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Fabrication of Aluminum-Based Hybrid Nanocomposite for Photocatalytic Degradation of Methylene Blue Dye: A Techno-Economic Approach †

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Abstract: Al_2O_3–MgO nanocomposite was synthesized using the co-precipitation method for photocatalytic degradation of methylene blue (MB) dye under UV–Vis light. Box–Behnken design (BBD) in response to surface methodology (RSM) was used for the optimization and modelling of the photocatalytic degradation of MB dye. An analysis of variance (ANOVA) revealed a quadratic model with an R^2 of 0.9880. MB removal followed the first-order kinetic model (R^2 = 0.9520, k_1 = 0.007 min^{-1}). Economic feasibility study at optimized conditions showed that the wastewater treatment cost is USD 16.50/m^3 and the payback period is 3.17 years.

Keywords: photodegradation mechanism; dye-laden solution; kinetic model; optimum operating condition; running cost

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1. Introduction

Methylene blue (MB) is a highly toxic cationic dye widely used in textile, pharmaceutical and printing industries. Exposure to MB dye results in physiological disorders, leading to acute and chronic illnesses such as vomiting, eye irritation and jaundice [1,2]. The discharge of MB-laden wastewater has detrimental effects on aquatic biota. MB changes the aesthetics of aquatic systems, leading to low sunlight available for photosynthesis, resulting in stunted growth and the death of aquatic plants. MB dye forms complex products in aqueous systems, leading to low dissolved oxygen and the death of aquatic organisms, resulting in a loss of biodiversity in marine ecosystems [2].

MB dye can be removed by conventional wastewater treatment methods such as adsorption, coagulation and phytoremediation [1]. However, the major drawback of conventional systems is the formation of secondary pollutants. Additionally, there is a high cost for the regeneration of adsorbents and disposal of pollutant-laden sludge [3].

Currently, advanced oxidation processes (AOPs) have been adopted for the degradation of organic pollutants by utilizing highly reactive hydroxyl radicals [4]. AOPs such as photocatalysis and photo-Fenton reaction can degrade MB dye into smaller and non-toxic molecules [3]. Due to the high stability and efficiency of TiO_2 and ZnO nano-semiconductors, they are widely used in the photodegradation of organic dyes [4].

Al_2O_3 has high thermal stability, a large surface area and well-defined nanopore structures [5]. It is widely used in sensors, energy storage and pharmaceutical applications [6]. Al_2O_3 has significant optical properties; hence, it can be used as a photocatalyst [5]. Al_2O_3 can be synthesized from abundant waste aluminum cans [7], resulting in lower economic costs in comparison to TiO_2 and ZnO.

Al_2O_3 has a relatively high band gap energy of 5.97 eV [8], and hence a lower photocatalytic activity. Al_2O_3 can be combined with MgO to form a nanocomposite with higher photocatalytic efficiency. MgO has a large surface area and structural defects that allow for the generation of reactive radicals under UV radiation [9]. MgO can form a heterojunction with Al_2O_3 to lower the latter's band gap energy. This leads to an improved photocatalytic degradation efficiency.

This study focuses on the synthesis of Al_2O_3–MgO nanocomposite using co-precipitation for the photodegradation of MB dye. The effect of operating parameters in MB photodegradation is investigated. An economic feasibility analysis is carried out to assess the costs of the photocatalytic degradation of MB using Al_2O_3–MgO.

2. Materials and Methods

2.1. Materials

Aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) was purchased from Qualikems Fine Chem Ltd., Vadodara, Gujarat, India. Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) was purchased from Tekkim, Bursa, Turkey. Methylene blue ($C_{16}H_{18}ClN_3S$, 99%) was bought from Alpha Chemical group, 6th of October, Egypt. Methanol (CH_3OH, 99.8%) and sulfuric acid (H_2SO_4, 97%) were purchased from Piochem, 6th of October, Egypt. Sodium hydroxide pellets (NaOH, 97%) were bought from SD fine Chem Ltd., Mumbai, India.

2.2. Photocatalyst Synthesis

The photocatalyst was prepared via a simple co-precipitation technique [8] as shown in Figure S1. Briefly, 0.2 M $Al(NO_3)_3 \cdot 9H_2O$ was mixed with 0.2 M $MgCl_2 \cdot 6H_2O$, and 1 M NaOH was added dropwise until pH was 11. A white precipitate formed with constant stirring for 30 min. The precipitate was washed with distilled water, filtered, dried for 12 h at 105 °C and finally calcined at 800 °C for 3 h to obtain Al_2O_3–MgO nanocomposite.

2.3. Characterization

The optical band gap energy was measured using a Jasco V-570 UV-DRS spectrophotometer (Tokyo, Japan) in the range of 220–2000 nm. The point of zero charge was determined using the batch equilibrium method [4].

2.4. Experimental Setup

A stock solution of 50 ppm of methylene blue solution was prepared by dissolving 50 mg of methylene blue dye in 1L of distilled water. The required solutions were prepared using the stock solution. Photodegradation of MB dye was carried out in a photoreactor with a 400 W metal halide lamp. The pH of the MB dye solution was adjusted using 1 M NaOH or 1 M H_2SO_4. The experiment was initially run in the dark for 60 min to achieve adsorption–desorption equilibrium. The concentration of MB after adsorption (C_o) was measured at 664 nm using a UV spectrophotometer (Jasco V-630 spectrophotometer (Tokyo, Japan). The light was turned on to initiate photocatalytic degradation. After photodegradation, samples of MB were withdrawn, quenched with methanol and centrifuged at 6000 rpm. The final concentration of MB (C_f) was measured. MB removal was calculated using Equation (1):

$$\text{MB removal} = [(C_o - C_f)/C_o] \times 100 \quad (1)$$

The experimental conditions in Table 1 are derived from BBD in RSM.

2.5. Statistical Analysis

Experimental results were analyzed by response surface methodology (RSM) and one-way ANOVA analysis in Design Expert 13.

Table 1. Experimental factors and limits in BBD.

Factor	Parameter	Unit	Levels		
			Low	Median	High
A	pH	-	3	7	11
B	Time	min	60	120	180
C	Photocatalyst dosage	mg/L	200	600	1000
D	Initial MB dye concentration	ppm	10	55	100

3. Results and Discussion

3.1. Material Characterization

Al_2O_3–MgO was characterized using UV–DRS. Figure 1a shows the plot of absorbance and wavelength for Al_2O_3–MgO. The maximum absorbance of Al_2O_3–MgO was 290 nm.

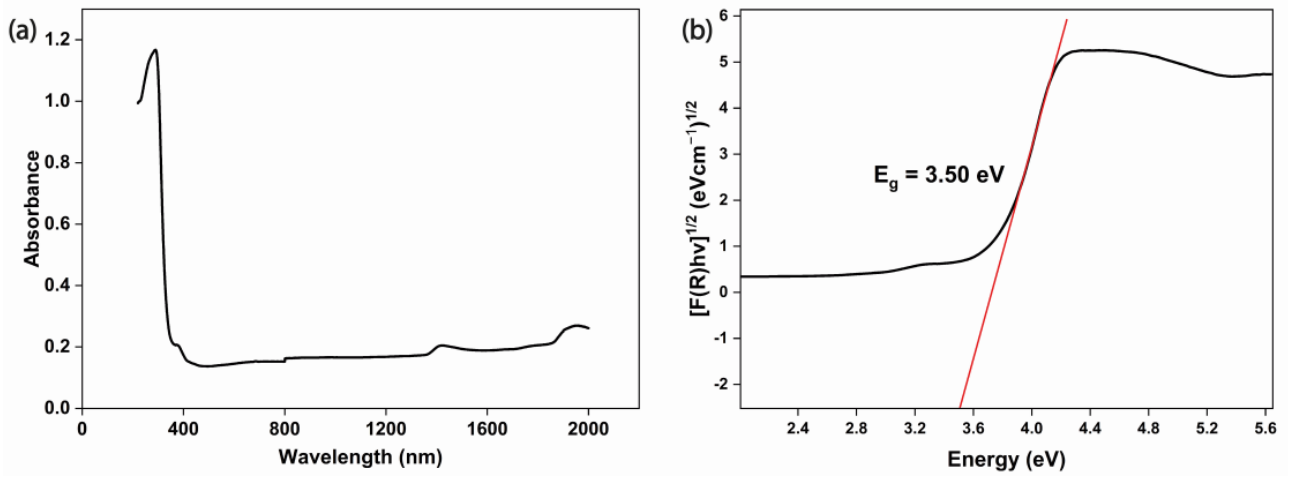

Figure 1. UV–DRS: (**a**) absorbance and (**b**) Kubelka–Munk plots for Al_2O_3–MgO.

The band gap of Al_2O_3–MgO was calculated from the Kubelka–Munk function, [F(R)], using the Tauc equation as shown in Equation (2) [10]:

$$[F(R)hv]^{(1/\gamma)} = B(hv - E_g) \quad (2)$$

where h is Planck's constant, v is the frequency of the photon, B is constant and E_g is the band gap energy of Al_2O_3–MgO; γ is equal to 2 for indirect band gap transition [10]. From the Kubelka–Munk plot in Figure 1a, the E_g for Al_2O_3–MgO is 3.50 eV. The E_g for pure Al_2O_3 is reported to be 5.97 eV [8]. Al_2O_3–MgO has a lower E_g than pure Al_2O_3 due to the presence of defects and heterojunction in the Al_2O_3–MgO nanocomposite [6,11].

3.2. Initial Photocatalyst Tests and Effect of Operational Parameters

Figure 2a shows the photodegradation tests of 11 ppm MB dye with pH, time and photocatalyst dosage as 7, 180 min and 500 mg/L, respectively. Pure Al_2O_3 has a photodegradation efficiency of 43.57%, whereas Al_2O_3–MgO has 72.72%. Al_2O_3–MgO has a lower band gap energy than Al_2O_3 and hence a higher photocatalytic activity.

The effect of pH is shown in Figure 2b. As pH increased from 3 to 11, MB removal increased from 0% to 57%. In acidic pH, MB exists as a neutral molecule below its pKa value of 3.8 [12]. The point of zero charge (pH_{zc}) of Al_2O_3–MgO is 10.04, as shown in Figure S2. In acidic conditions, the surface of Al_2O_3–MgO is positively charged and MB molecules have low adsorption on the catalyst surface, leading to a low photodegradation efficiency. MB dye exists as cations above the pKa value. As the pH approaches the pH_{zc}, the repulsive force against MB cations is reduced [13]. In alkaline conditions, above the pH_{zc}, the surface

of Al_2O_3–MgO is negatively charged and attracts the MB cations. This leads to an uptake of photogenerated holes and electrons, leading to higher photodegradation efficiency.

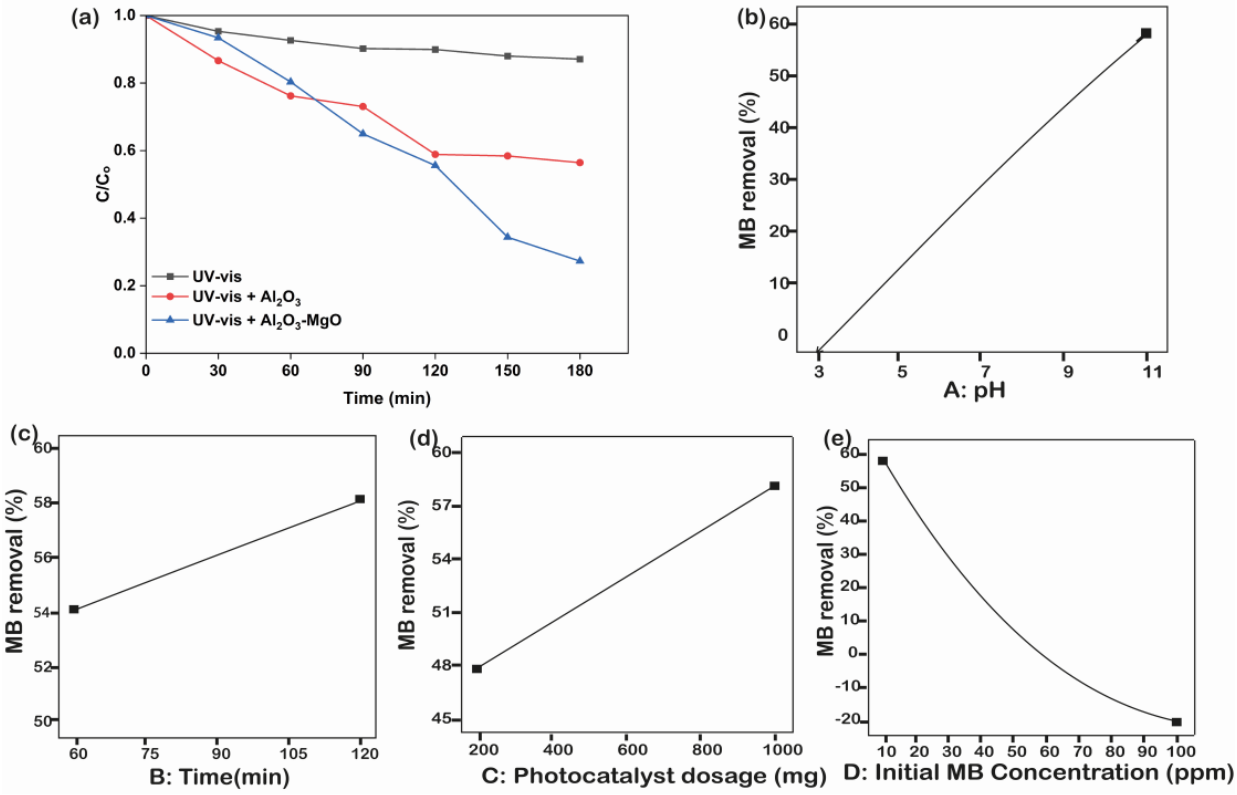

Figure 2. (**a**) Initial photocatalyst test; effect of (**b**) pH; (**c**) time; (**d**) photocatalyst dosage; (**e**) initial MB dye concentration on MB photodegradation.

Figure 2c shows the effect of time on the photodegradation of MB dye. MB removal increased from 54% at 60 min to 58% at 180 min. At constant photocatalyst dosage, more electrons and holes are generated by Al_2O_3–MgO as irradiation time increases. This leads to the production of more reactive radical species, leading to an increment in the photocatalytic degradation efficiency [14].

The effect of photocatalyst dosage is shown in Figure 2d. MB removal increased from 48% at 200 mg/L to 58% at 1000 mg/L. An increasing Al_2O_3–MgO dosage leads to the generation of more active sites and subsequently leads to a higher photodegradation efficiency for MB degradation [11]. However, a high Al_2O_3–MgO dosage causes agglomeration of particles. This results in low photon uptake by Al_2O_3–MgO and a low generation of electrons and holes, and hence, a decrease in MB photodegradation efficiency [15].

The effect of the initial MB dye concentration is shown in Figure 2e. MB removal was reduced from 57% to 0% as the initial MB dye increased from 10 to 100 ppm. As the concentration of MB dye increases, more MB molecules are adsorbed on the surface of Al_2O_3–MgO. This limits the influx of photons on the photocatalyst surface, resulting in a low generation of electrons and holes [11]. At constant Al_2O_3–MgO dosage and light radiation, the number of reactive radicals generated is insufficient for MB photodegradation. Intermediates will also compete with the parent MB molecule for radicals, leading to a lower photodegradation efficiency.

Figure S3 shows the 3D contour plots for the interaction of parameters. Each parameter contributes to achieving MB photodegradation.

3.3. Optimization of Operational Factors3.4. Model Validation and Kinetics

The operating factors can be adjusted by the following equation:

$$(\text{MB removal} + 22.5)^{0.81} = 12.63 + 1.56A - 0.9753B + 0.4529C - 5.39D + 1.97AB + 0.3677AC - 10.15AD - 14.3BD - 1.01CD - 1.38A^2 - 0.0321B^2 - 0.0093C^2 + 4.86D^2 \quad (3)$$

3.4. Model Validation and Kinetics

The optimized conditions of pH, time, photocatalyst dosage and initial MB concentration were 11, 115.6 min, 996.846 mg/L and 10 ppm, respectively, resulting in an MB dye removal of 57.82%, as shown in Figure S4a. The verification experiment at optimized conditions revealed that MB removal was 59.20%, as shown in Figure S4b, with an error of 1.68%. The photodegradation of MB dye with Al_2O_3–MgO followed first-order kinetics with an R^2 of 0.9520 and a k_1 of 0.007 min^{-1}, as shown in Figure S5.

3.5. Suggested Removal Mechanism

The mechanism for MB degradation by Al_2O_3–MgO is shown in Figure S6. It is assumed that MB degradation is due to the attack of generated hydroxyl (OH•) and superoxide (O_{2-}•) radicals. The radicals are generated when photons of light are incident on Al_2O_3–MgO, leading to the excitation of electrons from the valence band (VB) to the conductance band (CB). This leads to the generation of holes (h^+_{VB}) and electrons (e^-_{CB}). Hydroxyl ions from the water will then react with the holes to produce OH•. Oxygen present in the MB solution reacts with electrons to produce O_{2-}•. The radicals will react with MB dye molecules, resulting in degradation products, carbon dioxide and water. Equations (4)–(8) summarize the degradation mechanism [10,12]:

$$Al_2O_3\text{-MgO} + hv\ (\text{Vis region}) \rightarrow Al_2O_3\text{-MgO}\ (e_{cb}^- + h_{vb}^+) \quad (4)$$

$$h_{vb}^+ + H_2O(OH\text{-}) \rightarrow OH\bullet + H^+ \quad (5)$$

$$e_{cb}^- + O_2 \rightarrow O_2^-\bullet \quad (6)$$

$$O_2^-\bullet + MB \rightarrow \text{degradation products} + CO_2 + H_2O \quad (7)$$

$$OH\bullet + MB \rightarrow \text{degradation products} + CO_2 + H_2O \quad (8)$$

3.6. Economic Evaluation

An economic evaluation for the synthesis of Al_2O_3–MgO and its application in the photodegradation of MB dye was conducted. The textile wastewater treatment plant was assumed to be treating 80 m^3 of wastewater per day under optimized conditions. The annual operating time was 300 days. Table S2 summarizes the economic evaluation. The amortization cost (A) was calculated using Equation S5 [15] for a period of 25 years at an interest rate of 6% per annum and was found to be USD 365,765.78. The annual cost (AC) of treating textile wastewater cost per m^3 was evaluated using Equation (S6). For 300 working days, the AC was USD 16.50/m^3. The revenue generated from selling the Al_2O_3–MgO nanocomposite was calculated as USD 3.25 for treating 1 m^3 of wastewater. The estimated cost after wastewater reuse and pollution reduction was USD 0.46/m^3 and USD 0.16/m^3, respectively. The payback period was 3.17 years, as shown in text S1.

3.7. Conclusions

An Al_2O_3–MgO nanocomposite was prepared using the co-precipitation method. UV–DRS analysis showed that the band gap energy was 3.50 eV. Al_2O_3–MgO nanocomposite was used in the photocatalytic degradation of MB dye. The effect of operating parameters was investigated using RSM. The RSM model had an R^2 of 0.9880, indicating a good

prediction of MB removal. MB photocatalytic degradation using Al_2O_3–MgO followed first-order kinetics. Economic estimation revealed that the wastewater treatment cost was USD 16.50/m^3 with a payback period of 3.17 years.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ECP2023-14638/s1. Figure S1: Synthesis of Al_2O_3–MgO; Figure S2: pH_{zc} of Al_2O_3–MgO; Figure S3: Three-dimensional contour plots for the interaction of parameters; Table S1: ANOVA analysis for quadratic model MB photodegradation; Figure S4: Optimized conditions and the result of validation experiment; Equations (S1)–(S4): zero-, half-, first- and second-order kinetic models; Figure S5: Kinetic models for (a) zero order, (b), half order, (c) first order, (d) second-order; Figure S6: Mechanism of photocatalytic degradation of MB dye by Al_2O_3–MgO; Table S2: CAPEX and OPEX; Equation (S5): Amortization cost; Equation (S6): Annual cost; Equation (S7): payback period.

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