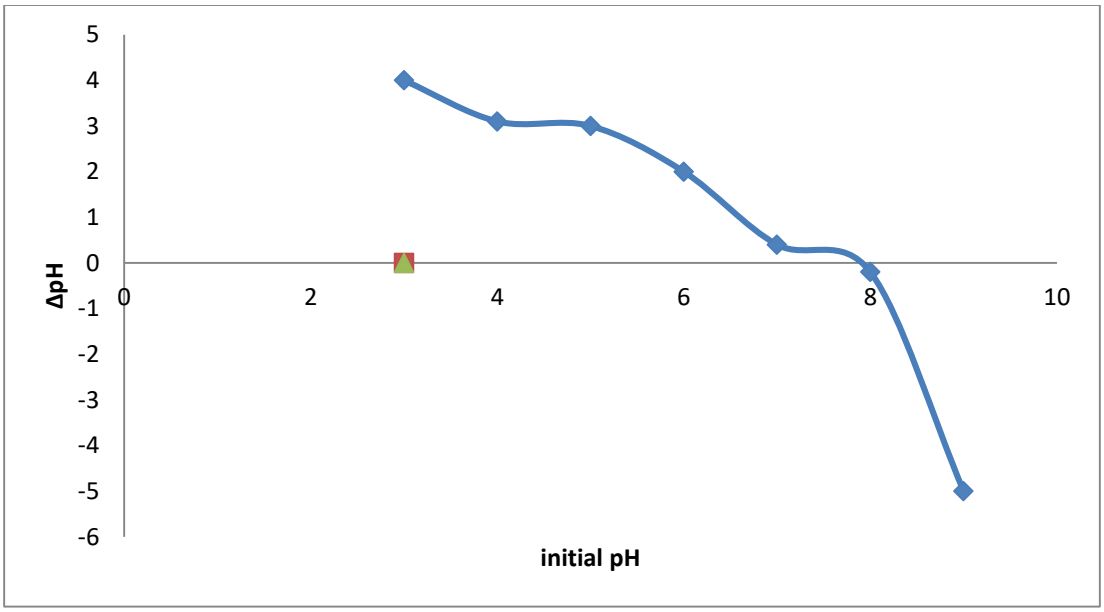

Figure 1: Determination of pHZpC for the synthesized $ZnFe_2O_4$ / TiO_2 composite

Kusvuran et al; 2004 reported that rate of photocatalytic decolorization of azo dyes usually at pH 6 was faster and higher than at pH 3. Assumption can be made that MG molecule is positively charge; therefore, an electrostatic attraction is established. The pHZpC for the synthesized $ZnFe_2O_4$/ TiO_2 was at pH value of 8.1, Figure 1. Additionally, strong adsorption can be developed and this can leads to a major decrease of the active centers on surface of the photocatalyst. This also means the absorption of the light quanta by the photocatalyst decreased. Furthermore, the amount decolorization of MG increment may be explained by the fact that at higher pH the surface of photocatalyst is deprotonated and turn to negatively charge; hence attraction between the positively metal cations established (Lohani e*t al.,* 2008). Therefore, $ZnFe_2O_4$/ TiO_2 surface is negatively charged in basic media (pH > 8), and then positively charged under acidic conditions (pH < 8).

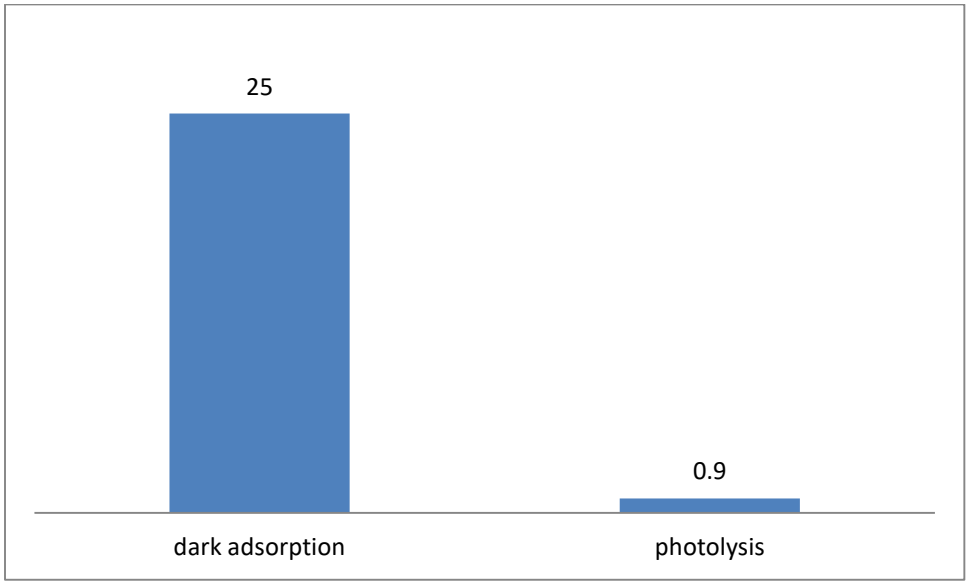

Figure 2: Dark Adsorption. *[MGo]* = 5 mg/L, pH = 5.42, $ZnFe_2O_4$/ TiO_2 dosage = 0.53 mg/L, Photolysis *[MGo]* = 5mg/L, pH = 5.42

Very small changes were observed for the duration of 30 minutes, and (< 1%) of the MG solution decolorized under visible light alone. This implied that the MG in the solution was very stable to visible light, as it was reported by Tesfaye and Aynalem, (2014). From the results obtained it is also possible to understand that the dye can be adsorbed by the photocatalyst and the adsorption efficiency can also be reached up to 25% (figure 2). But this is not decolorization because there was no irradiation. Design Expert software 6 has excellent function in color removal based on results obtained experimentally and is given below:

$Y\ (\%100) = -37.23 + 0.18A + 61.28B + 1.58C + 20.32D - 0.05A^2 - 42.11B^2 - 0.01C^2 - 1.78D^2 + 0.05AB - 0.02AD - 0.02BD$

Where initial MG concentration (A), photocatalyst dosage (B), and irradiation time (C), initial pH (D).

From the derived mathematical model, the ANOVA (see Table 2) showed an F-value of 1114.81 which suggests that the model is significant. All model terms i.e. MG dye initial concentration, photocatalyst dose, irradiation time and pH are all significant with Prob>" values <0.05. The predicted R-squared 0.995 agrees with the Adj R-squared 0.998. Adequate precision greater than 4.00 by the model shows desirability and indicates adequate signal. F-values implied that MG dye initial concentration has the highest influence in color removal among the other parameters involved.

Table 2. ANOVA using Central Composite Design

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	12632.77248	14	902.3408911	1114.809312	<0.0001	No significant
A	1367.645	1	1367.645	1689.675594	<0.0001	
B	1270.08	1	1270.08	1569.13759	<0.0001	
C	1131.293889	1	1131.293889	1397.672403	<0.0001	
D	259.1605556	1	259.1605556	320.183429	< 0.0001	
A^2	22.57421252	1	22.57421252	27.88961752	< 0.0001	
B^2	233.9159171	1	233.9159171	288.9945974	< 0.0001	
C^2	256.5969398	1	256.5969398	317.0161751	< 0.0001	
D^2	667.5705762	1	667.5705762	824.7591371	< 0.0001	
AB	0.600625	1	0.600625	0.742050316	0.4026	
AC	0.180625	1	0.180625	0.22315561	0.6434	
AD	1.890625	1	1.890625	2.33579834	0.1472	
BC	0.005625	1	0.005625	0.006949483	0.9347	
BD	0.015625	1	0.015625	0.019304119	0.8913	
CD	0.015625	1	0.015625	0.019304119	0.8913	
Residual	12.14119152	15	0.809412768			
Lack of Fit	8.12619152	10	0.812619152	1.011979019	0.5290	No significant
Adj R-squared	0.998					
Pred R-squared	0.995					
R- squared	0.999					
Adequate precision	115.83					

The effect of operating parameters showed that the color removal increases when photocatalyst dose, irradiation time and initial pH are increased to a certain level then it start decreasing. For instance, the color removal decreases as MG dye initial concentration, increases. More active sites on surface of the photocatalyst were formed by increasing photocatalyst dose and this cause number of •OH radicals to multiply and take part in the decolorization of dyes. On the other hand, MG dye initial concentration increases, make dyes adsorption equilibrium on the photocatalyst active sites also increases, hence adsorption competition of •OH radicals on the same site decreases. This indicate rate of formation of •OH radical responsible for dye discoloration (Akyol *et al.,* 2004). Path length of quanta passing through the solution decreases, as MG dye initial concentration is increased, this result in deceleration of quanta adsorption by photocatalyst molecules, and hence photocatalytic reaction rates decreases (Habibi and Nasr-Esfahani, 2007). The result also suggests the importance of contact time between the catalyst and target pollutant. The optimum conditions and full factorial central composite design showing the actual and predicted values are presented in Table 3.

Table 3: Optimization results of full factorial central composite design.

	Process variables				**Response**	
					% Decolorization of MG	
Run order	Initial dye conc. **(A)**	Photocatalyst dose **(B)**	Irradiation time **(C)**	Initial pH **(D)**	Actual values	Predicted values
1	20	0.05	90	9	47.1	47.65
2	12.5	0.53	60	6	30.3	30.31
3	5	1	30	3	64.6	64.09
4	5	0.05	30	3	47.2	47.52
5	12.5	0.53	60	9	64.2	63.2
6	12.5	0.53	30	6	45.7	46.27
7	12.5	0.05	60	6	78.7	79.71
8	12.5	0.53	60	6	64.7	63.56
9	20	1	90	3	40.1	40.75
10	5	0.05	90	3	22.5	22.03
11	12.5	1	60	6	57.1	57.06
12	12.5	0.53	60	6	38.1	39.12
13	20	0.05	90	3	56.2	56.42
14	5	1	90	9	38.1	38.12
15	20	1	30	3	73.3	72.81
16	20	0.05	30	3	55.3	55.29
17	5	0.53	60	6	95.25	96.10
18	12.5	0.53	60	6	78.1	78.28
19	12.5	0.53	90	6	72.6	72.07
20	20	0.05	30	9	88.5	88.85
21	12.5	0.53	60	6	73.1	72.07
22	20	1	90	9	87.1	87.93
23	5	1	90	3	77.5	77.69
24	20	0.53	60	6	70.5	70.1
25	5	1	30	9	89.2	89.95
26	12.5	0.53	60	3	90.2	89.95
27	5	0.05	30	9	89.5	89.95
28	5	0.05	90	9	91.2	89.95
29	12.5	0.53	60	6	90.3	89.95
30	20	1	30	9	88.7	89.95

Therefore, RSM result predicted 96.1%. After laboratory work was conducted in line with optimized parameters, 95.3% decolorization was obtained as the actual value. Agreement between the predicted results and laboratory results indicated that CCD design is viable for optimization of MG decolorization.

Optimization and Response surface (contour) plots

RSM is a mathematical approach to examine the overall shape of the curve, to locate the stationary point of the response surface, and to decide whether it describes a maximum, minimum, or saddle point. Three-dimensional (3D) and contour (2D) plots for the predicted responses were also formed, based on the model polynomial functions to assess the change of the response surface as shown in Figures 3a – 6b. The relationship between the dependent and independent variables can be also further understood by these plots. Since the model has more than two factors, one factor was held constant for each diagram.

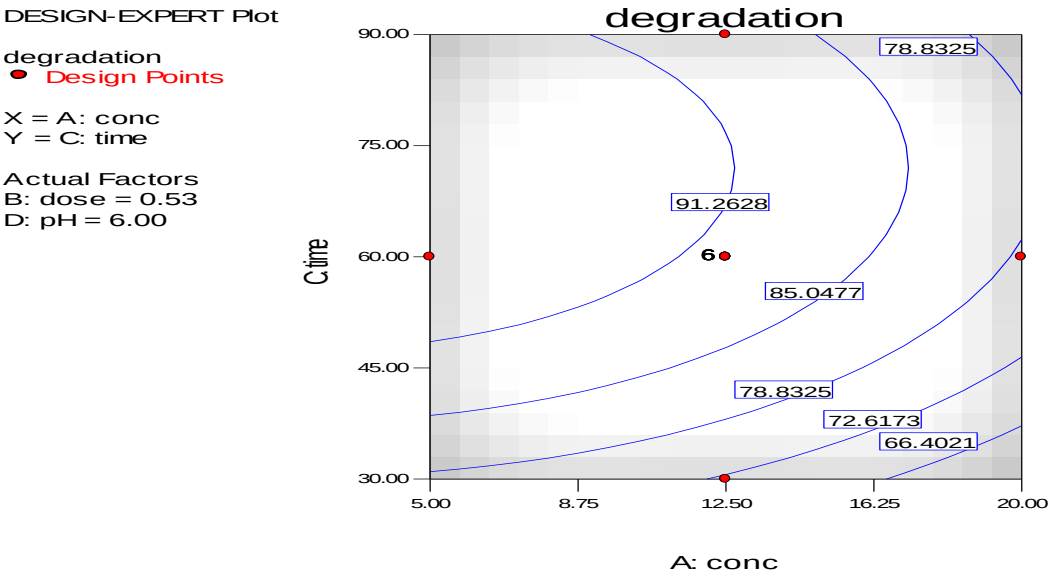

Figure 3a. Contour plot of Simultaneous effects of the initial MG concentration and irradiation time on the decolorization of MG using $ZnFe_2O_4$ /TiO_2

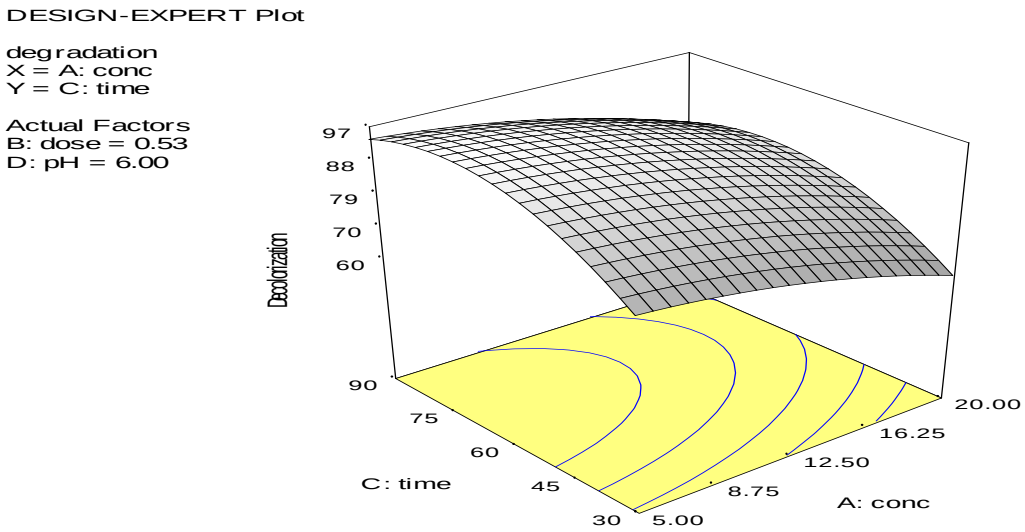

Figure 3b: 3D Simultaneous effects of the initial MG concentration and irradiation time on the decolorization of MG using $ZnFe_2O_4$ /TiO_2

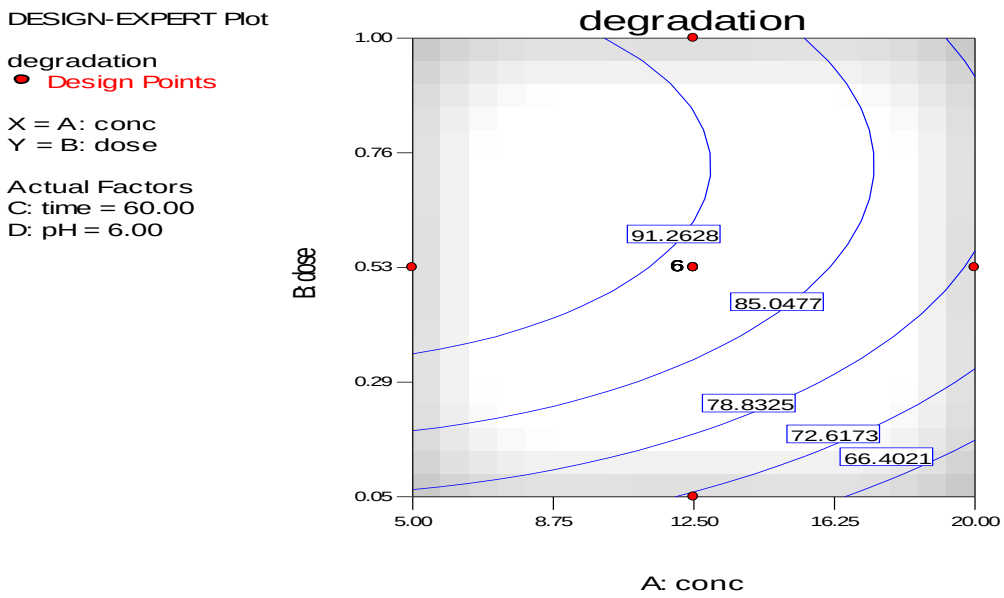

Figure 4a: Contour plot of Simultaneous effects of the initial MG concentration and photocatalyst dosage on the decolorization of MG using $ZnFe_2O_4$ /TiO_2

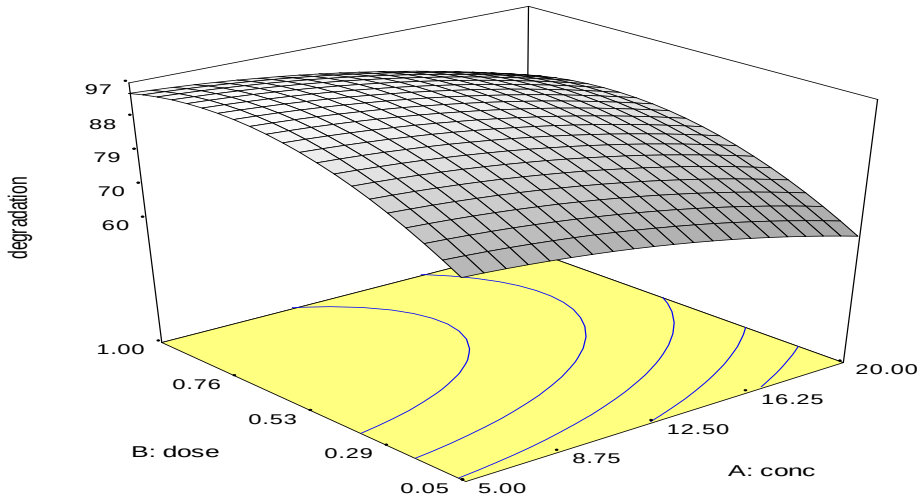

Figure 4b: 3D Simultaneous effects of the initial MG concentration and photocatalyst dose on the decolorization of MG using $ZnFe_2O_4$ /TiO_2.

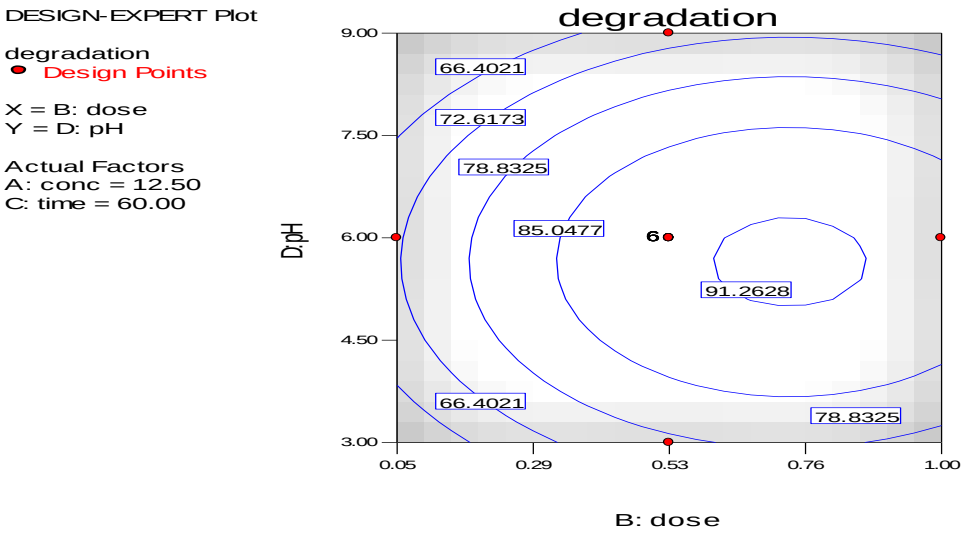

Figure 5a: Contour plot of Simultaneous effects of the initial MG pH and photocatalyst dosage on the decolorization of MG using $ZnFe_2O_4$ /TiO_2

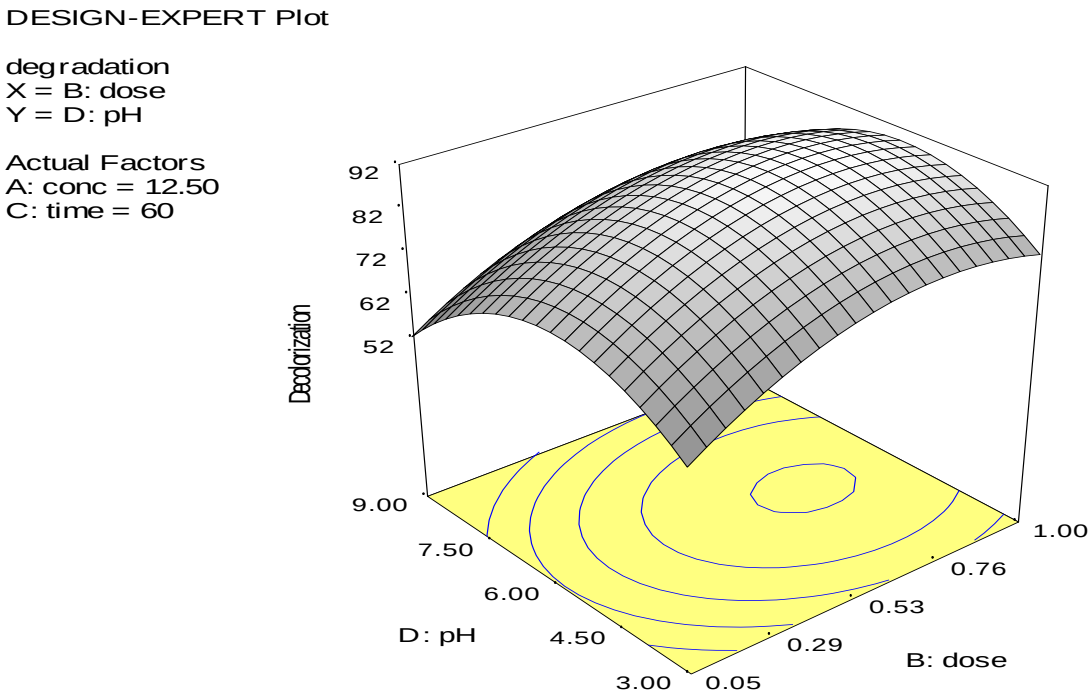

Figure 5b: 3D Simultaneous effects of the photocatalyst dose and pH on the decolorization of MG using $ZnFe_2O_4$ /TiO_2

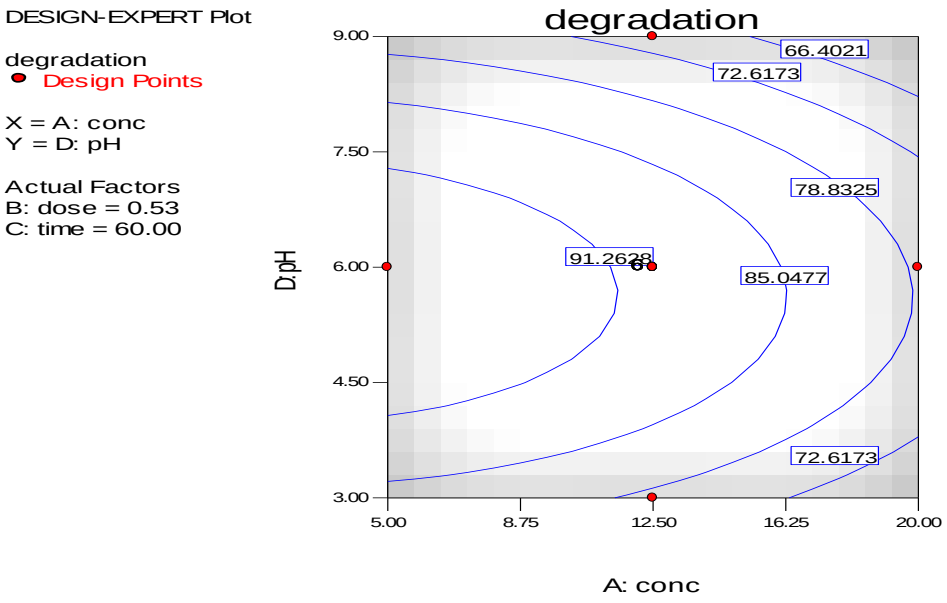

Figure 6a: Contour plot of Simultaneous effects of the initial MG concentration and initial MG pH on the decolorization of MG using $ZnFe_2O_4$ /TiO_2

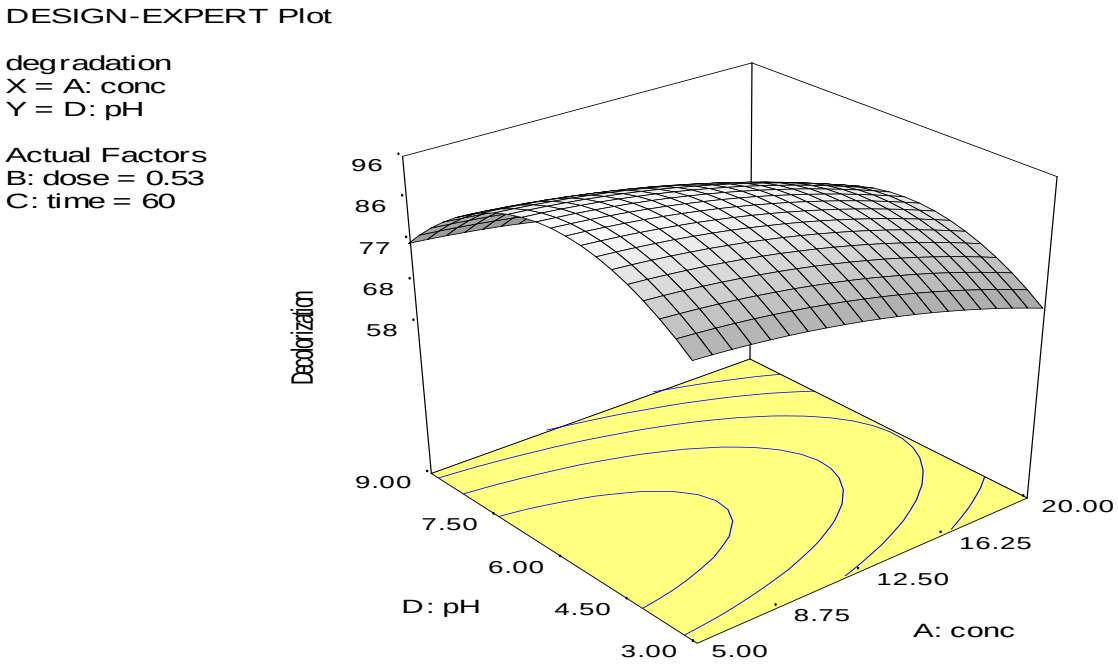

Figure 6b: 3D Simultaneous effects of the initial MG concentration and initial MG pH on the decolorization of MG using $ZnFe_2O_4$ /TiO_2

CONCLUSIONS

It was concluded from the analysis that the synthesized $ZnFe_2O_4/TiO_2$ composite has a specific surface area 243.80 m^2g^{-1} and P_{HpZC} 8.1.The material has rough surfaces, and the particles are of non-uniform shape and size as the SEM image implies. In laboratory investigation, the model derived for this system is significant with an *F-value* of 1114.81. ANOVA implied a high coefficient of determination (R^2=0.999), indicating a satisfactory fit between the second order regression model and the experimental results. The predicted R-squared of

0.995 is a reasonable agreement with the adjusted R-squared of 0.998, adequate precision greater than 4.00 shows that it is desirable and indicates an adequate signal.

Only 0.9% of it decolorized within irradiation period of one hour figure 2. The synthesized photocatalyst adsorbs 25% of the MG in the dark with one hour of contact. The optimal conditions, which yielded a maximized MG decolorization of 95.3%, were carried out in replicate, and identified using RSM with Design-Expert software v 6, these determined as follows: photocatalyst dosage of 0.53g/L, pH of 5.48, irradiation time of 90 minutes, and initial MG concentration of 5.12 mg/L.

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