

Article

Assessment of the Effect of Zn Co-Doping on Fe/TiO₂ Supports in the Preparation of Catalysts by Wet Impregnation for Photodegradation Reactions of Food Coloring Effluents

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Abstract: This study explores the photocatalytic efficiency of Zn/Fe/TiO₂ catalysts, synthesized via the wet impregnation method, for degrading the food colorings Allura Red and Tartrazine Yellow. A 2² factorial design with a central point replication guided the catalyst synthesis. Characterization involved BET surface area analysis, SEM-EDX, XRD, and PZC determination. Photocatalytic tests were conducted in batch mode under natural sunlight with 10 mg L⁻¹ food coloring solutions. Kinetic modeling and statistical analysis were performed, and catalyst reuse was evaluated under artificial light. Results showed that low calcination temperatures (200–273 °C) and Zn loadings of 2–10% led to nearly 99% discoloration and degradation efficiency. The Behnjady–Modirshahla–Ghanbery kinetic model best described the discoloration data, confirming the significant impact of both variables. The optimal catalyst for Allura Red degradation was 2%Zn/2%Fe/TiO₂ calcined at 200 °C, while for Tartrazine Yellow, 6%Zn/2%Fe/TiO₂ calcined at 300 °C was most effective. Both catalysts exhibited excellent stability, maintaining efficiency over four reuse cycles. These findings demonstrate the potential of Zn/Fe/TiO₂ catalysts for sustainable wastewater treatment.

Keywords: food dyes; photocatalysis; food industry effluents; Zn/Fe/TiO₂; advanced oxidative processes



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1. Introduction

Colorants play a key role in the food industry, where they are used extensively to enhance the visual appeal of products, influence consumer perception, and ensure consistency in food appearance [1]. Among synthetic colorants, Allura Red (AR) and Tartrazine Yellow (TY) are two of the most widely used azo dyes due to their vibrant hues, stability, and cost-effectiveness [2,3]. These dyes are commonly found in beverages, candies, ice creams, baked goods, and processed snacks, particularly in Brazil, where they are integral to the food industry due to their widespread use and low cost [4]. In Brazil, these dyes are added to a variety of food products to meet consumer demands for attractive colors and consistent appearance. However, during production, large amounts of dye-laden wastewater are discharged into the environment, contributing to effluent pollution. The widespread use

of synthetic colorants has led to significant environmental challenges, as large volumes of dye-laden effluents are discharged into water bodies during production and processing [5]. The persistence of these colorants in the environment poses risks to aquatic ecosystems and human health, as they are resistant to conventional wastewater treatment methods [6].

Synthetic colorants, particularly azo dyes like AR and TY, are characterized by complex aromatic structures that make them highly stable and difficult to degrade [7]. When released into water bodies, they can interfere with sunlight penetration, disrupting photosynthetic processes and harming aquatic life [8]. Moreover, some colorants and their degradation byproducts have been linked to carcinogenic and mutagenic effects, raising concerns about their impact on human health [9]. Despite these risks, the treatment of wastewater containing synthetic colorants remains a challenge, as conventional methods such as biological degradation, coagulation, and adsorption often prove ineffective in completely removing these persistent pollutants [10,11].

In recent years, advanced oxidation processes (AOP) have emerged as a promising solution for the degradation of synthetic colorants [12]. AOP generate highly reactive oxygen species, such as hydroxyl radicals ($\bullet\text{OH}$), which can oxidize and mineralize complex organic pollutants into harmless byproducts like CO_2 and H_2O [13]. Among AOP, photocatalysis has gained significant attention due to its ability to harness solar energy for environmental remediation [14]. Photocatalysis involves the activation of a semiconductor material, such as titanium dioxide (TiO_2), by light irradiation, leading to the production of electron–hole pairs that drive redox reactions for pollutant degradation [15]. This approach is particularly relevant for synthetic colorants, as their complex structures require advanced treatment methods for effective breakdown [16].

The use of solar light in photocatalysis offers several advantages over conventional treatment methods [17]. Solar-driven photocatalysis is a sustainable and cost-effective approach, as it utilizes renewable energy and reduces reliance on external power sources [18]. Additionally, it can achieve higher degradation efficiencies for persistent pollutants like synthetic colorants, making it an attractive option for wastewater treatment [19]. However, the widespread application of TiO_2 -based photocatalysts is limited by their relatively wide bandgap, which restricts their activity to ultraviolet (UV) light [20]. To overcome this limitation, doping TiO_2 with transition metals such as zinc (Zn) and iron (Fe) has been explored as a strategy to enhance light absorption in the visible spectrum and improve photocatalytic performance [21,22].

Zinc and iron are particularly attractive dopants due to their ability to modify the electronic structure of TiO_2 , reduce electron–hole recombination, and enhance photocatalytic activity under visible light [23]. The wet impregnation method is a widely used technique for preparing such catalysts, as it allows for uniform dispersion of dopants on the TiO_2 support and is relatively simple to implement. This method involves impregnating a surface area of TiO_2 with a metal precursor solution, followed by evaporation at a high temperature, which leads to the reduction of the metal precursor into metal particles on the support. The advantages of the wet impregnation method over other synthesis techniques include its simplicity, cost-effectiveness, and ability to achieve uniform metal dispersion. Unlike more complex methods such as sol–gel or hydrothermal processes, wet impregnation allows for precise control of the metal loading, is less resource-intensive, and is easier to scale up for practical applications [24]. However, one potential drawback is the weak interaction between the metal particles and the support, which can result in larger particle sizes and the formation of impurities if not optimized. Despite these challenges, the wet impregnation method remains a viable option for synthesizing TiO_2 -based photocatalysts for the degradation of synthetic colorants. The synergistic effects of Zn and Fe doping on TiO_2 supports and their influence on the photodegradation of complex colorants like AR

and TY, however, remain underexplored [25]. Understanding these effects is crucial for optimizing catalyst design and improving the efficiency of solar-driven photocatalysis for the treatment of colorant-laden wastewater [26].

This study aims to assess the effect of Zn doping on Fe/TiO₂ support in the preparation of catalysts via the wet impregnation method for the photodegradation of AR and TY, two of the most widely used synthetic colorants in the food industry. The catalysts will be characterized using advanced techniques. Photocatalytic tests will be conducted under sunlight exposure, and the degradation efficiency will be evaluated through kinetic data modeling, chemical oxygen demand (COD) reduction, and statistical analysis. By optimizing the synthesis parameters, this work seeks to contribute to the development of efficient and sustainable photocatalytic systems for the treatment of wastewater containing synthetic colorants, addressing environmental challenges.

2. Materials and Methods

2.1. Materials

Titanium dioxide (TiO₂, ≥91%), zinc chloride (ZnCl₂, ≥97%), iron chloride (FeCl₃·6H₂O, ≥99%), sodium hydroxide (NaOH, ≥97%), hydrochloric acid (HCl, ≥37%), Allura Red dye (AR, ≥85%), and Tartrazine Yellow dye (TY, ≥85%) were purchased from Merck Sigma-Aldrich (St. Louis, MO, United States). All chemicals used in this study were of analytical grade and were used as received, without further purification. The main solvent used in the synthesis process was ultrapure Milli-Q® water (resistivity of 18 MΩcm).

2.2. Synthesis and Preparation of Zn/Fe/TiO₂ Catalysts

The Fe/TiO₂ catalyst support was synthesized using the wet impregnation method, targeting an iron loading of 2% (m m^{−1}), following the procedure described by Castro et al. [6]. For this, approximately 30 g of TiO₂ was used as the base material. The iron precursor, FeCl₃·6H₂O, was weighed to achieve the desired 2% (m m^{−1}) loading, corresponding to approximately 2.96 g of FeCl₃·6H₂O. The precursor was dissolved in 30 mL of ultrapure Milli-Q® water (resistivity of 18 MΩcm) to form a homogeneous solution. The resulting mixture was stirred at room temperature (~25 °C) in a rotary evaporator for 17 h to ensure complete impregnation of the support. After impregnation, the solvent was evaporated by maintaining the rotary evaporator at 70 °C for 1 h. The partially dried material was then transferred to a vacuum oven and dried at 120 °C under vacuum for 21 h. Subsequently, the dried material was calcined in a muffle furnace at three different temperatures—200 °C, 300 °C, or 400 °C—for 5 h, at a heating rate of 5 °C min^{−1}. This Fe/TiO₂ material served as the support for the subsequent Zn co-doping step.

For the Zn co-doping, the same wet impregnation procedure was employed. ZnCl₂ was used as the zinc precursor, with Zn loadings adjusted to 2%, 6%, and 10% (m m^{−1}) relative to the mass of the Fe/TiO₂ support. Specifically, for each synthesis batch, approximately 30 g of Fe/TiO₂ was impregnated with approximately 1.27 g, 3.99 g, or 6.94 g of ZnCl₂, corresponding to 2%, 6%, and 10% Zn, respectively. The ZnCl₂ was first dissolved in 30 mL of ultrapure Milli-Q® water, and the Fe/TiO₂ support was then added to the solution. The suspension was stirred at room temperature in a rotary evaporator for 17 h, followed by solvent evaporation at 70 °C for 1 h. The resulting material was dried at 120 °C under vacuum for 21 h.

Finally, the Zn/Fe/TiO₂ catalysts were calcined at three selected temperatures—200 °C, 300 °C, or 400 °C—for 5 h, following the same heating protocol as for the support preparation. A 2² central factorial experiment (CFE) was designed to evaluate the effects of calcination temperature and Zn loading on the photodegradation efficiency of AR and TY. The central points were prepared in triplicate to ensure statistical reliability. The levels

of each variable are presented in Table 1. Tests with the Fe/TiO₂ catalyst support were conducted at calcination temperatures of 200, 300, and 400 °C to serve as controls for evaluating the effect of Zn co-doping.

Table 1. Control variables considered in the 2² factorial design and experiments for Zn/Fe/TiO₂ catalyst synthesis.

Experiment	Codified Variables		Non-Codified Variables	
	X ₁	X ₂	Calcination Temperature (°C)	Zn (%)
1	−1	−1	200	2
2	+1	−1	400	2
3	−1	+1	200	10
4	+1	+1	400	10
5	0	0	300	6
6	0	0	300	6
7	0	0	300	6

2.3. Characterization of Zn/Fe/TiO₂ Catalysts

The catalysts were characterized by their morphological, structural, surface, and compositional properties.

N₂ adsorption/desorption isotherms at 77 K were measured using a sorption analyzer (Quantachrome Instruments, model NOVA 2000e, Boynton Beach, USA). Specific surface area (S_o), average pore volume (V_p), and average pore diameter (dp) were calculated using the Brunauer–Emmert–Teller (BET) method, and pore size distribution using the Barrett–Joyner–Halenda (BJH) method.

Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDS, TESCAN, microscope model VEGA3, Brno, Czech Republic) was used to obtain micrographs and determine elemental composition of the adsorbents.

X-ray diffraction (XRD) was performed using a diffractometer with a copper emission line (Cu Kα, λ = 1.54056 Å), operated at 30 kV acceleration voltage, 20 mA current, and a scanning velocity of 2° 2θ min^{−1}.

Surface charge distribution was determined by the point of zero charge (PZC), where 50 mg of the adsorbent was added to 50 mL aqueous solutions at pH ranging from 2 to 12, and pHPZC was measured after 24 h [10,11].

2.4. Photocatalytic Assay

The photocatalytic assays were conducted under sunlight, as illustrated in Figure 1a. The experimental system consisted of a tank-type reactor (a 250 mL beaker) operating in batch mode, with a magnetic stirrer to ensure sample homogenization throughout the 2 h experiment. In the AR and TY discoloration tests (Table 2), reactions were carried out with each catalyst suspension, consisting of 150 mL of a 10 mg L^{−1} aqueous food coloring solution and 50 mg of catalyst, irradiated under sunlight. To evaluate the photocatalytic activity, experiments were performed at two different food coloring solution pH levels, 7 and 4. At reaction times of 0, 30, 60, 90, and 120 min, aliquots were collected for further discoloration analysis. These aliquots were vacuum-filtered using cellulose ester membranes (47 mm in diameter, 0.45 µm porosity) and stored in a refrigerator. The photocatalytic tests were performed from 5 January to 7 January 2025, between 11:00 a.m. and 1:00 p.m. During this period, the average solar radiation was measured using a UV radiation meter (model

LI-200, SIMEPAR, Curitiba, Brazil) in the 390–1100 nm range, with values ranging from 1038.0 to 1087.5 W m^{−2}.

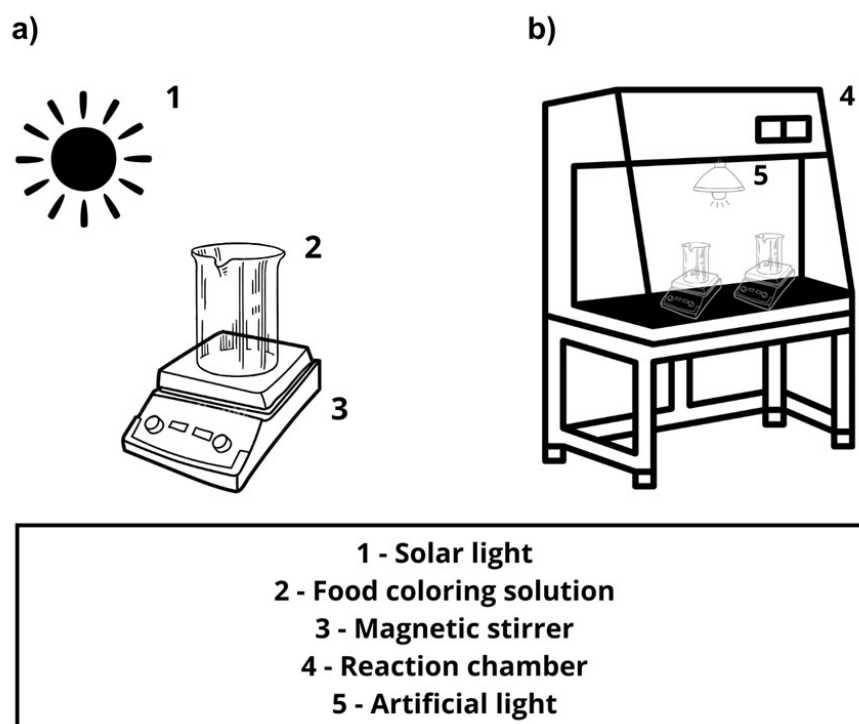


Figure 1. Schematic diagram of the photocatalytic apparatus for food coloring degradation: (a) Under solar light. (b) Under artificial light.

Table 2. Physical–chemical properties of the food coloring.

Food Coloring	C.I. Number	Molecular Formula	$\lambda_{\max}$ (nm)	Solubility (g L ^{−1})	pKa	Chemical Structure
Allura Red AC	16035	C ₁₈ H ₁₄ N ₂ Na ₂ O ₈ S ₂	504.0	~180.0	10.5	
Tartrazine Yellow	19140	C ₁₆ H ₉ N ₄ Na ₃ O ₉ S ₂	427.0	~20.0	4.0	

C.I.—Color index; solubility in water at 25 °C; data obtained from [27].

To better understand the photocatalytic behavior, preliminary adsorption tests were conducted to evaluate the capacity of the catalysts to discolor AR and TY in the absence of light for 30 min, under the same conditions as the photocatalytic assays. Additionally, a photolysis test was performed in the absence of the catalysts to assess the photosensitivity of the food coloring under solar light during a 120 min process.

The discoloration of the solutions over time was determined using a UV-Vis spectrophotometer (Drawell, Model EEQ9011I. UV-B, Chongqing, China), with the measured wavelengths listed in Table 2. Absorbance values were recorded, and concentrations

were determined using the calibration curve method. The discoloration percentage was calculated using Equation (1).

$$D_{AR/TY} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where D represents the percentage of discoloration of the food coloring solutions (AR and TY) (%), C_0 the food coloring concentration before the photocatalytic tests (10 mg L^{-1}) and C_t the food coloring concentration after the photocatalytic test at t time (mg L^{-1}).

2.5. Photodiscoloration Kinetics

To evaluate the discoloration kinetics of the solar photocatalytic process of AR and TY, three models were used: pseudo-first-order (PFO) (Equation (2)), pseudo-second-order (PSO) (Equation (3)), and the Behnajady–Modirshahla–Ghanbery (BMG) (Equation (4)) kinetic model (Table 3).

$$C_t = C_0 e^{(-k_1 t)} \quad (2)$$

$$C_t = \frac{C_0}{1 + (k_2 t C_0)} \quad (3)$$

$$C_t = C_0 \left(1 - \frac{t}{(m + bt)} \right) \quad (4)$$

Table 3. Kinetics models used in the experiment.

Kinetic Model	Equation	Reference
Pseudo-first order	Equation (2)	[28]
Pseudo-second order	Equation (3)	
BMG	Equation (4)	[29]

where C_0 and C_t (mg L^{-1}) are the concentrations of the food coloring at time 0 min and time t, respectively, k_1 is the first-order rate constant, k_2 is the second-order rate constant, and m and b are the two constants of BMG model related to the reaction kinetics and oxidative potential.

2.6. Photodegradation Assessment

The photodegradation of the AR and TY food colorings was evaluated through the reduction in the chemical oxygen demand (COD) percentage at the end of the photocatalytic process (120 min), according to the Standard Methods for Examination of Water and Wastewater [30].

2.7. Catalyst Reusability Test

To assess catalyst reusability, the tests were conducted following the same procedure as the previous batch experiments (Section 2.4). However, in this evaluation, the photocatalytic activity was tested under artificial irradiation using a 250 W mercury vapor lamp, as illustrated in Figure 1b. The reuse tests were repeated four times using the best catalyst and the best conditions from the batch assays.

2.8. Statistical Analysis

The results were analyzed using analysis of variance (ANOVA) to assess statistically significant factors and interaction effects between variables. Significant differences were tested using Tukey's method ($p \leq 0.05$). The experimental results for COD and discoloration percentage were evaluated using response surface methodology (RSM), described by second-order equations (Equation (5)). The regression coefficients for the response variables were determined through RSM, and their significance was confirmed by ANOVA ($p \leq 0.05$). Additionally, the response variables were optimized using the Simplex method.

All statistical analyses were conducted in MiniTab® software (version 19, Minitab, LLC., State College, PA, USA).

$$Y_1 = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i=1}^3 \sum_{j>i}^3 \beta_{ij} X_i X_j \quad (5)$$

where Y_1 is the studied response variable; β_0 is a constant; β_i are coefficients related to linear effects; β_{ii} are coefficients associated with quadratic effects; and β_{ij} are coefficients for second-order cross terms.

3. Results and Discussion

3.1. Catalyst Characterization

The isotherm measurements shown in Figure 2a provide valuable insights into the porous structure and adsorption behavior of the different catalysts, all calcined at the highest temperature of the CFE (2%Fe/TiO₂, 2%Zn/2%Fe/TiO₂, 6%Zn/2%Fe/TiO₂, and 10%Zn/2%Fe/TiO₂). The N₂ adsorption–desorption isotherms at 77 K can be classified according to IUPAC, and for all the catalysts, the isotherm resembles a Type II isotherm, which is characteristic of non-porous or macroporous materials, where adsorption occurs primarily on the external surface rather than within a well-defined porous network [31]. This characteristic can significantly influence the photocatalytic degradation of food coloring, as the efficiency of the process depends on the interaction between the food coloring molecules and the active sites of the photocatalyst [7]. The large external surface area allows for better light exposure and increased accessibility of reactive sites, facilitating the generation of reactive oxygen species, such as hydroxyl radicals, and superoxide anions. These species play a crucial role in breaking down complex food coloring molecules into smaller, less toxic compounds [6]. Additionally, the presence of Zn and Fe dopants in TiO₂ can enhance charge carrier separation and reduce recombination rates, further improving photocatalytic efficiency. The predominance of external surface adsorption in Type II materials ensures that food coloring molecules are readily available for photocatalytic reactions without diffusion limitations, making them highly effective for food coloring degradation under light irradiation [32].

Finally, the BJH pore size distribution (Figure 2b) further supports these observations. The pore size distributions of the catalysts are concentrated between 15.8 to 17.7 Å, falling within the mesoporous range [31]. This range is commonly observed in studies involving co-doped catalysts and composite materials, highlighting their potential for enhanced adsorption and catalytic activity due to their intermediate pore sizes that facilitate better accessibility and interaction with food coloring [6,7,33].

Table 4 presents the textural properties and elemental composition of the synthesized catalysts, highlighting the effects of calcination temperature and metal doping on surface area, pore volume, and pore diameter. Across all catalysts, calcination generally leads to a reduction in surface area, which is expected due to particle sintering and pore collapse at higher temperatures [34–36]. For instance, the 2%Fe/TiO₂ catalyst shows a gradual decrease in S_0 from 15.56 m² g^{−1} in the non-calcined sample to 10.98 m² g^{−1} at 400 °C. A similar trend is observed for the 10%Zn/2%Fe/TiO₂ catalyst, where S_0 drops from 7.56 m² g^{−1} to 6.37 m² g^{−1} after calcination at 400 °C.

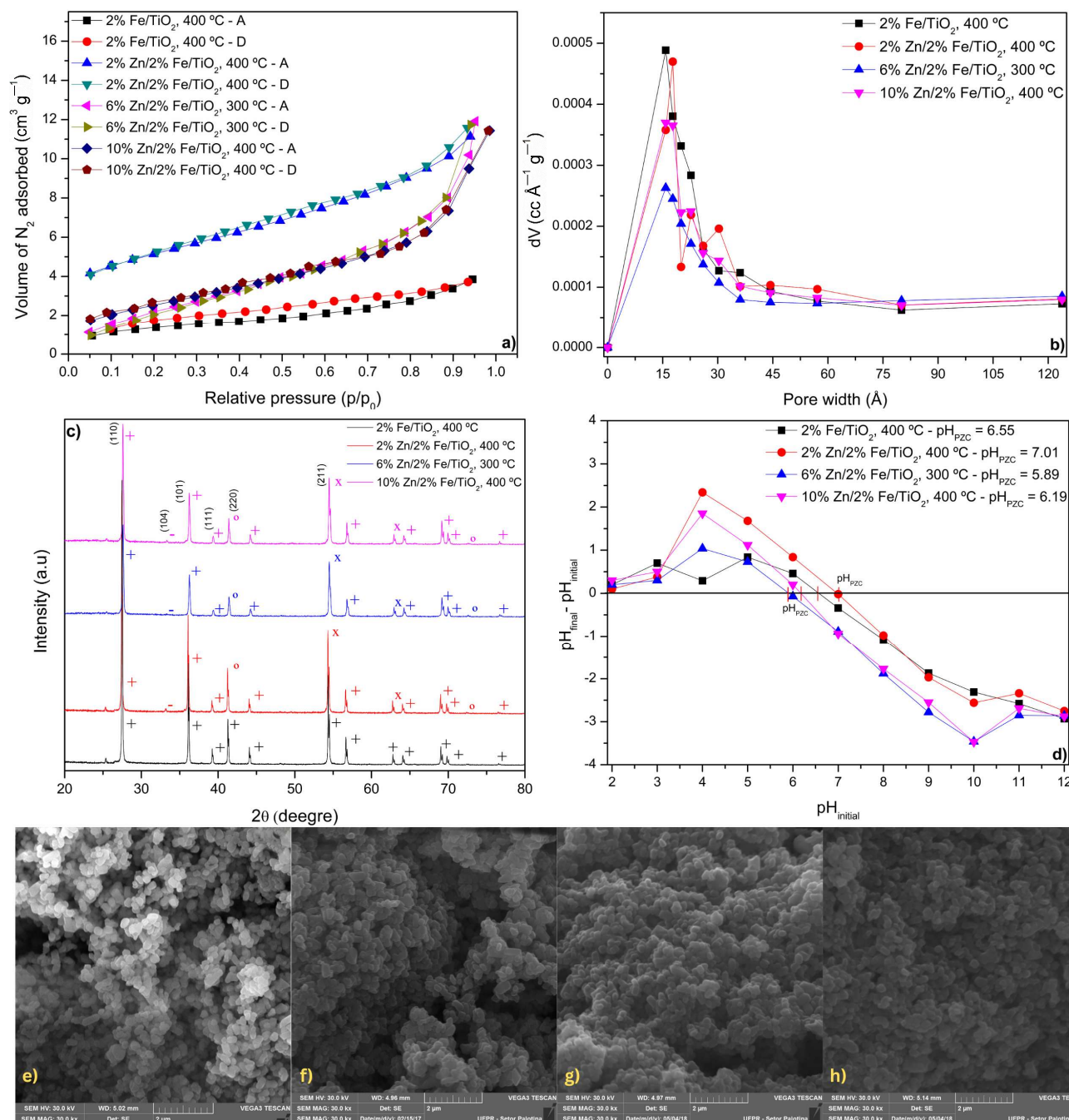


Figure 2. Catalyst characterization results: (a) N₂ adsorption/desorption isotherms; (b) BJH pore size distribution; (c) XRD pattern; (d) Surface charge distribution; SEM micrographs at 30,000× for: (e) 2% Fe/TiO₂; (f) 2% Zn/2% Fe/TiO₂; (g) 6% Zn/2% Fe/TiO₂; and (h) 10% Zn/2% Fe/TiO₂. Legend—XRD peak phases: + TiO₂ (Rutile), × TiO₂ (Anatase), − Fe₂O₃ (Hematite), ° Fe₃O₄ (Magnetite).

While surface area decreases with calcination, pore volume tends to increase slightly, especially at higher temperatures. In the case of 2%Fe/TiO₂, V_p rises from 0.0152 cm³ g⁻¹ in the non-calcined sample to 0.0217 cm³ g⁻¹ at 400 °C, likely due to structural rearrangements and the formation of larger interparticle voids [7].

Table 4. Textural properties and elemental analysis of the catalysts.

Catalyst	Calcination Temperature (°C)	S_o ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$)	d_p (Å)
2%Fe/TiO ₂	non-calcined	15.56	0.0152	27.76
	200	11.36	0.0159	28.56
	300	11.12	0.0163	28.61
	400	10.98	0.0217	28.76
2%Zn/2%Fe/TiO ₂	non-calcined	12.59	0.0134	21.28
	200	11.98	0.0154	25.76
	400	11.90	0.0167	28.00
6%Zn/2%Fe/TiO ₂	non-calcined	9.43	0.0391	85.82
	300	9.10	0.0416	88.29
10%Zn/2%Fe/TiO ₂	non-calcined	7.56	0.0276	73.12
	200	6.62	0.0218	66.12
	400	6.37	0.0306	89.62
Elemental analysis				
Catalyst			Zn (%)	Fe (%)
2%Fe/TiO ₂			-	1.91
2%Zn/2%Fe/TiO ₂			1.90	1.86
6%Zn/2%Fe/TiO ₂			5.74	1.74
10%Zn/2%Fe/TiO ₂			9.21	1.83

The pore diameter remains in the mesoporous range (20–50 Å) for 2%Fe/TiO₂ and 2%Zn/2%Fe/TiO₂, with a slight increase upon calcination. However, for 6%Zn/2%Fe/TiO₂ and 10%Zn/2%Fe/TiO₂, significantly larger pores are observed, with the non-calcined samples already exhibiting pore sizes above 70 Å, reaching 89.62 Å at 400 °C in the case of 10%Zn/2%Fe/TiO₂.

This suggests that higher Zn loading promotes pore expansion, possibly due to the agglomeration of Zn species and changes in structural morphology [6]. Increasing Zn content leads to a progressive decrease in surface area while significantly increasing pore diameter. The 10%Zn/2%Fe/TiO₂ catalyst exhibits the lowest S_o (6.37 $m^2 g^{-1}$) and the largest pores (89.62 Å at 400 °C), indicating that high Zn loading may induce sintering effects, reducing overall surface area but creating larger pores. Fe doping alone in 2%Fe/TiO₂ results in moderate surface area reduction and maintains mesoporosity, whereas co-doping with Zn in 2%Zn/2%Fe/TiO₂ leads to a more pronounced increase in pore diameter, suggesting that Zn contributes more significantly to structural modifications [6,37].

Elemental analysis confirms the successful incorporation of Fe and Zn, with Fe content remaining relatively stable between 1.74% and 1.91%, while Zn content increases proportionally with nominal doping, reaching 9.21% in 10%Zn/2%Fe/TiO₂.

XRD patterns presented in Figure 2c provide insights into the crystalline phases of the synthesized catalysts. The main diffraction peaks correspond to TiO₂ in both its rutile (+) and anatase (×) phases, with additional peaks assigned to iron oxides, specifically Fe₂O₃ (hematite, −) and Fe₃O₄ (magnetite, °). The XRD pattern of 2%Fe/TiO₂ exhibits characteristic peaks for anatase TiO₂ at 25.3° (101), 37.8° (004), 48.0° (200), and 55.1° (211), as well as peaks for rutile TiO₂ at 27.4° (110), 36.0° (101), 41.2° (111), and 54.3° (211).

The dominance of rutile suggests that the wet impregnation synthesis method inherently favors the formation of rutile over anatase [6]. The presence of hematite Fe_2O_3 is indicated by peaks at 33.2° (104) and 49.5° (024), suggesting oxidation of Fe species within the TiO_2 matrix [2].

For the 2%Zn/2%Fe/ TiO_2 catalyst, the diffraction peaks remain similar to those of 2%Fe/ TiO_2 , but with additional peaks attributed to zinc incorporation. Zn doping appears to slightly influence the anatase-to-rutile transformation, potentially stabilizing the anatase phase, as indicated by the persistence of its peaks [6,38]. Hematite and magnetite Fe_3O_4 phases are also detected, with Fe_3O_4 peaks at 30.1° (220), 35.4° (311), and 57.2° (511).

The 6%Zn/2%Fe/ TiO_2 catalyst shows a more prominent anatase phase, with reduced intensity for rutile peaks compared to the previous samples. The main anatase peaks remain at 25.3° (101), 37.8° (004), and 48.0° (200). The presence of hematite and magnetite are still evident, particularly at 33.2° (104) and 35.4° (311). In the case of the 10%Zn/2%Fe/ TiO_2 catalyst, the XRD pattern shows a more pronounced rutile phase, with peaks at 27.4° (110), 36.0° (101), 41.2° (111), and 54.3° (211). Zn incorporation might contribute to structural modifications, as reflected in slight shifts in peak positions and intensities [39,40]. Hematite and magnetite phases remain present, reinforcing the role of Fe species in the overall phase composition.

No peaks related to Zn were detected in the catalysts, likely because Zn ions are not incorporated into the TiO_2 crystal lattice. Instead, they are probably highly dispersed within the material [7]. Overall, the XRD results indicate that Zn and Fe doping introduce additional phases, particularly iron oxide phases. The retention of anatase suggests that Zn might contribute to phase stabilization, while Fe species undergo oxidation, forming hematite and magnetite. These structural changes could significantly impact the catalytic properties of the materials, influencing their photocatalytic and adsorption performance.

Figure 2d presents the results of the point of zero charge analysis performed on the materials. The PZC evaluates the surface characteristics of catalysts, providing information on whether their surfaces exhibit acidic or basic tendencies. A pH_{PZC} value higher than the solution's pH indicates a negatively charged surface, while a pH_{PZC} lower than the solution's pH suggests a positively charged surface. AR solution at 10 mg L^{-1} had a pH of 6.91, while TY solution had a pH of 6.88. The analysis revealed varying pH_{PZC} values among the catalysts. All the catalysts, except for 2%Zn/2%Fe/ TiO_2 , exhibited pH_{PZC} values lower than the pH of the food coloring solution, indicating positively charged surfaces. In contrast, 2%Zn/2%Fe/ TiO_2 displayed a pH_{PZC} higher than the pH of the AR and TY solutions, signifying a negatively charged surface [10,41].

3.2. Photocatalytic Tests

3.2.1. Adsorption and Photolysis Tests

To evaluate the effect of a non-photocatalytic process in the discoloration of the AR and TY aqueous solution, adsorption and photolysis tests were carried out, and the results are shown in Table 5.

Observing the data presented in Table 5, neither adsorption nor photolysis contributed significantly to the overall discoloration process, as the reported percentages remain strikingly low across all tested conditions. For Allura Red at pH 7, adsorption discoloration ranged from 4.44% to 10.03%, suggesting that the adsorption mechanism alone is insufficient for effective food coloring removal. Meanwhile, photolysis was nearly negligible, with discoloration values as low as 0.10–0.15%, reinforcing its minimal role in the process. Similarly, for Tartrazine Yellow at pH 4, adsorption discoloration varied between 1.08% and 8.33%. However, these results still indicate a weak adsorption capacity. Photolysis, though slightly more effective than for Allura Red, remained ineffective, with discoloration values

only reaching 1.05–3.50%. The results suggest that Zn doping can moderately enhance adsorption, particularly for Tartrazine Yellow, but the overall discoloration percentages are too low to be practically meaningful. The photolysis results are particularly striking in their inefficacy, as they consistently failed to exceed 3.5% discoloration under any condition. This implies that photocatalysis under sunlight may be necessary to achieve substantial food coloring removal.

Table 5. Adsorption and photolysis tests for the discoloration of food coloring solutions.

Catalyst	Calcination Temperature	Adsorption Assay				Photolysis Assay			
		Allura Red		Tartrazine Yellow		Allura Red		Tartrazine Yellow	
		pH 7	pH 4	pH 7	pH 4	pH 7	pH 4	pH 7	pH 4
		Discoloration (%)				Discoloration (%)			
2%Fe/TiO ₂	200 °C	5.70	8.75	2.16	8.74	0.15	3.50	0.10	1.05
	300 °C	6.55	9.54	1.08	6.08				
	400 °C	6.77	7.55	3.86	7.35				
2%Zn/2%Fe/TiO ₂	200 °C	7.01	9.77	7.74	9.24				
	400 °C	8.79	9.23	8.33	10.38				
6%Zn/2%Fe/TiO ₂	300 °C	8.14	10.03	2.25	9.99				
10%Zn/2%Fe/TiO ₂	200 °C	5.93	8.88	6.16	8.74				
	400 °C	4.44	7.54	7.35	9.66				

3.2.2. Food Coloring Photodiscoloration Under Sunlight

Figure 3 shows the discoloration of the food coloring during sunlight-driven photocatalytic assays. For all the assays, both for AR and TY, and for the two pH values (7 and 4), the Zn loading positively affects the discoloration of the food coloring, as the lowest values for discoloration were obtained from the 2%Fe/TiO₂ supports.

Zn co-doping onto Fe/TiO₂ can enhance photocatalytic performance in photodiscoloration assays by improving charge carrier separation, increasing surface area, and promoting better food coloring adsorption [6]. The combination of Zn and Fe can create synergistic effects, boosting the generation of reactive oxygen species for more efficient food coloring degradation [42]. When observing the assays for both AR and TY, the effect of calcination temperature on the doped catalysts is also evident. The lowest calcination temperatures (200 and 300 °C) promoted the highest discoloration of the solutions, reaching values higher than 90%; this is probably due to better retention of active sites, optimized crystallinity, and improved surface reactivity [6,7]. Lower temperatures prevent sintering and phase transitions, which can reduce the catalyst's effectiveness [43,44].

And finally, the pH level also clearly affects the photodiscoloration of food coloring, where pH 4 (open symbols) have higher discoloration percentages than pH 7 (close symbols) for both of the solutions, due to the pH-dependent ionization of the food colorings and the electrostatic interactions between the catalyst and the food colorings [45,46]. At pH 4, the catalyst surface is positively charged (due to its pHPZC being between 5.89 and 7.01—Figure 2d), which favors the adsorption of the neutral or weakly negatively charged forms of both AR (pKa 10.5) and TY (pKa 4) [27]. These electrostatic attractions enhance the photocatalytic degradation process [6]. At pH 7, the catalyst surface is near neutral or slightly negative, while both food colorings are anionic, leading to repulsive interactions that reduce adsorption and thus lower the photodegradation efficiency [7,41]. Therefore, the stronger electrostatic interactions at pH 4 improve the catalyst's performance in photodegradation assays [8].

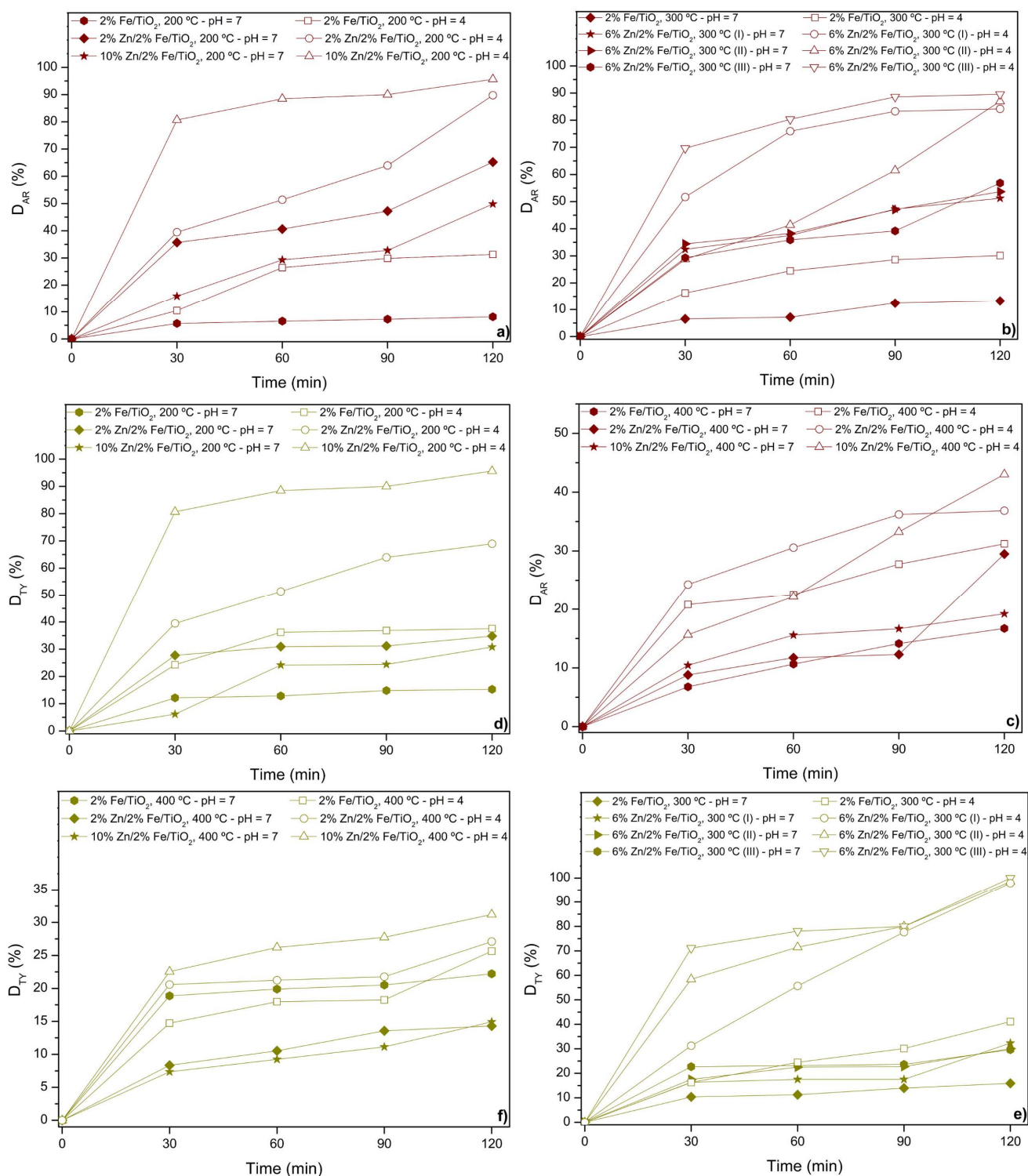


Figure 3. Photocatalytic discoloration under sunlight: assays for catalysts calcined at (a) 200 °C, (b) 300 °C, (c) 400 °C for Allura Red solution, and (d) 200 °C, (e) 300 °C, (f) 400 °C for Tartrazine Yellow solution. Legend: open symbols (pH 4), closed symbols (pH 7).

In summary, the best catalyst for AR photodiscoloration was 10%Zn/2%Fe/TiO₂ calcined at 200 °C, achieving values close to 95.6% at pH 4. For TY photodiscoloration, the best catalysts were 6%Zn/2%Fe/TiO₂ calcined at 300 °C and 10%Zn/2%Fe/TiO₂ calcined at 200 °C, achieving values close to 99.9% and 95.6%, respectively. These results highlight the influence of both catalyst composition and calcination temperature on the efficiency of

photodiscoloration, with optimal performance observed at specific pH conditions for each food coloring.

The photodegradation mechanism of dyes Allura Red (AR) and Tartrazine Yellow (TY) by TiO_2 catalysts co-doped with Zn and Fe involves a series of photo-induced processes that promote the generation of reactive oxygen species (ROS). Under conditions of irradiation, the photocatalyst absorbs photons and generates electron–lacuna pairs (e^-/h^+). The doping of Zn^{2+} has been shown to modify the band structure and enhance light absorption, while Fe^{3+} functions as an electron trap through the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox cycle, thereby promoting charge separation and reducing recombination. The excited electrons react with molecular oxygen, thereby generating superoxide anions (O_2^-). Concurrently, the gaps participate in the oxidation of water or hydroxyl ions, which results in the formation of hydroxyl radicals ($\text{OH}^\bullet$). These ROS promote the oxidative degradation of the dyes adsorbed on the catalyst surface.

Furthermore, the pH of the solution is a pivotal factor in the efficacy of the process, as the surface charge of the catalysts becomes positive in an acidic environment (pH 4), thereby promoting electrostatic attraction and the adsorption of the anionic dyes AR and TY. The porous nature of the materials under scrutiny exerts a direct influence on the photocatalytic activity. Textural analyses indicate the presence of mesopores with diameters that are suitable for the diffusion and interaction of the dyes with the active sites. This phenomenon is particularly evident in catalysts with a higher Zn content, which possess larger pores and facilitate enhanced mass transport. The high decolorization efficiency observed under optimized conditions is attributable to a synergistic set of structural, electronic, and surface effects. Figure 4 presents a schematic representation of the adsorption and photocatalytic degradation mechanism, as outlined in the text.

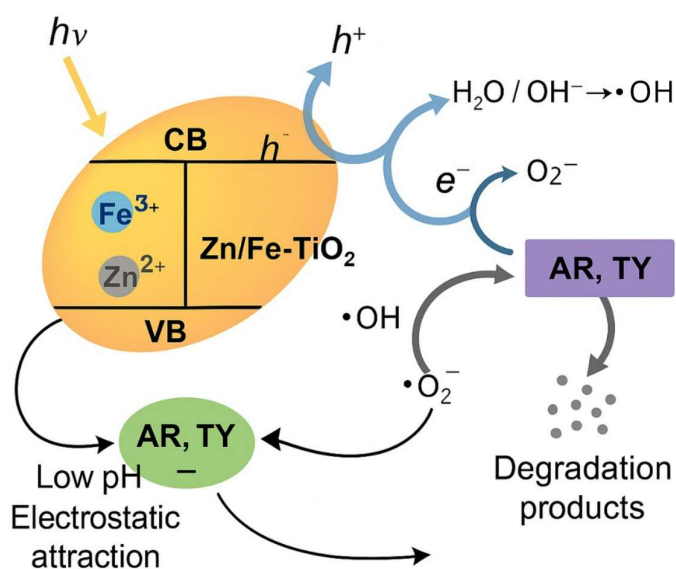


Figure 4. Schematic representation of the adsorption and photocatalytic degradation mechanism.

3.2.3. Kinetic Modeling of Photodiscoloration Process Under Sunlight

The kinetics of the photocatalysis process can be quite complex due to the numerous steps occurring simultaneously [6]. Three kinetic models—the first-order, second-order, and Behnajady–Modirshahla–Ghanbery models—have been used to assess the fit of experimental data obtained from the discoloration processes. The kinetic parameters for the discoloration of AR and TY, using different catalysts and pH conditions, were calculated based on the models shown in Table 3. The results are presented in Table 6.

Table 6. Kinetic parameters determined for the Zn/Fe/TiO₂ photocatalysis assays.

Food Coloring	Model	Parameters	Catalysts							
			2%Fe/TiO ₂			2%Zn/2%Fe/TiO ₂		6%Zn/2%Fe/TiO ₂	10%Zn/2%Fe/TiO ₂	
			Calcination Temperature (°C)							
			200	300	400	200	400	300	200	400
AR (pH 7)	PFO	k ₁ (10 ^{−3} min ^{−1})	0.85	1.32	1.66	8.74	2.3	7.29	5.31	2.09
		R ² _{adj}	0.635	0.906	0.960	0.907	0.834	0.867	0.971	0.817
		SD (mg L ^{−1})	0.194	0.163	0.131	0.727	0.436	0.738	0.316	0.326
	PSO	k ₂ (10 ^{−4} L mg ^{−1} min ^{−1})	0.89	1.42	1.81	13.10	2.57	10.40	6.77	2.35
		R ² _{adj}	0.658	0.918	0.973	0.942	0.820	0.942	0.963	0.855
		SD (mg L ^{−1})	0.188	0.153	0.108	0.573	0.455	0.487	0.360	0.290
	BMG	m (dimensionless)	214.8	440.5	375.9	63.78	347.9	51.88	151.0	165.4
		b (dimensionless)	11.00	3.81	2.89	1.16	1.22	1.565	1.33	3.91
		R ² _{adj}	0.991	0.938	0.999	0.928	0.915	0.984	0.950	0.994
		SD (mg L ^{−1})	0.030	0.133	0.024	0.642	0.142	0.251	0.419	0.06
AR (pH 4)	PFO	k ₁ (10 ^{−3} min ^{−1})	3.75	3.66	3.71	13.79	4.93	21.77	47.86	4.59
		R ² _{adj}	0.913	0.858	0.772	0.958	0.787	0.980	0.977	0.989
		SD (mg L ^{−1})	0.405	0.465	0.580	0.680	0.700	0.506	0.603	0.174

Table 6. *Cont.*

Food Coloring	Model	Parameters	Catalysts								
			2%Fe/TiO ₂			2%Zn/2%Fe/TiO ₂		6%Zn/2%Fe/TiO ₂	10%Zn/2%Fe/TiO ₂		
			Calcination Temperature (°C)								
			200	300	400	200	400	300	200	400	
AR (pH 4)	PSO	k_2 (10 ⁻⁴ L mg ⁻¹ min ⁻¹)	4.52	4.44	45.20	23.50	6.40	43.90	133.0	5.68	
		R ² _{adj}	0.941	0.912	0.836	0.926	0.872	0.990	0.999	0.983	
		SD (mg L ⁻¹)	0.332	0.366	0.492	0.899	0.543	0.355	0.143	0.215	
	BMG	m (dimensionless)	163.3	108.8	73.38	42.87	59.30	23.68	7.16	174.5	
		b (dimensionless)	1.65	2.35	2.75	1.33	2.19	1.47	1.00	1.96	
		R ² _{adj}	0.946	0.998	0.974	0.901	0.997	0.986	0.998	0.977	
		SD (mg L ⁻¹)	0.320	0.059	0.196	0.993	0.087	0.420	0.163	0.248	
		TY (pH 7)	PFO	k_1 (10 ⁻⁴ min ⁻¹)	3.07	16.80	27.10	46.10	15.40	34.70	32.80
R ² _{adj}	0.548			0.748	0.473	0.586	0.815	0.593	0.923	0.898	
SD (mg L ⁻¹)	0.432			0.309	0.667	0.911	0.247	0.730	0.369	0.177	
PSO	k_2 (10 ⁻⁴ L mg ⁻¹ min ⁻¹)		1.95	1.85	3.16	5.95	1.67	4.21	3.85	1.53	
	R ² _{adj}		0.600	0.782	0.555	0.700	0.843	0.673	0.930	0.912	
	SD (mg L ⁻¹)		0.398	0.287	0.613	0.775	0.227	0.654	0.351	0.163	

Table 6. Cont.

Food Coloring	Model	Parameters	Catalysts							
			2%Fe/TiO ₂			2%Zn/2%Fe/TiO ₂		6%Zn/2%Fe/TiO ₂	10%Zn/2%Fe/TiO ₂	
			Calcination Temperature (°C)							
			200	300	400	200	400	300	200	400
TY (pH 7)	BMG	m (dimensionless)	72.10	155.2	28.68	26.29	223.5	35.24	245.9	346.8
		b (dimensionless)	6.07	5.33	4.43	2.77	5.13	3.45	1.15	4.30
		R ² _{adj}	0.991	0.971	0.995	0.993	0.991	0.953	0.907	0.958
		SD (mg L ⁻¹)	0.059	0.105	0.065	0.119	0.055	0.247	0.403	0.113
TY (pH 4)	PFO	k ₁ (10 ⁻³ min ⁻¹)	5.27	4.41	3.88	11.73	2.66	23.56	47.86	3.12
		R ² _{adj}	0.744	0.975	0.673	0.953	0.798	0.971	0.977	0.595
		SD (mg L ⁻¹)	0.811	0.241	0.711	0.594	0.425	0.635	0.603	0.666
	PSO	k ₂ (10 ⁻⁴ L mg ⁻¹ min ⁻¹)	6.98	5.45	4.80	19.30	3.06	51.10	133.0	3.71
		R ² _{adj}	0.844	0.984	0.760	0.995	0.836	0.967	0.999	0.668
		SD (mg L ⁻¹)	0.633	0.194	0.609	0.187	0.383	0.675	0.144	0.603
	BMG	m (dimensionless)	51.97	178.3	48.08	47.07	123.4	21.20	7.16	40.84
		b (dimensionless)	2.13	1.06	2.93	1.06	3.32	1.63	1.01	3.74
		R ² _{adj}	0.983	0.979	0.993	0.995	0.931	0.954	0.998	0.958
		SD (mg L ⁻¹)	0.206	0.223	0.104	0.187	0.248	0.797	0.163	0.215

As the correlation coefficient (R^2) approaches 1, the experimental kinetic data align more closely with the kinetic model. As seen in Table 5, the first-order and second-order models do not fit the experimental data well due to their low correlation coefficients. However, the correlation coefficients for the BMG model are generally higher than those of the first-order and second-order models. Therefore, the BMG kinetic model is the most suitable for describing the discoloration of food coloring under various reaction conditions via photocatalysis under sunlight. The BMG model has been successfully applied to describe the discoloration kinetics of AR and TY, and its plot is shown in Figure 5.

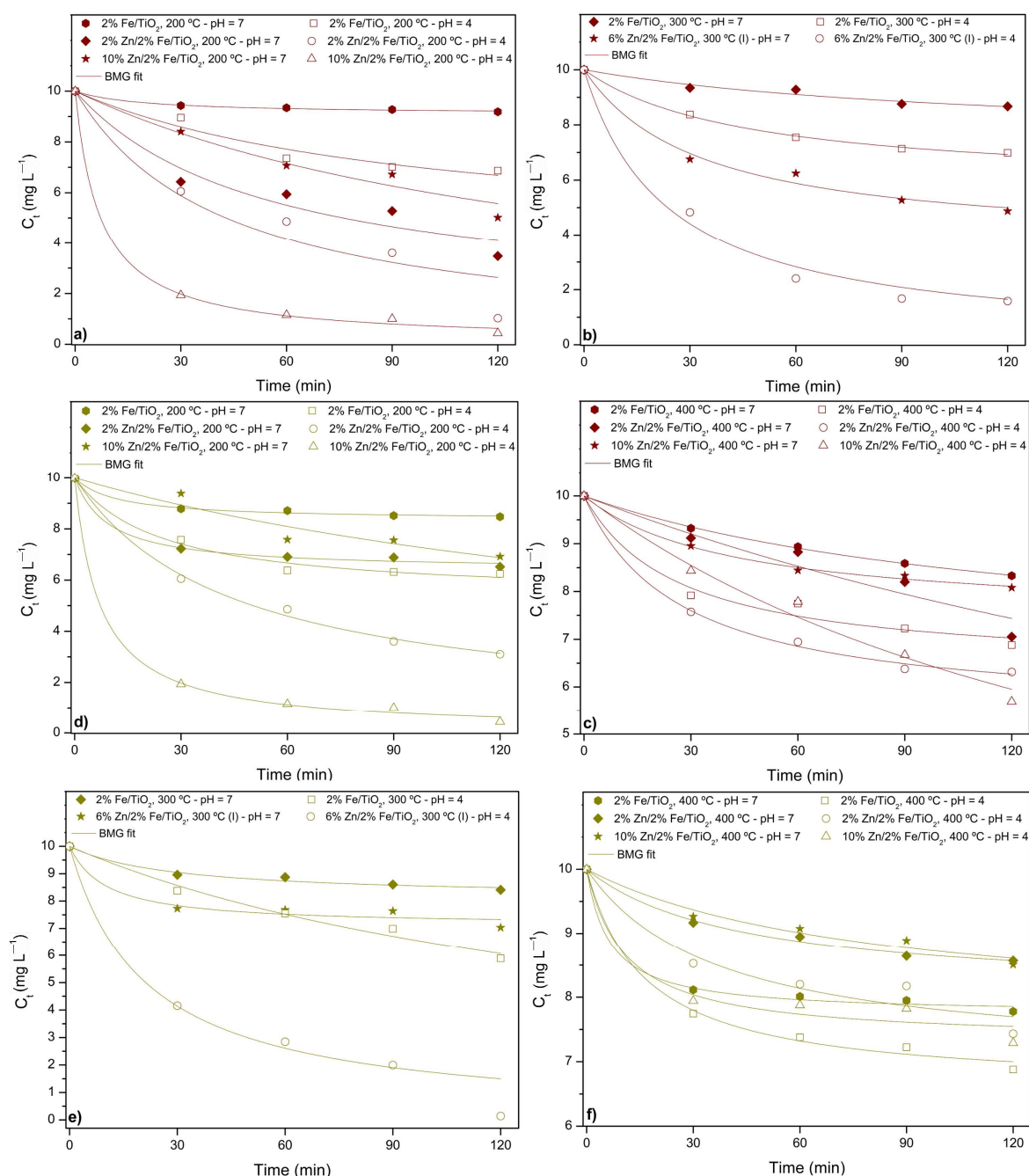


Figure 5. BMG kinetic curves for photocatalytic assays with catalysts calcined at (a) 200 °C, (b) 300 °C, (c) 400 °C for Allura Red solution, and (d) 200 °C, (e) 300 °C, (f) 400 °C for Tartrazine Yellow solution. Legend: open symbols (pH 4), closed symbols (pH 7).

3.2.4. Food Coloring Photodegradation Assessment

The degradation of the complex structure of the food coloring into less polluting compounds was assessed by measuring the reduction in the chemical oxygen demand of the solutions after the photocatalytic reaction. The results are presented in Figure 6.

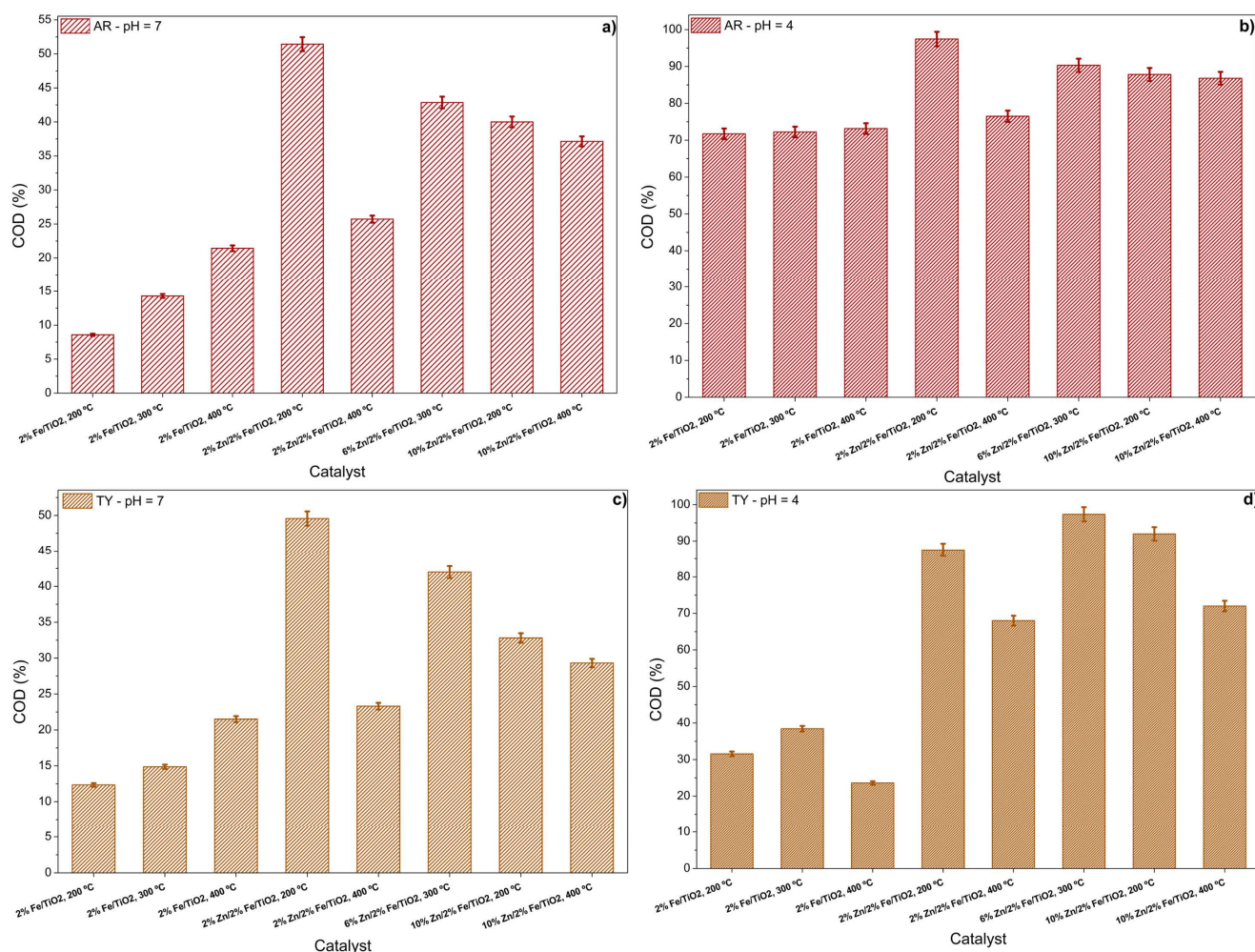


Figure 6. COD removal by different catalysts for food coloring solution degradation: (a) Allura Red at pH 7, (b) Allura Red at pH 4, (c) Tartrazine Yellow at pH 7, and (d) Tartrazine Yellow at pH 4.

It was observed that in the tests conducted at pH 7 for both AR and TY (Figure 6a and c), the maximum COD reduction was approximately 50%, achieved using the 2%Zn/2%Fe/TiO₂ catalyst calcined at 200 °C for both food colorings. This reinforces the fact that neutral pH conditions hinder the catalysts' ability to break down food coloring molecules into compounds with a lower organic load. However, under more acidic conditions (pH 4), both food colorings exhibited COD reductions exceeding 95% (Figure 6b and d). For AR, the most effective catalyst was again the 2%Zn/2%Fe/TiO₂ calcined at 200 °C, while for TY, the best performance was observed with the 6%Zn/2%Fe/TiO₂ catalyst calcined at 300 °C. These results demonstrate that the synthesized materials can effectively degrade a wide range of food colorings, breaking them down into compounds with lower organic loads and potentially harmless byproducts.

Studies in the literature have reported similar behavior in dye degradation using different catalysts. Modirshahla et al. (2013) [47] achieved a COD reduction of approximately 92% when degrading Tartrazine Yellow using ZnO catalysts. Similarly,

Gupta et al. (2011) [48] reported a COD reduction of around 94% when degrading Tartrazine Yellow with TiO_2 catalysts.

3.2.5. Catalyst Reusability Assessment

Figure 7 illustrates the reusability of the studied catalysts for the photodegradation of AR and TY over four cycles under UV irradiation. In this study, the most effective catalyst for AR degradation was 2%Zn/2%Fe/ TiO_2 calcined at 200 °C, while for TY, it was 6%Zn/2%Fe/ TiO_2 calcined at 300 °C, as previously observed in Section 3.2.3.

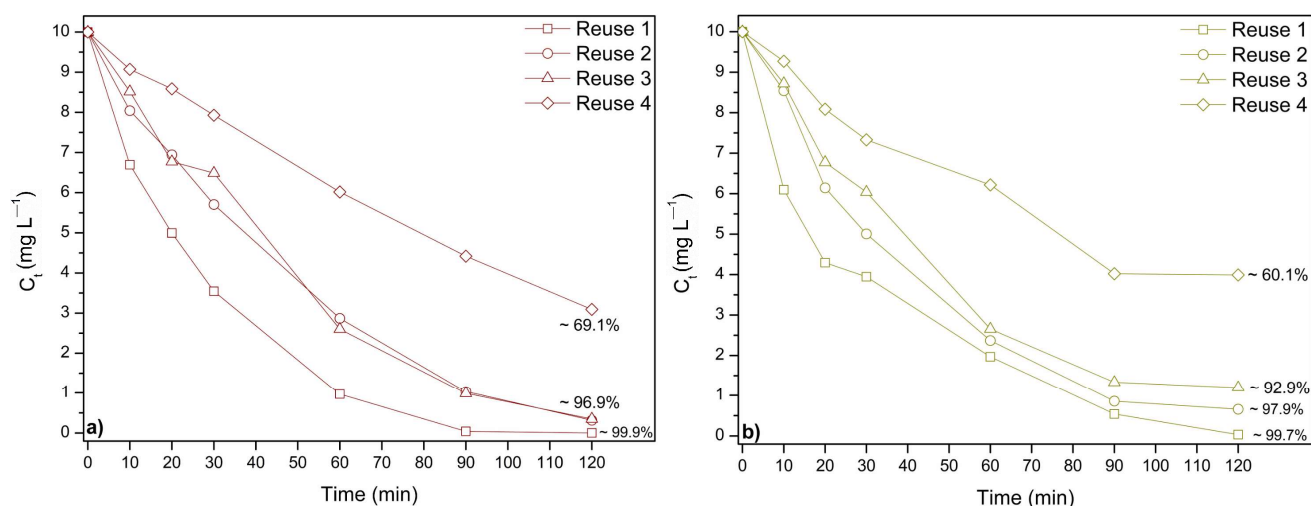


Figure 7. Reuse performance of the optimal catalyst in the photodegradation of food coloring: (a) Allura Red, and (b) Tartrazine Yellow.

The food coloring concentration was readjusted to its initial value before each cycle. All catalysts exhibited a significant decline in performance from the first to the last cycle. For AR (Figure 7a), the first reuse achieved approximately 99.9% degradation, while by the fourth cycle, this value dropped to around 69%. Similarly, for TY (Figure 7b), the first reuse resulted in approximately 99.7% degradation, decreasing to about 60% in the fourth cycle.

These results indicate that although the catalysts maintain a considerable degradation capacity over multiple cycles, their efficiency decreases over time, likely due to catalyst deactivation caused by surface fouling, structural modifications, or active site depletion [6,7]. Further studies on catalyst regeneration strategies could help improve their long-term stability and reusability.

3.3. Statistical Analysis and Optimization

The effects of different temperatures and pH levels were investigated using a 2^2 response surface methodology design with replication at the central point. A statistical model incorporating second-order functions was evaluated for all response variables obtained from the photocatalytic assays and analyzed using ANOVA. Table 7 presents the ANOVA results for the response variables.

For AR discoloration and TY COD, factor x (calcination temperature), factor y (Zn %), and factor x^2 had a statistically significant effect at a 5% significance level (p -value < 0.05). Additionally, for AR COD, the factors x, x^2 , and the interaction between $x \times y$ (calcination temperature $\times$ Zn %) also exhibited a significant statistical effect at the same significance level. Finally, for TY discoloration, all factors and interactions had a statistically significant effect at a 5% significance level (p -value < 0.05).

Table 7. Analysis of variance.

Source	df	AR Discoloration (%)				AR COD (%)				TY Discoloration (%)				TY COD (%)			
		SS	MS	f-Value	p-Value	SS	MS	f-Value	p-Value	SS	MS	f-Value	p-Value	SS	MS	f-Value	p-Value
A	1	5451.2	5451.2	2050.6	0.001	244.01	244.01	590.1	0.001	6168.8	6168.8	5928.9	0.001	678.8	678.8	520.8	0.001
B	1	65.84	65.84	24.77	0.003	0.15	0.15	0.36	0.571	459.5	459.5	441.6	0.001	56.13	56.13	43.07	0.001
A ²	1	909.4	909.4	342.1	0.001	30.30	30.30	73.24	0.001	4249.1	4249.1	4083.8	0.001	715.1	715.1	548.7	0.001
A × B	1	0.81	0.81	0.31	0.600	192.8	192.8	466.0	0.001	347.6	347.6	334.0	0.001	1.93	1.93	1.48	0.269
Error	6	15.95	2.66			2.48	0.41			6.20	1.04			7.82	1.30		
Lack of fit	3	10.63	3.54	2.00	0.26	1.65	0.55	1.83	0.20	4.10	1.37	1.96	0.27	5.22	1.74	2.02	0.25
Total	10	6443.2				469.8				11,231.2				1459.8			

A—Calcination temperature, and B—Zn content; *df* = degree of freedom; SS = sum of squares; MS = mean square.

The residual error for AR discoloration, AR COD, TY discoloration, and TY COD was found to be 1.63, 0.64, 1.02, and 1.14, respectively. The low residual error values indicate that the model effectively predicts the behavior of the variables used in the experiment.

Level curves were generated for the statistically valid variables (Figure 8). The AR discoloration percentage was maximized at a lower temperature range, in the dark greenish region between 200 and 270 °C (Figure 8a), independent of Zn % variation. This result suggests that calcination temperature is the dominant factor influencing the discoloration of Allura Red solutions. However, for AR COD reduction (Figure 8b), the highest values were achieved at the lowest calcination temperatures (between 200 and 240 °C) and the lowest Zn % (between 2 and 3.5%).

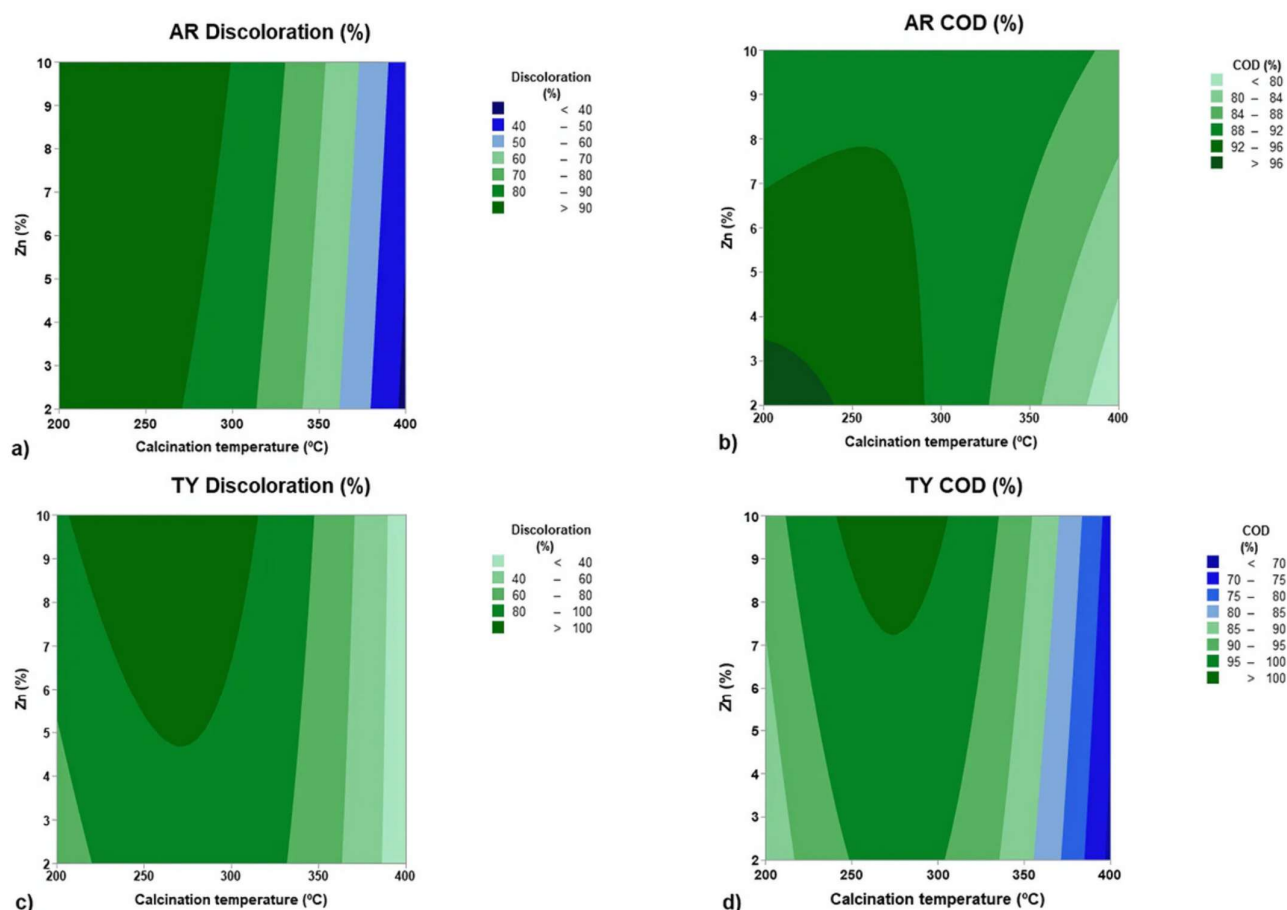


Figure 8. Response surface plots of the statistical analysis: (a) 2D—level curve for AR discoloration; (b) 2D—level curve for AR COD; (c) 2D—level curve for TY discoloration; and (d) 2D—level curve for TY COD.

For TY discoloration and TY COD reduction (Figure 8c,d), the highest removal efficiencies were observed at intermediate temperatures (between 250–300 °C) and Zn % values in the middle-to-high range (~5–10%). These findings suggest that different operational parameters can be adjusted to optimize calcination temperature and Zn %, depending on the desired outcome for each response variable.

The equations for AR discoloration (Equation (6)), AR COD (Equation (7)), TY discoloration (Equation (8)), and TY COD (Equation (9)), were derived, along with the determination coefficients for the adjusted regression models based on second-order functions.

The determination coefficient was found to be greater than 0.984 for all models, indicating that the models accurately fit the experimental data. To optimize the factorial design and maximize the response variables, the obtained models were subjected to Simplex

method analysis to determine the optimal values of the factors that yield the highest discoloration and/or COD reduction.

The calculations were performed using the Solver tool in Microsoft Office Excel®. The constraints applied in the software were based on the factorial design limits: $200 \leq x \leq 400$ °C and $2 \leq y \leq 10$, with the objective function being the response variable itself. The optimization results were as follows:

- AR discoloration: T = 236 °C, Zn % = 10, with 97.9% discoloration;
- AR COD reduction: T = 200 °C, Zn % = 2, with 97.8% COD reduction;
- TY discoloration: T = 261 °C, Zn % = 10, with 100% discoloration;
- TY COD reduction: T = 273 °C, Zn % = 10, with 100% COD reduction.

These different optimization conditions demonstrate the flexibility of the photocatalytic process, allowing adjustments in operational parameters depending on the desired outcome. The ability to fine-tune calcination temperature and Zn % offers a valuable advantage in tailoring the process for specific food coloring degradation needs, improving both efficiency and adaptability in practical applications.

$$\text{AR Discoloration (\%)} = -21.39 + 0.959 \times A + 0.478 \times B - 0.002 \times A^2 + 0.0008 \times A \times B$$

$$(S = 1.63; R^2 = 0.997; R_{\text{adj}}^2 = 0.994) \quad (6)$$

$$\text{AR COD (\%)} = 96.14 + 0.095 \times A - 3.65 \times B - 0.0004 \times A^2 + 0.0123 \times A \times B$$

$$(S = 0.64; R^2 = 0.995; R_{\text{adj}}^2 = 0.984) \quad (7)$$

$$\text{TY Discoloration (\%)} = -256.11 + 2.469 \times A + 6.838 \times B - 0.004 \times A^2 - 0.0165 \times A \times B$$

$$(S = 1.02; R^2 = 0.999; R_{\text{adj}}^2 = 0.998) \quad (8)$$

$$\text{TY COD (\%)} = -43.52 + 1.001 \times A + 1.031 \times B - 0.0018 \times A^2 - 0.0012 \times A \times B$$

$$(S = 1.14; R^2 = 0.995; R_{\text{adj}}^2 = 0.991) \quad (9)$$

where x represents the calcination temperature (°C) and y represents the Zn content (%) used in the photocatalytic process.

4. Conclusions

In this work, Zn/Fe/TiO₂ catalysts were successfully synthesized using the wet impregnation method. The variation in Zn content and calcination temperature had a significant influence on both the discoloration and degradation efficiency of aqueous solutions containing the food colorings Allura Red and Tartrazine Yellow.

Statistical analysis confirmed that both calcination temperature and Zn loading played a crucial role in discoloration efficiency and COD removal. The optimal conditions were achieved at low calcination temperatures ranging from 200 °C to 273 °C, with Zn loadings varying between 2% and 10%, resulting in up to 98% discoloration and COD removal for both food colorings.

Among the catalysts tested, the best performance for Allura Red was observed with 2%Zn/2%Fe/TiO₂ calcined at 200 °C, while for Tartrazine Yellow, the most effective catalyst was 6%Zn/2%Fe/TiO₂ calcined at 300 °C. Additionally, both catalysts demonstrated stability, maintaining effectiveness over four reuse cycles.

These findings provide valuable insights for future studies exploring a wider range of calcination temperatures and metal loadings. Furthermore, while optimizing catalytic

performance is crucial, it is equally important to consider the economic and environmental implications, as higher synthesis temperatures and increased metal content can elevate production costs. The results of this study contribute to the development of cost-effective and efficient photocatalysts for the degradation of organic pollutants in wastewater treatment applications.

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