INDIVIDUAL AND INTERACTION EFFECTS OF OPERATING PARAMETERS ON THE PHOTOCATALYTIC DEGRADATION UNDER VISIBLE LIGHT ILLUMINATION: RESPONSE SURFACE METHODOLOGICAL APPROACH

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In this study, for the first time a statistical analysis based on the response surface methodology (RSM) was employed to investigate individual and interaction effects of key operating parameters of the photocatalytic degradation under visible-light irradiation using Ag-S/PEG/TiO2. Ag-S/PEG/TiO2 is a visible-light-driven photocatalyst and was synthesized (based on earlier research) by co-doping of TiO2 with silver and sulphur and addition of polyethylene glycol (as a reagent template). In addition, the model pollutant was methylene orange (MO) and the studied operating parameters included the photocatalyst loading, initial concentration of the pollutant, and pH of the solution. The statistics-based experimental design and RSM was utilized to find a quadratic model as a functional relationship between the degradation efficiency and the three operating parameters. The regression analysis with R2 value of 0.9678 showed a close fit between the model prediction and experimental data of the degradation efficiency. The analysis of variance based on the model indicated that pH of the solution was the most influential factor, while the two other operating parameters were also significant. The efficiency of MO degradation reached 94.0 % under the optimum conditions (i.e. photocatalyst loading of 1.20 g/L, MO concentration of 5 mg/L, and pH of 2).

Keywords: photocatalytic degradation, RSM, operating parameters, visible light, interaction effect

INTRODUCTION

Advanced oxidation processes (AOPs) have attracted great attention for wastewater treatment and air purification in the recent years.[1–3] These methods provide an advantage of destroying the pollutants, in contrast to conventional techniques such as activated carbon or air stripping which only transfer the contaminants from one phase to another.[4–7] The mechanism of degradation in AOPs is based on the formation of very reactive radicals, principally hydroxyl radicals (OH•).[8–10]

Among AOPs, heterogeneous photocatalysis using titanium dioxide (TiO2) semiconductor has been proven to be an efficient approach for degrading both aquatic and atmospheric contaminants.[11–13] The unique properties of TiO2, such as its high oxidizing power, non-toxicity, high stability, low cost, and resistance to photo and chemical corrosion, make this photocatalyst suitable for the photocatalytic degradation processes.[14,15] However, the photocatalytic region of TiO2 is narrow and it only corresponds to photons with wave length shorter than 387 nm (anatase phase).[4,16] This is one of the most important drawbacks of TiO2 which limits its practical applications. Hence, shifting TiO2 sensitivity to the visible range will significantly increase its photocatalytic efficiency.[17–19]

Several scientific studies on the modification and development of TiO2 catalyst in order to increase its visible light sensitivity have been reported over the past decades.[20–24] Doping TiO2 with metals and non-metals (such as silver and sulphur respectively) has been known as an efficient strategy to extend its optical response from UV to visible light range.[25–27] Doping these impurities into the TiO2 matrix can decrease the band gap of the semiconductor and increase the photocatalytic activity of TiO2 under the visible light significantly without modifying its surface properties.[28,29] Furthermore, it has been proved that using poly ethylene glycol (PEG) as a template reagent could act as a significant factor to improve the efficiency of the photocatalytic system under visible light irradiation.[30,31]

In the study of operating parameters’ effects on photocatalytic degradation processes, most of the earlier researchers have utilized the classical method of investigating, which is based on optimizing one parameter at a time keeping others constant. It is not only a time-consuming study, but it is also impractical to reach the correct optimum point due to ignoring the interaction effects between the studied variables.[32–34] In order to overcome these problems, the response surface methodology (RSM) has been proposed to determine the effects of individual variables and their interaction effects.
interactive effects, and ultimately, to find the real optimum condition with a limited number of planned experiments.

In our previous research to enhance the photocatalytic activity of TiO₂, we successfully synthetized a novel visible-light-driven TiO₂ photocatalyst doped with silver and sulphur, using PEG as a synthesis reagent.[28] Here, this efficient synthesized photocatalyst was utilized to remove methylene orange (MO), as a model pollutant, under visible light illumination. The RSM was employed to analyze the simultaneous effects of the three operating parameters that are photocatalyst loading, concentration of the pollutant, and pH of the solution. In addition, the optimized values of the operating parameters and the degradation efficiency were found.

EXPERIMENTAL AND METHODS

Materials
Titanium tetraisopropoxide (TTIP, > 98 %, Sigma–Aldrich) was used as a titanium precursor, while precursors for silver and sulphur were silver nitrate (Merck KgaA, Darmstadt, Germany) and thiourea (Merck KgaA, Darmstadt, Germany), respectively. Polyethylene glycol (Merck KgaA, Darmstadt, Germany) was utilized as a synthesis reagent, and NaOH (Merck KgaA, Darmstadt, Germany) and HCl (Merck KgaA, Darmstadt, Germany) were used for adjusting the solution pH. Moreover, methylene orange (the model pollutant) and ethanol and ethanolamine (synthesis solvents) were purchased from Merck KgaA, Darmstadt, Germany.

Preparation of Photocatalyst
Ag-S/PEG/TiO₂ photocatalyst was prepared based on our previous work[28] using the sol-gel method. Briefly, 15 mL of ethanol and 5 mL of ethanolamine were dissolved in 5 g of TTIP. Then, 1 g of PEG 4000 was added to the prepared mixture to give solution A. Meanwhile, the required volumes of AgNO₃ and thiourea (for 0.8 % Ag and 1 % S molar ratio) were dissolved in 15 mL of ethanol and 5 mL of deionized water. This solution was then added drop wise to the solution A for 70 min, while mixing with an electromagnetic stirrer. The prepared solution was ultrasonicated at 0 °C for 20 min and stirred continuously for 260 min. Subsequently, the solution was ultrasonicated for the second time, and was kept for a day at room temperature in dark area. Then, it was gelated at 76 °C for 12 h, and the obtained gel was dried by heating at 120 °C for 3 h. Finally, the dried gel was calcined at 550 °C for 3 h. The prepared sample was labelled as Ag-S/PEG/TiO₂. Un-promoted TiO₂ was labelled pure TiO₂ and was synthesized similarly to the above method, without addition of PEG as well as the silver and sulphur precursors.

Photocatalyst Characterization
The X-ray diffraction (XRD) analysis of the synthesized photocatalyst was carried out on a Philips (X’pert Pro MPD) X-ray diffractometer, employing the Cu Kα radiation (wavelength 1.5406 Å) equipped with a Ni filter over the range of 10–90° (2θ). The crystallite sizes of the samples were calculated using the Scherrer equation.[29] In addition, the morphologies of the modified photocatalyst were observed by transmission electron microscopy (TEM, Philips CM10). The result for the photocatalyst’s characterizations can be found in the Supporting Information (Figures S1, S2).

In order to study the photocatalyst agglomeration tendency, focused beam reflectance measurement (FBRM) was used for the in situ measurement of the particle size. A FBRM probe was inserted in the solution of the photocatalyst with different loading from the top of the photoreactor.

Evaluation of Photocatalytic Activity
Effects of operating parameters (i.e. photocatalyst loading, MO initial concentration, and pH of solution) on the degradation of MO in a reactor containing 100 mL solution were evaluated.

According to the experimental design, for each run, the proper amounts of the photocatalyst and MO were added into the solution. The initial pH was adjusted to the design values using HCl or NaOH before starting the experiments, and pH was not controlled during tests (like what is usually happened in the industrial wastewater treatment units). Ten 3-W low-voltage LED lamps served as the visible light source. The spectrum distribution of the visible-light source provided by LED lamps was shown in Figure 1. It clearly determined that the interval of the lamp irradiation wavelength was located in the visible region (430 nm ≤ λ ≤ 500 nm).

During the process, oxygen was continuously bubbled to provide a steady state condition for dissolved oxygen concentration. The reaction mixture was initially stirred in the dark for 30 min to ensure the adsorption equilibrium, then it was exposed to the visible-light irradiation for 120 min. During the photocatalytic degradation, the solution was mixed using a magnetic stirrer at 600 rpm. In the preliminary experiments, the rotation frequency of the mixer was increased to find the minimum frequency which is completely enough to avoid mass transfer to be the controlling step. This value was 600 rpm. In other words, increasing the mixer rotation frequency above this value (600 rpm) had almost no impact on the efficiency of the photocatalytic degradation.

Samples were withdrawn from the mixture and centrifuged to separate solid particles. Finally, UV–Vis spectrophotometer (Perkin Elmer Lambda2S) was utilized to determine the absorbance of the resulting samples. The concentration of MO was calculated from an absorbance versus concentration calibration curve. The degradation efficiency (%) was calculated by the following equation:

\[
E = \frac{C_0 - C_f}{C_0} \times 100\%
\]  

where \(E\) is the degradation efficiency, and \(C_0\) and \(C_f\) are the concentrations of the MO at the beginning and the end of the experiments, respectively.

![Figure 1. Spectrum distribution of the visible light source provided by 3-W LED lamps.](image-url)
Table 1. Values and levels of the variables for experimental design

<table>
<thead>
<tr>
<th>Variables</th>
<th>Ranges and levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photocatalyst loading (A, g/L)</td>
<td>–α  1  0  +1  +α</td>
</tr>
<tr>
<td>MO concentration (B, mg/L)</td>
<td>0.50  0.80  1.25  1.70  2.00</td>
</tr>
<tr>
<td>pH (C)</td>
<td>5  8.04  12.5  16.96  20</td>
</tr>
</tbody>
</table>

α = 1.68

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares (SS)</th>
<th>Degree of freedom (df)</th>
<th>Mean squares (MS)</th>
<th>F value</th>
<th>Prob &gt; F</th>
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<tbody>
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<td>Model</td>
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<td>752.30</td>
<td>33.40</td>
<td>&lt;0.0001</td>
</tr>
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<td>A-photocatalyst loading</td>
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<td>144.11</td>
<td>6.40</td>
<td>0.0299</td>
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<tr>
<td>B-MO concentration</td>
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<td>144.17</td>
<td>30.61</td>
<td>0.0003</td>
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<tr>
<td>C-pH</td>
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<td>4367.64</td>
<td>193.89</td>
<td>&lt;0.0001</td>
</tr>
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<td>10.04</td>
<td>0.45</td>
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</tr>
<tr>
<td>AC</td>
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<td>30.50</td>
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<tr>
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<tr>
<td>A^2</td>
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<tr>
<td>B^2</td>
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<td>120.91</td>
<td>5.37</td>
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<tr>
<td>C^2</td>
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<td>Residual</td>
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<td>41.06</td>
<td>10.29</td>
<td>0.0115</td>
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<td>Pure error</td>
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<td>5</td>
<td>3.99</td>
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</table>

A: Photocatalyst loading (g/L); B: MO concentration (mg/L); C: pH.
R-Squared = 0.9678; Adj R-Squared = 0.9388; Adequate Precision = 18.577.

Experimental Design and Statistical Analysis

In the present study, RSM was employed to evaluate the influence of three selected parameters (photocatalyst loading (A, g/L), MO initial concentration (B, mg/L), and pH (C)) on the degradation efficiency of MO under visible light illumination. The three parameters (A, B, C) were chosen as independent variables, while the degradation efficiency of MO was the output response.

It is worth mentioning that the applicability of using “MO concentration/photocatalyst” ratio as an operating parameter (instead of using MO concentration and photocatalyst loading separately) was investigated. The results showed that there is no clear relationship between the mentioned ratio and the degradation efficiency. Moreover, if that ratio was utilized as a parameter, the interpretation of the effects of MO concentration and the photocatalyst would be difficult.

The experimental ranges and the levels of the independent variables for MO photocatalytic degradation are shown in Table 1. It should be pointed out that the range of the chosen operating parameters were selected in accordance with our initial experiments.

The RSM based on the central composite experimental design (CCD), which is one of the most usual methods of using response surface methodological approach, was utilized to evaluate the combined effects of the three independent variables using twenty sets of experiments. Moreover, a second-order polynomial equation was obtained to relate the response variable to the three independent variables, as follows:

\[ Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \]  

(2)

where Y (%) is the predicted response (degradation efficiency of MO), b1, b2, and b3 are the coefficients for linear effects, b11, b13, and b23 are the interaction coefficients, b12, b22, and b33 are the quadratic terms, b0 is the interception coefficient and A, B, and C are the independent variables (photocatalyst loading, MO initial concentration, and pH, respectively).

Degradation conditions determined by the CCD method along with the predicted and experimental values of the response were presented in Table 2. Data were analyzed by the analysis of variance (ANOVA), and the optimal values of the operating parameters were obtained using Design Expert® software (Trial version 9.0.3 Stat-Ease, Inc., Minneapolis, USA).

Table 2. Experimental design matrix and the value of responses based on experiment run

<table>
<thead>
<tr>
<th>Run</th>
<th>Photocatalyst loading (A, g/L)</th>
<th>MO concentration (B, mg/L)</th>
<th>pH (C)</th>
<th>Actual</th>
<th>Predicted</th>
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<tr>
<td>1</td>
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<td>12.50</td>
<td>8.00</td>
<td>22.8</td>
<td>21.3</td>
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<td>2</td>
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<td>16.96</td>
<td>6.78</td>
<td>31.5</td>
<td>31.8</td>
</tr>
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<td>5.00</td>
<td>62.3</td>
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</tr>
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<td>63.9</td>
</tr>
<tr>
<td>5</td>
<td>0.80</td>
<td>16.96</td>
<td>3.22</td>
<td>51.3</td>
<td>52.7</td>
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<td>5.00</td>
<td>46.7</td>
<td>47.3</td>
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<td>5.00</td>
<td>35.1</td>
<td>32.3</td>
</tr>
<tr>
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<td>12.50</td>
<td>5.00</td>
<td>63.1</td>
<td>63.9</td>
</tr>
<tr>
<td>9</td>
<td>1.70</td>
<td>8.04</td>
<td>6.78</td>
<td>34.6</td>
<td>37.6</td>
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<td>64.8</td>
<td>63.9</td>
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<td>5.00</td>
<td>41.7</td>
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<td>6.78</td>
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<td>18</td>
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<td>5.00</td>
<td>76.0</td>
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</table>

Figure 2. Plot of the predicted value versus experimental data for various MO photocatalytic degradation.
RESULTS AND DISCUSSION

Model Fitting and Statistical Analysis

Based on the results of the MO photocatalytic degradation, the following second-order polynomial equation was obtained:

\[
\text{Degradation efficiency} \% = 43.78 + 103.96 \times A - 0.623 \\
- 4.174 \times B + 0.5632 \times A \times B + 2.45 \times A \times C \\
+ 0.385 \times B \times C - 46.43 \times A^2 - 0.144 \times B^2 - 1.377 \times C^2
\]  

where A, B, and C were photocatalyst loading, MO initial concentration (mg/L), and pH, respectively. The positive coefficients of B, AB, AC, and BC showed a constructive effect to increase the degradation efficiency, while the negative coefficients of A, C, A^2, B^2, and C^2 affected the degradation efficiency in a reverse manner.

The interactive effects depend on the value and sign of main and quadratic terms as well as binary interaction terms. The optimum value of main terms can provide a conclusive evidence of interactive effects; by equalling the partial derivative of Equation (3) respect to independent variables (i.e. A, B, and C) to zero, the optimum values can be found. For example, the following relation can be obtained for the photocatalyst loading (A).

\[
\text{Optimum of } A = \frac{\text{coeff. of } A + \text{coeff. of } AB \times \text{value of } B + \text{coeff. of } AC \times \text{value of } C}{-2 \times \text{coeff. of } A^2}
\]

Since coefficients of A, AB, and AC are positive, but the coefficient of A^2 is negative (based on Equation (3)), if the amount of parameter B or C is increases, the optimum value of A will increase (see Figure S3).

Table 3 shows the ANOVA results of the quadratic response surface model for the MO photocatalytic degradation. The ANOVA has provided a powerful tool for investigating the effect of variables and their interaction in experiments as well as studying significance of the model.\[37\]

The model p-values and F-values were used as a tool to check the relative significance of the variables.\[38\] In general, coefficients with a higher F-value and lower p-value indicate that their corresponding variables have more significance in comparison with other variables.\[37\] Therefore, based on Table 3, the effect of pH was highly significant and causes the main impact on the MO photocatalytic degradation efficiency. In terms of interactive effects, BC was more significant than AB and AC.

In addition to the very low model p-value, the “model F-value” of 33.40 also showed adequacy of the model since it was much greater than the theoretical F-value (4.35). In addition, the lack of fit F-value of 10.29 indicated good predictability of the model and implied that the lack of fit was not significant relative to the pure error.

The model adequacy was further checked using the diagnostic plots (Figures 2–5). The experimental results of the MO degradation were plotted versus corresponding predicted values in Figure 2. According to this figure, the values of R^2 and Adj R^2 were calculated as 0.9678 and 0.9388, respectively, implying that the experimental data were fitted very well by the proposed model. In addition to the correlation coefficient, the normal probability plot of the internally studentized residuals was also studied to evaluate the adequacy of the model (Figure 3). According to Figure 3, the residual points fell near to the straight line, indicating that
there was almost no severe departure of the assumptions underlying the analysis and also a good agreement between the actual and predicted values. The plot of the internally studentized residuals versus predicted responses is illustrated in Figure 4. As seen, all design points of the experimental runs were scattered randomly within the constant range of residuals across the graph, suggesting that the variance of original observations is constant for all values of the response, and the approximation of the fitted model to the response surface was completely acceptable and adequate. Figure 5 presents leverage for the photocatalytic degradation runs. The leverage values below 1.0 indicate that the approximation of the fitted model to the response surface is fairly good with no data recording error, and the scattering shows the influence of all runs on the fitted model.

Analysis of Response Surface
Using RSM, the effects of the operating parameters (photocatalyst loading, MO concentration, and pH of the solution) and their interaction effect on the degradation efficiency of MO are graphically represented by three-dimensional response surface plots and two-dimensional contour plots in Figure 6. The interaction effect of the photocatalyst loading and pH on the degradation efficiency of MO is depicted as a bell-shaped curve in

Figure 6. Response surface showing the effects of photocatalyst loading, MO initial concentration, and pH on degradation efficiency of MO under visible light when (a) MO initial concentration was kept constant at 12.5 mg/L, (b) pH was kept constant at 5, and (c) photocatalyst loading was kept constant at 1.25 g/L.
adsorbed dye molecules may occupy the active sites of TiO\textsubscript{2} for several reasons. Firstly, at high dye concentration, the fact that at low concentration of the dye, the photocatalytic range of 5\textsuperscript{–9} mg/L as seen in the contour plot of Figure 6b. The interaction effect of the MO initial concentration on the degradation efficiency was shown in Figure 6c. From this figure, MO degradation efficiency displayed a dramatic increase with a decrease in the solution pH regardless of the dye initial concentration. Such a result could be explained by the fact that for pH values lower than the pH\textsubscript{zpc} of titania (\(\text{pH} = 6.25\))\textsuperscript{[60]} the catalyst surface becomes positively charged whereas for pH values higher than pH\textsubscript{zpc}, the surface becomes negatively charged according to the following reactions:\textsuperscript{[51]}

\[
\text{pH < pH}_{zpc}: \text{Ti}^{IV} - \text{OH}^+ + \text{H}^+ \rightarrow \text{Ti}^{IV} - \text{OH}_2^-
\]

\[
\text{pH > pH}_{zpc}: \text{Ti}^{IV} - \text{OH} + \text{OH}^- \rightarrow \text{Ti}^{IV} - \text{O}^- + \text{H}_2\text{O}
\]

Therefore, for MO, which is an anionic dye (like most dyes)\textsuperscript{[52]} a strong adsorption of the dye on the photocatalyst surface was expected at low pH, as a result of the electrostatic attraction of the positively charged TiO\textsubscript{2} with the negatively charged dye. This can lead to the conclusion that at acidic pH, the photocatalysis system works more efficiently than alkaline medium for MO degradation.

Optimization of the Operating Parameters and Verification of the Model

For the optimization, Design Expert Version 9.0.3 software was employed to maximize the degradation efficiency based on the suggested model (Equation (3)). The model predicted a maximum degradation efficiency of 94.0 % under the optimum conditions of Ag-S/PEG/TiO\textsubscript{2} loading of 1.20 g/L, MO initial concentration of 5 mg/L, and pH of 2. In order to confirm the accuracy of the proposed model, three replicate experiments were conducted under the optimum conditions. The degradation efficiency was found to be at 93.7 \pm 1.8 % which was reasonably close to the predicted value. Further validations for three more points were done in four important conditions, and the result can be found in Table S1 which shows that there is a good agreement between the model predictions and the experimental data. Therefore, the optimum point determined by the model was successfully validated, and it was confirmed that RSM can be utilized to optimize the MO photocatalytic degradation under visible light illumination.

To ensure that the modified synthesized nanophotocatalyst (Ag-S/PEG/TiO\textsubscript{2}) is efficient under solar light irradiation, two additional experiments were conducted to compare the activity of Ag-S/PEG/TiO\textsubscript{2} and pure synthesized TiO\textsubscript{2}. Experiments were carried out at the optimum condition (Figure 7). As seen, Ag-S/PEG/TiO\textsubscript{2} had much more efficiency (93.7 %) compared to the pure TiO\textsubscript{2} (23.2 %) under visible light irradiation. In addition, to make sure that under a very acidic condition (i.e. optimum pH; pH = 2), the pollutant removal is due to the photocatalysis, an experiment was carried out by adjusting the initial pH at 2, in the absence of both the photocatalyst and light. The result showed that the MO degradation in this condition was 8 % and significantly lower than 93.7 % that obtained at the optimum condition in the presence of both the photocatalyst and light (see Figure S5).

CONCLUSIONS

In the present study, RSM was employed to investigate the individual and interaction effects of three important operating conditions in photocatalytic Ag-S/PEG/TiO\textsubscript{2} and pure TiO\textsubscript{2} under visible light irradiation.
parameters (i.e. photocatalyst loading, pollutant initial concentration, and pH of solution) on the photocatalytic degradation under visible light irradiation. For this purpose, Ag-S/PEG/TiO2 and MO were selected as the visible-light-driven photocatalyst and the model pollutant, respectively. The obtained model fit very well to the experimental data as confirmed by the high R² (0.9678) and Adj-R² (0.9388). ANOVA based on the model indicated that pH of the solution was the most influential factor, while two other factors were also significant. Moreover, the present model (which takes into account the interaction effects of the operating parameters) suggested that the optimum conditions were 1.20 g/L, 5 mg/L, and 2 for photocatalyst loading, MO concentration, and pH, respectively. Under the optimum condition, the dye degradation efficiency was predicted to be 94.0 % and the corresponding experimental data (93.7 %) was in a good agreement with the predicted value. As a result, this work demonstrates the application and benefits of the experimental design approach based on RSM to study and optimize the photocatalytic degradation process under visible light illumination.

REFERENCES
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