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# Comparative Optimization of Photocatalysis and Adsorption of Methylene Blue Using Aluminum Doped Magnetic Iron Oxide by Central Composite Design

***Chima Golda C[1], Nleonu Emmanuel C[2,3] and Ilham Ben Amor[4]***

[1]Chemical Engineering Department, Federal Polytechnic Nekede, Owerri, P.M.B 1036, Imo State Nigeria.
[2]Chemistry Department, Federal Polytechnic Nekede, Owerri, P.M.B 1036, Imo State Nigeria.
[3]Material and Electrochemical Research Unit (MERU), Chemistry Department, Federal Polytechnic Nekede, Owerri, P.M.B 1036, Imo State Nigeria.
[4]Department of Process Engineering and Petrochemical, Faculty of Technology, University of El Oued, El Oued 39000, Algeria
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**ABSTRACT**

Water pollution still remains a major issue in developing countries due to poor disposal systems. Therefore, this study was to optimize methylene blue removal from aqueous solutions through adsorption and photocatalysis methods using aluminium-doped magnetic iron oxide. The synthesis of aluminium-doped magnetic iron oxide ($AlFe_3O_4$) as an adsorbent and photocatalyst was successfully prepared using the co-precipitation method. The removal efficiency of the $AlFe_3O_4$ was evaluated as a function of two input parameters, viz., catalyst/ adsorbent dose (0.1–0.5 g) and contact time (20-100 min) by using central composite design (CCD) adopted from response surface methodology (RSM). Using removal and degradation efficiency as responses, a 13 run experiment matrix was generated by the CCD to investigate the interaction effects of the two input factors. From the results, a linear model was generated for the two treatment methods of adsorption and photocatalytic processes, which didn't show good predictability of results agreeable to the experimental data. The analysis of variance (ANOVA) showed the selected models for adsorption and degradation were significant ($P < 0.05$) with poor coefficients of determination ($R^2$) values of 0.6323 and 0.6535, respectively. The highest efficiency of MB removal for the adsorption process (59.68%) and the photocatalysis process (49.02%) were obtained in optimum conditions of adsorbent/photocatalyst = 0.23g, contact time = 38.96 min, and MB concentration = 40mg/l. The kinetic studies showed that the adsorption data fitted well to a pseudo-first-order kinetic model, whereas the photocatalysis data fitted well to a pseudo-second-order kinetic model.

**Keywords:** Photocatalysis, adsorption, central composite design, $AlFe_3O_4$, methylene blue.

## Introduction

One vital constituent that seriously affects human beings and life on earth is the use of contaminated and unhygienic water due to environmental pollution via industrial effluents (Asif et al., 2021). With recent industrialization and globalisation, large volumes of textile effluents containing high concentrations of pollutants such as dyes and pigments contribute to a great extent to water contamination and environmental pollution, specifically in developing or underdeveloped countries (Tetteh *et al.*, 2021). Consequently, the presence of dyes in effluents at concentrations as low as 1 ppm can lead to high-strength colours associated with reductions in sunlight penetration, photosynthetic activities of aquatic ecosystems, reductions in oxygen dissolution, and increases in biochemical oxygen demand (Talebi *et al.*, 2017; Gurses *et al.*, 2016).

Despite their low concentration in the environment, dye contaminants can lead to toxicity, resulting in negative effects on aquatic and human life. Therefore, it is important to remove dyes from aqueous solutions before discharging them into the environment (Karim *et al*., 2019). Recently, investigators have paid great attention to numerous treatment technologies for the removal and degradation of dyes in wastewater through biodegradation, adsorption, chemical treatment, coagulation, membrane processes, and photocatalysis (Razani *et al*., 2017; Tetteh and Rathial, 2020). Photocatalysis is considered a promising alternative for the degradation of various organic pollutants or dyes (Nleonu *et al*., 2023a). Photocatalysis uses a photocatalyst, generally a semiconductor material, and light to enhance the degradation of organic compounds in wastewater. Metal oxides such as $TiO_2$ , $Al_2O_3$, $CeO_2$, $Fe_2O_3$, and ZnO are still the most widely used photocatalysts being studied because of their abundance, cost effectiveness, and excellent properties such as non-toxicity, high excitation, binding energy, and photocatalytic active crystal phases (Ezeibe *et al*., 2022; Emil-Kaya, *et al.*, 2022; Su *et al.*, 2021). However, magnetic iron oxide ($Fe_3O_4$) has recently been investigated due to its environmental stability, low cost, and high abundance as compared to other metal oxides (Ezeibe *et al.*, 2019).

Magnetic iron oxide is a potential photocatalyst for remediation of aqueous contaminants under ultraviolet or visible irradiation because of its outstanding catalytic activities, low production cost, and excellent optical and chemical properties. Despite its unique properties, $Fe_3O_4$ has major drawbacks attributed

to its wide band gap, which is between 4 - 6 eV (Saeed *et al*., 2020). Recently, researchers have adopted a variety of methods to reduce the wide band gap, quick recombination of electrons, and narrow range of light responses (Su *et al.*, 2021). Hence, the photocatalytic efficiency of $Fe_3O_4$ can be improved by doping with metal atoms of different band gaps to form hetero-junctions in the photocatalytic system that have unique properties not present in the individual nanomaterial arising from the interfacial interaction (Gindose, 2019). Doping with aluminium (III) is thought to have considerable potential because the ionic radius of $Al^{3+}$ (0.50 Å) is between $Fe^{3+}$ (0.63 Å) and $Fe^{2+}$ (0.76 Å), as this is expected to reduce the band gap energy required for excitation and improve photocatalytic activity (Nleonu *et al*., 2023a).

In this study, aluminium-doped magnetic iron oxide ($AlFe_3O_4$) was synthesised by the co-precipitation method as an effective adsorbent and photocatalyst for the removal of methylene blue in aqueous solution. Methylene blue is a popular industrial dye used to colour wool, leather, silk, fibre, polyester, and nylon. Currently, there is no literature on the photocatalytic degradation of methylene blue by $AlFe_3O_4$. Response surface methodology (RSM) with a central composite rotatable design (CCRD) was used to improve and optimise the adsorption and photocatalytic removal efficiency of the prepared metal oxide. The aim of the present work was to study the photocatalytic performance of synthesised $AlFe_3O_4$ on methylene blue dye. The effect of two operating parameters, including irradiation time and catalyst dosage, on the dye removal efficiency was optimised and analysed using research surface methodology based on the central composite rotatable design (CCRD) method.

## Materials and Methods

### *Chemicals*

Methylene Blue dye with absorbance (λ = 662nm), iron (II) chloride tetrahydrate ($FeCl_3.4H_2O$), iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), and aluminium chloride ($AlCl_3$) were products of British Drug House (BHD). Ammonium hydroxide was a product of Chemie Ltd., India. All chemicals were of Analytical grade and were used as received. All solutions were prepared with deionized water.

### $AlFe_3O_4$ Synthesis and Characterization

The doping of $Fe_3O_4$ with $Al^{3+}$ was achieved using the co-precipitation method. Specifically, 17.5 g of $FeCl_3.6H_2O$, 7.5g of $FeCl_2.4H_2O$ and 1.17g of $AlCl_3$ were dissolved in 100 ml of deionized water, then 25 % $NH_4OH$ was added dropwise to the earlier reaction mixture under continuous stirring at 70 ℃ until the reaction pH reached approximately 10 and refluxed at 100 ℃ for 1 h. The resultant precipitate was filtered, washed, and dried at 105 ℃ for 12 hours. The morphology of the $AlFe_3O_4$ was recorded on a scanning electron microscopy (SEM) instrument at an accelerating voltage of 10 kv and 1000x magnification.

### Photocatalytic Experiments

The photochemical batch reactor was a beaker containing 100 ml of a 40 mg methylene blue solution in which $AlFe_3O_4$ was suspended. The solution was continuously magnetically stirred in the dark for 30 minutes to reach the equilibrium of the dye molecule on the catalyst particles. The irradiation in the UV region was provided by a 254 nm, 220 V, 15 W lamp in a continuously closed chamber. The distance between the UV source and reaction mixture was kept at 30 cm. The experiments were monitored based on the influence of contact time (20, 40, 60, 80, and 100 min) and metal oxide dose (0.1, 0.2, 0.3, 0.4, and 0.5 g). The concentration of methylene blue in the test sample was determined using a UV–Vis spectrophotometer (D-8 Drawell) at a wavelength of 660 nm.

### Adsorption Study

Adsorptive experiments were carried out in a batch process containing 100 ml of methylene blue. The removal efficiency of $AlFe_3O_4$ was studied at different contact time (20, 40, 60, 80, and 100 min) and adsorbent doses (0.1, 0.2, 0.3, 0.4, and 0.5), respectively. Methylene blue removal efficiency was determined by measuring MB concentration before and after treatment with aluminium doped magnetic iron oxide using a UV-Vis spectrophotometer (D-8 Drawell) at a wavelength of 660 nm. The dye removal efficiency was estimated as follows:

$$\text{Removal/Degradation Performance (\%)} = \frac{A_o - A_t}{A_o} \times 100 \quad (1)$$

Where $A_o$ is the initial dye absorbance and $A_t$ is the final dye absorbance.

### Optimization Design

Optimization of variables in adsorption and photocatalysis was studied using Central Composite Design (CCD) provided by the design expert 9.0.6 software (Stat-Ease Inc., USA). The variables and their ranges selected for the photocatalysis and adsorption of methylene blue by $AlFe_3O_4$ were metal oxide dosage (0.1–0.5 g) and contact time (20–100 min), which implies 13 experiments. The employed designs are presented in Table 1. The degradation and removal efficiency calculated using equation 1 is designated as the experimental response. The design was used to obtain predicted responses, response surfaces, and regression models.

**Table 1:** Central Composite Rotatable Design (CCRD) matrix for input variables

| Factor | Low level (-1) | Medium (0) | High Level (+1) |
|---|---|---|---|
| A: Contact time (min) | 20 | 60 | 100 |
| B: Metal oxide dose (g) | 0.1 | 0.3 | 0.5 |

**Kinetic Studies**

The kinetic studies of the adsorption and photocatalysis removal of MB were evaluated using pseudo-first-order and pseudo-second order models expressed by equations (2) and (3), respectively.

$$\text{In}\frac{A_o}{A_t} = K_1 t \quad (2)$$

$$\frac{1}{A_t} - \frac{1}{A_o} = K_2 t \quad (3)$$

Where $A_t$ is the absorbance of MB at time t and $A_o$ is the initial absorbance of MB

## Result and Discussion

***Statistical Model Assessment***

The experimental runs, as discussed earlier, were designed by the RSM through the CCD to examine key operating parameters such as metal oxide load (A) and reaction contact time (B). The CCD model fittings and the statistical analysis of the adsorption and photocatalysis process experimental data were fitted to the linear model for methylene blue removal using $AlFe_3O_4$ metal oxide. The equation model for adsorption and photocatalysis could be described by equations (4) and (5), respectively.

Adsorption removal efficiency (%) = +68.57 + 11.41A + 79.09B (4)

Photocatalysis degradation efficiency (%) = +56.88 + 10.43A + 7.44B (5)

Where A and B are the terms for the coded values of contact time (min) and adsorbent dose (g). The model equations show only the actual values of the input variables (A and B) without any interactions between the variables. The positive sign indicates the synergistic effect of the two variables on the response. The actual and predicted adsorption removal efficiency and photocatalytic degradation efficiency results obtained are presented in Table 2. The results in Table 2 show a good relationship between the experimental and predicted values of adsorption removal efficiency and photocatalytic degradation efficiency.

**Table 2:** Experimental and predicted values of methylene blue adsorption removal and photocatalytic degradation efficiencies.

| Run | Factor 1 A: Contact Time (min) | Factor 2 B: Metal Oxide Load (g) | Adsorption Experimental (%) | Adsorption Predicted (%) | Photocatalytic Experimental (%) | Photocatalytic Predicted (%) |
|---|---|---|---|---|---|---|
| 1 | 60 | 0.3 | 74.38 | 68.57 | 62.88 | 56.88 |
| 2 | 60 | 0.3 | 74.38 | 68.57 | 62.88 | 56.88 |
| 3 | 20 | 0.5 | 68.20 | 66.25 | 54.54 | 53.89 |
| 4 | 100 | 0.5 | 83.37 | 89.07 | 68.94 | 74.75 |
| 5 | 3.43 | 0.3 | 37.47 | 52.44 | 25.00 | 42.13 |
| 6 | 60 | 0.3 | 74.38 | 68.57 | 62.88 | 56.88 |
| 7 | 60 | 0.5 | 77.19 | 81.42 | 68.18 | 67.40 |
| 8 | 60 | 0.3 | 74.38 | 68.57 | 62.88 | 56.88 |
| 9 | 100 | 0.1 | 75.51 | 70.90 | 60.60 | 59.87 |
| 10 | 60 | 0.3 | 74.38 | 68.57 | 62.88 | 56.88 |
| 11 | 20 | 0.1 | 60.34 | 48.08 | 46.21 | 39.01 |
| 12 | 60 | 0.02 | 36.91 | 55.72 | 37.88 | 46.35 |
| 13 | 116 | 0.3 | 80.56 | 84.71 | 63.64 | 71.63 |

Statistical model analysis was analyzed using analysis of variance (ANOVA), as presented in Table 3 and 4 respectively. Based on the results obtained, contact time and adsorbent dose have significant effects on the dye adsorption and degradation. The Fisher variation ratio (F-value) of the model (8.60) for adsorption and 9.43 for photocatalytic degradation with P-value of 0.0067 for dye adsorption and 0.0050 for photocatalytic degradation of MB. The P-values obtained being less than 0.05 shows that the model is significant at the 95% confidence level. The independent variables were also found to be significant for both responses because of their P-values <0.05. The coefficient of determination ($R^2$) quantitatively evaluates the relationship between the experimental data and the predicted responses. The predicted values of both treatment methods were not relatively close to the experimental values as seen in the $R^2$ values of 0.6323 and 0.6535 for the adsorption and photocatalysis processes respectively. Figure 1a and 1b shows the comparison of the model predicted values with the actual values of the test for the methylene blue adsorption and degradation respectively. According to the results displayed in Figure 1a and 1b, the points given in this chart were not relatively close to the straight line and also showed weak correlations.

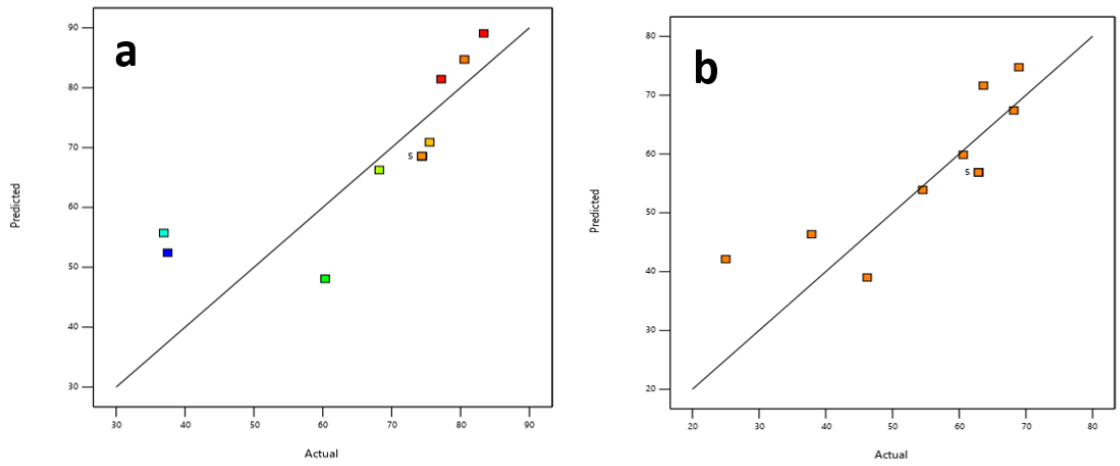


**Figure 1: Values predicted by the model against the actual values obtained from the experiment for MB (a) adsorption (b) photocatalysis processes.**

***Model Validation***

The results of the correlation and validation coefficients of the model are tabulated in Table 5. According to the correlation and validation coefficients obtained, the values of R-squared and adjusted R-squared were 0.6323 and 0.5588 for adsorption removal, while photocatalytic degradation efficiency showed R-square as 0.6535 and adjusted R-square as 0.5842, respectively. The difference between the predicted $R^2$ and adjusted $R^2$ was greater than 0.2 in both removal techniques adopted in this study, suggesting poor predictability of the linear model. The coefficient of variation (CV) was 14.51 % and 14.67 % for the dependent variables of adsorption and photocatalysis processes, which indicated the accuracy of the measurement and reliability of the tests. The linear model showed an adequate precision greater than 4.00, which indicates that the model is desirable and implies an adequate signal. The result also implies that the model can be used to navigate the design space for the adopted treatment methods. The Press value of the model of 2020.18 and 1350.69 for the adsorption and photocatalysis process indicates extremely high signal to noise ratio.

**Table 3**: Analysis of variance (ANOVA) results for adsorption linear models

| Source | Sum of Squares | Degree of Freedom | Mean Square | F-Value | p-Value | |
|---|---|---|---|---|---|---|
| Model | 1701.85 | 2 | 850.92 | 8.60 | 0.0067 | Significant |
| A: Contact time | 1041.47 | 1 | 1041.47 | 10.52 | 0.0088 | |
| B: Metal oxide load | 660.38 | 1 | 660.38 | 6.67 | 0.0273 | |
| Residual | 989.63 | 10 | 98.96 | | | |
| Lack of Fit | 989.63 | 6 | 164.94 | | | |
| Pure error | 0.0000 | 4 | 0.0000 | | | |
| Cor Total | 2691.48 | 12 | | | | |

**Table 4:** Analysis of variance (ANOVA) results for photocatalytic linear models

| Source | Sum of Squares | Degree of Freedom | Mean Square | F-Value | p-Value | |
|---|---|---|---|---|---|---|
| Model | 1313.02 | 2 | 656.51 | 9.43 | 0.0050 | Significant |
| A: Contact time | 870.18 | 1 | 870.18 | 12.50 | 0.0054 | |
| B: Metal oxide load | 442.84 | 1 | 442.84 | 6.36 | 0.0303 | |
| Residual | 696.31 | 10 | 69.63 | | | |
| Lack of Fit | 969.31 | 6 | 116.05 | | | |
| Pure error | 0.0000 | 4 | 0.0000 | | | |
| Cor Total | 2009.33 | 12 | | | | |

**Table 5:** Analysis of variance (ANOVA) results for the response linear models.

| Parameter | Adsorption | Photocatalysis |
|---|---|---|
| Standard deviation | 9.95 | 8.34 |
| Mean | 68.57 | 56.88 |
| Coefficient of variance (CV,%) | 14.51 | 14.67 |
| Coefficient of determination ($R^2$) | 0.6323 | 0.6535 |
| Adjusted $R^2$ | 0.5588 | 0.5842 |
| Predicted $R^2$ | 0.2531 | 0.3278 |
| Adequate precision | 8.58 | 8.92 |

***Effect of Parameters on the Removal Efficiency***

The effects of the studied operating variables for the adsorption and photocatalysis processes on the removal of methylene blue are presented by the 3D response surfaces in Figure 1. It was observed that the percentage of dye removal increased with increasing adsorbent/catalyst and contact time for both treatment methods. The response surface plots of adsorption removal efficiency and photocatalytic degradation efficiency as a function of $AlFe_3O_4$ concentration and contact time are displayed in Figures 2a and 2b and show that there is synergy between catalyst/adsorbent concentration and contact time as they increase.

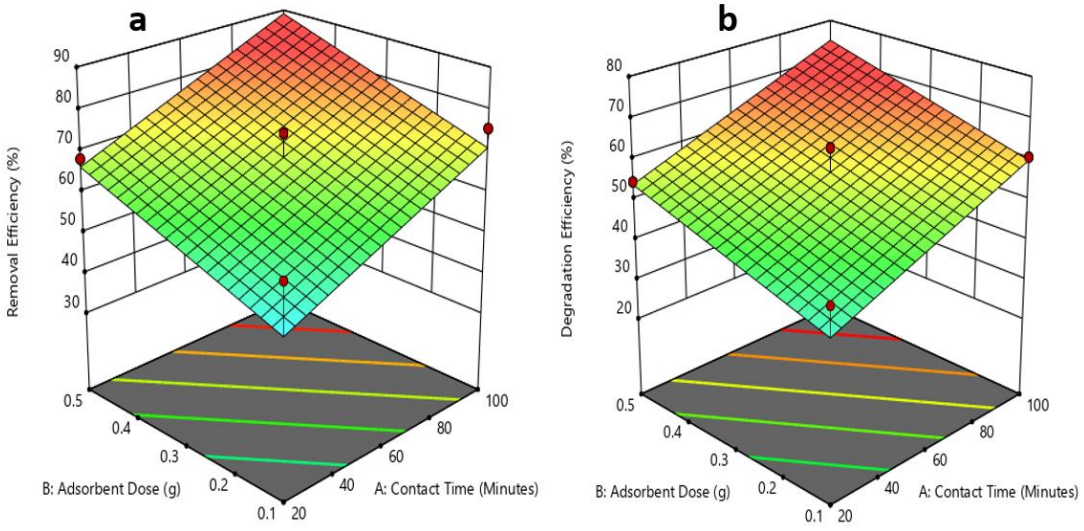


**Figure 2: Response surface 3D plot of metal oxide MB (a) adsorption (b) photocatalysis processes.**

***Numerical Optimization Model***

In order to determine the maximum removal efficiency of MB by $AlFe_3O_4$ through adsorption and photocatalytic processes and optimum conditions, the optimization function of the software was used. The best prediction and conditions for the model were 0.22 g for metal oxide dose at 65.40 min adsorption and degradation processes for contact time, respectively. The proposed maximum removal efficiency of the model was found to be 66.44 % and 55.28 % for adsorption and photocatalysis processes, respectively. The results show that a higher percentage of MB removal cannot be achieved with a low amount of $AlFe_3O_4$ metal oxide and for a short period of time. Chima *et al*. (2023) obtained a similar result on the degradation of MB using CuO-doped $Fe_3O_4$. It could be observed that composite central design via response surface methodology is not a good model for optimization of two experimental variables.

***Kinetic Modeling of the Removal Process***

The Kinetic models can be used as a tool for removal efficiency design and scale-up studies. Kinetic modelling based on pseudo first order and pseudo-second-order rate equations (Eqs 2 and 3), respectively, was plotted for experiments at catalyst/adsorbent dosage (0.2 g) and initial MB concentration (40 mg/L). The rate constants corresponding to pseudo-first-order and pseudo-second-order were obtained from the slope and are displayed in Table 7. The fitting of the adsorption process data to the two models and their corresponding coefficients of determination ($R^2$) show that the kinetics of MB removal on the $AlFe_3O_4$ metal oxide followed a pseudo-first-order kinetic model. The kinetic rate constants were evaluated as $5.63 \times 10^{-3}$ and $1.22 \times 10^{-2}$ $min^{-1}$ for pseudo-first-order and pseudo-second-order, at $R^2$ values of 0.9890 and 0.9865 for the adsorption process, respectively. The photocatalytic degradation

of MB over $AlFe_3O_4$ agreed with the pseudo-second-order kinetic model with a rate constant of 0.0 4.85 x $10^{-2}$ and an $R^2$ value of 0.9289. However, the photocatalytic degradation of MB under a pseudo-first-order kinetic scheme shows a rate constant of 1.04 x $10^{-2}$ with an $R^2$ value of 0.9191.

The pseudo-first-order kinetic mechanism considers the rate of occupation of adsorbent sites to be equal to the number of unoccupied sites (Nleonu et al., 2023b), whereas the pseudo-second-order kinetic mechanism implies that the rate-limiting step is monolayer chemical sorption via photo-induced electron transfer between MB molecules and the aluminium-doped magnetic iron oxide particles (Talebi et al., 2017).

**Table 6:** Pseudo first order and pseudo second order kinetic parameters of methylene blue removal

| Removal Process | Pseudo first order | | Pseudo second order | |
|---|---|---|---|---|
| | **K** | **$R^2$** | **K** | **$R^2$** |
| Adsorption | $5.63 \times 10^{-3}$ | 0.9890 | $1.22 \times 10^{-2}$ | 0.9865 |
| Photocatalysis | $1.04 \times 10^{-2}$ | 0.9191 | $4.85 \times 10^{-2}$ | 0.9289 |

## Conclusion

This study synthesised aluminium-doped magnetic iron oxide through the co-precipitation method as a potential adsorbent and photocatalyst metal oxide for the removal of methylene blue from aqueous solutions. The CCD method of RSM was used to analyse and optimize the process through the operating conditions of adsorbent/catalyst dose and contact time. According to ANOVA, a linear model for adsorptive and photocatalytic processes was used to predict the results of the study. The optimum system conditions for MB removal via adsorption were achieved at MB = 40mg/l, $AlFe_3O_4$ = 0.22 g, and time = 65.40 min with a removal efficiency of 66.44 %, whereas the optimal conditions for photocatalytic degradation of MB in the presence of $AlFe_3O_4$ were found at a catalyst dose of 0.23 g and a contact time of 65.40 min for a degradation efficiency of 55.28 % through numerical optimization. The adsorption removal process and photocatalysis degradation process of MB in the presence of $AlFe3O_4$ followed the pseudo-first-order and pseudo-second-order kinetics models, respectively. Consequently, it can be concluded that the use of CCD via RSM is not viable for optimization and modelling of a system under two experimental variables.

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