Research Article

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Modeling the removal of methylene blue dye using a graphene oxide/TiO₂/SiO₂ nanocomposite under sunlight irradiation by intelligent system

<https://doi.org/10.1515/chem-2021-0025>

received September 30, 2020; accepted January 26, 2021

Abstract: In this study, a model to improve the degradability of methylene blue (MB) dye using graphene oxide/TiO₂/SiO₂ nanocomposite under sunlight irradiation is investigated. The effect of operative parameters comprising catalyst concentration, initial dye concentration, and pH on the photocatalytic batch during removal of MB is studied. Fractional factorial design (FFD) and response surface methodology (RSM) are used to design the experiment layout. Graphene oxide (GO)/TiO₂/SiO₂ nanoparticles are synthesized through sonication and sol–gel methodologies. In the experiments, three levels of catalyst varied in the percentage of TiO₂ pointed as (I) TiO₂:GO (100%), (II) TiO₂:GO:SiO₂ (50%), and (III) TiO₂:GO:SiO₂ (25%) are used. The irradiation interval was 7 h at solar radiation energy 6.35–5.00 kW h/m²/day. In the experiments, three levels of catalyst varied in the percentage of TiO₂ pointed as (I) TiO₂:GO (100%), (II) TiO₂:GO:SiO₂ (50%), and (III) TiO₂:GO:SiO₂ (25%) are used. The synthesized catalysts are characterized by X-ray diffraction, Fourier-transform infrared spectroscopy, scanning electron microscope, and X-ray photoelectron spectroscopy. ANOVA under 2³ FFD is conducted to evaluate the effect of independent factors depending on the value of F as pH of solution, weight of catalyst, and concentration of MB. The adsorption kinetics, experimental design with FFD, and RSM are investigated in this study. The Surface Adsorption kinetics were statistically analyzed, the model that best described the results of each experiment was determined out of the two evaluated kinetics (pseudo-first order, pseudo-second order), for the three photocatalyst composites I, II, and III with the parameters; weight of the catalyst, pH, and initial MB concentration, also percentage

degradation is evaluated. RSM results are consistent with the kinetic model; first, the pH is considered as the most significant parameter affecting the removal of the organic pollutant, and second, catalyst II gives the highest percentage removal efficiency of MB. FFD results are consistent with both models where the effect of the independent factor depending on the value of F was pH of solution > weight of catalyst > initial concentration of MB. The percentage removal was in the range from 30 to 99%.

Keywords: response surface methodology, fractional factorial design, Langmuir, photocatalysis, sunlight

1 Introduction

Treatment of wastewater becomes essential and mandatory because they contain many contaminated compounds (organic and inorganic) that cause risk to the living beings and environment if released without treatment. Many of these compounds are stable and pass through conventional wastewater treatment systems, without major changes in their chemistry [1]. Advanced oxidation processes (AOPs) are known as being operative for the degradation of many biotic recalcitrant compounds, these processes are technologies that generally use the hydroxyl radicals for oxidizing organic molecules (breaking them down), and can be enhanced by catalysts and/or light [2].

The heterogeneous photocatalytic degradation involves three main steps: adsorption on the surface, surface reaction, and finally desorption of reacted product from the pores. The adsorption mechanism and the reactions put in place have been widely studied, according to the objective of each work, different models, and characterization techniques used. Nevertheless, the common point is the optimization of the process. Optimization of the adsorption process was usually performed in a routine and conventional way [3].

TiO₂ is considered as a unique photocatalyst comparing to the other metal oxides were used, but to remove its limitations some advanced approaches were used,

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such as adding metal oxides (transition or rare metals) also nonmetal was added to its bulk. Photocatalytic degradation mechanism is highly affected and enhanced by the modifications made on it [4–6].

There are many kinds of nanomaterials, which carried a large potential to treat wastewater (containing organic and inorganic pollutants and metal toxin substances) very effectively because of their properties like a greater surface area. The nano photocatalyst-based approaches to remove pollutants from wastewater are eco-friendly and efficient, but they require more energy and more investment to purify the wastewater [7].

Yet, the catalyst most used is TiO_2 photocatalysis, and the simplified Langmuir–Hinshelwood kinetic model is used to explain the photocatalytic processes.

Ateia and his colleagues used models of reaction kinetics to define time-dependent relation between the operating conditions of the system and the degradation rate of organic contaminants [4]. The photocatalytic degradation rate depends on the water chemistry factors (e.g., pH, temperature, contaminant concentration, natural organic matter, dissolved oxygen, and inorganic species) and the system factors (e.g., light intensity, light wavelength, catalyst type, and catalyst loading) [8]. Several researchers make efforts to improve models that can describe and estimate the photocatalytic degradation kinetics [1,9,10].

Moreover, photocatalytic experiments provide different results. Therefore, it is challenging to form effective models to optimize photocatalytic activity. Artificial neural networks are used to model photocatalytic efficiency [11], and response surface methodology (RSM) is used for experimental design and to improve (optimize) operational conditions [11,12]. RSM is a statistical method based on the multivariate nonlinear model and allowed the design of mathematical models with a better match with the data obtained by the experimental design. Using an elaborate model with the statistical analysis of factors, it gives the chance to evaluate the interactions between factors and explain the relations very well [3,11,12].

Several adsorption kinetic models are used among them the Langmuir model, which is the most fitting for the experimental results found by Udrea and Ion in removing methylene blue (MB) dye present in wastewater by using adsorbent materials obtained from vegetable waste [13].

This study aimed to apply mathematical modeling on MB dye photodegradation results to find the optimized conditions and the most effective variable. Three modeling systems were investigated in this study, experimental design with FFD (ANOVA under 23), RSM and surface adsorption kinetics. And the factors contain; pH of solution, weight of

catalyst (with three % composites), and the amount of MB dye at time t (q_t).

2 Methods

2.1 Synthesis and characterization

Three types of photocatalysis were under study, which varied in the percentage of TiO_2 pointed as (I) $\text{TiO}_2\text{:GO}$ (100%), (II) $\text{TiO}_2\text{:GO:SiO}_2$ (50%), and (III) $\text{TiO}_2\text{:GO:SiO}_2$ (25%). The synthesis was by sol–gel method under sonication (sonicating with a probe sonicator for 20 min impulse mode with 2s on and 5s off at 35% amplitude). The modification was confirmed by X-ray diffraction, Fourier-transform infrared spectroscopy, scanning electron microscope, and X-ray photoelectron spectroscopy analysis. Details for both the synthesis and full characterization are given in the previous study [14]. The catalysis is chosen as models for the mathematical modeling study.

Weight/weight percentage for the three prepared catalyzes I, II, and III out of the total weight of the catalyst:

Catalyst	GO%	Ti%	Si%
I	1.96	98	0
II	1.29	45.5	50
III	0.966	24.15	74.9

2.2 Experiment procedure

The assessment of MB removal is handled in a specific time. The absorbance is measured on UV-Vis spectrophotometer at several wavelengths according to MB charge. 100 mL of DW is spiked with a mixture of MB (with the desired concentration).

The absorption spectrum of MB generally is characterized by an absorption band at high energy ($\pi\text{--}\pi^*$ of benzene ring) and a band at low energy around 580–741 nm (affecting correspondent to the pH of the solution) and corresponding to the $n\text{--}\pi^*$ transitions (n is the free doublet on the nitrogen atom of the $\text{C}=\text{N}$ bond and free doublet of S atom on $\text{S}=\text{C}$ bond) [15,16].

For establishing adsorption equilibrium, the spiked samples were placed in the dark for around an hour, and then the degradation undergo sunlight irradiation.

The irradiation interval was 7 h at solar radiation energy 6.35–5.00 kW h/m²/day. The measured temperature ranged from 35 to 45°C in summer season. At an interval of 30 min, an aliquot of 10 mL was collected, and then the absorbance of MB was measured on UV-Vis spectrophotometer.

Three variables were studied: first, catalyst loading (weight of catalyst) 0.05, 0.10, 0.15, 0.20, 0.25, and 0.30 g with fixing pH of solution at pH 6, and the initial concentration of MB at 20 ppm. The second variable was the pH of the solution (the pH were; 2, 4, 6, 8, and 10) with fixing the initial concentration of MB at 20 ppm, with catalyst weight 0.15 g. The last variable was the initial concentration of MB 0.50, 1.00, 3.00, 5.00, 10.00 ppm fixing the pH of solution at pH 6 and 0.15 g weight of catalyst.

2.3 Mathematical modeling

Three modeling systems were investigated in this study, experimental design with FFD (ANOVA under 23), RSM and surface adsorption kinetics. And the factors contain; pH of solution, weight of catalyst (with three % composites), and the amount of MB dye at time t (q_t). An experimental design is performed using SPSS (16.0 package) with FFD to assess the effect of the independent factors under study. RSM was performed on the parameters using Minitab [19] package.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussions

3.1 Adsorption kinetics

The heterogeneous photocatalytic degradation involves three main steps: adsorption on the surface, surface reaction, and finally desorption of reacted product from the pores. When studying the mechanism of removing pollutants from water, a set of models explaining the adsorption between the pollutant and the active sites in the catalyst are used. Several adsorption kinetic models are used, among them the Langmuir model, which is the most fitting for the experimental results, two fitting model plotted with experimental data under different conditions

the pseudo-first-order model ($\log(q_e - q_t)$ vs t) and the pseudo-second-order model (t/q_t vs t) [2,4].

3.1.1 Effect of initial solution pH on the adsorption efficiency

The pH of the aqueous solution is an important controlling parameter in the adsorption process as it is related to the ionization state of the surface for the catalyst and the pollutant [2,17]. The pH range was chosen to adopt the whole pH ranges of wastewater (industrial, domestic, and pharmaceutical wastewater). The pH plays a critical character both in the characteristics of dye wastes and in the generation of hydroxyl radicals [18]. The effect of pH on the removal of MB is studied in the range of 2–10. Figure 1 shows the plotting of q_t vs time for pH ranges [2/4/6/8/10] for the three composites % I (100%), II (50%) and III (25%).

For the composite % I (100%) and III (25%), the basic media is favored in the removal of MB (pH 8 and 10, respectively); meanwhile pH of catalyst composite % II (50%) is 6, which is almost neutral. The results are consistent with [17] and others where the quantities of MB adsorbed increase with pH and that the disappearance of MB is favored at basic pH [17].

The influence of pH on the ionization state of the TiO₂ surface becomes positively charged, and MB adsorption is favored in alkaline solution because it has a cationic configuration [17].

The experimental data fitted with a pseudo-second-order (equation 1) adsorption model with regression (R^2) ranged 0.99917–0.9961 (Figures 2 and 3).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}. \quad (1)$$

3.1.2 Effect of weight of catalyst dosage on the adsorption efficiency

Obtaining the optimal quantity of catalyst loading is a major stage in scaling up the photocatalytic process. It affects the financial side of the process and the downstream processing to separate the photocatalyst from the reaction medium. Catalyst dosage effect on the removal of MB varied as 0.05, 0.10, 0.15, 0.20, 0.25, and 0.30 g with fixing pH 6, and the initial concentration of MB at 20 ppm for the three composites (I, II, and III).

The catalyst's loading effect on the decolorization efficiency is shown in Figure 4. The amount of catalyst

Figure 1: pH ranges (2/4/6/8/10) of catalysts I, II, and III plotting of q_t (mg/g) vs time in minutes.

Figure 2: Percentage degradation to pH values.

added to the reaction medium is significant in the process effectiveness.

Figure 5 shows the degradation of efficiency for the catalysts. The maximum % degradation for catalyst I (100%)

was at 0.15 g, catalyst II (50%) at 0.30 g, and catalyst III (25%) at 0.25 g. The obtained increase in the decolorization efficiency is designated by the increase in the number of the catalyst's active sites, which results in the creation of more active radicals (hydroxyl and superoxide) that initiate the degradation reaction. At higher catalyst loading, the TiO_2 particles act as a barrier for the incident UV irradiation and prevent their arrival to some particles. A second possibility is the agglomeration of the catalyst nanoparticles, which is preferred by high surface energy and surface area. Therefore, the operative surface area of the catalyst decreases, and the decolorization efficiency is expected to reduce [19].

The experimental data fitted with pseudo-second-order (Figure 6) adsorption model with regression (R^2) ranged between 0.998 and 0.987.

3.1.3 Effect of initial concentration of MB on the adsorption efficiency

The disparity in the color intensity (dye concentration) influences the intensity of light transitory through the reaction

Figure 3: The applicability of the pseudo-second-order kinetic model to pH parameter for catalysts I, II, and III.

medium to reach the surface of the photocatalyst. Therefore, examining the effect of dye concentration on the photocatalytic process is of great importance [19]. The effect of the initial dye concentration on the decolorization of MB is investigated between a wide range of concentrations (0.50, 1.00, 3.00, 5.00, and 10.00 ppm). Figure 6 illustrates the q_t vs time for the catalyst composites at the concentration range.

The influence of initial MB concentration on degradation efficiency is shown in Figure 7. A significant reduction in the percentage of degradation is observed with an increase in the initial MB concentration. This is because of the coverage of the catalyst's active sites with higher adsorption of MB molecules. This is because of the coverage of the catalyst's active sites (suppress the generation of active $\text{OH}^\bullet$ radicals) at higher concentration of MB (adsorption) [19].

Moreover, here the experimental data fitted with a pseudo-second-order (Figures 8 and 9) adsorption model with regression (R^2) is ranged between 0.999 and 0.998.

3.1.4 Degradation efficiency

The degradation efficiency in equation 2 of MB under the selected parameters is shown in Figure 10. The highest percentage degradation was found for catalyst I at an initial concentration of 1 ppm, but the highest percentage degradation for the parameters were for the catalyst II (50% of TiO_2 : 50% of SiO_2), here the GO works as both a photocatalyst and an adsorption material. The percentage removal ranged from 30 to 99%, where the pH was considered as the most significant parameter affecting the removal of the organic pollutant.

Figure 4: Weight ranges (0.05/0.10/0.15/0.20/0.25/0.30 g) of catalysts I, II, and III q_t (mg/g) vs time in minutes.

Figure 5: Percentage degradation of MB for the catalysts composites I (100%), II (50%), and III (25%) versus catalyst weight.

% Degradation (removal efficiency)

$$= \frac{C_0 - C_t}{C_0} \times 100\% \quad (2)$$

3.2 Experiment design and descriptive analysis

SPSS 16.0 package was used for performing the experimental designs. FFD is used to evaluate the effect of the independent factors; weight, pH, and initial concentration on the response variable (q_t), q_t represents the amount of MB dye onto catalyst at time t , q_t (mg g⁻¹) was calculated by mass balance relationship:

$$q_t = (C_0 - C_t)V/m,$$

where C_0 is the initial MB concentration (mg L⁻¹), C_t is the concentration of MB at any time t , V is the volume of solution (L), and m is the mass catalyst (g).

Figure 6: The applicability of the pseudo-second-order kinetic model to catalyst weight parameter for catalysts I, II, and III.

Table 1 summarizes the results of ANOVA analysis under 2^3 FFD. Looking at the F and P -values at a significance level of 0.05, we see that the P -values are less than 0.05 for all factors under consideration; this indicates that there is significant evidence of the effect of each factor on the response variable (q_t). We can order the effect of the independent factor depending on the value of F as pH of solution > weight of catalyst > initial concentration of MB.

Table 2 shows the lower and upper limits for the weight of the factors of catalyst, pH of the solution, and concentration of MB in our experiment. In Tables 3–5, we computed the 95% confidence intervals for the q_t under different levels of factor values, which are weight, pH, and concentration, respectively.

From Table 3, it is obvious that the shortest interval length for the mean q_t is attained at weight 0.15 g. Therefore, statistically, we may recommend working with this level of weight to achieve better estimates and results for any future experiment in this field.

The same can be noted in Tables 4 and 5, where the shortest interval length is attained at pH = 7 and a concentration of 10 mg/L, respectively.

In our experiment, we used three levels of catalyst varied in the percentage of TiO_2 pointed as (I) $\text{TiO}_2\text{:GO}$ (100%), (II) $\text{TiO}_2\text{:GO:SiO}_2$ (50%), and (III) $\text{TiO}_2\text{:GO:SiO}_2$ (25%). Table 6 summarizes all the descriptive results and confidence intervals for the mean q_t under these catalyst levels.

To distinguish between these three levels of catalyst and depending on the real statistical analysis, we can say that 50% (II) level is recommended; the reason for that is the smallest standard error is obtained at this level which is **0.44061**, and the smallest mean q_t value is at 50% (II) level which equals to **5.7678**. Finally, we can realize that the shortest interval length is at a 50% (II) level. Therefore, it supports our choice of 50% (II) as an optimal catalyst level among others. These results are consistent with the percentage degradation of the MB dye as shown in Figure 1. This result is consistent with the assumption

Figure 7: Initial concentration of MB (0.50/1.00/3.00/5.00/10.00 ppm) of catalysts I, II, and III q_t (mg/g) vs time in minutes.

Figure 8: Degradation percentage of MB at different initial concentrations.

that mixing the photocatalysts with the material helps to increase absorption, and has a significant effect by increasing the efficiency of photo-degradation. In addition,

it affects the physical properties in terms of converting the material from a powder to a crystalline substance that is easy to handle and reuse.

3.3 RSM

RSM is a classic method used to optimize operational parameters so that its idea is to change one parameter while keeping the others constant. This technique saves time and effort to search for a local area of parameter space. In addition, there is a risk in which there may be only a local maximum. On the contrary, in some cases, RSM can define optimal operational conditions more quickly by modeling the empirical relationship between the dependent responses. RSM models contain a variety of mathematical and statistical equations that can connect the operational parameters and optimize the design of experiments. It is an advanced technique for fitting mathematical models to the observed experimental results. These mathematical models may include linear, quadratic, or polynomial equations, etc. The strategy of

Figure 9: The applicability of the pseudo-second-order kinetic model to initial MB concentration for catalysts I, II, and III.

experimental design is used to obtain a suitable set of data that can be successfully used in an RSM [4].

Modeling is used to optimize the selected independent (explanatory) variables on the response variable, and for that reason RSM is performed using Minitab [19] package. RSM provides a background to study the parameters and their interaction effects on output responses, and then finally extracts a mathematical model that is useful in plotting the effect of parameters and their interactions. We divided our work into three parts: the first one at the catalyst I level, the second at catalyst II level, and the third at catalyst III level.

3.3.1 Part I

Table 7 shows the ANOVA results for assessing q_t using RSM design under the catalyst I; it is clear that all factors

have an effect on the response variable q_t and we can order their effects depending on F -value as $B > A > C$. Therefore, the most effect on the response variable is because of the pH level and the lowest effect is because of the initial concentration of MB.

The model F -value of 17.56 implies that the model is significant. The “lack of-fit F -value” of 4.19 implies that the lack of fit is significant with a pure error of 0.3443.

The reliability of a model can be checked by determining the R^2 coefficient. In this study, R^2 is 0.812 for the nonlinear model, implying that 81.2% of response variability is obtained by a nonlinear regression model.

From Table 7, we conclude that the linear model is a better fit than the quadratic model, this appears from the F -values of A^2 , B^2 , and C^2 with small values (Not significant). The interaction between factors can't be estimated using RSM, in this case, we used a nonlinear regression model, and the regression equation is given by equation.

Figure 10: A comparison of the degradation efficiency for the three parameters.

Table 1: ANOVA table for 2^3 FFD

Source	Mean square	F-value	P-value	
Model	4.044	11.746	<0.0001	Significant
Weight	2.966	8.615	<0.0001	Significant
pH	5.794	16.827	<0.0001	Significant
Concentration	1.863	5.411	0.001	Significant

Table 2: Lower and upper limits of parameters and their 95% confidence intervals in RSM design

Parameter	Lower	Upper
Weight (g)	0.05	0.3
pH	2	10
Concentration (mg/L)	0.5	10

The interaction between factors cannot be estimated using RSM; in this case, we used a nonlinear regression model, and the regression equation is given by equation (3).

Table 3: 95% confidence intervals for q_t with respect to weight factor

Weight	95% confidence interval for the mean of q_t	
	Lower bound	Upper bound
0.05	10.4146	12.5939
0.1	10.4077	12.6463
0.15	5.5870	6.9557
0.20	8.3495	10.8421
0.25	7.8545	10.8343
0.30	7.0887	10.4056

The regression model equation reduces to

$$q_{t1} = -3.302 + 61.563X_1 + 1.435X_2 - 0.97X_3 - 14.196X_1X_2 + 3.286X_1X_3 + 0.111X_2X_3 - 10.001X_1^2 - 0.01X_2^2 - 0.013X_3^2, \quad (3)$$

where X_1 , X_2 , and X_3 represent the weight, pH, and initial concentration, respectively.

From equation (3), the model under 100% indicates a strong effect of weight, followed by pH level with a weak effect of concentration. It also appears that the interaction effect between some factors are strong such

Table 4: 95% confidence intervals for q_t with respect to pH factor

pH	95% confidence interval for the mean of q_t	
	Lower bound	Upper bound
2	9.8757	13.4034
4	8.5649	10.8542
6	6.4261	10.0417
8	6.4857	10.4860
10	4.2687	7.7523

Table 5: 95% confidence intervals for q_t with respect to pH factor

Concentration mg/L	95% confidence interval for the mean of q_t	
	Lower bound	Upper bound
0.5	0.4411	0.6937
1	0.5488	1.0226
3	1.3069	2.5820
5	2.4935	4.4143
10	8.9588	9.8666

as weight with pH and weight with initial concentration, whereas a weak interaction effect is obtained between pH and initial concentration factors.

Figure 11 illustrates the q_t response surface and contour plots as a function of the weight versus pH, weight versus initial concentration, and pH versus initial concentration. Similar to the above result in equation (3), there is a noticeable change in the trend of q_t variation at low and high levels of the parameters weight versus pH and weight versus initial concentration. It can be noticed from the response surface plot of weight versus pH that q_t attains its maximum value at the minimum level of weights and maximum level of pH. This result is clear from the contour plot as well. Similar argument can be obtained for other response surface and contour plots. This means there is a significant interaction between the two parameters.

Table 7: ANOVA table for RSM design with respect to catalyst I

Source	Mean square	F-value	P-value	
Model	7.5136	17.56	<0.0001	Significant
Linear	14.3235	33.47	<0.0001	Significant
A-weight	15.7470	36.79	<0.0001	Significant
B-PH	17.1173	40.00	<0.0001	Significant
C-concentration	14.3071	33.43	<0.0001	Significant
Square	0.1204	0.28	0.839	Not significant
A^2	0.0233	0.05	0.816	Not significant
B^2	0.1771	0.41	0.521	Not significant
C^2	0.1468	0.34	0.559	Not significant
Residual	0.4280			
Lack-of-fit	1.4424	4.19	0.000	Significant
Pure error	0.3443			

Table 8: ANOVA table for RSM design with respect to catalyst II

Source	Mean square	F-value	P-value	
Model	12.5169	15.11	0.000	Significant
Linear	13.5031	16.30	0.000	Significant
A-weight	4.2662	5.15	0.025	Significant
B-PH	13.1227	15.84	0.000	Significant
C-concentration	26.9062	32.47	0.000	Significant
Square	7.9685	9.62	0.000	Significant
A^2	5.7109	6.89	0.010	Significant
B^2	11.1160	13.42	0.000	Significant
C^2	0.2946	0.36	0.552	Not significant
Residual	0.8286			
Lack-of-fit	4.3498	8.08	0.000	Significant
Pure error	0.5381			

3.3.2 Part II

Table 8 shows the ANOVA results for assessing q_t using RSM design under catalyst III. All factors have an effect on the response variable q_t and their order of effect depending on F-value is $C > B > A$. Therefore, the most

Table 6: Descriptive statistics and 95% confidence intervals for q_t with respect to catalyst levels

	N	Mean	Std. deviation	Std. error	95% confidence interval for mean		Minimum	Maximum
					Lower bound	Upper bound		
100% (I)	80	8.7885	4.45411	0.49798	7.7973	9.7797	0.05	14.84
25% (III)	80	7.8881	4.13933	0.46279	6.9670	8.8093	0.45	14.53
50% (II)	80	5.7678	3.94091	0.44061	4.8908	6.6448	0.27	12.49

Figure 11: Plots of response surface and contours of the q_t efficiency percentage as a function of the explanatory factors on q_t (mg/g) amount at 100%.

Figure 12: Plots of response surface and contours for q_t efficiency percentage as a function of the explanatory factors on q_t (mg/g) amount at 25%.

effect on the response variable is because of concentration and the lowest effect is because of weight.

The model F -value of 15.11 indicates that the model is significant. In addition, the lack of-fit F -value of 4.3498

implies that the lack of fit is significant with a pure error of 0.5381.

The reliability of a model can be checked by determining the R^2 coefficient. In this study, R^2 is 0.979 for the nonlinear model, implying that 97.9% of response variability is obtained by a regression model.

From Table 8, we may conclude that the linear and quadratic models are both significant and can be used to model q_t value. The F -values of A^2 and B^2 indicated a significant effect of these quadratic forms on q_t , whereas C^2 is not significant in this model. Moreover, the interaction between the factors cannot be estimated using RSM, and so we used a nonlinear regression model; the regression equation, in this case, is given by equation (4).

$$q_t = 3.333 - 70.913X_1 - 0.663X_2 + 1.368X_3 \\ + 14.279X_1X_2 - 5.573X_1X_3 - 0.018X_2X_3 \\ + 61.663X_1^2 - 0.087X_2^2 - 0.017X_3^2. \quad (4)$$

From equation (2), the model under catalyst III indicates a strong effect of weight, followed by initial concentration and weak effect of pH level. It also appears that the interaction effect between some factors is strong such as weight with pH and weight with initial concentration, whereas a weak interaction effect is obtained between pH and initial concentration factors.

Figure 12 shows the q_t response surface and contour plots as a function of weight versus pH, weight versus initial concentration, and pH versus initial concentration. Similar to the above result in equation (4), there is a clear change in the trend of q_t variation at low and high levels of the weight versus pH and weight versus initial concentration. From the response surface plot of weight versus pH, it can be concluded that q_t attains its maximum value at the maximum level of pH and a minimum level of weight. This result is clear from the contour plot as well. Similar argument can be obtained for other response surface and contour plots. Therefore, there is a significant interaction between these two parameters.

3.3.3 Part III

Table 9 shows the ANOVA results for assessing q_t using RSM design under catalyst II. All factors have an effect on the response variable q_t and their order of effect depending on F -value are $C > A > B$. Therefore, the most effect on the response variable is because of the initial concentration and the lowest effect is because of the pH level.

Table 9: ANOVA table for RSM design with respect to catalyst III

Source	Mean square	F -value	P -value	
Model	9.1813	8.47	0.000	Significant
Linear	13.6073	12.55	0.000	Significant
A-weight	4.3632	4.02	0.047	Significant
B-PH	0.2535	0.23	0.630	Significant
C-concentration	37.8847	34.95	0.000	Significant
Square	2.7771	2.56	0.059	Not significant
A^2	0.0296	0.03	0.869	Not significant
B^2	3.1003	2.86	0.094	Not significant
C^2	5.1156	4.72	0.032	Significant
Residual	1.0841			
Lack-of-fit	7.2873	12.73	0.000	Significant
Pure error	0.5725			

The F -value of the model is 8.47, which indicates that the model is significant. The lack-of-fit F -value of 12.73 implies that the lack of fit is significant with a pure error of 0.5725.

The reliability of a model can be examined by determining the value of R^2 . In this study, R^2 is 0.968 for the nonlinear model, implying that 96.8% of response inconsistency is obtained by the regression model.

From Table 9, we may conclude that the linear model is significant, whereas the quadratic models are not significant. The F -values of A^2 and B^2 indicated a non-significant effect of these quadratic forms on q_t , whereas C^2 is the only significant factor in this model. Moreover, the interaction between the factors cannot be estimated using RSM, and so we used a nonlinear regression model; the regression equation, in this case, is given by equation (5).

$$q_t = -1.775 + 58.509X_1 + 1.190X_2 - 0.692X_3 \\ - 16.372X_1X_2 + 5.077X_1X_3 + 0.082X_2X_3 \\ + 0.009X_1^2 + 0.038X_2^2 - 0.036X_3^2. \quad (5)$$

In equation (5), the model under catalyst II indicates a strong effect of weight, followed by pH, and then the initial concentration. It also appears that the interaction effect between some factors is strong such as weight with pH and weight with initial concentration, whereas a weak interaction effect is obtained between pH and initial concentration factors.

Figure 13 represents q_t response surface and contour plots as a function of the weight versus pH, weight versus initial concentration, and pH versus initial concentration. Similar to the above result in equation (5), there is a clear change in the trend of q_t variation at low and high levels of the parameters weight versus pH. From the response

Figure 13: Plots of response surface and contour for q_t efficiency percentage as a function of the explanatory factors on q_t (mg/g) amount at 50%.

surface plot of weight versus pH, it can be concluded that q_t attains its maximum value at the maximum level of pH and a minimum level of weight. This result is clear from the contour plot as well. Similar argument can be obtained for other response surface and contour plots. This leads to a considerable interaction between these two parameters.

4 Conclusions and recommendations

The results gave an inference of the importance of the pH of wastewater in promoting the removal of pollutants, bearing in mind that the optimum pH varies with different chemicals. Therefore, consideration should be given in the future to modification and/or synthesis of novel photocatalysis applied to a wide range of pH.

Further investigation can be performed on the recycling and stability of catalyst as a future point of research work. The recycling process is influenced by manufactured materials as it has good packing and crystal shape.

Acknowledgment: The authors extend their appreciation to the Deputyship for Research and Innovation, Ministry of Education in Saudi Arabia for funding this research work through the project grant number IFT20158.

Funding information: This research work was funded by the Ministry of Education in Saudi Arabia through the project grant number IFT20158.

Author contributions: Hanan Haj Ahmad: writing – review and editing. Waed Alahmad: writing – original draft.

Conflict of interest: The authors declare no conflict of interest.

Data availability statement: The authors confirm that the data supporting the findings of this study are available within the article.

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