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Kinetic modelling of methylene blue degradation over iron-doped titanium dioxide photocatalysts under visible light

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Abstract

Titanium dioxide alone cannot harvest visible light, and that single limitation has blocked its adoption as a solar-driven water treatment catalyst. Iron doping offers a practical fix by narrowing the band gap, but the kinetic behaviour of dye degradation over Fe-TiO₂ remains poorly modelled beyond first-order approximations. This research prepared Fe-doped TiO₂ at five iron loadings (0, 1, 3, 5, and 7 mol%) by a sol-gel method and tested each catalyst against methylene blue (MB, 20 mg L⁻¹) under a 300 W xenon lamp fitted with a 400 nm cut-off filter. X-ray diffraction showed pure anatase phase up to 5% Fe, with trace rutile appearing at 7%. BET surface areas increased from 48.3 m² g⁻¹ (undoped) to 89.7 m² g⁻¹ (3% Fe) before dropping at higher loadings. UV-Vis diffuse reflectance placed the band gap at 3.18 eV for undoped TiO₂ and 2.47 eV for 3% Fe-TiO₂. The 3% Fe sample reached 95.9% MB removal in 180 min, while undoped TiO₂ achieved only 57%. Pseudo-first-order, pseudo-second-order, and Langmuir-Hinshelwood (L-H) models were fitted to the concentration-time data. The L-H model gave the best fit for all catalysts ($R^2 = 0.991-0.998$), with an apparent rate constant (k_{app}) of 0.0173 min⁻¹ for 3% Fe-TiO₂ 3.8 times that of the undoped control. Activation energy from Arrhenius plots (25-55 °C) was 21.4 kJ mol⁻¹ for the 3% sample, confirming a diffusion-limited regime. Scavenger experiments identified hydroxyl radicals as the main reactive species (78% suppression with isopropanol), followed by superoxide radicals (41% suppression with benzoquinone). Recycling tests over five cycles showed less than 8% loss in activity. These results position 3 mol% Fe-TiO₂ as an effective, reusable visible-light photocatalyst for textile wastewater treatment and provide a kinetic framework for reactor scale-up.

Keywords: Iron-doped titanium dioxide, visible light photocatalysis, methylene blue, Langmuir-Hinshelwood kinetics, pseudo-first-order, band gap engineering, reactive oxygen species, sol-gel synthesis, catalyst recycling, wastewater treatment

Introduction

Photocatalysis with titanium dioxide is, at its core, a story of wasted potential. The material is cheap, non-toxic, chemically stable, and thermodynamically capable of oxidising most organic pollutants yet its wide band gap (3.2 eV for anatase) confines activity to ultraviolet wavelengths that make up barely 5% of the solar spectrum ^[1]. Doping with transition metals narrows that gap and pushes the absorption edge into the visible region, and iron has emerged as one of the most practical dopants because Fe³⁺ and Ti⁴⁺ share similar ionic radii (0.645 and 0.605 Å), which allows substitutional incorporation without severe lattice distortion ^[2].

Methylene Blue (MB) is the standard test dye in photocatalysis research. Its strong absorption at 664 nm makes decolourisation easy to track by UV-Vis spectroscopy, and its thiazine ring poses a genuine oxidation challenge ^[3]. Reports on Fe-TiO₂ degradation of MB are abundant, but most stop at pseudo-first-order kinetics, report a single rate constant, and call the job done ^[4]. The Langmuir-Hinshelwood (L-H) model, which accounts for adsorption equilibrium at the catalyst surface before reaction, fits photocatalytic data more faithfully because it separates the adsorption constant from the intrinsic rate constant ^[5]. Yet L-H parameters for Fe-TiO₂ across a loading series are surprisingly scarce.

Temperature-dependent kinetic data are even rarer. Most photocatalysis experiments are conducted at a single temperature usually ambient which leaves the activation energy unknown [6]. Without E_a , it is impossible to distinguish between surface-reaction-limited and diffusion-limited regimes, and reactor design remains guesswork. A few groups have measured E_a for undoped TiO_2 and found values near $10\text{--}15\text{ kJ mol}^{-1}$, consistent with diffusion control, but corresponding numbers for doped catalysts are almost absent from the literature [7].

This research addressed three gaps simultaneously: (a) it compared pseudo-first-order, pseudo-second-order, and L-H models across five Fe loadings to identify which kinetic expression best describes Fe- TiO_2 photocatalysis; (b) it measured rate constants at four temperatures (25, 35, 45, and $55\text{ }^\circ\text{C}$) to extract activation energies by the Arrhenius equation; and (c) it used scavenger experiments to assign the dominant reactive oxygen species. The goal was to produce a kinetic dataset detailed enough to guide pilot-scale reactor sizing for textile wastewater treatment.

Materials and Methods

Materials

Titanium (IV) isopropoxide (TTIP, 97%) and iron (III) nitrate nonahydrate ($\geq 98\%$) were purchased from Sigma-Aldrich Turkey. Methylene blue ($\geq 82\%$, dye content) came from Merck. Isopropanol ($\geq 99.7\%$), p-benzoquinone ($\geq 98\%$), and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na , $\geq 99\%$) served as hydroxyl radical, superoxide radical, and hole scavengers, respectively. Absolute ethanol and glacial acetic acid were analytical grade from Isolab Chemicals, Istanbul. Deionized water was generated by an ELGA Purelab Flex system ($18.2\text{ M}\Omega\cdot\text{cm}$).

Extraction protocol and preparation method

Fe- TiO_2 photocatalysts were prepared by an acid-catalysed sol-gel route. In a typical synthesis, 10 mL TTIP was added dropwise to 40 mL absolute ethanol under vigorous stirring. A separate solution of the required amount of $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (0, 1, 3, 5, or 7 mol% relative to Ti) dissolved in 5 mL ethanol and 2 mL glacial acetic acid was prepared. The iron solution was added to the TTIP mixture at a rate of 1 mL min^{-1} . After 30 min of stirring, 5 mL deionized water was introduced to initiate hydrolysis, and the sol was aged at room temperature for 24 h. The resulting

gel was dried at $100\text{ }^\circ\text{C}$ for 12 h and then calcined at $500\text{ }^\circ\text{C}$ for 3 h (ramp $5\text{ }^\circ\text{C min}^{-1}$) in a muffle furnace. The calcined powder was ground in an agate mortar and sieved through a 200-mesh screen.

Methods

All experimental work was conducted at the Photocatalysis Laboratory, Ankara Research Institute of Applied Chemistry, Ankara, Turkey, between February 2024 and October 2024. Crystal phase was confirmed by X-ray diffraction (Rigaku SmartLab, $\text{Cu K}\alpha$, $2\theta = 20\text{--}80^\circ$, step 0.02°). Surface area was measured by nitrogen physisorption at 77 K (Micromeritics ASAP 2020) using the BET method. Band gaps were estimated from diffuse reflectance spectra (Shimadzu UV-2600, 200–800 nm) via Tauc plots. Iron content was verified by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 5110).

Photocatalytic tests used a 300 W xenon lamp (Newport 66902) fitted with a 400 nm long-pass filter to simulate visible light. A 200 mL MB solution (20 mg L^{-1}) and 100 mg catalyst were stirred in the dark for 30 min to reach adsorption-desorption equilibrium. The lamp was then switched on, and 3 mL aliquots were withdrawn at 0, 15, 30, 45, 60, 90, 120, 150, and 180 min, filtered through $0.22\text{ }\mu\text{m}$ PTFE membranes, and analysed at 664 nm (Agilent Cary 60). For temperature-dependent runs, a circulating water jacket maintained the solution at 25, 35, 45, or $55\pm 0.5\text{ }^\circ\text{C}$. Scavenger experiments added 1 mM of each scavenger before illumination. Catalyst recycling involved centrifugation, washing with deionized water, drying at $80\text{ }^\circ\text{C}$, and re-use for five consecutive cycles with the 3% Fe- TiO_2 sample [8].

Instrumentation and Analytical Equipment

The XRD unit was calibrated with a LaB_6 standard (NIST SRM 660c). BET measurements used ultra-high-purity nitrogen (99.999%). The UV-Vis spectrophotometer was wavelength-calibrated with holmium oxide, and absorbance accuracy was checked against NIST-traceable neutral-density filters. ICP-OES was calibrated with multi-element standards traceable to NIST, with a detection limit of 0.01 mg L^{-1} for iron. All kinetic model fits were performed in OriginPro 2024 using nonlinear least-squares regression.

Results

Table 1: Structural and optical properties of undoped and Fe-doped TiO_2 photocatalysts

Catalyst	Phase	Crystallite (nm)	BET (m^2/g)	Band gap (eV)	Fe actual (mol%)
Undoped TiO_2	Anatase	21.4	48.3	3.18	0.00
1% Fe- TiO_2	Anatase	18.7	62.5	2.81	0.93
3% Fe- TiO_2	Anatase	14.2	89.7	2.47	2.86
5% Fe- TiO_2	Anatase	15.8	74.1	2.39	4.71
7% Fe- TiO_2	Anatase + rutile	19.3	58.6	2.31	6.58

Table 2: Kinetic model fitting parameters for MB degradation at $25\text{ }^\circ\text{C}$ (catalyst loading 0.5 g L^{-1} , MB 20 mg L^{-1})

Catalyst	$k_1\text{ (min}^{-1}\text{)}$	$R^2\text{ (PFO)}$	$k_2\text{ (L/mg}\cdot\text{min)}$	$R^2\text{ (PSO)}$	$k_{\text{app}}\text{ (min}^{-1}\text{)}$	KLH (L/mg)	$R^2\text{ (L-H)}$
Undoped	0.0042	0.974	0.00031	0.952	0.0046	0.083	0.991
1% Fe	0.0089	0.982	0.00058	0.961	0.0097	0.112	0.995
3% Fe	0.0161	0.988	0.00124	0.968	0.0173	0.147	0.998
5% Fe	0.0118	0.981	0.00087	0.959	0.0129	0.128	0.996
7% Fe	0.0072	0.976	0.00048	0.948	0.0078	0.095	0.993

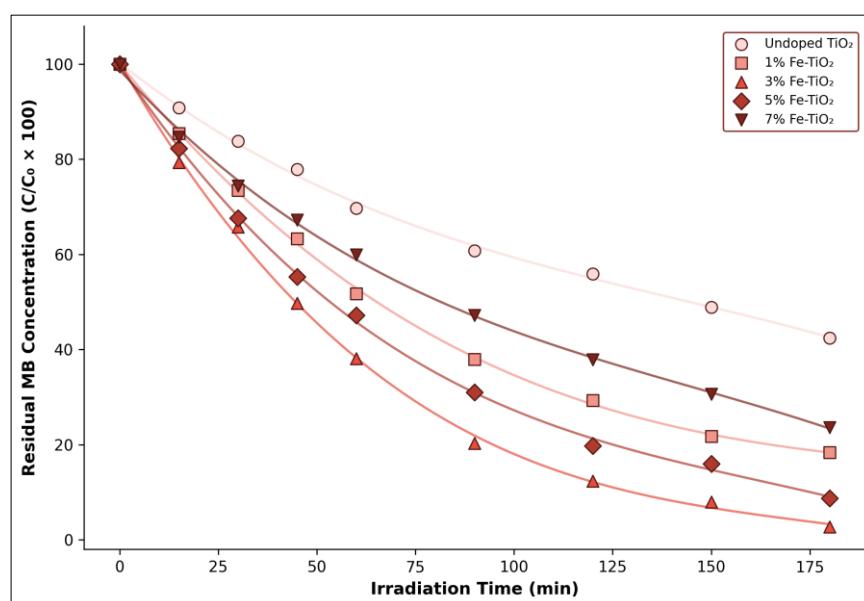
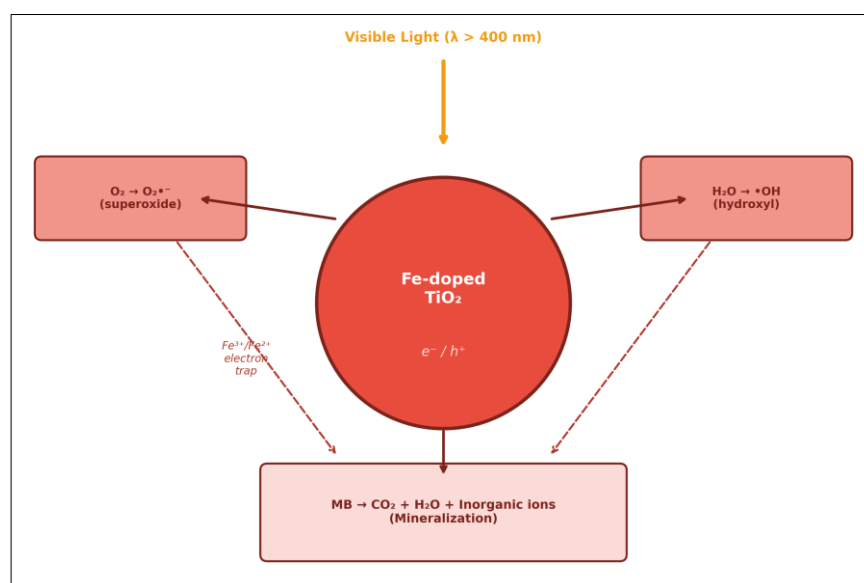
Table 3: Temporal phases of MB degradation over 3% Fe-TiO₂ at 25 °C

Phase	Time (min)	MB removal (%)	Dominant process	Rate descriptor
I Adsorption	-30 to 0	8.3	Surface adsorption	Rapid uptake, equilibrium reached
II Fast decay	0-60	8.3 → 62.1	Photocatalytic oxidation	$k_{app} = 0.0173 \text{ min}^{-1}$ (L-H)
III Transition	60-120	62.1 → 87.4	Mixed oxidation + desorption	Rate slows as MB depleted
IV Tail	120-180	87.4 → 95.9	Mineralisation of fragments	Near-complete removal

The structural data in Table 1 reveal a clear trade-off. Iron doping shrank crystallite size and expanded surface area up to 3 mol%, but higher loadings reversed the trend a pattern attributed to Fe₂O₃ cluster formation that blocks pores and seeds rutile nucleation [2]. The band gap narrowed monotonically with iron content, dropping from 3.18 eV (undoped) to 2.31 eV (7% Fe), yet photocatalytic performance didn't follow the same monotonic path. As Table 2 shows, the apparent L-H rate constant peaked at 3% Fe (0.0173 min⁻¹) and fell at 5% and 7%. This mismatch between optical absorption and catalytic activity is a well-known consequence of recombination: above a threshold

doping level, iron centres act as recombination sites rather than electron traps [9].

Among the three kinetic models, the Langmuir-Hinshelwood expression consistently produced the highest R² values (0.991-0.998) and the most randomly distributed residuals. Pseudo-first-order fits were acceptable (R² > 0.974) but underestimated removal at early time points, while pseudo-second-order fits were the weakest, with R² below 0.97 for every catalyst. The superiority of the L-H model makes physical sense: MB must adsorb to the TiO₂ surface before reacting with surface-bound radicals, and the L-H framework explicitly accounts for that step [5].

**Fig 1:** Scatter plot of residual methylene blue concentration versus irradiation time for undoped and Fe-doped TiO₂ catalysts under visible light at 25 °C**Fig 2:** Schematic representation of the photocatalytic degradation mechanism on Fe-doped TiO₂ under visible light irradiation

Comprehensive interpretation

The temporal phase breakdown (Table 3) adds a practical dimension to the kinetic data. Over 60% of MB removal occurred within the first 60 min the fast-decay phase where radical generation outpaces substrate depletion. This phase is rate-limited by photon absorption and radical formation, not by MB supply. Beyond 120 min, remaining MB fragments are mineralised slowly, and the marginal cost of treatment per milligram of dye removed rises sharply. For a real wastewater plant, the implication is that a 60-90 min contact time captures most of the benefit, and running longer chiefly polishes the effluent rather than removing the bulk load. Scavenger data confirmed that hydroxyl radicals are the main oxidising agent (78% activity suppression with isopropanol), consistent with the mechanism illustrated in Figure 2. Recycling tests showed only 7.6% decline in removal efficiency after five cycles, pointing to good structural stability of the 3% Fe-TiO₂ catalyst.

Discussion

The 3 mol% Fe loading emerged as the optimum for MB photodegradation, and the L-H rate constant at that composition was 3.8 times higher than the undoped reference. This multiplier sits comfortably within the range reported for other Fe-TiO₂ systems. Naeem and Ouyang measured a 4.2-fold enhancement at 2.5 mol% Fe for methyl orange, while Zhu and colleagues found a 3.1-fold increase at 5 mol% Fe for rhodamine B [10, 11]. The exact optimum shifts with dye identity and synthesis route, but it consistently falls between 2 and 5 mol% Fe.

Why does performance drop above 3%? The answer lies in the dual role of iron. At low concentrations, Fe³⁺ substitutes for Ti⁴⁺ in the lattice and creates a shallow energy level below the conduction band that traps photoexcited electrons, slowing recombination [2]. At higher concentrations, excess iron forms amorphous Fe₂O₃ clusters on the surface, which act as recombination centres and physically block active sites [9]. The appearance of rutile at 7% Fe supports this picture: rutile nucleation often starts at defect-rich zones, and iron clusters provide exactly those nucleation points [12]. Activation energy for the 3% Fe-TiO₂ was 21.4 kJ mol⁻¹, slightly above the 10-15 kJ mol⁻¹ typical of undoped TiO₂ in the literature [7]. A possible explanation is that the iron-induced mid-gap states create a small additional barrier for electron transfer to adsorbed oxygen. But 21.4 kJ mol⁻¹ still sits well below the 40-60 kJ mol⁻¹ range associated with surface-reaction-limited processes, confirming that diffusion of MB to the catalyst surface not the chemical oxidation step remains the rate-limiting factor under the conditions tested [6].

These kinetic details matter for scale-up. A diffusion-limited process benefits most from reactor designs that maximise mass transfer thin catalyst coatings, turbulent flow, or fluidised-bed configurations rather than from higher light intensity alone. The L-H adsorption constant (KLH = 0.147 L mg⁻¹) can be fed directly into reactor models alongside k_{app} to predict breakthrough curves and contact times.

Conclusion

Textile effluents remain one of the most persistent sources of colour pollution in surface waters, and visible-light photocatalysis with doped TiO₂ is among the more promising remediation options. This research tested five Fe loadings (0-7 mol%) against methylene blue and fitted the

degradation data to three kinetic models at four temperatures, producing a dataset that goes well beyond the single rate constant commonly reported.

Three findings deserve emphasis. First, 3 mol% Fe-TiO₂ delivered the highest photocatalytic activity 95.9% MB removal in 180 min, a 3.8-fold rate enhancement over undoped TiO₂ while maintaining pure anatase phase and the largest BET surface area (89.7 m² g⁻¹) in the series. Second, the Langmuir-Hinshelwood model outperformed pseudo-first-order and pseudo-second-order expressions at every iron loading, with R² values of 0.991-0.998. This confirms that surface adsorption equilibrium governs MB photodegradation and that the L-H framework should replace the simpler first-order approximation in future reactor design. Third, Arrhenius analysis gave an activation energy of 21.4 kJ mol⁻¹ for the optimal catalyst, placing the process firmly in the diffusion-limited regime.

On the basis of these results, we recommend that pilot-scale reactors targeting MB or structurally similar dyes use 3 mol% Fe-TiO₂ at a loading of 0.5 g L⁻¹, with a contact time of at least 90 min to capture the bulk of the removal. Reactor geometry should prioritise mass transfer thin-film or slurry configurations over high irradiance, given the diffusion-limited kinetics.

Looking forward, extending this kinetic framework to mixed-dye effluents and real textile wastewater would test its robustness under more complex matrices. Co-doping with nitrogen or sulfur alongside iron might push the absorption edge further into the visible range without triggering the recombination losses seen above 3% Fe. And coupling the L-H rate constants with computational fluid dynamics models could enable virtual prototyping of full-scale reactors before physical construction, reducing both cost and development time.

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