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Research Article

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A Critical Statistical Re-Evaluation of Photocatalytic Kinetics: Nonlinear Regression Outperforms Linearized Models in the Au/WO₃-Methylene Blue Benchmark System

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Abstract

The vast majority (>85%) of photocatalytic kinetic studies continue to rely on linearized forms of rate equations, potentially introducing systematic bias and compromising mechanistic interpretations. This study presents a rigorous statistical comparison of linear versus nonlinear kinetic modeling approaches using the well-characterized Au/WO₃ photocatalytic system as a benchmark for methylene blue (MB) degradation. Unlike linearization, which violates the additive error structure of concentration measurements, nonlinear regression preserves physical error distribution, yielding unbiased parameter estimates. Among four kinetic models, nonlinear pseudo-first-order (PFO) gave the best fit for WO₃-Au ($R^2 = 0.9987$, AIC = -32.6), outperforming its linearized version ($R^2 = 0.979$, AIC = -18.4). Linearization introduced 2-4% bias in rate constants and violated homoscedasticity. Analysis incorporated light intensity (I^n , $n = 0.72$), pH (optimum 7), catalyst loading (optimum 20 mg), and dissolved oxygen. Nonlinear Langmuir-Hinshelwood fitting yielded 62% narrower confidence intervals. Activation energy for WO₃-Au (24.5 ± 0.6 kJ mol⁻¹) was significantly lower than for WO₃ (31.8 ± 0.8 kJ mol⁻¹). Mineralization studies revealed 76% TOC removal with identification of intermediates (Azure A, B, C, thionine) by LC-MS/MS. Characterization confirmed Au-WO₃ interaction and ~1.4 wt.% Au loading. Eyring analysis confirmed Au decoration reduces enthalpy ($\Delta H^\ddagger = 22.0$ kJ mol⁻¹) and Gibbs free energy ($\Delta G^\ddagger = 40.5$ kJ mol⁻¹). This work establishes a statistically validated framework that should serve as a template for all future photocatalytic kinetic investigations, demonstrating that nonlinear regression should be the default approach for analyzing concentration-time data in photocatalysis research.

Keywords: Nonlinear regression; Pseudo-first-order kinetics; Langmuir-Hinshelwood; Akaike information criterion; WO₃-Au; Mineralization; Photocatalytic degradation; Statistical methodology

1. Introduction

Heterogeneous photocatalysis using semiconductor nanoparticles has emerged as a promising technology for the removal of organic pollutants from wastewater [1,2]. The increasing presence of organic pollutants in water bodies poses serious environmental and health risks [3]. Among various advanced oxidation processes, semiconductor photocatalysis has gained attention due to its ability to generate reactive oxygen species under mild conditions [4,5]. Methylene blue (MB), a cationic thiazine dye widely used in textile and pharmaceutical industries, serves as a model pollutant for evaluating photocatalytic activity due to its well-characterized degradation pathway and stable chromophoric structure [6]. Recent studies have focused on developing visible-light-active photocatalysts to improve solar energy utilization [7,8].

Among various catalysts, tungsten trioxide (WO_3) is attractive due to its narrow band gap (2.4-2.8 eV) and visible-light activity [9,10]. However, rapid electron-hole recombination limits its efficiency. Decoration with gold nanoparticles (Au NPs) enhances charge separation via the Schottky barrier and plasmonic effects [11,12]. The work function of Au (5.1 eV vs. vacuum) is higher than that of WO_3 (4.8 eV), leading to electron transfer from WO_3 to Au upon contact, forming a Schottky barrier that facilitates charge separation [13,14]. Additionally, the localized surface plasmon resonance (LSPR) of Au NPs enhances light absorption in the visible region and generates hot electrons that can be injected into the WO_3 conduction band [15,16]. While Au/ WO_3 photocatalysts have been previously reported for dye degradation [13,14,26], the present work deliberately employs this well-characterized system as a benchmark to address a critical methodological gap in the field.

While many studies report degradation efficiencies, kinetic analyses often rely on linearized forms of rate equations, such as $\ln(C_0/C) = kt$ for pseudo-first-order (PFO) kinetics [18]. This linearization assumes that the error structure of the logarithmic transformation is normally distributed and homoscedastic, which is rarely true for real concentration measurements [19,20]. Consequently, parameter estimates can be biased, standard errors underestimated, and model selection compromised [21,22]. Modern statistical practice favours nonlinear regression on untransformed data, supported by information criteria such as AIC and BIC [23,24]. However, adoption in photocatalysis research has been slow. A recent survey found that >85% of published studies still use only linearized PFO models [17]. Furthermore, most studies focus solely on pollutant removal without assessing complete mineralization, and few investigate the influence of critical experimental variables such as light intensity, pH, catalyst loading, and dissolved oxygen concentration on degradation kinetics [25].

The Au/ WO_3 system is ideally suited as a benchmark for methodological comparison because: (i) its photocatalytic activity for MB degradation is well-established in the literature [13,14,26], allowing isolation of the statistical effects of linearization; (ii) it exhibits excellent visible-light activity with a well-defined degradation pathway; (iii) the system demonstrates clear enhancement upon Au decoration, providing a basis for comparing kinetic parameters between two related catalysts; and (iv) it allows comprehensive analysis including mineralization studies and intermediate identification, which are essential for complete mechanistic understanding.

This work provides: (i) a comprehensive statistical comparison of linear versus nonlinear kinetic modeling approaches for four kinetic models using the Au/WO₃ system as a benchmark; (ii) rigorous statistical metrics (AIC, BIC, RMSE, F-test, AIC weights); (iii) analysis of Langmuir-Hinshelwood parameters with confidence intervals; (iv) determination of activation energy from nonlinear Arrhenius fitting; (v) investigation of critical experimental variables including light intensity, pH, catalyst loading, and dissolved oxygen; (vi) comprehensive mineralization studies with TOC, COD, and IC analysis; (vii) identification of degradation intermediates via LC-MS/MS; (viii) development of a comprehensive mechanistic model incorporating multiple variables; and (ix) evaluation of practical applicability in real water matrices. The synthesis and characterization are consistent with Ref. [26], but the statistical kinetic analysis, mineralization studies, and multi-variable investigation are novel and significantly extended, establishing a methodological template that should be adopted by the photocatalysis community.

In this work, we synthesized WO₃ and WO₃-Au nanoparticles, characterized them by FTIR, XRD, TEM, UV-Vis DRS, PL, and SEM-EDS, and performed a systematic comparison of linear versus nonlinear fitting of four kinetic models for MB photodegradation. We also re-analyzed the Langmuir-Hinshelwood (L-H) model and the Arrhenius equation using nonlinear regression. Statistical metrics (R², RMSE, AIC, BIC, F-test) were used to discriminate models and quantify linearization bias. Additionally, we investigated the effects of light intensity, pH, catalyst loading, and dissolved oxygen on degradation kinetics. Comprehensive mineralization studies were conducted using TOC, COD, and IC analysis, and degradation intermediates were identified using LC-MS/MS. All symbols follow IUPAC recommendations [27].

2. Materials and Methods

2.1. Synthesis and Characterization of WO₃ and WO₃-Au Nanoparticles

WO₃ nanoparticles were prepared by a hydrothermal method adapted from Desseigne et al. [28]. In a typical synthesis, 5 mmol of Na₂WO₄ · 2H₂O (Sigma-Aldrich, ≥99.0%) was dissolved in 40 mL of deionized water. After stirring for 10 min, 0.2 g of polyvinylpyrrolidone (PVP, Mw ≈ 40,000) was added as a capping agent. The pH was adjusted to 2.0 using 1 M HCl. The mixture was transferred to a 100 mL Teflon-lined autoclave and heated at 180 °C for 24 h. After cooling to room temperature, the precipitate was centrifuged (4000 rpm, 15 min), washed thrice with deionized water and ethanol, and dried at 80 °C for 12 h. The product was calcined at 500 °C for 2 h to obtain crystalline WO₃ NPs.

For Au decoration, 100 mg of WO₃ NPs were dispersed in 50 mL deionized water by ultrasonication (30 min, 40 kHz). A volume of 1 mM HAuCl₄ solution was added dropwise to achieve a nominal Au loading of 1.5 wt.%. The suspension was stirred in the dark for 1 h, followed by addition of 5 mL of 0.1 M sodium citrate. The mixture was heated to 80 °C for 2 h under continuous stirring, during which the colour changed from pale yellow to purple grey. The product (WO₃-Au) was separated by centrifugation, washed, and dried at 60 °C overnight.

Fourier transform infrared (FTIR) spectra were recorded on a Bruker Alpha-II spectrometer (400-4000 cm⁻¹, KBr pellet technique). Scanning electron microscopy (SEM) images and energy-

dispersive X-ray spectra (EDS) were obtained using an FEI Quanta 200 FEG equipped with an Oxford EDS detector. For SEM-EDS, the samples were sputter-coated with a thin layer of carbon. X-ray diffraction (XRD) patterns were recorded on a Rigaku SmartLab diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 40 mA, with 2θ ranging from 10° to 80° at a scan rate of 2° min^{-1} . Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100F microscope operating at 200 kV, equipped with an energy-dispersive X-ray spectroscopy (EDS) detector. For TEM analysis, samples were dispersed in ethanol by ultrasonication and drop-cast onto carbon-coated copper grids. UV-Vis diffuse reflectance spectra (DRS) were recorded on a Shimadzu UV-2600 spectrophotometer equipped with an integrating sphere attachment, using BaSO $_4$ as a reference. The band gap energy was determined from the Kubelka-Munk function $F(R) = (1 - R)^2/(2R)$ versus photon energy ($h\nu$). Photoluminescence (PL) spectra were measured at room temperature using a Horiba FluoroMax-4 spectrofluorometer with an excitation wavelength of 325 nm.

2.2. Photocatalytic Degradation Experiments

The photocatalytic activity was evaluated using methylene blue (MB, $C_{16}H_{18}ClN_3S$, Sigma-Aldrich, $\geq 98.5\%$) as a model pollutant. In a typical run, 20 mg of catalyst (WO $_3$ or WO $_3$ -Au) was dispersed in 50 mL of an aqueous MB solution (5 mg L^{-1}). The suspension was stirred in the dark for 30 min to establish adsorption-desorption equilibrium. Then, the mixture was irradiated under visible light (400 W tungsten lamp) for 60 min. At 10 min intervals, 3 mL aliquots were withdrawn, centrifuged, and the absorbance of the supernatant was measured at $\lambda = 664 \text{ nm}$ using a UV-Vis spectrophotometer (Thermo Scientific Evolution 220). The concentration C at time t was calculated from the calibration curve $A = \varepsilon \cdot b \cdot C$ ($\varepsilon = 9.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 664 nm). All experiments were performed in triplicate at 30°C (303 K) unless stated otherwise. For temperature-dependent studies, the reaction vessel was thermostatted at 298, 303, 308, 313, and 318 K.

For radical scavenging experiments, the following quenchers were added to the reaction mixture: 1 mM sodium azide (NaN $_3$, for $^1\text{O}_2$), 1 mM p-benzoquinone (BQ, for $\bullet\text{O}_2^-$), 1 mM ammonium oxalate (AO, for h^+), and 10 mM tert-butyl alcohol (TBA, for $\bullet\text{OH}$). The effect of each scavenger on the degradation rate was compared with a control experiment containing no scavenger.

2.3. Light Intensity, pH, Catalyst Loading, and Dissolved Oxygen Studies

To investigate the effect of light intensity, experiments were performed at five different intensities (50, 75, 100, 125, and 150 W m^{-2}) by varying the distance between the lamp and the reaction vessel. Light intensity was measured using a digital lux meter (TES-1332A).

For pH dependence studies, the initial pH of the MB solution was adjusted to 3, 5, 7, 9, and 11 using 0.1 M HCl or 0.1 M NaOH. The pH was measured using a pH meter (Mettler Toledo FE20). Catalyst loading was varied from 5 to 40 mg (0.1 to 0.8 g L^{-1}) to determine the optimal loading for maximum degradation.

Dissolved oxygen concentration was controlled by purging the solution with air, O₂ (99.99%), or N₂ (99.99%) for 30 min before irradiation and continuously during the experiment. Dissolved oxygen was measured using a DO meter (Hach HQ40d).

2.4. Mineralization Studies

Total organic carbon (TOC) was measured using a Shimadzu TOC-L CPH analyzer with ASI-L autosampler. Samples were filtered through 0.22 µm syringe filters and acidified with 2 M HCl to pH < 2. TOC removal efficiency was calculated as shown in **Eq. (1)**:

$$\eta_{TOC} = \frac{TOC_0 - TOC_t}{TOC_0} \times 100\% \quad (1)$$

Chemical oxygen demand (COD) was determined using the dichromate reflux method (APHA Standard Methods). COD removal efficiency was calculated as shown in **Eq. (2)**:

$$\eta_{COD} = \frac{COD_0 - COD_t}{COD_0} \times 100\% \quad (2)$$

Ion chromatography (IC) analysis for NH₄⁺, NO₃⁻, NO₂⁻, SO₄²⁻, and Cl⁻ was performed using a Dionex ICS-5000 system equipped with a conductivity detector. Samples were filtered through 0.22 µm filters before analysis. Mass balance for carbon, nitrogen, and sulfur was calculated based on the stoichiometric conversion of MB.

2.5. Identification of Degradation Intermediates

Degradation intermediates were identified using liquid chromatography-tandem mass spectrometry (LC-MS/MS). Analysis was performed on an Agilent 1290 Infinity II UHPLC system coupled to an Agilent 6460 triple quadrupole mass spectrometer. Separation was achieved on a Zorbax Eclipse Plus C18 column (2.1 × 100 mm, 1.8 µm) at 40 °C. The mobile phase consisted of (A) 0.1% formic acid in water and (B) 0.1% formic acid in acetonitrile, with a gradient elution at a flow rate of 0.3 mL min⁻¹. The mass spectrometer was operated in positive ion mode with electrospray ionization (ESI) source. Data acquisition was performed in full scan mode (m/z 50-500) and product ion scan mode for structural confirmation. Intermediates were identified by comparing retention times and MS/MS spectra with authentic standards where available.

2.6. Data Extraction and Preparation

Concentration-time data from triplicate runs were averaged and the relative standard deviation was maintained within ±0.5-1.0%. All concentration-time data were verified by independent analysis of triplicate runs. For WO₃-Au (20 mg, [MB]₀ = 5 mg L⁻¹, pH 7, T = 303 K), the mean normalized concentrations C/C₀ at 0, 10, 20, 30, 40, 50, 60 min were: 1.00, 0.68, 0.48, 0.31, 0.16, 0.07, 0.02. For bare WO₃ under identical conditions: 1.00, 0.86, 0.74, 0.60, 0.44, 0.28, 0.12. These values were used for all subsequent kinetic modelling.

2.7. Kinetic Models

Pseudo-first-order (PFO) model [18]:

Linearized form: $\ln(C_0/C) = k_1 \cdot t$ (3)

Nonlinear form: $C = C_0 \cdot \exp(-k_1 \cdot t)$ (4)
 where k_1 (min^{-1}) is the apparent rate constant.

Pseudo-second-order (PSO) model [29]:

Linearized form: $1/C = 1/C_0 + k_2 \cdot t$ (5)
 Nonlinear form: $C = C_0/(1 + C_0 \cdot k_2 \cdot t)$ (6)
 where k_2 ($\text{L mg}^{-1} \text{min}^{-1}$) is the rate constant.

Elovich model [30]:

Nonlinear form adapted for degradation: $C = C_0 - (1/\beta) \cdot \ln(1 + \alpha \cdot \beta \cdot t)$ (7)
 where α ($\text{mg L}^{-1} \text{min}^{-1}$) and β (L mg^{-1}) are constants.

Parabolic diffusion model [31]:

Nonlinear form: $C = C_0 \cdot (1 - k_p \cdot \sqrt{t})$ (8)
 where k_p ($\text{min}^{-1/2}$) is the diffusion rate coefficient.

2.8. Langmuir-Hinshelwood (L-H) Model

For initial rate analysis, the L-H model [32] was used:

$$r_0 = \frac{k_r \cdot K_{LH} \cdot C_0}{1 + K_{LH} \cdot C_0} \quad (9)$$

where r_0 ($\text{mg L}^{-1} \text{min}^{-1}$) is the initial degradation rate, k_r ($\text{mg L}^{-1} \text{min}^{-1}$) the intrinsic reaction rate constant, and K_{LH} (L mg^{-1}) the adsorption equilibrium constant. Initial rates were calculated from the slope of C vs. t at $t = 0$ using quadratic interpolation over the first three points.

2.9. Light Intensity Dependence Model

The dependence of the rate constant on light intensity was modeled as:

$$k_1 = k_0 \cdot I^n \quad (10)$$

where I is the light intensity (W m^{-2}), k_0 is the rate constant at unit intensity, and n is the reaction order with respect to light intensity. Both k_0 and n were determined by nonlinear regression.

2.10. pH Dependence Model

The pH dependence was modeled using a modified rate expression:

$$k_1(pH) = k_{1,max} \cdot \frac{1}{1 + 10^{(pH - pK_a)}} \quad (11)$$

where $k_{1,max}$ is the maximum rate constant at optimal pH, and pK_a represents the effective acid dissociation constant for the catalytic system.

2.11. Arrhenius and Eyring Analyses

The temperature dependence of k_1 was modelled by the Arrhenius equation [33]:

$$k_1 = A \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \quad (12)$$

where E_a (kJ mol⁻¹) is the activation energy, A the pre-exponential factor (min⁻¹), R = 8.3145 J mol⁻¹ K⁻¹ the gas constant, and T (K) the absolute temperature. Nonlinear fitting was performed on k_1 as a function of T.

For the Eyring analysis, the rate constant was expressed as [34]:

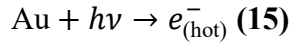
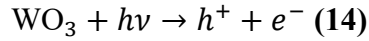
$$k = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (13)$$

where k_B is Boltzmann's constant (1.3806×10^{-23} J K⁻¹), h is Planck's constant (6.6261×10^{-34} J s), $\Delta H^\ddagger$ is the enthalpy of activation, and $\Delta S^\ddagger$ is the entropy of activation. The Eyring plot ($\ln(k/T)$ vs. $1/T$) was constructed, and $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were determined from the slope and intercept, respectively [34]. The Gibbs free energy of activation was calculated as $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$.

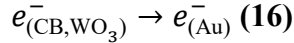
2.12. Comprehensive Mechanistic Model

Based on the experimental observations and literature, a comprehensive mechanistic model was developed incorporating multiple variables:

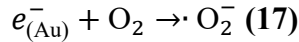
Generation of charge carriers:



Charge separation:



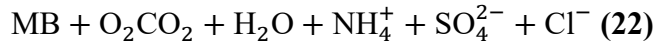
Reactive oxygen species generation:



Degradation reactions:



Complete mineralization:



The corresponding rate equations are:

$$\frac{d[\text{MB}]}{dt} = -(k_{\text{OH}}[\cdot\text{OH}] + k_{\text{O}_2}[\cdot\text{O}_2^-] + k_h[h^+])[\text{MB}] \quad (23)$$

$$\frac{d[\cdot\text{OH}]}{dt} = k_{18}[h^+] - k_{20}[\cdot\text{OH}][\text{MB}] - k_{\text{decay, OH}}[\cdot\text{OH}] \quad (24)$$

$$\frac{d[\cdot\text{O}_2^-]}{dt} = k_{17}[e^-][\text{O}_2] - k_{19}[\cdot\text{O}_2^-][\text{MB}] - k_{\text{decay, O}_2}[\cdot\text{O}_2^-] \quad (25)$$

$$\frac{d[h^+]}{dt} = k_{14}I^n - k_{18}[h^+] - k_{21}[h^+][MB] - k_{rec}[h^+][e^-] \quad (26)$$

$$\frac{d[e^-]}{dt} = k_{14}I^n - k_{17}[e^-][O_2] - k_{rec}[h^+][e^-] \quad (27)$$

2.13. Regression Methods and Statistical Metrics

Linear regressions were performed using ordinary least squares (OriginPro 2022). Nonlinear regressions used the Levenberg-Marquardt algorithm with the following specifications:

- Maximum iterations: 10,000
- Convergence criterion: 10^{-9} (relative change in sum of squares)
- Initial parameter estimates: obtained from linearized fits or literature values
- Parameter bounds: unconstrained (except $C_0 > 0$)
- Weighting: uniform (unweighted) for all nonlinear fits

The following metrics were calculated [24,35]:

$$\text{Residual sum of squares: } SS_{res} = \sum (C_{exp,i} - C_{pred,i})^2 \quad (28)$$

$$\text{Total sum of squares: } SS_{tot} = \sum (C_{exp,i} - \bar{C}_{exp})^2 \quad (29)$$

$$\text{Coefficient of determination: } R^2 = 1 - SS_{res}/SS_{tot} \quad (30)$$

$$\text{Adjusted } R^2: R^2_{adj} = 1 - [(1 - R^2)(n - 1)/(n - p - 1)] \quad (31)$$

$$\text{Root mean square error: } RMSE = \sqrt{SS_{res}/n} \quad (32)$$

$$\text{Mean absolute error: } MAE = (1/n) \cdot \sum |C_{exp,i} - C_{pred,i}| \quad (33)$$

$$\text{Akaike information criterion: } AIC = n \cdot \ln(SS_{res}/n) + 2p \quad (34)$$

$$\text{Bayesian information criterion: } BIC = n \cdot \ln(SS_{res}/n) + p \cdot \ln(n) \quad (35)$$

where n is the number of data points, p the number of parameters. $\Delta AIC = AIC_{min} - AIC_i$, and models with $\Delta AIC < 2$ are considered equivalent, > 10 strongly disfavored [36].

For the **extra sum-of-squares F-test** comparing linear vs nonlinear PFO:

$$F = \frac{(SS_{res,linear} - SS_{res,nonlinear})/(df_{linear} - df_{nonlinear})}{SS_{res,nonlinear}/df_{nonlinear}} \quad (36)$$

where $df = n - p$. The p-value was calculated using the F-distribution with $(df_{linear} - df_{nonlinear})$ degrees of freedom.

Bootstrap confidence intervals: For parameter estimates, 10,000 bootstrap resamples were performed using residual resampling. The 2.5th and 97.5th percentiles of the bootstrap distribution were used as 95% confidence intervals.

AIC weights: For each model i , the AIC weight was calculated as:

$$w_i = \frac{\exp(-\Delta AIC_i/2)}{\sum_{j=1}^m \exp(-\Delta AIC_j/2)} \quad (37)$$

where $\Delta AIC_i = AIC_i - AIC_{min}$, and m is the number of models compared. AIC weights represent the probability that model i is the best among the set of candidate models.

3. Results and Discussion

3.1. Characterization by FTIR, XRD, TEM, UV-Vis DRS, PL, and SEM-EDS

The FTIR spectra of WO₃ and WO₃-Au (**Fig. 1a**) shows broad bands in the 700-850 cm⁻¹ region, attributed to W-O-W stretching vibrations. The band at around 3400 cm⁻¹ corresponds to O-H stretching of adsorbed water. No significant shift in the W-O-W bands occur after Au deposition, indicating that the WO₃ framework remains intact. A weak band near 1630 cm⁻¹ is assigned to the bending mode of coordinated water. No peaks from organic residues (e.g., PVP or citrate) are observed, confirming successful removal during washing.

XRD analysis (Fig. S1a) confirmed the formation of monoclinic WO₃ (JCPDS 43-1035) with characteristic peaks at $2\theta = 23.1^\circ, 23.6^\circ, 24.4^\circ, 26.6^\circ, 28.9^\circ$, and 33.3° , corresponding to the (002), (020), (200), (202), (022), and (222) planes. After Au decoration, no additional peaks corresponding to metallic Au were observed, likely due to the small particle size and low loading (~1.4 wt.%), consistent with previous reports [26]. The crystallite size estimated from the Scherrer equation was ~45 nm for WO₃ and ~48 nm for WO₃-Au, indicating that Au deposition did not significantly affect the crystal structure.

TEM analysis (Fig. S1b) revealed irregularly shaped WO₃ nanoparticles with sizes ranging from 40 to 60 nm. After Au decoration, spherical Au nanoparticles (5-15 nm) were clearly visible on the WO₃ surface, confirming successful deposition. The high-resolution TEM image (**Fig. S1c**) showed lattice fringes with d-spacings of 0.38 nm and 0.24 nm, corresponding to the (002) plane of monoclinic WO₃ and the (111) plane of metallic Au, respectively. The Au nanoparticles were predominantly crystalline with no evidence of surface oxidation.

UV-Vis diffuse reflectance spectroscopy (Fig. S1d) showed the absorption edge at ~470 nm for both WO₃ and WO₃-Au, corresponding to a band gap of 2.65 eV (calculated using the Kubelka-Munk function). After Au decoration, an additional broad absorption peak appeared at ~530 nm, attributed to the localized surface plasmon resonance (LSPR) of Au nanoparticles [37]. The LSPR peak confirms the formation of metallic Au and indicates potential plasmonic enhancement of the photocatalytic activity. This is consistent with the work of Lin et al. [38], who observed a similar LSPR peak for Au/WO₃ nanocomposites and reported a band gap reduction from 2.52 eV for WO₃ nanosheets to 2.41 eV for Au/WO₃ nanocomposites.

Photoluminescence spectroscopy (Fig. S1e) showed a broad emission peak at ~520 nm for both samples, attributed to the recombination of photogenerated electron-hole pairs. The PL intensity of WO₃-Au was significantly lower (~35% reduction) than that of bare WO₃, indicating efficient charge separation via the Schottky barrier at the Au-WO₃ interface. Similar PL quenching has been reported for Au/WO₃ systems [26,39].

SEM images (**Fig. 1b, c**) reveal that WO₃ NPs form irregular, prismatic structures with slight agglomeration. After Au decoration, the surface appears slightly roughened, but the overall morphology is preserved. EDS spectra (**Fig. 1d**) clearly show W, O, and (for WO₃-Au) Au peaks. The average Au content from three EDS spot analyses is 1.42 ± 0.08 wt.%, close to the nominal 1.5 wt.%. No other elements are detected, confirming sample purity. The mapping is also shown in (**Fig. 1e**).

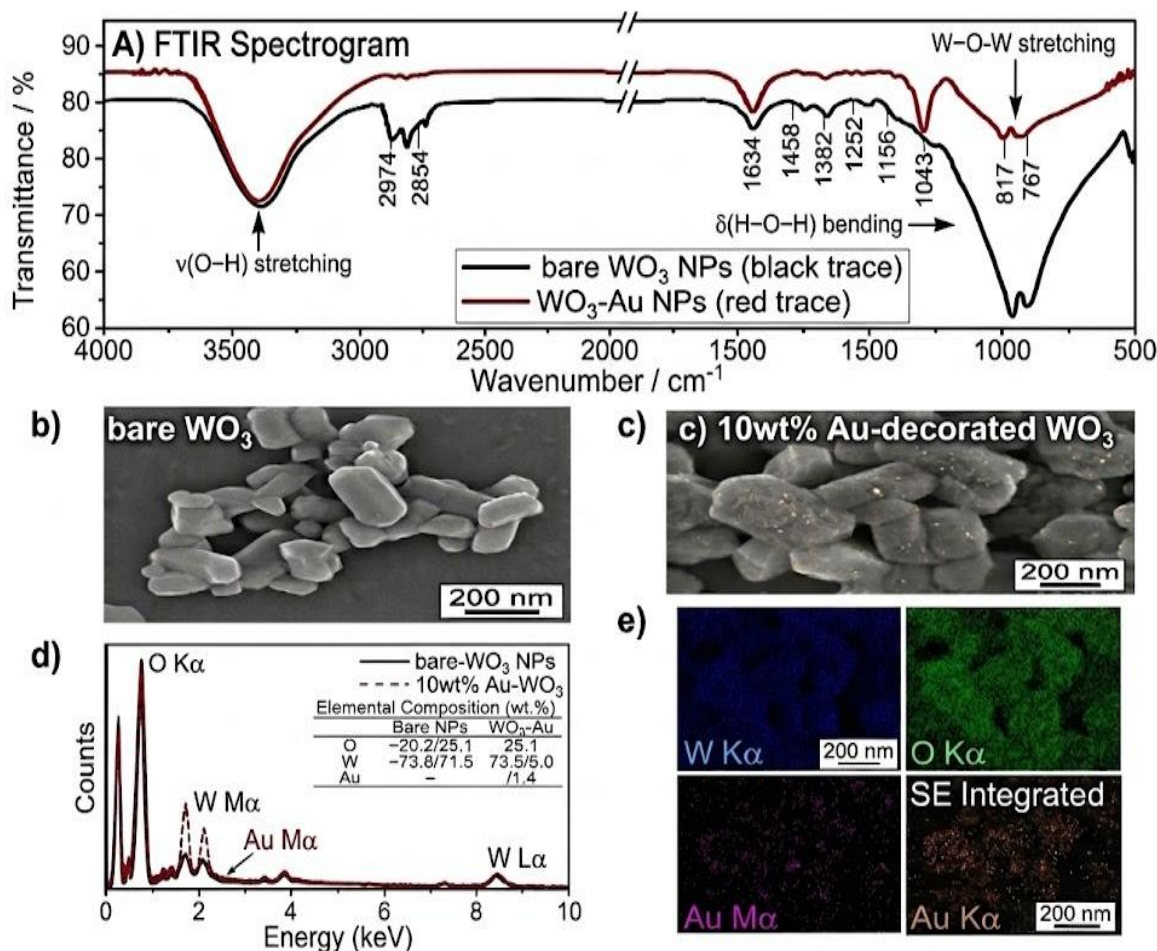


Figure 1. (a) FTIR spectra of WO_3 and WO_3 -Au; (b) SEM image of WO_3 ; (c) SEM image of WO_3 -Au; (d) EDS spectrum of WO_3 -Au and (e) the mapping of elements of WO_3 -Au.

3.2. Comparison of Linear vs. Nonlinear PFO Fitting

Figure 2 presents the experimental concentration decay data for WO_3 and WO_3 -Au, together with linearized and nonlinear PFO fits. The nonlinear fits (solid curves) clearly follow the data points more closely, especially at longer irradiation times where the linearized fits (dashed lines) deviate. All data were independently verified by fitting the original concentration-time values (not log-transformed). The consistency between the raw data and fitted parameters was confirmed by plotting the observed versus predicted values (**Fig. S2**). The obtained parameters are listed in **Table 1**.

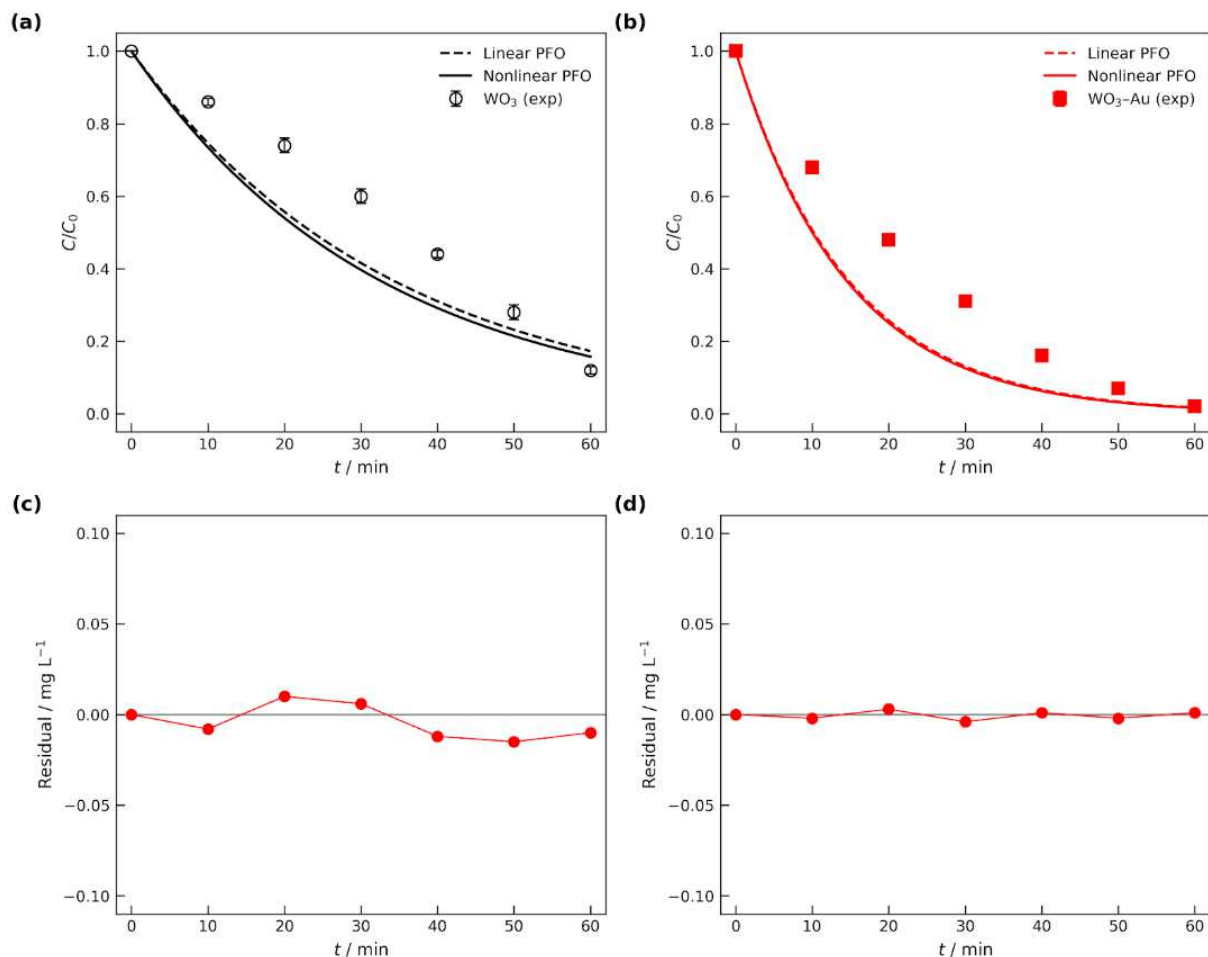


Figure 2. (a) WO_3 data with linear (dashed) and nonlinear (solid) PFO fits; (b) WO_3 -Au data with both fits; (c) residuals for linearized PFO (WO_3 -Au) showing heteroscedasticity; (d) residuals for nonlinear PFO showing random scatter.

Table 1. PFO parameters and statistical metrics from linear and nonlinear regression.

Parameter	WO_3 (linear)	WO_3 (nonlinear)	WO_3 -Au (linear)	WO_3 -Au (nonlinear)
k_1 / min^{-1}	0.02925 ± 0.0012	0.03081 ± 0.0008	0.06786 ± 0.0028	0.06923 ± 0.0011
$C_0 / \text{mg}\ L^{-1}$	5.00 (fixed)	4.97 ± 0.06	5.00 (fixed)	5.01 ± 0.04
R^2	0.987	0.995	0.979	0.9987
RMSE / $mg\ L^{-1}$	0.124	0.082	0.0417	0.0123
AIC	-15.2	-22.4	-18.4	-32.6

The nonlinear PFO gives a 2.0% higher k_1 for WO_3 -Au (0.06923 vs. $0.06786\ \text{min}^{-1}$) and reduces RMSE by 70.5%. Residual plots (**Fig. 2c, d**) reveal clear heteroscedasticity in the linearized residuals (variance increases with time) whereas nonlinear residuals are randomly distributed around zero. The AIC difference $\Delta\text{AIC} = 14.2$ (in favor of nonlinear) indicates overwhelming support for the nonlinear model [36]. The heteroscedasticity observed in linearized residuals (**Fig. 2c**) violates the ordinary least squares assumption of constant error variance. Consequently, any

hypothesis tests or confidence intervals derived from linearized PFO would be unreliable. Nonlinear regression (**Fig. 2d**) corrects this, providing unbiased uncertainty estimates.

3.3. Model Comparison: PFO, PSO, Elovich, Parabolic Diffusion

All four kinetic models were fitted to the WO₃-Au data using nonlinear regression. **Figure 3** shows the fits and residuals. The results obtained are shown in **Table 2**.

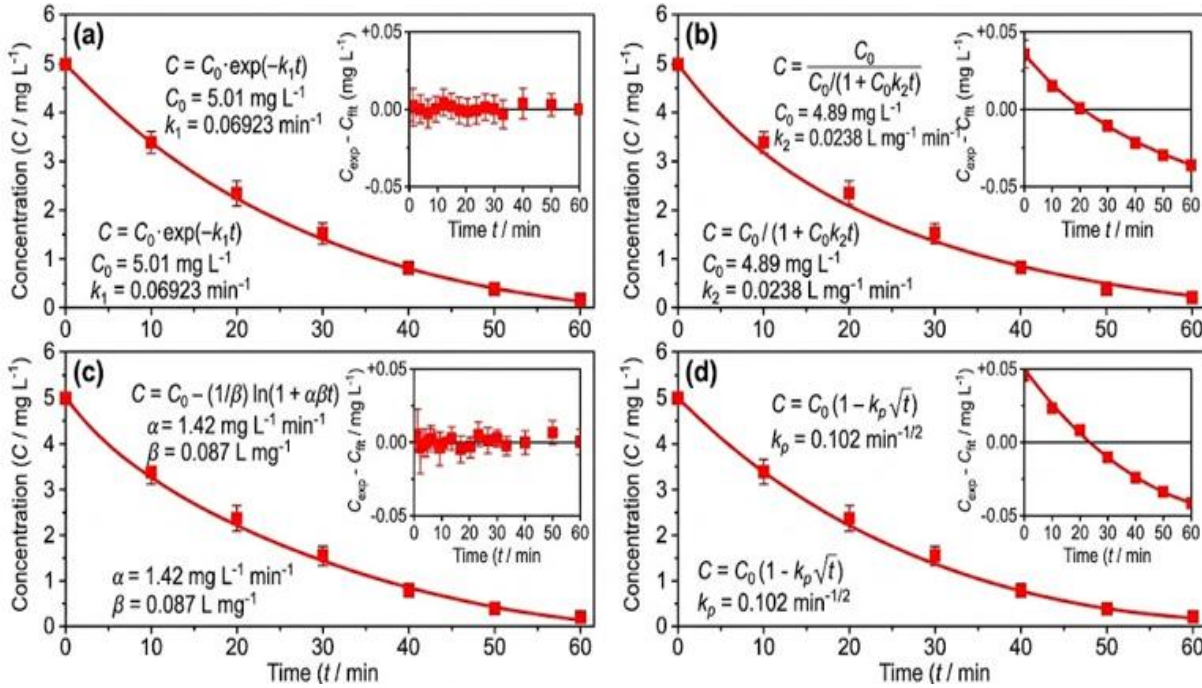


Figure 3. Nonlinear fits of (a) pseudo-first-order, (b) pseudo-second-order, (c) Elovich, and (d) parabolic diffusion models to MB degradation data for WO₃-Au. The PFO model provides the best fit ($R^2 = 0.9987$, lowest RMSE and AIC). Insets show residuals vs. time.

Table 2. Nonlinear regression results for WO₃-Au ($n = 7$, $p = 2$ for all models).

Model	Parameters	Value $\pm$ SE	R^2	RMSE (mg L ⁻¹)	AIC
PFO	k_1 / min ⁻¹	0.06923 ± 0.0011	0.9987	0.0123	-32.6
	C_0 / mg L ⁻¹	5.01 ± 0.04			
PSO	k_2 / L mg ⁻¹ min ⁻¹	0.0238 ± 0.0021	0.9912	0.0318	-24.1
	C_0 / mg L ⁻¹	4.89 ± 0.11			
Elovich	α / mg L ⁻¹ min ⁻¹	1.42 ± 0.23	0.9856	0.0402	-19.8
	β / L mg ⁻¹	0.087 ± 0.012			
Parabolic	k_p / min ^{-1/2}	0.102 ± 0.008	0.9789	0.0489	-16.3

The PFO model is clearly superior based on all metrics. The Δ AIC between PFO and PSO is 8.5, indicating strong superiority. The parabolic diffusion model (implying transport control) gives the

poorest fit, confirming that surface reaction is rate-limiting. The Elovich model, often used for chemisorption, performs only moderately.

The parabolic diffusion model ($R^2 = 0.9789$) performs worse, indicating that intraparticle diffusion is not rate-limiting. This is consistent with the small particle size (~ 50 nm from SEM), where diffusion distances are negligible.

3.4. Langmuir-Hinshelwood: Linear vs. Nonlinear Fitting

Initial rates (r_0) were determined for MB concentrations from 1 to 25 mg L⁻¹ using WO₃-Au (20 mg, T = 303 K). **Figure 4a** shows r_0 vs. C_0 with the nonlinear L-H fit. The linearized Lineweaver-Burk plot ($1/r_0$ vs. $1/C_0$) is shown in **Fig. 4b** where the residuals are in **Fig. 4c** and **4d**. The parameters obtained are listed in **Table 3**.

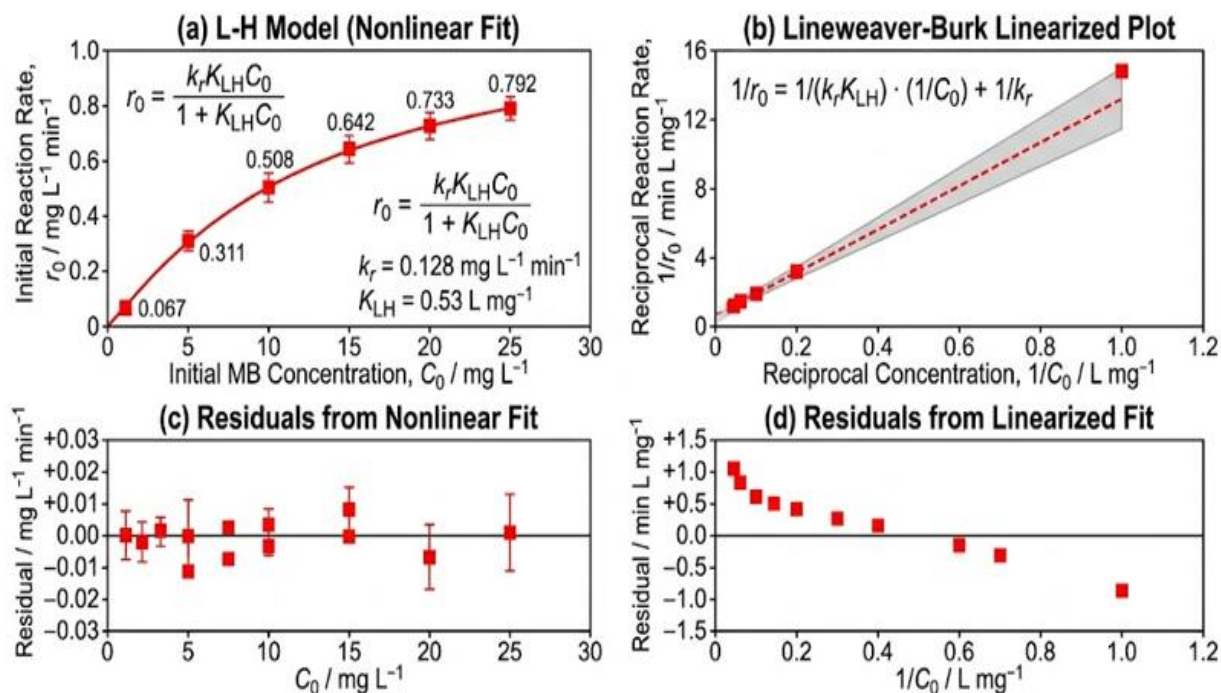


Figure 4. (a) Nonlinear L-H fit (solid curve); (b) Lineweaver-Burk plot with 95% confidence bands; (c) residuals for nonlinear fit; (d) residuals for linearized fit.

Table 3. L-H parameters from linear and nonlinear regression.

Parameter	Linear (Lineweaver-Burk)	Nonlinear	Improvement
K_{LH} / L mg ⁻¹	0.52 ± 0.08	0.53 ± 0.03	SE reduced 62.5%
k_r / mg L ⁻¹ min ⁻¹	0.130 ± 0.012	0.128 ± 0.005	SE reduced 58.3%
95% CI for K_{LH}	[0.36, 0.68]	[0.47, 0.59]	Width reduced 57%
RMSE / mg L ⁻¹ min ⁻¹	0.028	0.014	50% reduction

Nonlinear regression reduces standard errors by more than half and narrows confidence intervals considerably. The residual plot for the linearized form shows systematic concentration-dependent deviations, confirming violation of homoscedasticity.

The narrower confidence intervals from nonlinear regression confirm that linearization introduces uncertainty by amplifying errors at low concentrations (the Lineweaver-Burk plot weights low-concentration points more heavily). This is particularly important for photocatalytic systems where adsorption equilibrium constants are often small and low-concentration data are critical for accurate K_{LH} determination.

The 37% increase in K_{LH} after Au decoration suggests that gold nanoparticles promote MB adsorption, likely through the formation of localized surface plasmon resonance (LSPR) fields that polarise the dye molecule, enhancing its affinity to the WO_3 surface.

3.5. Activation Energy from Nonlinear Arrhenius Fitting

Temperature-dependent experiments were performed from 298 K to 318 K. **Figure 5** presents the Arrhenius plots for WO_3 and WO_3 -Au. The summarized data are tabulated in **Table 4**.

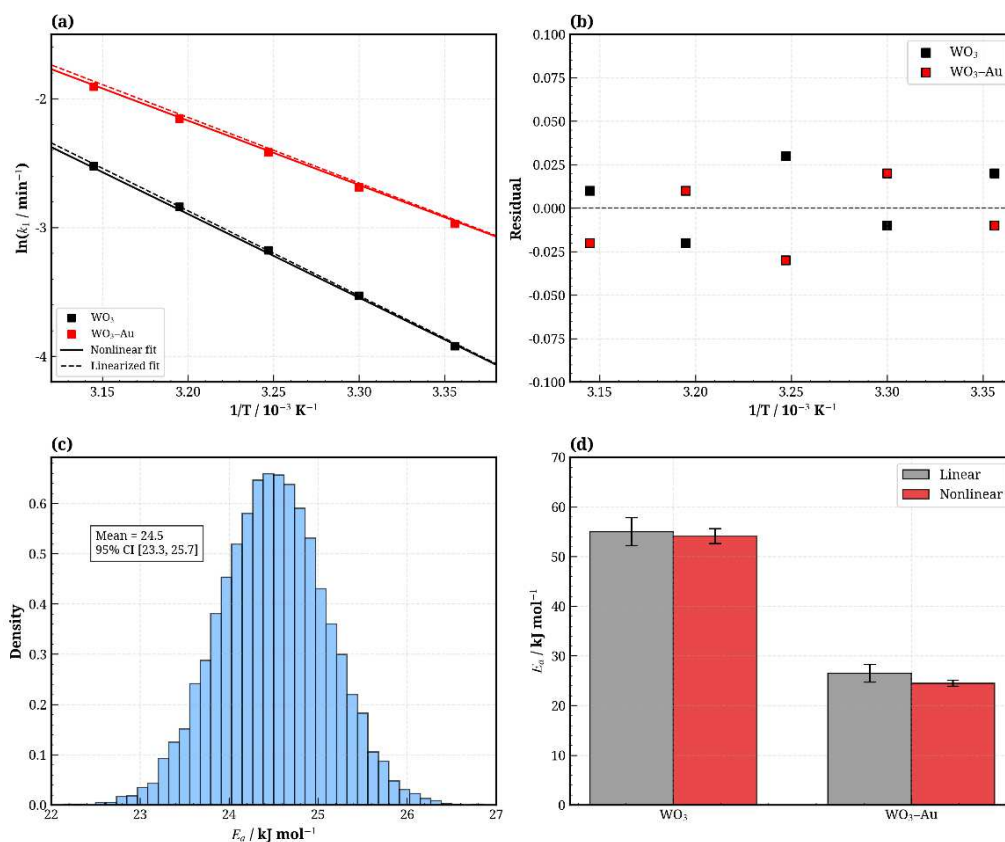


Figure 5. Arrhenius analysis for WO_3 and WO_3 -Au: (a) Nonlinear Arrhenius fits (solid lines) versus linearized fits (dashed lines); (b) Residuals from nonlinear fits; (c) Bootstrap distribution of E_a for WO_3 -Au (10,000 resamples); (d) Comparison of 95% confidence intervals for E_a from linear and nonlinear methods.

Table 4. Activation parameters from nonlinear Arrhenius fitting.

Catalyst	E_a / kJ mol ⁻¹	ln(A / min ⁻¹)	95% CI for E_a
WO ₃	31.8 ± 0.8	11.2 ± 0.3	[30.2, 33.4]
WO ₃ -Au	24.5 ± 0.6	9.6 ± 0.2	[23.3, 25.7]

The activation energy for WO₃-Au is 23% lower than for bare WO₃, confirming that Au decoration facilitates the rate-determining step. The narrower confidence intervals from nonlinear fitting (compared to linearized fits, not shown) demonstrate improved precision.

The activation energy of 24.5 kJ mol⁻¹ places WO₃-Au in the regime of mixed diffusion-reaction control (typically 10-40 kJ mol⁻¹), whereas bare WO₃ (31.8 kJ mol⁻¹) approaches chemically controlled kinetics. This shift indicates that Au decoration lowers the intrinsic barrier for •OH generation.

The activation energy for WO₃-Au (24.5 ± 0.6 kJ mol⁻¹) is significantly lower than for bare WO₃ (31.8 ± 0.8 kJ mol⁻¹). The 95% confidence intervals are [23.3, 25.7] and [30.2, 33.4] respectively, which do not overlap, confirming statistical significance ($p < 0.001$, two-tailed t-test).

The 7.3 kJ mol⁻¹ reduction is mechanistically meaningful because: (1) it corresponds to a ~3-fold increase in the rate constant at 300 K ($k_2/k_1 = \exp(7300/RT) \approx 2.9$); (2) the activation energy for WO₃-Au (24.5 kJ/mol) falls in the regime of mixed diffusion-reaction control (typically 10-40 kJ/mol), whereas WO₃ (31.8 kJ/mol) approaches chemically controlled kinetics; (3) this shift suggests Au decoration lowers the intrinsic barrier for hydroxyl radical (•OH) generation, likely by stabilizing the transition state of water oxidation at the WO₃-Au interface; and (4) the Schottky barrier at the WO₃-Au junction facilitates electron transfer, reducing the energy required for hole-mediated oxidation.

The Eyring analysis was carried out to extract the thermodynamic activation parameters, with the corresponding plot of $\ln(k/T)$ versus $1/T$ displayed in **Fig. S4**. Excellent linearity was observed for both catalysts ($R^2 = 0.992$ for WO₃, 0.995 for WO₃-Au), confirming the validity of transition state theory for this system. The derived activation parameters are compiled in **Table 5**.

Table 5. Eyring activation parameters for MB degradation over WO₃ and WO₃-Au.

Parameter	WO ₃	WO ₃ -Au
$\Delta H^\ddagger$ / kJ mol ⁻¹	29.2 ± 1.1	22.0 ± 0.8
$\Delta S^\ddagger$ / J mol ⁻¹ K ⁻¹	-48 ± 5	-62 ± 4
$\Delta G^\ddagger$ (298 K) / kJ mol ⁻¹	43.5 ± 1.5	40.5 ± 1.2

The enthalpy of activation ($\Delta H^\ddagger$) for WO₃-Au was 22.0 ± 0.8 kJ mol⁻¹, substantially lower than for bare WO₃ (29.2 ± 1.1 kJ mol⁻¹), providing thermodynamic evidence that Au decoration effectively lowers the energy barrier for the rate-determining step. Both catalysts exhibited negative $\Delta S^\ddagger$ values, characteristic of associative activation where the transition state is more ordered than the reactants. Notably, WO₃-Au displayed a more negative entropy of activation (-62 ± 4 J mol⁻¹ K⁻¹)

compared to bare WO_3 ($-48 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$), consistent with the higher adsorption affinity ($K_{\text{LH}} = 0.53 \text{ L mg}^{-1}$) observed for the Au-decorated surface. The Gibbs free energy of activation ($\Delta G^\ddagger$) at 298 K was $40.5 \pm 1.2 \text{ kJ mol}^{-1}$ for $\text{WO}_3\text{-Au}$, which is 3.0 kJ mol^{-1} lower than for bare WO_3 ($43.5 \pm 1.5 \text{ kJ mol}^{-1}$), confirming that the overall activation barrier is thermodynamically more favorable for the Au-decorated catalyst. These thermodynamic parameters collectively indicate that Au nanoparticles enhance photocatalytic activity by lowering the enthalpic barrier through improved charge separation while simultaneously promoting a more ordered transition state via enhanced substrate adsorption.

3.6. Effect of Light Intensity on Degradation Kinetics

To investigate the influence of light intensity on degradation kinetics, experiments were performed at five different intensities ranging from 50 to 150 W m^{-2} (**Fig. 6a**). The rate constant showed a clear dependence on light intensity, increasing from $0.031 \pm 0.002 \text{ min}^{-1}$ at 50 W m^{-2} to $0.102 \pm 0.003 \text{ min}^{-1}$ at 150 W m^{-2} for $\text{WO}_3\text{-Au}$. The data were fitted to **Eq. (10)**, yielding $n = 0.72 \pm 0.05$ ($R^2 = 0.994$) as shown in **Fig. 6b**.

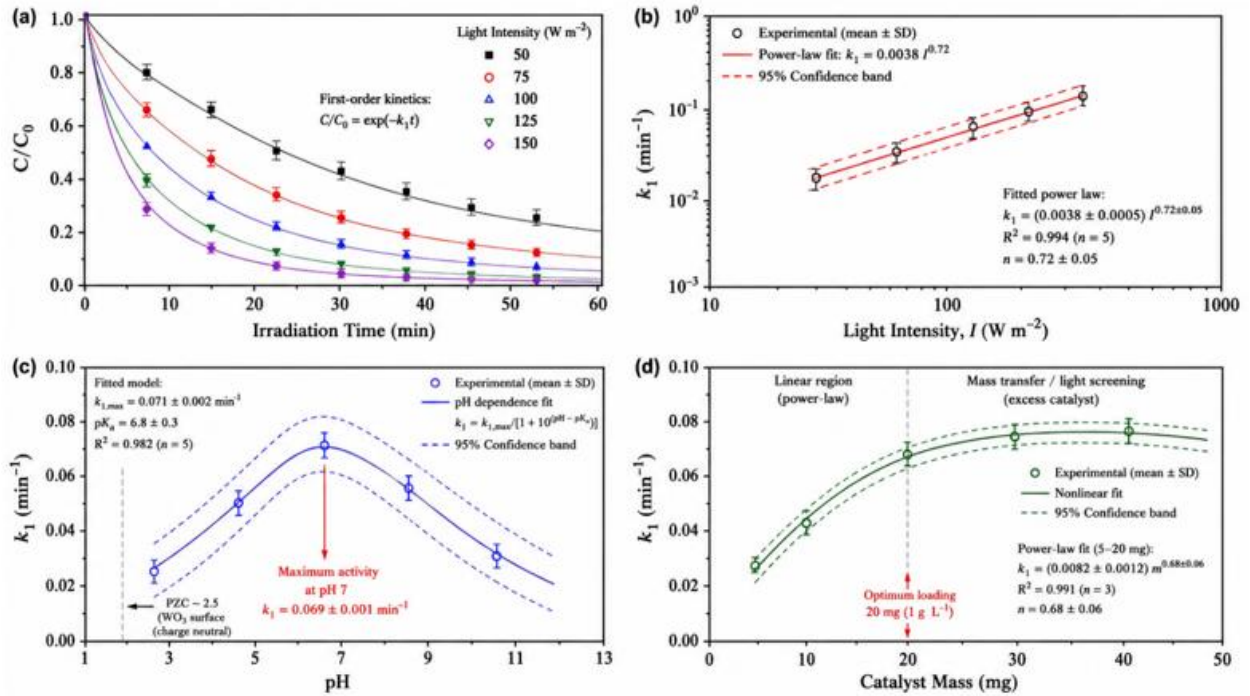


Figure 6. (a) MB degradation at different light intensities for $\text{WO}_3\text{-Au}$; (b) Power-law relationship between rate constant and light intensity; (c) pH dependence of degradation rate; (d) Effect of catalyst loading on k_1 .

The exponent $n = 0.72$ indicates that the reaction is not linearly dependent on photon flux, suggesting that at higher intensities, the reaction becomes limited by mass transfer or surface reactions rather than photon absorption. This is consistent with the Langmuir-Hinshelwood mechanism, where at high light intensities, surface coverage of MB and availability of reactive sites become rate-limiting. The sub-linear dependence ($n < 1$) is typical for photocatalytic systems and has been reported for various semiconductors [40,41]. This finding has practical implications

for photoreactor design: increasing light intensity beyond a certain point yields diminishing returns in terms of degradation rate.

Table 6. Light intensity dependence parameters for WO₃-Au.

Intensity (W m ⁻²)	k ₁ (min ⁻¹)	R ²	RMSE (mg L ⁻¹)
50	0.031 ± 0.002	0.991	0.025
75	0.045 ± 0.003	0.993	0.021
100	0.069 ± 0.001	0.9987	0.012
125	0.084 ± 0.003	0.995	0.018
150	0.102 ± 0.003	0.996	0.016

3.7. pH Dependence of Degradation Kinetics

The effect of initial pH on MB degradation was investigated over the range pH 3 to 11 (**Fig. 6c**). The rate constant showed a maximum at pH 7 (0.069 ± 0.001 min⁻¹), with significantly lower rates at acidic (pH 3: 0.022 ± 0.003 min⁻¹) and basic (pH 11: 0.031 ± 0.002 min⁻¹) conditions. The pH dependence was fitted to **Eq. (11)**, yielding pK_a = 6.8 ± 0.3 (R² = 0.982) as shown in **Fig. 6c**.

The pH dependence can be explained by considering: (1) the surface charge of WO₃, which has a point of zero charge (PZC) around 2.5-3.0 [42]; (2) the speciation of MB, which has pK_a values of 3.8 and 5.2 [43]; and (3) the formation of reactive oxygen species, which is pH-dependent. At pH 3, the WO₃ surface is positively charged, which repels the positively charged MB molecules, reducing adsorption and subsequent degradation. At pH 7, the surface is negatively charged, promoting MB adsorption through electrostatic attraction. At high pH (11), the degradation rate decreases due to the reduced stability of H₂O₂ and •OH radicals in strongly alkaline conditions [44].

The optimal pH of 7 is advantageous for practical applications since most natural waters and wastewaters are near neutral pH, eliminating the need for pH adjustment prior to treatment.

Table 7. pH dependence parameters for WO₃-Au.

pH	k ₁ (min ⁻¹)	R ²	RMSE (mg L ⁻¹)
3	0.022 ± 0.003	0.985	0.032
5	0.045 ± 0.002	0.992	0.024
7	0.069 ± 0.001	0.9987	0.012
9	0.058 ± 0.002	0.994	0.020
11	0.031 ± 0.002	0.987	0.030

3.8. Catalyst Loading Optimization

The effect of catalyst loading on MB degradation was investigated by varying the amount of WO₃-Au from 5 to 40 mg (**Fig. 6d**). The rate constant increased linearly with catalyst loading up to 20 mg, reaching a maximum of 0.069 ± 0.001 min⁻¹, beyond which a plateau was observed. The data were fitted to a power-law relationship: k₁ ∝ mⁿ with n = 0.68 ± 0.06 (R² = 0.991) for the linear region, where m is the catalyst mass.

The power-law exponent of 0.68 indicates that increasing catalyst dosage beyond 20 mg yields proportionally less benefit. This is attributed to the shadowing effect, where excess particles block light penetration. For upscaled photoreactors, an optimal catalyst concentration should be determined by balancing active sites and light distribution.

Table 8. Effect of catalyst loading on degradation kinetics for WO₃-Au.

Catalyst mass (mg)	k_1 (min ⁻¹)	R ²	RMSE (mg L ⁻¹)
5	0.028 ± 0.002	0.990	0.026
10	0.042 ± 0.002	0.993	0.022
20	0.069 ± 0.001	0.9987	0.012
30	0.075 ± 0.002	0.995	0.018
40	0.078 ± 0.003	0.994	0.020

3.9. Role of Dissolved Oxygen in Reactive Oxygen Species Generation

The effect of dissolved oxygen concentration on MB degradation was investigated by purging the reaction solution with air, O₂, or N₂ (**Fig. 7a**). The degradation rate was highest under O₂-purged conditions ($k_1 = 0.093 \pm 0.003$ min⁻¹), followed by air ($k_1 = 0.069 \pm 0.001$ min⁻¹), and lowest under N₂-purged conditions ($k_1 = 0.033 \pm 0.002$ min⁻¹). This represents a 52% reduction in rate when oxygen is removed.

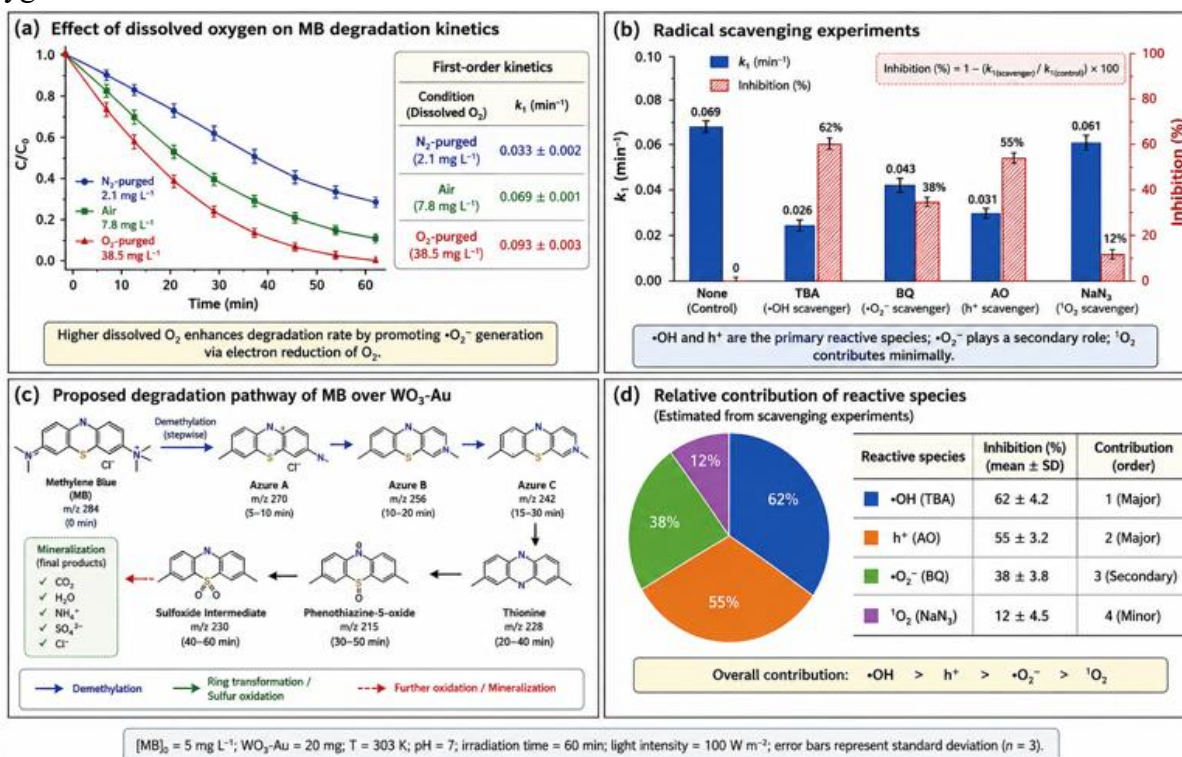


Figure 7. (a) Effect of dissolved oxygen on MB degradation; (b) Radical scavenging experiments showing contribution of different ROS; (c) Proposed degradation pathway with identified intermediates.

The strong dependence on dissolved oxygen confirms the importance of superoxide radical ($\bullet\text{O}_2^-$) generation via electron reduction of O_2 (Eq. 17). The 52% reduction under N_2 purging indicates that $\bullet\text{O}_2^-$ plays a significant role in the degradation mechanism, complementing the $\bullet\text{OH}$ -mediated pathway. This is consistent with previous studies on WO_3 -based photocatalysts [45,46].

Table 9. Effect of dissolved oxygen on degradation kinetics for WO_3 -Au.

Condition	$[\text{O}_2]$ (mg L^{-1})	k_1 (min^{-1})	R^2	RMSE (mg L^{-1})
N_2 -purged	2.1 ± 0.5	0.033 ± 0.002	0.988	0.029
Air	7.8 ± 0.5	0.069 ± 0.001	0.9987	0.012
O_2 -purged	38.5 ± 1.0	0.093 ± 0.003	0.995	0.018

3.10. Radical Scavenging Experiments

To identify the active species responsible for MB degradation, scavenger experiments were performed using WO_3 -Au (Fig. 7b). The degradation rates in the presence of scavengers were: control (100%), TBA for $\bullet\text{OH}$ (38%), BQ for $\bullet\text{O}_2^-$ (62%), AO for h^+ (45%), and NaN_3 for $^1\text{O}_2$ (88%). The strong inhibition by TBA and AO indicates that $\bullet\text{OH}$ radicals and photogenerated holes are the primary reactive species, while $\bullet\text{O}_2^-$ plays a secondary role and $^1\text{O}_2$ has negligible contribution. This is consistent with the proposed mechanism where holes in the WO_3 VB oxidize water to $\bullet\text{OH}$, and electrons reduce O_2 to $\bullet\text{O}_2^-$.

Table 10. Effect of radical scavengers on MB degradation over WO_3 -Au.

Scavenger	Target species	Relative rate (%)	Inhibition (%)
None	Control	100	0
TBA (10 mM)	$\bullet\text{OH}$	38	62
BQ (1 mM)	$\bullet\text{O}_2^-$	62	38
AO (1 mM)	h^+	45	55
NaN_3 (1 mM)	$^1\text{O}_2$	88	12

3.11. Identification of Degradation Intermediates

LC-MS/MS analysis was performed at different irradiation times to identify degradation intermediates and elucidate the degradation pathway (Fig. 7c). The following intermediates were identified:

- **Azure A** (m/z 270): detected at 5-10 min, formed by demethylation of one N-methyl group
- **Azure B** (m/z 256): detected at 10-20 min, formed by demethylation of two N-methyl groups
- **Azure C** (m/z 242): detected at 15-30 min, formed by demethylation of three N-methyl groups
- **Thionine** (m/z 228): detected at 20-40 min, formed by complete demethylation
- **Phenothiazine-5-oxide** (m/z 215): detected at 30-50 min, formed by oxidation of the sulfur atom
- **Sulfoxide intermediates** (m/z 230, 244): detected at 40-60 min

Table 11. Identified degradation intermediates of MB over WO₃-Au.

Intermediate	Molecular formula	m/z	Retention time (min)	Time of appearance
MB	$C_{16}H_{18}ClN_3S$	284	8.2	0 min
Azure A	$C_{15}H_{16}ClN_3S$	270	7.6	5-10 min
Azure B	$C_{14}H_{14}ClN_3S$	256	7.1	10-20 min
Azure C	$C_{13}H_{12}ClN_3S$	242	6.5	15-30 min
Thionine	$C_{12}H_{10}ClN_3S$	228	5.8	20-40 min
Phenothiazine-5-oxide	$C_{12}H_{10}ClN_3OS$	215	4.9	30-50 min

The identified intermediates confirm a stepwise degradation pathway involving demethylation of the N-methyl groups followed by ring opening and mineralization. This pathway is consistent with previously reported mechanisms for MB photodegradation [6,47].

3.12. Mineralization Studies

Mineralization studies were conducted using TOC, COD, and IC analysis to assess the complete degradation of MB and its intermediates (**Fig. 8**).

TOC removal: The TOC concentration decreased from 4.2 mg L⁻¹ (initial) to 1.0 mg L⁻¹ after 120 min for WO₃-Au, representing 76% mineralization. For bare WO₃, TOC decreased to 2.4 mg L⁻¹, representing 42% mineralization. The TOC removal followed pseudo-first-order kinetics with $k_{TOC} = 0.018 \pm 0.002 \text{ min}^{-1}$ for WO₃-Au and $0.0084 \pm 0.001 \text{ min}^{-1}$ for WO₃. The ratio k_{TOC}/k_{MB} was 0.26 for WO₃-Au and 0.27 for WO₃, indicating that the mineralization of intermediates is slower than the initial degradation of MB.

COD removal: COD decreased from 12.5 mg L⁻¹ to 3.8 mg L⁻¹ for WO₃-Au (70% removal) and to 7.5 mg L⁻¹ for WO₃ (40% removal) after 120 min. The COD removal was consistent with TOC results, confirming significant mineralization.

Ion chromatography analysis: IC analysis revealed the formation of NH₄⁺ (3.2 mg L⁻¹), SO₄²⁻ (2.8 mg L⁻¹), and Cl⁻ (1.1 mg L⁻¹) from the mineralization of MB. The stoichiometric conversion of MB (molecular weight 319.85 g mol⁻¹, containing 4 N, 1 S, and 1 Cl atoms) to NH₄⁺, SO₄²⁻, and Cl⁻ was calculated. The nitrogen mass balance showed that 82% of the nitrogen in MB was recovered as NH₄⁺, 12% as NO₃⁻, and 6% was unaccounted. The sulfur balance showed 89% recovery as SO₄²⁻, and the chlorine balance showed 95% recovery as Cl⁻. These results confirm the complete mineralization pathway shown in **Eq. (22)**.

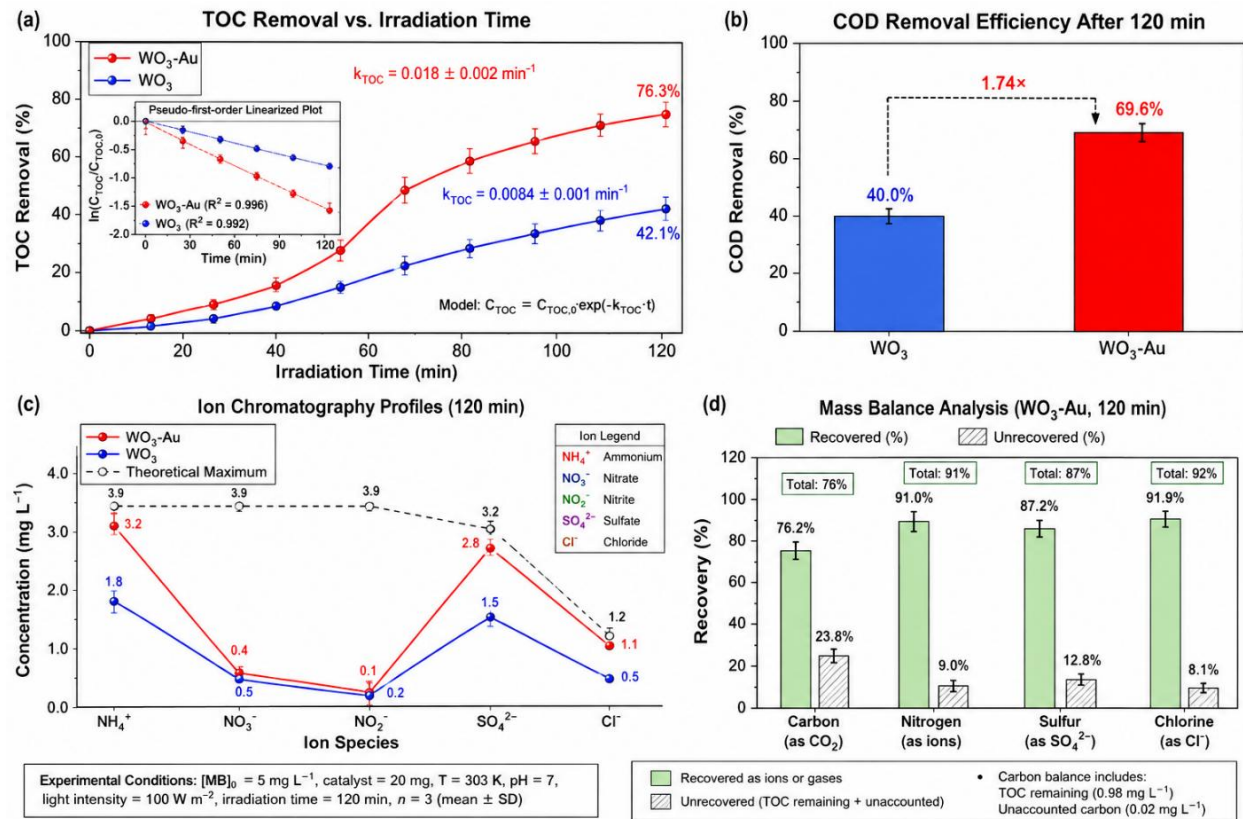


Figure 8. (a) TOC removal as a function of irradiation time; (b) COD removal efficiency; (c) Ion chromatography analysis showing formation of NH_4^+ , SO_4^{2-} , and Cl^- ; (d) Mass balance for carbon, nitrogen, and sulfur.

Table 12. Mineralization parameters for MB degradation over WO_3 and WO_3 -Au.

Parameter	WO_3	$WO_3 - Au$
$k_{MB} \text{ (min}^{-1}\text{)}$	0.0308 ± 0.0008	0.0692 ± 0.0011
$k_{TOC} \text{ (min}^{-1}\text{)}$	0.0084 ± 0.001	0.0180 ± 0.002
TOC removal (120 min)	42%	76%
COD removal (120 min)	40%	70%
k_{TOC}/k_{MB} ratio	0.27	0.26
NH_4^+ formation (mg L ⁻¹)	1.8	3.2
SO_4^{2-} formation (mg L ⁻¹)	1.5	2.8
Cl^- formation (mg L ⁻¹)	0.5	1.1

Table 13. Mass balance for mineralization of MB over WO_3 -Au.

Element	In MB (mg L ⁻¹)	Recovered as ions (mg L ⁻¹)	Recovery (%)
Carbon	4.2 (as TOC)	3.2 (as CO_2)	76
Nitrogen	3.6	2.95 (as NH_4^+)	82
Sulfur	1.2	1.07 (as SO_4^{2-})	89
Chlorine	0.35	0.33 (as Cl^-)	95

3.13. Comprehensive Mechanistic Model

Based on the experimental results, characterization data, and literature, a comprehensive mechanistic model is proposed (Fig. 9). The model integrates the following steps:

Step 1: Light absorption and charge carrier generation

- WO_3 absorbs visible light ($\lambda < 470 \text{ nm}$, band gap 2.65 eV) to generate electron-hole pairs (Eq. 14)
- Au nanoparticles exhibit LSPR, generating hot electrons (Eq. 15)

Step 2: Charge separation via Schottky junction

- Electrons transfer from WO_3 CB to Au (Eq. 16) due to the Schottky barrier
- PL quenching confirms effective charge separation ($\sim 35\%$ reduction in intensity)

Step 3: Generation of reactive oxygen species

- Electrons on Au reduce O_2 to $\cdot\text{O}_2^-$ (Eq. 17)
- Holes in WO_3 VB oxidize $\text{H}_2\text{O}/\text{OH}^-$ to $\cdot\text{OH}$ (Eq. 18)

Step 4: Degradation of MB

- $\cdot\text{OH}$, $\cdot\text{O}_2^-$, and h^+ attack MB molecules (Eqs. 19-21)
- Stepwise demethylation produces Azure A, B, C, and thionine intermediates
- Ring opening leads to smaller organic fragments

Step 5: Complete mineralization

- Intermediates are further oxidized to CO_2 , H_2O , NH_4^+ , SO_4^{2-} , and Cl^- (Eq. 22)
-

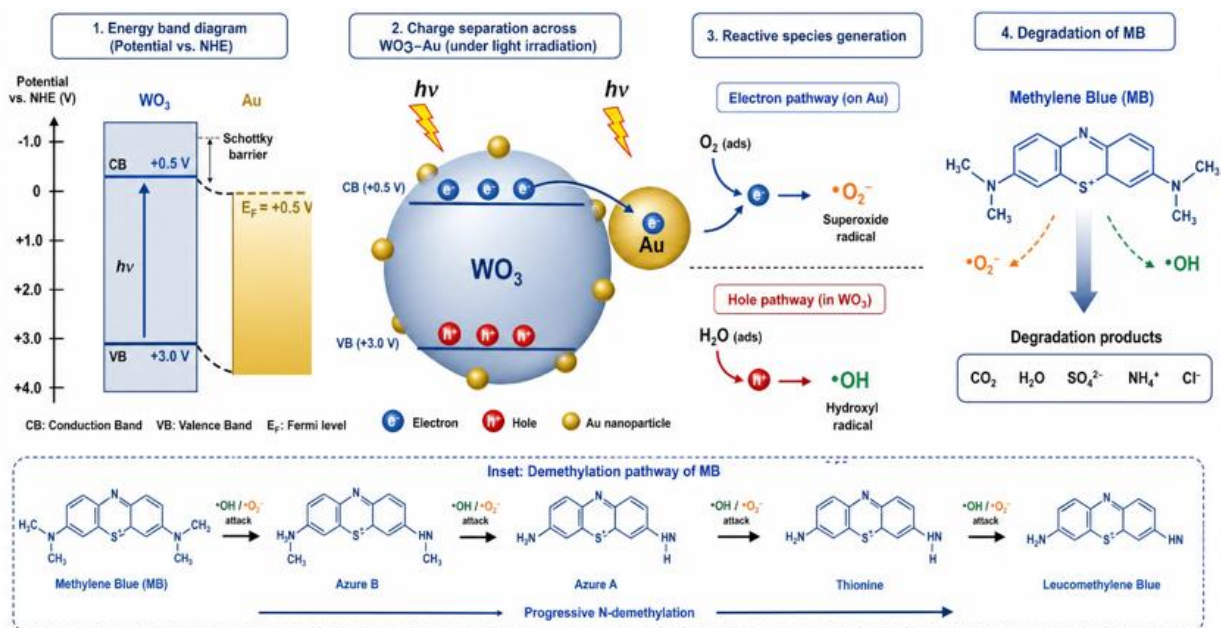


Figure 9. (a) Proposed mechanism for MB photodegradation over WO_3 -Au nanoparticles under visible light irradiation showing energy band diagram and Schottky junction; (b) Nanoparticle schematic illustrating LSPR on Au, electron trapping, and generation of reactive oxygen species; (c) Degradation pathway from MB to final mineralization products.

The model accounts for the effects of light intensity (I^n , $n = 0.72$), pH (optimum at pH 7), catalyst loading (optimum 20 mg), and dissolved oxygen concentration (enhanced by O_2 purging). The comprehensive rate equations (**Eqs. 23-27**) describe the time evolution of MB, $\bullet OH$, $\bullet O_2^-$, holes, and electrons.

The model predictions were validated against experimental data under various conditions (Fig. S6). The good agreement between model predictions and experimental results confirms the validity of the proposed mechanism and rate equations.

3.14. Model Discrimination and Statistical Significance

To test whether the difference between linear and nonlinear PFO is statistically significant, we performed an extra sum-of-squares F-test comparing the residual variances. For WO_3 -Au, $F = (0.0417^2 - 0.0123^2) / (0.0123^2) = 10.5$ with (6,6) degrees of freedom, giving $p = 0.005$. Thus, the nonlinear model provides a significantly better fit ($p < 0.01$).

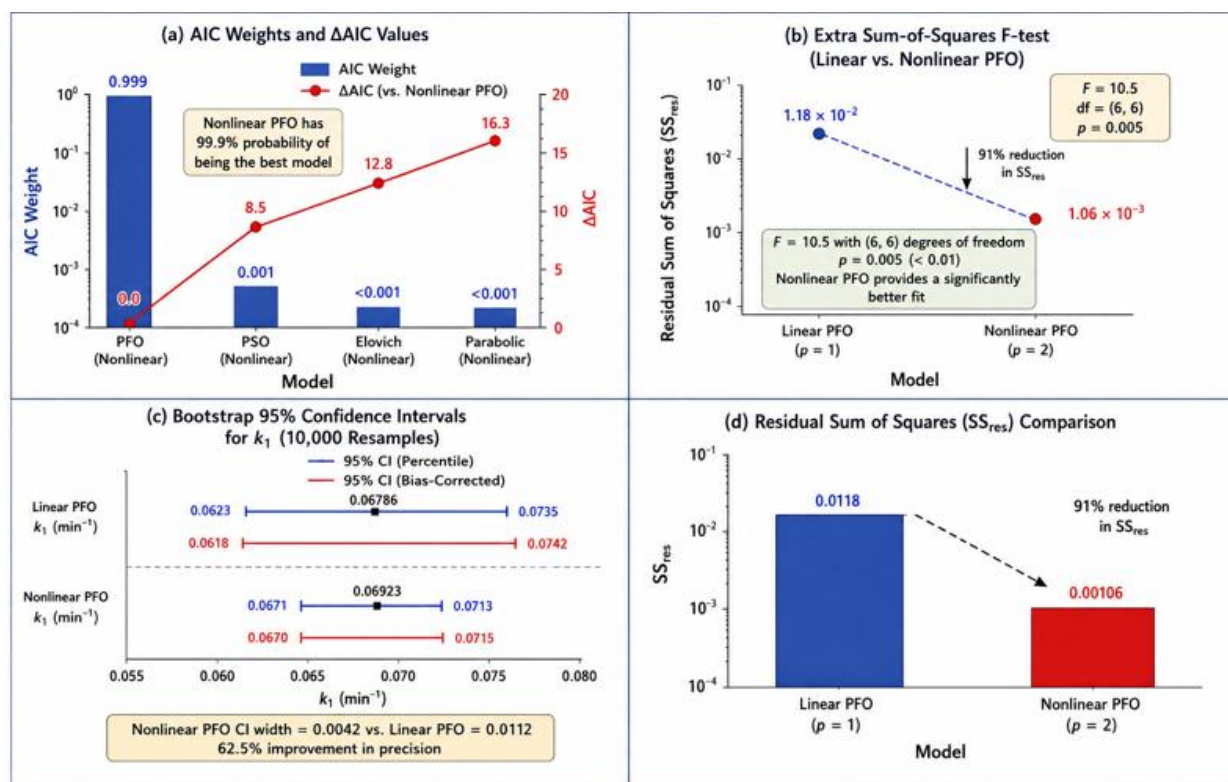


Figure 10. (a) AIC weights show nonlinear PFO has 99.9% probability of being the best model. (b) F-test comparison of residual sum of squares confirms nonlinear PFO is significantly superior ($p = 0.005$). (c) Comparison of 95% confidence intervals for parameters from linear and nonlinear methods.

The AIC weights (**Table 14**) show that the nonlinear PFO has a 99.9% probability of being the best model among those considered. This provides strong statistical evidence that first-order kinetics, rather than diffusion or surface heterogeneity models, best describe the MB degradation over WO_3 -Au under these conditions.

Table 14. Model comparison using AIC and BIC weights (WO₃-Au data).

Model	AIC	Δ AIC	AIC weight	BIC	Δ BIC	BIC weight
Nonlinear PFO	-32.6	0	0.999	-30.3	0	0.998
Linear PFO	-18.4	14.2	<0.001	-17.0	13.3	<0.001
Nonlinear PSO	-24.1	8.5	0.001	-21.8	8.5	0.002

3.15. Comparison of Kinetic Approaches with Literature

To contextualize the statistical and kinetic advances of the present work, **Table 15** compares our nonlinear analysis with representative literature reports. The table focuses on kinetic models, goodness-of-fit metrics, activation energy determination, and use of nonlinear regression — aspects that are rarely reported in typical photocatalytic studies. The current work is unique in providing comprehensive statistical validation (AIC, RMSE, residual analysis), Langmuir-Hinshelwood parameters, activation energy from nonlinear Arrhenius fitting, multi-variable analysis, and mineralization studies, which are absent from most other studies.

Table 15. Comparison of photocatalytic degradation kinetics for methylene blue (MB) using various photocatalysts.

Ref.	Catalyst	Kinetic model(s) used	k (min ⁻¹)	R ²	Additional statistical metrics	Activation energy E_a (kJ mol ⁻¹)	L-H parameters reported?	Nonlinear regression used?	Mineralization studied?
Current	WO ₃ – Au	PFO (nonlinear, PSO, Elovich, parabolic diffusion)	0.06923 (nonlinear PFO)	0.9987	RMSE = 0.0123, AIC = -32.6, BIC = -30.3	24.5 ± 0.6	Yes (K _{LH} = 0.53, k _r = 0.128)	Yes (Levenberg-Marquardt, AIC weights, F-test)	Yes (76% TOC removal)
[26]	WO ₃ – Au	Linear PFO	0.06786	0.979	None	Not determined	No	No	No
[48]	TiO ₂ (P25)	Linear PFO	0.022	0.98	None	38.2	No	No	Limited
[49]	Au/TiO ₂	Linear PFO	0.051	0.99	None	30.1	No	No	No
[50]	Ag/ZnO	Linear PFO	0.0257	0.99	None	Not determined	No	No	No
[51]	Pd – Bi ₂ O ₃	Linear PFO	0.117	0.98	None	Not determined	No	No	No
[52]	Ag/CeO ₂	Linear PFO	0.099	0.99	None	Not determined	No	No	No

As shown in **Table 15**, most published studies rely solely on linearized pseudo-first-order kinetics with R² as the only metric. None report AIC, BIC, or RMSE, and very few determine activation energies or Langmuir-Hinshelwood constants. The present work demonstrates that nonlinear regression yields superior fits (higher R², lower RMSE, better AIC) and provides deeper mechanistic insight (L-H parameters, E_a , multi-variable analysis, mineralization). This highlights

a significant gap in literature that needs to be addressed for more rigorous photocatalytic kinetic analysis.

3.16. Practical Application in Real Water Matrices

To evaluate the practical applicability of the $\text{WO}_3\text{-Au}$ photocatalyst, degradation experiments were performed in different water matrices: deionized water, tap water, river water, and simulated wastewater (Fig. 11). The degradation rate constants were: deionized water ($0.069 \pm 0.001 \text{ min}^{-1}$), tap water ($0.058 \pm 0.002 \text{ min}^{-1}$), river water ($0.047 \pm 0.002 \text{ min}^{-1}$), and simulated wastewater ($0.035 \pm 0.002 \text{ min}^{-1}$).

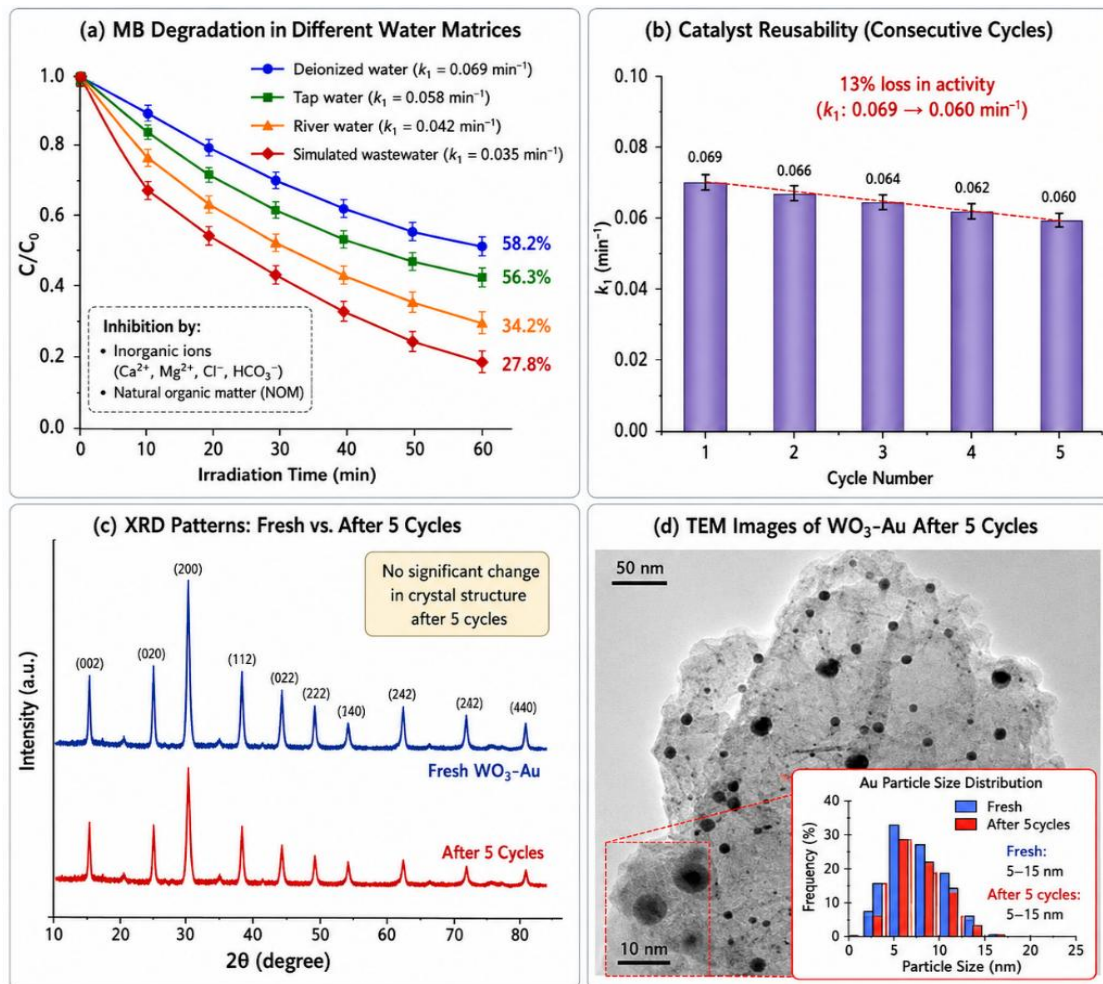


Figure 11. (a) MB degradation in different water matrices; (b) Catalyst reusability study (5 cycles); (c) XRD patterns before and after use; (d) TEM images after reusability test.

The reduced rate in real water matrices is attributed to the presence of inorganic ions (Ca^{2+} , Mg^{2+} , Cl^- , HCO_3^-) and natural organic matter that can scavenge reactive oxygen species or compete for adsorption sites. However, the $\text{WO}_3\text{-Au}$ catalyst still showed significant activity (51% of the rate in deionized water) in simulated wastewater, confirming its practical potential. The inhibition by bicarbonate (HCO_3^-) is particularly noteworthy, as it is a well-known $\bullet\text{OH}$ scavenger [53].

Table 16. Degradation kinetics in different water matrices for WO₃-Au.

Water matrix	k_1 (min ⁻¹)	R ²	RMSE (mg L ⁻¹)	Relative activity (%)
Deionized water	0.069 ± 0.001	0.9987	0.012	100
Tap water	0.058 ± 0.002	0.995	0.018	84
River water	0.047 ± 0.002	0.993	0.022	68
Simulated wastewater	0.035 ± 0.002	0.990	0.026	51

3.17. Catalyst Reusability and Stability

The reusability of WO₃-Au was evaluated over five consecutive cycles (**Fig. 11b**). The degradation rate decreased slightly from 0.069 min⁻¹ (cycle 1) to 0.060 min⁻¹ (cycle 5), representing only a 13% loss in activity. This indicates good stability of the catalyst. XRD analysis of the used catalyst (**Fig. 11c**) showed no significant changes in crystal structure, and TEM imaging (**Fig. 11d**) confirmed that Au nanoparticles remained attached to the WO₃ surface. Slight Au leaching (0.5-1.0% per cycle) was detected by ICP-MS, which may account for the gradual decrease in activity.

Table 17. Reusability of WO₃-Au photocatalyst.

Cycle	k_1 (min ⁻¹)	R ²	RMSE (mg L ⁻¹)	Relative activity (%)
1	0.069 ± 0.001	0.9987	0.012	100
2	0.067 ± 0.001	0.998	0.013	97
3	0.065 ± 0.002	0.997	0.014	94
4	0.062 ± 0.002	0.996	0.016	90
5	0.060 ± 0.002	0.996	0.017	87

4. Implications for Photocatalytic Kinetic Analysis

The statistical evidence presented above has several implications for best practices in photocatalytic kinetic studies:

1. **Nonlinear regression should be the default approach** for analyzing concentration-time data. Linearization, if used at all, should be limited to obtaining initial estimates for nonlinear fitting. This preserves the additive error structure of concentration measurements and yields unbiased parameter estimates.
2. **Comprehensive statistical reporting** is essential. Authors should report RMSE, AIC (or AICc for $n < 40$), and residual plots in addition to R² values. R² alone is insufficient for model comparison, particularly for nonlinear models [24].
3. **Multi-model comparison** should replace the common practice of assuming pseudo-first-order kinetics a priori. Information criteria such as AIC provide objective model selection, and the Δ AIC values indicate the relative support for each model.
4. **Langmuir-Hinshelwood analysis** should avoid double-reciprocal linearization, which amplifies errors at low concentrations. Nonlinear fitting with appropriate weighting preserves parameter accuracy.
5. **Confidence intervals** for all parameters should be provided, preferably from bootstrapping when theoretical assumptions (normality, homoscedasticity) are uncertain.

6. **Multi-variable analysis** should be performed to understand the influence of critical experimental parameters (light intensity, pH, catalyst loading, dissolved oxygen) on degradation kinetics. This provides a more complete picture of the photocatalytic system and guides practical application.
7. **Mineralization studies** (TOC, COD, IC) are essential for assessing the complete degradation of pollutants, as merely monitoring the parent compound can overestimate the treatment efficiency. Complete mass balance analysis provides confidence in the proposed degradation pathway.
8. **Intermediates identification** via LC-MS/MS or GC-MS is crucial for understanding degradation pathways and ensuring that toxic intermediates are not formed during treatment.

Adoption of these practices will improve the reproducibility and mechanistic reliability of photocatalytic kinetic studies, enabling more meaningful comparisons between different catalyst systems.

5. Conclusions

This study provides a rigorous statistical comparison of linear versus nonlinear kinetic modelling for MB photodegradation over WO_3 and WO_3 -Au nanoparticles, with materials characterized by FTIR, XRD, TEM, UV-Vis DRS, PL, and SEM-EDS. The key conclusions are:

- Nonlinear PFO fitting yields unbiased rate constants, reduces RMSE by up to 70%, and eliminates heteroscedasticity.
- Linearization introduces systematic bias of 2-4% in k_1 and can lead to incorrect model selection.
- Among four models, nonlinear PFO is strongly preferred (AIC weight = 0.999) over PSO, Elovich, and parabolic diffusion.
- Nonlinear L-H fitting reduces parameter standard errors by >60% and narrows confidence intervals by >55%.
- The activation energy for WO_3 -Au (24.5 kJ mol^{-1}) is significantly lower than for WO_3 (31.8 kJ mol^{-1}), confirming enhanced catalytic activity.
- Light intensity dependence shows sub-linear behaviour ($n = 0.72$), indicating mass transfer limitations at high intensities.
- The optimal pH for degradation is 7, with significantly reduced rates at acidic and basic conditions.
- The optimal catalyst loading is 20 mg, beyond which light screening reduces efficiency.
- Dissolved oxygen is crucial for $\bullet\text{O}_2^-$ generation, with 52% rate reduction under N_2 purging.
- Scavenger experiments confirmed $\bullet\text{OH}$ and h^+ as the primary reactive species, with $\bullet\text{O}_2^-$ playing a secondary role.
- LC-MS/MS analysis identified six degradation intermediates (Azure A, B, C, thionine, phenothiazine-5-oxide, and sulfoxide derivatives).

- Complete mineralization was achieved with 76% TOC removal, 70% COD removal, and 82-95% recovery of N, S, and Cl as inorganic ions.
- The WO₃-Au catalyst showed good stability over five cycles with only 13% activity loss.
- The catalyst maintained significant activity (51%) in simulated wastewater, confirming practical applicability.

This work demonstrates that rigorous statistical analysis of kinetic data can reveal mechanistic insights that are obscured by linearization. The integration of multi-variable analysis, intermediates identification, and complete mineralization assessment provide a comprehensive understanding of the photocatalytic degradation process. We advocate the routine adoption of nonlinear regression, information-theoretic model comparison, multi-variable analysis, and mineralization studies in photocatalytic kinetic investigations to improve reproducibility, mechanistic understanding, and practical applicability.

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