

Article

Influence of Fe and Zn Loading and Calcination Temperature on Sol–Gel-Derived TiO₂ Photocatalysts for Food-Industry Effluent Treatment

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Abstract

Fe/Zn-modified TiO₂ photocatalysts were synthesized by the sol–gel method to investigate the influence of Fe loading, Zn loading, and calcination temperature on the degradation of food-industry pollutants. A 2³ factorial design combined with Response Surface Methodology was employed to optimize the synthesis parameters. The catalysts were characterized by N₂ adsorption–desorption, SEM/EDS, X-ray diffraction coupled with Rietveld refinement and point of zero charge analyses. The materials exhibited mesoporous structures with type IV isotherms, while Fe/Zn modification altered the crystalline phase composition and surface charge of TiO₂. Low metal loading stabilized the anatase phase, whereas higher Fe contents promoted the formation of hematite and rutile. Photocatalytic performance was evaluated through the discoloration and degradation of Red 40 and Tartrazine under natural sunlight and the degradation of cheese whey under artificial irradiation. F10Z2-400 exhibited the highest activity toward Red 40 (99.85% discoloration and 77.02% COD removal), whereas T-400 showed the best performance for tartrazine (86.25% discoloration and 87.61% COD removal). For cheese whey, F10Z10-400 achieved the highest degradation (41.01% COD removal). Reactive-species scavenging indicated that hydroxyl radicals made the predominant contribution to the discoloration of both dyes, followed by superoxide radicals and photogenerated holes. Kinetic analyses indicated that the Behnajady–Modirshahla–Ghanbery model best described the degradation process. RSM identified calcination temperature as the most influential synthesis parameter and showed that the effects of Fe and Zn loading were pollutant-dependent. No single catalyst formulation provided the best performance for all evaluated matrices.

Keywords: Fe/Zn-modified TiO₂; sol–gel synthesis; heterogeneous photocatalysis; food wastewater treatment; Response Surface Methodology; reactive-species scavenging



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1. Introduction

The continuous growth of the global population and the increasing demand for processed foods have substantially expanded the food-manufacturing industry in recent decades [1]. Although this expansion has improved food availability, it has also resulted in the generation of large volumes of industrial wastewater containing high concentrations of organic matter, nutrients, and synthetic additives [2]. Among food-industry wastewaters, effluents containing synthetic colorants and dairy-processing residues are of particular concern because of their complex compositions and the environmental challenges associated with their treatment [3,4].

Synthetic azo dyes such as Red 40 and Tartrazine are extensively used in beverages, confectionery products, dairy products, and other processed foods because of their high coloring efficiency and chemical stability [5]. However, these same properties make them resistant to conventional biological treatment processes. Their release into aquatic environments can reduce light penetration, disrupt photosynthetic activity, and generate potentially toxic aromatic transformation products, thereby posing risks to aquatic ecosystems and human health [6]. Similarly, cheese whey, the principal by-product of cheese manufacturing, represents a major agro-industrial waste stream because of its exceptionally high organic load, as reflected by its elevated chemical oxygen demand (COD) [7,8]. When discharged without adequate treatment, cheese whey can rapidly deplete dissolved oxygen in receiving water bodies and cause severe environmental damage [9].

Given the potential effects of dye-containing wastewater and high-strength agro-industrial effluents on aquatic ecosystems and public health, their treatment remains a major environmental challenge [10]. Conventional treatment processes, including adsorption, membrane filtration, coagulation–flocculation, ion exchange, and biological treatment, are widely employed for industrial wastewater remediation [11,12]. Nevertheless, these methods may be limited by the incomplete degradation of recalcitrant organic compounds, the generation of secondary waste, high operating costs, or insufficient efficiency toward chemically stable synthetic dyes [11,13]. Consequently, increasing attention has been directed toward advanced oxidation processes (AOPs), which generate highly reactive oxygen species capable of oxidizing complex organic contaminants into simpler and potentially less harmful compounds [14,15].

Among AOPs, heterogeneous photocatalysis has emerged as a promising technology for wastewater treatment [16]. In this process, a semiconductor absorbs photons with sufficient energy to generate electron–hole pairs. These charge carriers subsequently participate in surface reactions that produce reactive oxygen species capable of degrading organic pollutants and, under favorable conditions, mineralizing them into carbon dioxide, water, and inorganic ions [17]. Titanium dioxide (TiO₂) remains one of the most extensively investigated photocatalysts because of its high chemical stability, relatively low toxicity, low cost, and strong oxidative potential [18]. However, its practical application is limited by its wide band gap, which restricts photoactivation primarily to ultraviolet radiation, and by the rapid recombination of photogenerated electron–hole pairs, which reduces the number of charge carriers available for surface reactions [19].

Several modification strategies have therefore been investigated to improve the photocatalytic performance of TiO₂, including the addition of metal species [20]. Fe modification has been reported to introduce electronic states that may affect light absorption and charge-carrier behavior, whereas Zn loading has been associated with changes in crystal growth, phase development, surface properties, and charge transport [21,22]. The simultaneous addition of Fe and Zn may therefore produce composition-dependent changes in several physicochemical properties of TiO₂. However, demonstrating a true Fe–Zn synergistic effect requires direct comparison with matched Fe-only and Zn-only catalysts prepared

and evaluated under identical conditions. In the absence of these controls, the observed effects should be described as combined or composition-dependent rather than synergistic.

The broader potential of multimetal modification is illustrated by Amin et al. (2026) [23], who reported that Co/Ni co-doping of TiO₂ photocatalysts synthesized by the sol–gel method enhanced photocatalytic hydrogen production, yielding a hydrogen evolution rate of 448 $\mu\text{mol h}^{-1} \text{g}^{-1}$. Although the photocatalytic material and target reaction investigated in that study differ from those examined here, the findings illustrate how the simultaneous addition of different metal species can alter photocatalytic behavior. Nevertheless, the performance of multimetal-modified TiO₂ depends strongly on synthesis parameters such as metal loading, precursor chemistry, thermal treatment, and calcination temperature, making systematic optimization essential [24].

TiO₂-based photocatalysts can be synthesized using several established routes, including sol–gel, hydrothermal, solvothermal, extraction–pyrolytic, microwave-assisted, and green synthesis methods [19,25]. The selected preparation route can strongly influence particle size, morphology, crystallinity, phase composition, surface chemistry, and, consequently, photocatalytic performance [19,25]. Hydrothermal and solvothermal methods generally provide good control over crystal growth and morphology but require pressurized reactors and relatively demanding operating conditions. Microwave-assisted synthesis can substantially reduce processing time through rapid and comparatively uniform heating, although it requires specialized equipment and may present scale-up challenges [21,26]. Green synthesis routes can reduce the use of hazardous reagents, but variations in the composition of biological extracts may affect reproducibility [27].

In comparison, the sol–gel method enables molecular-level precursor mixing, relatively homogeneous distribution of multiple components, and systematic control of catalyst composition at moderate synthesis temperatures [19,22,27]. Nevertheless, the properties of sol–gel-derived materials remain highly sensitive to hydrolysis, condensation, aging, drying, and calcination conditions. In the present study, the sol–gel route was selected because it allowed Fe loading, Zn loading, and calcination temperature to be systematically investigated within the same experimental design [28,29]. This choice was not intended to establish sol–gel synthesis as universally superior to alternative preparation methods, but rather to employ a controllable route suitable for investigating composition–structure–performance relationships in Fe/Zn-modified TiO₂ materials [29,30].

Accordingly, this study aimed to determine how Fe loading, Zn loading, and calcination temperature influence the physicochemical properties and photocatalytic performance of sol–gel-derived TiO₂. Fe/Zn-modified TiO₂ photocatalysts were synthesized and evaluated using a 2³ factorial experimental design in which Fe loading, Zn loading, and calcination temperature were treated as independent synthesis variables. The photocatalytic performance of the materials was investigated using both synthetic dye solutions and a complex real effluent. Natural sunlight was employed for the discoloration and degradation of aqueous Red 40 and Tartrazine solutions, whereas artificial UV irradiation was used for the treatment of real cheese whey effluent. Photocatalytic performance was assessed by monitoring dye discoloration through UV–Vis spectrophotometry and organic-matter removal through COD measurements. Reactive-species scavenging experiments were additionally performed with the best-performing catalyst for each dye to evaluate the relative involvement of hydroxyl radicals, superoxide radicals, and photogenerated holes in the discoloration process.

The experimental design included Fe/Zn-modified catalysts and TiO₂ support samples but did not include matched Fe-only and Zn-only catalysts. Therefore, the study evaluates the combined and composition-dependent effects of Fe and Zn loading without claiming to demonstrate a true physicochemical synergy between the two metals. Accordingly, the

Fe $\times$ Zn terms obtained from the factorial design are interpreted strictly as statistical interactions within the investigated experimental domain and not as direct evidence of Fe–Zn synergy. By combining physicochemical characterization, photocatalytic testing, kinetic modeling, and statistical optimization, this study provides insight into the relationships among synthesis conditions, catalyst properties, and pollutant-dependent photocatalytic performance, thereby contributing to the development of TiO₂-based materials for the treatment of synthetic dye solutions and real food-industry effluents.

2. Results and Discussion

2.1. Catalyst Characterization

The N₂ adsorption–desorption isotherms of the TiO₂ support and Fe/Zn-modified catalysts are presented in Figure S1, and the corresponding textural properties are summarized in Table 1. All samples exhibit type 4 adsorption–desorption isotherms, according to the IUPAC classification, confirming the formation of mesoporous materials through the sol–gel synthesis route [28]. The presence of hysteresis loops at intermediate and high relative pressures (P/P_0) further indicates that nitrogen adsorption occurs via capillary condensation within the mesopores, demonstrating that the mesoporous structure was preserved after calcination [31].

The TiO₂ support undergoes a progressive evolution of its textural properties as the calcination temperature increases. The BET specific surface area increases from 72.0 m² g^{−1} for the non-calcined material (T-NC) to 84.0, 90.1, and 101.0 m² g^{−1} after calcination at 200, 300, and 400 °C, respectively. Simultaneously, the average pore diameter increases from 2.02 to 4.51 nm, whereas the total pore volume decreases slightly from 230.0 $\times 10^{-3}$ to 183.0 $\times 10^{-3}$ cm³ g^{−1}. This behavior suggests that calcination promotes the removal of residual organic species remaining from the sol–gel process, increasing pore accessibility while inducing partial pore coalescence and widening, which results in larger average pore diameters despite a modest reduction in pore volume [32].

A similar trend is observed for most Fe/Zn-modified catalysts, although the magnitude of the textural changes depends strongly on the metal loading. The F2Z2 series exhibits an increase in BET surface area from 96.3 to 146.0 m² g^{−1} after calcination at 400 °C, accompanied by an increase in pore diameter from 1.26 to 3.16 nm. Likewise, the F2Z10 catalyst reaches 140.6 m² g^{−1} with an average pore diameter of 4.03 nm, whereas F10Z10-400 presents the highest specific surface area among all synthesized materials (177.5 m² g^{−1}) together with a pore diameter of 3.03 nm. These results indicate that Fe/Zn-modification may suppress excessive structural densification during thermal treatment, allowing the development of highly accessible mesoporous structures after calcination [26].

The F10Z2 series exhibits distinct behavior. Although the non-calcined catalyst presents a remarkably high BET surface area (166.2 m² g^{−1}), calcination at 200 °C reduces this value to 99.8 m² g^{−1}, followed by a partial recovery to 142.1 m² g^{−1} at 400 °C. This evolution suggests that intermediate-temperature calcination can initially promote structural rearrangement and partial pore collapse before complete decomposition of residual precursor species at higher temperatures restores pore accessibility [33]. Such behavior highlights the strong influence of calcination temperature on the final porous architecture of highly Fe-loaded catalysts [34].

Despite the increase in BET surface area observed for most Fe/Zn-modified catalysts after calcination, the total pore volume does not follow the same trend. For example, F2Z2-400 and F2Z10-400 exhibit pore volumes of only 81.2 $\times 10^{-3}$ and 74.6 $\times 10^{-3}$ cm³ g^{−1}, respectively, which remain considerably lower than that of the TiO₂ support. This combination of high surface area and relatively low pore volume suggests that Fe/Zn modification

modifies the mesoporous network, increasing the accessible internal surface without proportionally increasing the total pore volume [35].

Table 1. Textural properties and elemental analysis of the catalysts.

Textural Properties			
Catalyst	S_{bet} ($\text{m}^2 \text{g}^{-1}$)	V_p ($10^{-3} \text{cm}^3 \text{g}^{-1}$)	d_p (nm)
T-NC	72.0	230.0	2.02
T-200	84.0	225.0	2.26
T-300	90.1	220.0	3.39
T-400	101.0	183.0	4.51
F2Z2-NC	96.3	61.0	1.26
F2Z2-200	101.0	4.0	1.99
F2Z2-400	146.0	81.2	3.16
F2Z10-NC	93.40	84.9	1.10
F2Z10-200	113.0	67.1	1.18
F2Z10-400	140.6	74.6	4.03
F6Z6-NC	96.90	9.6	1.54
F6Z6-300	115.4	13.2	1.70
F10Z2-NC	166.2	125.0	3.78
F10Z2-200	99.8	1.0	1.61
F10Z2-400	142.1	33.9	2.02
F10Z10-NC	94.9	6.5	1.86
F10Z10-200	125.3	2.0	1.58
F10Z10-400	177.5	117.0	3.03
Elemental Analysis			
Catalyst	Ti (%)	Fe (%)	Zn (%)
T-400	52.16	-	-
F2Z2-400	-	1.71	1.65
F2Z10-400	-	1.72	10.3
F6Z6-300	-	5.42	5.75
F10Z2-400	-	9.63	1.66
F10Z10-400	-	9.69	10.60

Overall, the N_2 physisorption results demonstrate that both calcination and Fe/Zn modification can play a decisive role in tailoring the textural properties of the synthesized catalysts [33].

The surface morphology of the TiO_2 support and Fe/Zn-modified catalysts after calcination was investigated by SEM, and the corresponding micrographs are presented in Figure 1. Independent of composition, all samples exhibit agglomerated particles with irregular morphology, a characteristic feature of oxide materials synthesized via the sol–gel method [27]. These agglomerates are formed by the assembly of fine primary particles, generating interparticle voids that contribute to the mesoporous texture previously identified by N_2 physisorption [36].

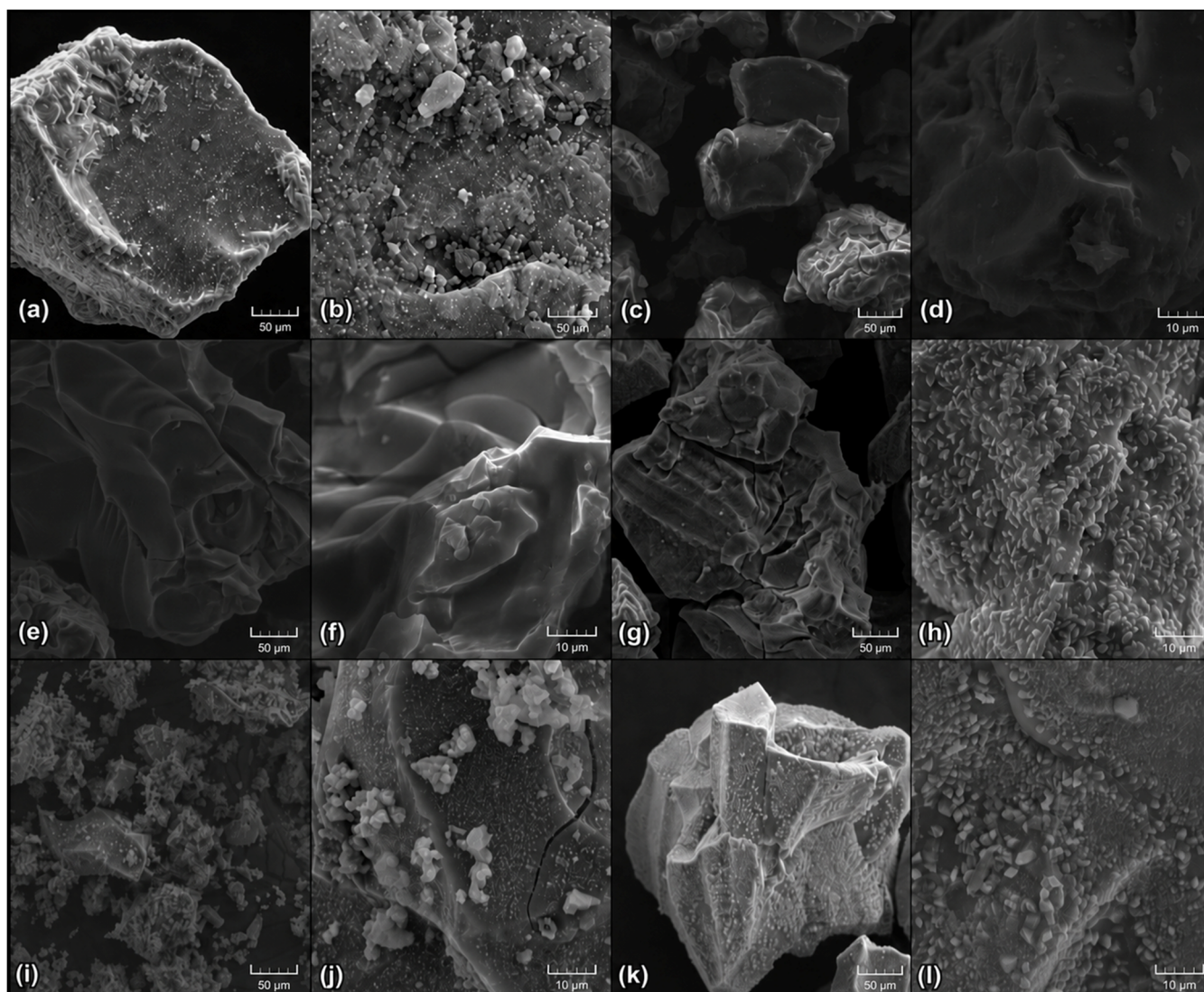


Figure 1. SEM micrographs of the catalysts calcined at 400 °C, except Fe_{6%}/Zn_{6%}/TiO₂ calcined at 300 °C. (a,b) T-400, (c,d) F2Z2-400, (e,f) F2Z10-400, (g,h) F6Z6-300, (i,j) F10Z2-400, and (k,l) F10Z10-400. For each sample, the first image (a,c,e,g,i,k) was acquired at 1000× magnification, while the second image (b,d,f,h,j,l) was acquired at 5000× magnification.

The TiO₂ support (T-400) exhibits compact agglomerates with relatively rough surfaces and no evidence of extensive particle coalescence (Figure 1a,b). This morphology indicates that calcination at 400 °C promoted crystallization while avoiding severe sintering, which is consistent with the preservation of a relatively high BET specific surface area and mesoporous structure [31]. The absence of dense fused particles suggests that the thermal treatment effectively removed residual organic species generated during the sol–gel process without inducing excessive grain growth [26].

Following Fe/Zn modification, no significant changes in the overall particle morphology are observed. The F2Z2-400, F2Z10-400, F6Z6-300, F10Z2-400 and F10Z10-400 catalysts retain the agglomerated structure characteristic of the TiO₂ support (Figure 1c–l), indicating that addition of Fe and Zn does not substantially alter the particle growth mechanism during the sol–gel synthesis [37].

Although SEM does not reveal distinct crystalline domains attributable to iron or zinc oxides, this result is expected considering both the relatively low metal loading and the nanometric dimensions of the synthesized particles [33,38].

The elemental distribution was further evaluated by SEM-EDS mapping (Figure S2). As expected, the TiO_2 support contains only Ti and O signals, whereas all Fe/Zn-modified catalysts present homogeneous distributions of Ti, O, Fe and Zn throughout the analyzed particles. No localized enrichment of Fe or Zn is detected, confirming elemental presence and a relatively homogeneous distribution of both metals at the micrometric scale [39]. This homogeneous elemental distribution indicates close spatial association of the metal species with TiO_2 at the micrometric scale; however, SEM-EDS does not establish oxidation state, lattice location, or charge-transfer behavior [40].

The semiquantitative EDS analysis further confirms the presence of Fe and Zn, with measured contents ranging from 1.71 to 9.69 wt.% for Fe and from 1.65 to 10.60 wt.% for Zn, in close agreement with the nominal compositions employed during synthesis (Table 1). These results indicate effective retention of the metal precursors and good compositional control during the sol-gel process; however, they do not establish lattice addition.

The crystalline structure of the TiO_2 support and Fe/Zn-modified catalysts was investigated by X-ray diffraction, and the diffraction patterns are presented in Figure 2a. The corresponding phase quantification obtained by Rietveld refinement is summarized in Table S2, while the refinement profiles and crystallographic parameters are shown in Figure S3 and Table S3, respectively.

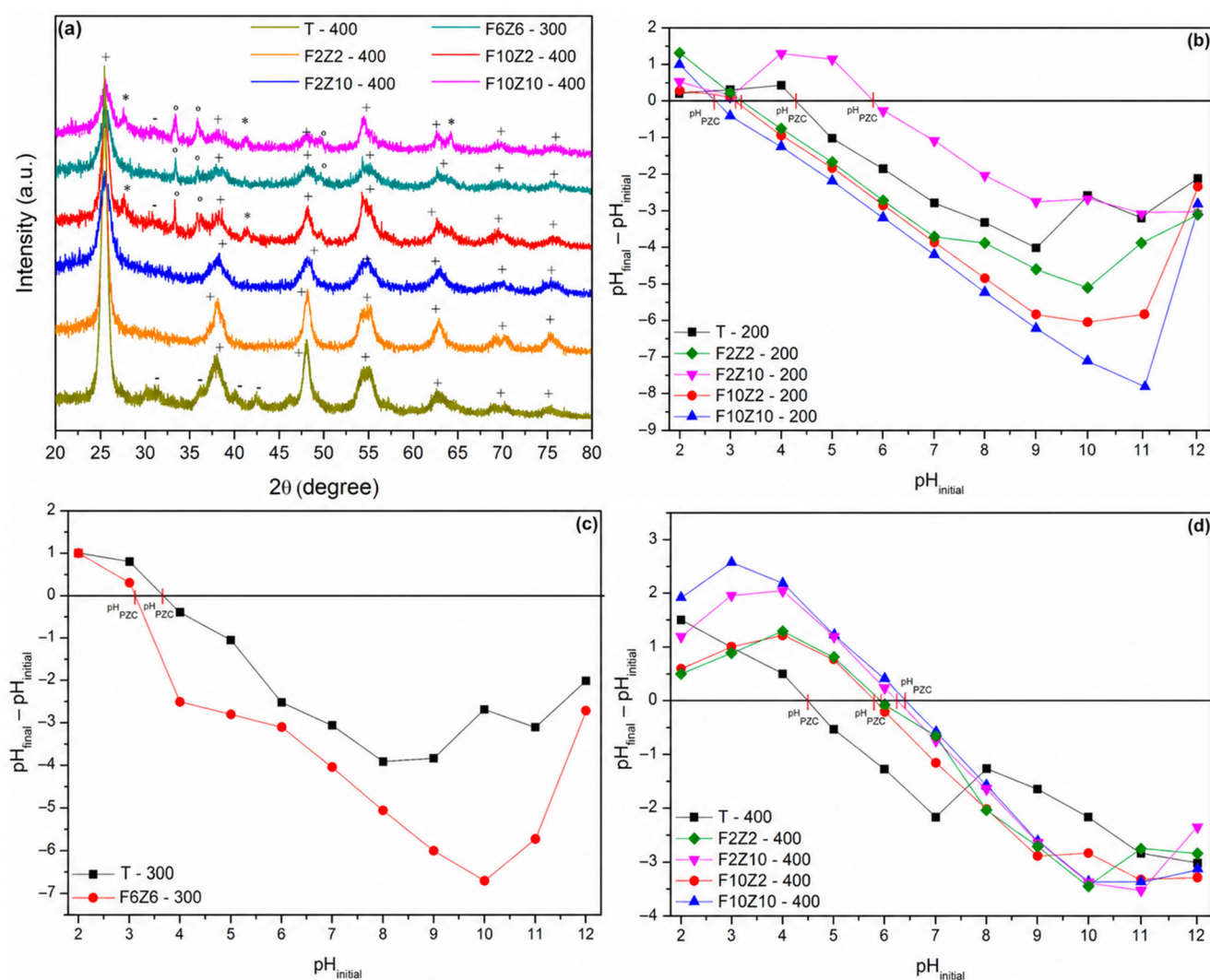


Figure 2. Catalyst characterization results: (a) XRD pattern and (b–d) surface charge distribution. Phase identification: + TiO_2 (anatase), - TiO_2 (brookite), * TiO_2 (rutile), and ° Fe_2O_3 (hematite).

The diffraction pattern of the TiO₂ support (T-400) exhibits the characteristic reflections of anatase TiO₂ at approximately 25.3°, 37.8°, 48.0°, 53.9°, 55.1°, and 62.7°, which are indexed to the (101), (004), (200), (105), (211), and (204) crystallographic planes, respectively (ICDD PDF No. 21-1272) [41]. Additional reflections centered at approximately 30.8° are assigned to brookite TiO₂ (ICDD PDF No. 29-1360) [41], confirming the coexistence of both polymorphs after calcination at 400 °C (Figure 2a). The predominance of the anatase (101) reflection at $2\theta \approx 25.3^\circ$ indicates that anatase is the major crystalline phase of the TiO₂ support [42]. As the Fe content increases, additional reflections appear at approximately 33.2°, 35.6°, 49.5°, 54.1°, and 62.4°, corresponding to the (104), (110), (024), (116), and (214) crystallographic planes of α -Fe₂O₃ (hematite; ICDD PDF No. 33-0664) [41]. The intensity of these reflections progressively increases from F6Z6-300 to F10Z2-400, indicating that higher Fe loadings promote the segregation and crystallization of hematite [33]. Furthermore, the emergence of a diffraction peak at $2\theta \approx 27.4^\circ$, assigned to the (110) plane of rutile TiO₂ (ICDD PDF No. 21-1276) [41], is observed only for F10Z2-400 and F10Z10-400, indicating that higher Fe contents can promote the partial anatase-to-rutile transformation during calcination [43].

These qualitative observations are supported by the Rietveld refinement results (Table S2). The TiO₂ support consists of 79.0 wt.% anatase and 21.0 wt.% brookite, in close agreement with the phase fractions obtained by the Spurr equation (81.0 and 19.0 wt.%, respectively), confirming the reliability of the refinement procedure. The coexistence of anatase and brookite indicates that calcination at 400 °C promotes crystallization of the TiO₂ support while preserving the metastable brookite phase generated during the sol–gel synthesis [28].

A markedly different crystallization behavior was observed after Fe/Zn modification. Both F2Z2-400 and F2Z10-400 exhibited diffraction patterns exclusively indexed to anatase, with Rietveld refinement indicating 100 wt.% anatase. At low Fe and Zn loadings, no diffraction peaks attributable to crystalline iron- or zinc-containing secondary phases were detected. However, the absence of detectable reflections cannot be interpreted as evidence of substitutional addition of Fe or Zn into the TiO₂ lattice. The metal species may be present below the XRD detection limit, as highly dispersed or amorphous surface species, or potentially within the TiO₂ structure. Because XPS, Raman spectroscopy, and local structural analyses were not performed, these possibilities cannot be distinguished using the present dataset. EDS confirms elemental presence and approximate composition but does not resolve oxidation state or lattice location. Accordingly, the materials are described as Fe/Zn-modified TiO₂ rather than assuming definitive lattice doping [33,39].

Increasing the Fe loading significantly alters the phase evolution of the catalysts. The diffraction pattern of F6Z6-300 remains predominantly anatase, although additional reflections assigned to hematite become evident. Rietveld refinement indicates a composition of 93.6 wt.% anatase and 6.2 wt.% hematite, demonstrating that part of the incorporated Fe crystallizes as a separate iron oxide phase even at the lower calcination temperature of 300 °C. A further increase in Fe content promotes the formation of additional crystalline phases. F10Z2-400 contains 71.0 wt.% anatase, 9.0 wt.% rutile and 20.0 wt.% hematite, whereas F10Z10-400 consists of 71.5 wt.% anatase, 16.4 wt.% rutile, 11.3 wt.% hematite and a minor fraction of 0.8 wt.% brookite. These results indicate that increasing the Fe concentration progressively destabilizes the single-phase anatase structure, promoting the crystallization of both hematite and rutile during calcination [38,40].

The appearance of hematite only in catalysts containing intermediate and high Fe contents strongly suggests that the solubility limit of Fe within the TiO₂ structure is exceeded under these synthesis conditions [44]. At low metal loading (2 wt.% Fe), iron species may remain highly dispersed without forming detectable crystalline oxides, whereas increasing

the Fe loading can favor segregation into crystalline α -Fe₂O₃, which becomes readily identified by XRD [45]. In contrast, no crystalline Zn-containing phases were detected in any catalyst. This finding establishes only that crystalline Zn-containing domains, if present, were below the XRD detection limit; it does not distinguish among highly dispersed, amorphous, surface-associated, or structurally incorporated Zn species in TiO₂ [46,47].

The refinement quality parameters further confirm the reliability of the structural model. The calculated diffraction profiles reproduce the experimental patterns with good agreement for all catalysts, as evidenced by the satisfactory refinement residuals shown in Figure S3 and the relatively low values of R_p , R_{wp} and χ^2 reported in Table S3. Furthermore, the refined lattice parameters of anatase, rutile, brookite and hematite remain very close to their reference crystallographic values, indicating that Fe/Zn modification does not produce significant distortions of the crystal structures detectable by XRD [48].

Overall, the XRD and Rietveld refinement results demonstrate that Fe/Zn modification strongly influences the crystallization behavior of TiO₂. Low metal loading stabilize a single anatase phase, whereas increasing the Fe content promotes the formation of hematite together with rutile, resulting in multiphase catalysts with distinct crystalline compositions.

The surface charge properties of the TiO₂ support and Fe/Zn-modified catalysts were evaluated by determining the point of zero charge (pH_{PZC}), and the results are presented in Figure 2b–d and Table 2. The pH_{PZC} values vary considerably with both catalyst composition and calcination temperature, indicating that Fe/Zn modification and thermal treatment significantly modify the surface acid-base properties of TiO₂.

Table 2. Surface charge distribution (pH_{PZC}) of the synthesized catalysts.

Catalyst	pH_{PZC}
T-200	4.26
T-300	3.81
T-400	4.47
F2Z2-200	3.27
F2Z2-400	6.03
F2Z10-200	5.88
F2Z10-400	6.17
F6Z6-300	2.96
F10Z2-200	3.09
F10Z2-400	5.73
F10Z10-200	2.78
F10Z10-400	6.39

The TiO₂ support exhibited pH_{PZC} values ranging from 3.81 to 4.47 after calcination at different temperatures (Table 2). The relatively small variation observed among the TiO₂ support samples suggests that calcination temperature alone has a limited influence on the surface charge properties compared with the addition of Fe and Zn [49].

In contrast, the Fe/Zn-modified catalysts exhibited pronounced changes in pH_{PZC} , depending on both the metal loading and calcination temperature. Except for F6Z6-300, all catalysts calcined at 400 °C displayed pH_{PZC} values close to neutrality, ranging from 5.73 to 6.39. For example, the pH_{PZC} increased from 3.27 to 6.03 for F2Z2, from 3.09 to 5.73 for F10Z2, and from 2.78 to 6.39 for F10Z10 after calcination. This shift toward higher pH_{PZC} values demonstrates that calcination modified the surface chemistry of the Fe/Zn-modified catalysts, likely due to dehydroxylation of the oxide surface and changes in the distribution

of Fe–O and Zn–O surface sites, which alter the acid–base properties and point of zero charge [50].

The observed variation in pH_{PZC} has important implications for the interfacial behavior of the catalysts during photocatalytic processes, as the surface charge governs the electrostatic interactions between the catalyst and charged species in solution [51]. Consequently, tuning the pH_{PZC} through Fe/Zn modification provides an additional strategy for tailoring the surface properties of TiO_2 according to the operating conditions [33].

Considering the experimental pH values, the surface charge of the catalysts was expected to differ between the dye solutions and cheese whey. Red 40 and Tartrazine were treated at pH 4; therefore, catalysts with pH_{PZC} values above 4 were expected to exhibit positively charged surfaces, whereas those with pH_{PZC} values below 4 were expected to exhibit negatively charged surfaces [33]. For cheese whey, which was treated at its original pH of 6.02, F2Z10-400 and F10Z10-400 were expected to exhibit positively charged surfaces, whereas F2Z2-400 was close to its point of zero charge. The remaining catalysts were expected to exhibit predominantly negatively charged surfaces under the cheese-whey treatment conditions. These different surface-charge states may influence the adsorption behavior of the organic species and the resulting catalyst–pollutant interactions. However, because adsorption and molecular speciation were not quantified, their individual contribution to photocatalytic performance cannot be conclusively established [52]. Overall, the pH_{PZC} results demonstrate that both Fe/Zn modification and calcination modified the surface chemistry of TiO_2 , complementing the structural and textural changes identified by XRD and N_2 physisorption.

2.2. Photocatalytic Tests

2.2.1. Adsorption and Photolysis Tests

To evaluate the contribution of non-photocatalytic processes, adsorption and catalyst-free irradiation experiments were conducted using aqueous Red 40 and Tartrazine solutions. A catalyst-free irradiation control was also performed for cheese whey under the same artificial-light conditions used in the photocatalytic experiments. The corresponding results are presented in Table 3.

As shown in Table 3, adsorption and direct photolysis made only minor contributions to the discoloration of either dye. For Red 40, removal by adsorption ranged from 2.18% to 8.88%, indicating that adsorption alone was insufficient to achieve substantial dye removal under the tested conditions. Direct photolysis resulted in only 3.41% discoloration, showing that solar irradiation in the absence of a photocatalyst had a negligible effect on Red 40 discoloration.

Similar behavior was observed for Tartrazine. Removal by adsorption ranged from 0.56% to 7.55%, demonstrating the limited contribution of adsorption under the experimental conditions. Direct photolysis was even less effective for Tartrazine than for Red 40, resulting in only 1.11% discoloration. These findings indicate that sunlight alone made a negligible contribution to Tartrazine discoloration during the evaluated reaction period.

These results are consistent with those reported by Castro et al. (2025) [33], who investigated Fe- and Zn-modified TiO_2 photocatalysts. In that study, adsorption and direct photolysis also made only minor contributions to dye discoloration. Removal by adsorption remained below approximately 10% for both Red 40 and Tartrazine, regardless of catalyst composition or calcination temperature, whereas direct photolysis resulted in less than 3.50% discoloration under all tested conditions. Although Fe/Zn modification produced small variations in dye removal by adsorption, no systematic improvement relative to the corresponding TiO_2 supports was observed.

Table 3. Photodiscoloration and photodegradation efficiencies of the synthesized catalysts for the treatment of food industry effluents.

Catalysts	Pollutant	Photodiscoloration (%)			Photodegradation (COD, %) *		
		Adsorption	Photolysis	Sunlight-Driven Photocatalysis	Photolysis	Artificial Light-Driven Photocatalysis	Sunlight-Driven Photocatalysis
T-200	Red 40	5.11 ± 0.49	3.41 ± 0.22	65.23 ± 5.44	n/a		41.74 ± 2.02
T-300		4.96 ± 0.33		55.13 ± 4.37			41.61 ± 3.33
T-400		8.44 ± 0.75		93.28 ± 8.05			70.81 ± 6.58
F2Z2-200		3.21 ± 0.11		41.75 ± 2.22			16.77 ± 0.99
F2Z2-400		7.77 ± 0.35		84.67 ± 7.45			66.58 ± 5.75
F2Z10-200		2.18 ± 0.10		32.24 ± 1.02			11.68 ± 1.03
F2Z10-400		6.55 ± 0.56		71.14 ± 5.55			54.16 ± 4.87
F6Z6-300		4.34 ± 0.30		54.44 ± 3.21			26.71 ± 1.11
F10Z2-200		5.63 ± 0.41		69.23 ± 4.80			46.34 ± 3.90
F10Z2-400		8.88 ± 0.77		99.85 ± 2.22			77.02 ± 7.01
F10Z10-200		7.12 ± 0.60		83.61 ± 6.98			64.47 ± 5.41
F10Z10-400		8.03 ± 0.79		90.59 ± 7.77			67.58 ± 4.02
T-200	Tartrazine	3.33 ± 0.21	1.11 ± 0.08	48.67 ± 3.21	n/a		60.35 ± 5.01
T-300		4.98 ± 0.48		58.17 ± 4.02			63.04 ± 6.33
T-400		7.55 ± 0.66		86.25 ± 7.77			87.61 ± 7.58
F2Z2-200		1.01 ± 0.03		21.41 ± 1.30			30.13 ± 2.22
F2Z2-400		6.12 ± 0.41		75.00 ± 5.55			64.03 ± 5.47
F2Z10-200		0.56 ± 0.02		12.67 ± 1.01			15.25 ± 1.02
F2Z10-400		3.05 ± 0.18		47.42 ± 3.32			53.01 ± 4.44
F6Z6-300		3.78 ± 0.22		47.33 ± 4.44			55.08 ± 3.78
F10Z2-200		1.89 ± 0.10		25.22 ± 1.33			38.31 ± 2.11
F10Z2-400		2.22 ± 0.23		39.57 ± 2.15			49.83 ± 3.02
F10Z10-200		3.87 ± 0.17		48.09 ± 3.98			58.52 ± 4.44
F10Z10-400		6.99 ± 0.55		77.91 ± 6.21			67.63 ± 2.22
T-200	Cheese whey		n/a		2.87 ± 0.13	18.98 ± 1.11	n/a
T-300						23.66 ± 2.58	
T-400						35.47 ± 3.08	
F2Z2-200						23.58 ± 2.02	
F2Z2-400						36.14 ± 3.33	
F2Z10-200						36.72 ± 2.41	
F2Z10-400						40.01 ± 3.58	
F6Z6-300						39.23 ± 2.01	
F10Z2-200						22.23 ± 1.55	
F10Z2-400						33.34 ± 2.85	
F10Z10-200						26.67 ± 1.88	
F10Z10-400						41.01 ± 3.00	

* Photodegradation was evaluated based on COD removal. Values are reported as mean ± standard deviation from three independent batch experiments ($n = 3$). n/a = not applicable.

A similar trend was observed in the present study. Fe/Zn modification did not consistently increase dye removal by adsorption compared with the TiO₂ support samples. For Red 40, the TiO₂ support samples T-200, T-300, and T-400 exhibited adsorption removals ranging from 4.96% to 8.44%, whereas the Fe/Zn-modified materials generally produced comparable values. The highest value, 8.88%, was obtained with F10Z2-400 and was only slightly higher than the 8.44% obtained with T-400. For Tartrazine, the TiO₂ support samples exhibited adsorption removals ranging from 3.33% to 7.55%. Fe/Zn modification generally resulted in comparable or lower adsorption, particularly for the materials calcined at 200 °C. Among the materials calcined at 400 °C, all Fe/Zn-modified catalysts exhibited lower adsorption removals than the T-400 support.

The catalyst-free control for cheese whey was evaluated under the same artificial-light irradiation conditions used in the photocatalytic experiments. After 4 h, catalyst-free irradiation resulted in only 2.87% COD removal, compared with 41.01% in the presence of F10Z10-400. This difference indicates that direct photolytic oxidation made only a minor contribution to cheese-whey COD removal and that most of the observed COD reduction was associated with the catalyst-mediated process.

Overall, adsorption and direct photolysis made only minor contributions to dye discoloration, while catalyst-free irradiation produced negligible COD removal from cheese whey. Fe/Zn modification did not consistently improve dye removal by adsorption relative to the TiO₂ supports. Therefore, the differences in photocatalytic performance among the investigated materials cannot be explained solely by increased adsorption and most likely reflect the combined influence of their crystalline, textural, and surface properties. Because adsorption isotherms and equilibrium capacities were not determined, these results should be interpreted as adsorption removals under the specific experimental conditions rather than as intrinsic adsorption capacities [53].

2.2.2. Food Dyes Photodiscoloration and Photodegradation Under Sunlight

The photocatalytic performance of the TiO₂ support and Fe/Zn-modified catalysts under sunlight was evaluated through the discoloration and degradation of Red 40 and Tartrazine, and the results are summarized in Table 3. Overall, the catalysts exhibited markedly different performances depending on both the calcination temperature and the nature of the pollutant, demonstrating that the photocatalytic activity can be governed by the interplay between catalyst physicochemical properties and the molecular characteristics of the target dye [54].

For Red 40, calcination at 400 °C substantially enhanced the photocatalytic activity of both the TiO₂ support and the Fe/Zn-modified catalysts. The TiO₂ support exhibited an increase in photodiscoloration from 65.23% (T-200) and 55.13% (T-300) to 93.28% (T-400), accompanied by an increase in COD removal from approximately 42% to 70.81%. This improvement was accompanied by increased crystallinity and favorable textural properties. Although these features may help rationalize the higher activity, the present data do not directly demonstrate reduced electron–hole recombination or increased reactive-oxygen-species generation [28].

The addition of Fe and Zn produced distinct effects depending on the metal loading. Among all investigated materials, F10Z2-400 exhibited the highest photocatalytic activity, achieving 99.85% photodiscoloration and 77.02% COD removal, outperforming the TiO₂ support. Although XRD revealed the presence of hematite and rutile in this catalyst, anatase remained the predominant crystalline phase (71 wt.%), providing a suitable balance between crystallinity and phase composition. Furthermore, F10Z2-400 presented a relatively high surface area and a p*H*_{PZC} of 5.73. Therefore, its surface was expected to be positively charged at the experimental pH of 4, which could favor interactions with the

anionic sulfonate groups of Red 40. However, the contribution of electrostatic interactions was not quantified independently [28]. $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox cycling has been proposed in previous literature as a pathway that may promote interfacial charge transfer and radical formation; however, this mechanism was not directly evaluated in the present study [33].

Conversely, catalysts containing lower calcination temperatures generally exhibited poorer photocatalytic performance [39]. For example, F2Z2-200 and F2Z10-200 achieved photodiscoloration efficiencies of only 41.75% and 32.24%, respectively, with COD removals below 20%. These results are consistent with the lower crystallinity and less favorable textural properties observed for these materials [39]. Likewise, increasing the Zn content while maintaining low Fe loading (F2Z10-400) reduced the photocatalytic efficiency relative to F2Z2-400, suggesting that excessive Zn loading may not further improve charge separation under the investigated conditions [28,39]. Overall, these results indicate that Red 40 degradation is favored by an optimized balance between Fe loading, crystallinity, and surface properties rather than by the highest metal loading.

A different behavior was observed during the degradation of Tartrazine. In this case, the highest photocatalytic activity was achieved by the TiO_2 support calcined at 400 °C, which reached 86.25% photodiscoloration and 87.61% COD removal. Most Fe/Zn-modified catalysts exhibited lower efficiencies than the TiO_2 support, indicating that metal addition did not universally improve photocatalytic activity. This behavior suggests that the degradation pathway of Tartrazine is more sensitive to modifications in the crystalline composition of the catalyst [55]. The formation of hematite and rutile at higher Fe loadings may reduce the anatase fraction. Their possible role as recombination centers is a literature-supported hypothesis that cannot be verified without direct charge-carrier measurements [25,56].

Among the Fe/Zn-modified materials, F10Z10-400 exhibited the best performance toward Tartrazine, reaching 77.91% discoloration and 67.63% COD removal, followed by F2Z2-400 with 75.00% and 64.03%, respectively. In contrast, F10Z2-400, which was the most active catalyst for Red 40 degradation, achieved only 39.57% photodiscoloration and 49.83% COD removal for Tartrazine. This pronounced difference clearly demonstrates that the optimum catalyst composition depends on the molecular structure of the target pollutant rather than solely on the intrinsic photocatalytic activity of the material [57]. The different adsorption affinities and degradation pathways of the two azo dyes likely determine the effectiveness of the active sites generated by Fe/Zn modification.

The pH_{PZC} results indicate that the catalyst surfaces exhibited different charge states at the experimental pH of 4. Catalysts with pH_{PZC} values above 4 were expected to be positively charged, whereas those with values below 4 were expected to be negatively charged. Therefore, electrostatic interactions may have contributed to the catalyst-dependent behavior of the dyes but cannot independently explain the observed photocatalytic trends [50,58].

For both dyes, photodiscoloration generally exceeded COD removal, particularly for Red 40, indicating that cleavage of the azo chromophore occurred more rapidly than complete mineralization of the resulting intermediates. The rapid disappearance of color reflects the efficient breakdown of the conjugated $-\text{N}=\text{N}-$ bond responsible for visible-light absorption, whereas the lower COD removal indicates that residual oxidizable organic matter remained in solution after photocatalysis; however, its chemical identity could not be determined without chromatographic and mass-spectrometric analyses [59]. This behavior highlights the importance of evaluating mineralization in addition to discoloration, since complete decolorization does not necessarily correspond to complete oxidation of the organic pollutants [33].

Overall, the photocatalytic results show that the performance of the Fe/Zn-modified catalysts depends on the combined influence of crystalline phase composition, textural properties, and surface chemistry. Calcination at 400 °C consistently enhanced photo-

catalytic performance by increasing crystallinity and stabilizing the anatase phase [39]. The F10Z2-400 formulation provided the highest Red 40 degradation, whereas the TiO₂ support remained the most active material for Tartrazine degradation. These findings demonstrate that the optimum catalyst composition is pollutant-dependent and emphasize the importance of tailoring the physicochemical properties of TiO₂-based photocatalysts according to the characteristics of the target contaminant rather than pursuing a universal catalyst formulation [60,61].

2.2.3. Reactive-Species Scavenging Experiments

Reactive-species scavenging experiments were conducted with F10Z2-400 and T-400, the best-performing catalysts for Red 40 and Tartrazine, respectively. The complete results are summarized in Table S7. In the simultaneously irradiated controls, Red 40 and Tartrazine discoloration reached $97.05 \pm 1.66\%$ and $82.33 \pm 3.65\%$, respectively, in close agreement with the efficiencies obtained in the original photocatalytic assays (99.85% and 86.25%, respectively). This agreement confirms that the selected dye–catalyst systems maintained their high activity during the parallel scavenging experiments.

For Red 40 discoloration with F10Z2-400, all three scavengers produced significant reductions relative to the control ($p < 0.05$). Isopropyl alcohol (IPA) caused the strongest effect, decreasing discoloration to 33.57% and producing 65.41% inhibition. In the presence of p-benzoquinone (p-BQ), discoloration decreased to 53.71%, corresponding to 44.66% inhibition. Ammonium oxalate (AO) produced the smallest, although still pronounced, reduction, with 72.14% discoloration and 25.67% inhibition. The inhibition order IPA > p-BQ > AO supports a pre-dominant contribution from hydroxyl radicals ($\bullet\text{OH}$), followed by superoxide radicals ($\text{O}_2\bullet^-$) and photogenerated holes (h^+), to Red 40 discoloration [62–65].

The Tartrazine–T-400 system exhibited the same inhibition sequence. Relative to the control, IPA reduced discoloration to $22.85 \pm 2.30\%$, corresponding to $72.24 \pm 3.02\%$ inhibition. The addition of p-BQ resulted in $46.11 \pm 3.44\%$ discoloration and $43.99 \pm 1.99\%$ inhibition, whereas AO resulted in $64.29 \pm 2.52\%$ discoloration and $21.91 \pm 3.54\%$ inhibition. All scavenger-containing treatments differed significantly from the control ($p < 0.05$). These results indicate that $\bullet\text{OH}$ also made the largest contribution to Tartrazine discoloration, with a relevant secondary contribution from $\text{O}_2\bullet^-$ and a smaller contribution from h^+ . The involvement of these reactive species in Tartrazine photocatalysis has also been reported previously, although their relative contributions may vary according to the photocatalyst and reaction conditions [64,66].

The consistent inhibition order observed for the two dyes provides experimental support for a radical-mediated oxidation pathway dominated by $\bullet\text{OH}$ under the investigated conditions and is consistent with the conceptual degradation pathways proposed in the mechanistic section below. [64,67,68]. Nevertheless, inhibition percentages should not be interpreted as additive or absolute fractions of the reaction mechanism because the scavengers differ in selectivity and reaction kinetics and may influence interconnected radical-formation pathways. Thus, the scavenging experiments provide indirect evidence of relative reactive-species involvement; direct identification and quantification would require complementary EPR spin-trapping measurements [69].

2.2.4. Cheese Whey Photodegradation Under Artificial Light

The photocatalytic performance of the TiO₂ support and Fe/Zn-modified catalysts toward cheese whey degradation under artificial irradiation is summarized in Table 3. In contrast to the dye solutions, only degradation was evaluated through COD removal, providing a direct assessment of the oxidation of the complex organic matter present in the effluent. Overall, all catalysts exhibited measurable photocatalytic activity, although

the degradation efficiencies were considerably lower than those obtained for Red 40 and Tartrazine. This behavior reflects the complex composition of cheese whey, whose organic load consists primarily of lactose, proteins, peptides, lipids, and other biodegradable compounds that require multiple oxidation steps before complete mineralization [70].

The TiO₂ support exhibited a progressive increase in photocatalytic activity with increasing calcination temperature, achieving COD removals of 18.98%, 23.66%, and 35.47% for T-200, T-300, and T-400, respectively. As observed during dye degradation, the higher activity at 400 °C was accompanied by improved crystallinity, stabilization of the anatase phase, and favorable textural properties. These correlations may help explain the observed trend, but they do not directly demonstrate increased reactive-oxygen-species generation or reduced charge-carrier recombination [2,26].

Unlike the trend observed for Tartrazine, several Fe/Zn-modified formulations provided relatively high COD removal from cheese whey. Among all investigated catalysts, F10Z10-400 exhibited the highest photocatalytic activity, achieving 41.01% COD removal, closely followed by F2Z10-400 (40.01%) and F6Z6-300 (39.23%). These results indicate that Fe/Zn formulations containing higher Zn loadings were favorable for this complex matrix under the tested conditions [26]. Because matched Fe-only and Zn-only controls were not evaluated, this behavior cannot be attributed to Fe-Zn synergy. It may instead reflect the combined effects of Fe and Zn loading, calcination-dependent phase composition, and surface chemistry of TiO₂, together with sufficient crystallinity for photocatalytic oxidation [26,33].

The beneficial effect of calcination is particularly evident when comparing catalysts of identical composition. For instance, the COD removal increased from 23.58% to 36.14% for F2Z2, from 36.72% to 40.01% for F2Z10, from 22.23% to 33.34% for F10Z2, and from 26.67% to 41.01% for F10Z10 after calcination at 400 °C. These improvements are consistent with the structural characterization, which demonstrated that calcination promotes crystallization and modifies the surface chemistry of the Fe/Zn-modified catalysts, leading to more efficient photocatalytic oxidation.

The p*H*_{PZC} results also provide valuable insight into the observed photocatalytic behavior. Cheese whey presented a pH of 6.02, which is close to the p*H*_{PZC} of several catalysts. Under these conditions, F2Z10-400 (p*H*_{PZC} = 6.17) and F10Z10-400 (p*H*_{PZC} = 6.39) are expected to exhibit predominantly positively charged surfaces, whereas the TiO₂ support and F6Z6-300 remain negatively charged [50]. Because cheese whey contains a heterogeneous mixture of organic compounds with different functional groups and ionization states, the proximity between the solution pH and the p*H*_{PZC} may enhance catalyst–substrate interactions by reducing electrostatic repulsion and facilitating the adsorption of oxidizable species [71].

Overall, the photocatalytic results demonstrate that the optimum catalyst composition is highly dependent on the nature of the target pollutant. While F10Z2-400 exhibited the highest activity toward Red 40 degradation, the TiO₂ support calcined at 400 °C (T-400) showed superior performance for Tartrazine, whereas F10Z10-400 achieved the greatest mineralization of cheese whey. These findings indicate that the photocatalytic performance of Fe/Zn-modified TiO₂ catalysts is governed by the combined effects of crystalline phase composition, surface chemistry, and catalyst–substrate interactions rather than by a single physicochemical property [33]. Consequently, tailoring the Fe/Zn loading according to the physicochemical characteristics of the target effluent represents an effective strategy for optimizing the performance of TiO₂-based photocatalysts under practical operating conditions.

Table 4 places the photocatalytic performance of the present materials in the context of representative TiO₂-based systems. F10Z2-400 achieved 99.85% discoloration of Red 40

under natural sunlight, demonstrating competitive activity relative to previously reported modified TiO₂ photocatalysts. However, its COD removal was 77.02%, indicating that discoloration was faster than the oxidation of the dye and its transformation products. For Tartrazine, the T-400 provided the best result, reaching 86.25% discoloration and 87.61% COD removal. This finding shows that metal addition does not necessarily improve photocatalytic performance for every pollutant, since the interaction between the catalyst surface, pollutant speciation, and irradiation conditions also influences the reaction.

Table 4. Comparison of the photocatalytic performance of the materials investigated in this study with representative TiO₂-based systems reported for dye-containing solutions and dairy-industry wastewaters.

Photocatalyst	Target Matrix	Main Experimental Conditions	Irradiation/Time	Reported Performance	Reference
Zn/Fe-modified TiO ₂ (optimized formulations)	Allura Red 40 and Tartrazine, 10 mg L ^{−1}	Catalyst loading: 0.333 g L ^{−1} ; pH 4	Natural sunlight; 120 min	95.6% Allura Red discoloration; 99.9% Tartrazine discoloration; COD removal above 95% for optimized systems	[33]
N/Fe/Zn-TiO ₂ immobilized on basalt fiber	Rhodamine B, 5 mg L ^{−1}	Fixed TiO ₂ loading: 3.04 mg cm ^{−2} ; solution volume: 7 L	42 W UV mercury lamp; 180 min	67.67% degradation	[26]
Zn-Fe co-doped TiO ₂ (ZFT_2.5)	Mixture of Rhodamine B, Malachite Green, and Methylene Blue	Sol-gel synthesized, visible-light-active nanoparticles	Visible light; 60 min	90.57%, 91.54%, and 88.39% degradation of RhB, MG, and MB, respectively	[72]
TiO ₂ /NiFe ₂ O ₄ composite	Real dairy wastewater	Batch-circulation parabolic-trough solar reactor; initial COD, dosage, and solar intensity optimized	Solar irradiation	Approximately 90% COD removal under optimized conditions	[73]
TiO ₂	Dairy-industry wastewater	TiO ₂ : 10 g L ^{−1} in a batch tank reactor	250 W UV light reactor; 24 h	Approximately 30% COD removal	[74]
Immobilized TiO ₂ followed by biological treatment	Dairy-industry wastewater; initial COD: 3782.5 mg O ₂ L ^{−1}	TiO ₂ fixed on a polyurethane-coated metallic plate, followed by an aeration pond	Solar irradiation for 3 h, followed by 72 h biological treatment	93.70% COD removal for the complete combined treatment	[75]
F10Z2-400	Red 40, 10 mg L ^{−1}	Catalyst loading: 0.333 g L ^{−1}	Natural sunlight; 120 min	99.85% discoloration and 77.02% COD removal	This work
T-400	Tartrazine, 10 mg L ^{−1}	Catalyst loading: 0.333 g L ^{−1}	Natural sunlight; 120 min	86.25% discoloration and 87.61% COD removal	This work
F10Z10-400	Real cheese whey	Catalyst loading: 0.333 g L ^{−1} ; solution volume: 150 mL	250 W mercury-vapor lamp; 240 min	41.01% COD removal	This work

Abbreviations: RhB, Rhodamine B; MG, Malachite Green; MB, Methylene Blue. The values should not be interpreted as a direct ranking because the studies used different matrices, catalyst loadings, irradiation sources, reactor configurations, and treatment times. The TiO₂/H₂O₂ result includes an added oxidant, whereas the 93.70% COD removal reported by Salazar et al. corresponds to the complete photocatalytic-biological treatment.

For the more complex cheese-whey matrix, F10Z10-400 achieved 41.01% COD removal after 4 h. Although higher COD removals have been reported for optimized solar-reactor

systems or combined photocatalytic-biological treatments, direct comparison is limited by differences in the initial organic load and reactor configuration. Moreover, some literature results were obtained with added H_2O_2 or subsequent biological polishing, whereas the present experiment was conducted without an added oxidant or a coupled biological treatment. Therefore, the observed COD reduction demonstrates the potential of the synthesized photocatalyst for the partial oxidation of a highly concentrated and complex real matrix, while also indicating the need for further optimization or integration with complementary treatment processes.

An exploratory Pearson correlation analysis was performed using the catalysts for which BET surface area, pH_{PZC} , and photocatalytic responses were available (Table S4). Calcination temperature was positively correlated with all five responses ($r = 0.606\text{--}0.711$, unadjusted $p < 0.05$). BET surface area and pH_{PZC} were associated with cheese-whey COD removal ($r = 0.729$, $p = 0.007$ and $r = 0.635$, $p = 0.027$, respectively), but their correlations with the dye responses were weaker and not statistically significant at $p < 0.05$. Fe and Zn contents did not show a uniform linear relationship with activity across pollutants. These results support a pollutant-dependent, multidescrptor interpretation rather than a universal surface-area or metal-loading effect.

The analysis is exploratory because the sample size is small, the predictors are coupled by the factorial synthesis design, multiple correlations were examined without multiplicity adjustment, and phase fractions were quantified for only a subset of selected catalysts. In addition, the solution pH is constant within each pollutant dataset; pH_{PZC} , rather than solution pH, is therefore the catalyst-specific surface-charge descriptor in this comparison. Correlation does not establish causality, and the RSM analysis remains the more appropriate framework for estimating synthesis-factor effects.

2.2.5. Kinetic Modeling of Photodiscoloration and Photodegradation Processes for the Food Dyes and Cheese Whey

The photocatalytic degradation kinetics of Red 40 and Tartrazine and the COD-removal kinetics of cheese whey wastewater were evaluated using the pseudo-first-order (PFO), pseudo-second-order (PSO), and Behnajady–Modirshahla–Ghanbary (BMG) kinetic models (Section S1, Supplementary Material). The corresponding fitting parameters and model-selection statistics, including the corrected Akaike information criterion (AICc) and ΔAICc values, are summarized in Table S5, whereas the BMG fitting curves are presented in Figure 3. Overall, the three models satisfactorily described most of the experimental datasets, with adjusted coefficients of determination generally exceeding 0.90. Nevertheless, model selection based on AICc consistently identified the BMG model as the best-performing model for all catalysts and matrices evaluated. The BMG model exhibited the lowest AICc value in every comparison and generally provided high adjusted R^2 values and low standard deviations, demonstrating its suitability for representing the photocatalytic degradation behavior under the investigated conditions [33].

For Red 40, the PFO and PSO models satisfactorily described the degradation kinetics for most catalysts, with adjusted R^2 values ranging from approximately 0.78 to 0.999. Nevertheless, the BMG model provided the lowest AICc value for all twelve catalysts evaluated. Its superior performance was particularly evident for F2Z10-400, for which the ΔAICc values of the PFO and PSO models were 27.62 and 16.82, respectively. Substantial differences were also observed for T-400 ($\Delta\text{AICc} = 7.33$ for PFO and 11.44 for PSO) and F2Z2-400 ($\Delta\text{AICc} = 11.95$ and 2.90, respectively). These results confirm that the BMG model provided the best overall representation of the Red 40 degradation profiles.

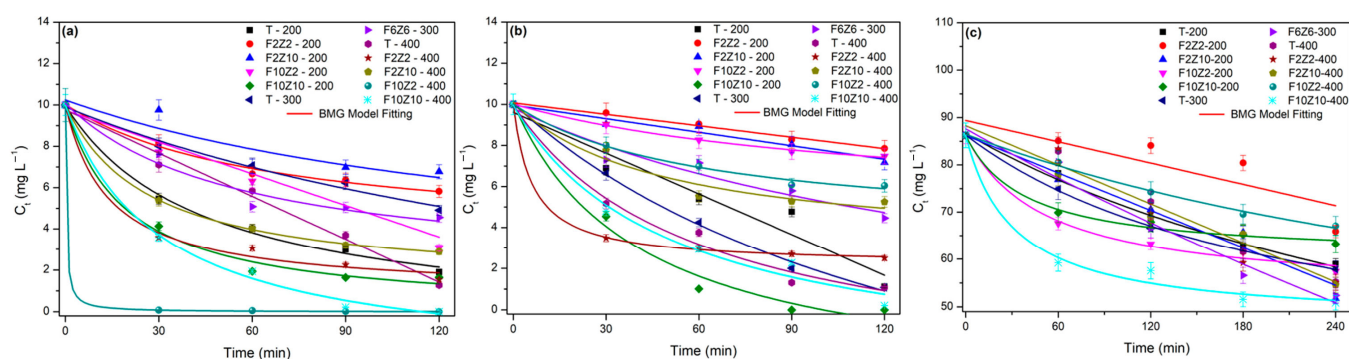


Figure 3. BMG kinetic curves for the photodegradation efficiencies of the synthesized catalysts in the treatment of food-industry effluents: (a) Red 40, (b) Tartrazine, and (c) Cheese whey. Symbols represent mean experimental values, and error bars indicate the standard deviation of three independent batch experiments ($n = 3$).

The outstanding photocatalytic performance of F10Z2-400 was reflected not only by its nearly complete discoloration (99.85%) but also by its high kinetic constants ($k_1 = 163.2 \times 10^{-3} \text{ min}^{-1}$ and $k_2 = 454.0 \times 10^{-3} \text{ L mg}^{-1} \text{ min}^{-1}$), together with an adjusted R^2 of 0.999 for all three models and one of the lowest standard deviations among the evaluated catalysts. The BMG parameter m , which is inversely related to the initial degradation rate, reached its lowest value ($m = 0.290$) for F10Z2-400, indicating a particularly rapid initial degradation stage. The BMG model also presented the lowest AICc value for this catalyst, further supporting its selection as the most appropriate model. These kinetic results are consistent with the photocatalytic experiments and confirm that F10Z2-400 exhibited the fastest Red 40 degradation kinetics under solar irradiation.

The degradation kinetics of Tartrazine followed a different catalyst-dependent trend. Although the BMG model again provided excellent fitting quality, the highest kinetic constants were obtained for the TiO_2 support calcined at 400°C and F10Z10-400, in agreement with their superior photocatalytic performances. In contrast, F10Z2-400, which was the most active catalyst for Red 40 degradation, exhibited one of the lowest kinetic constants for Tartrazine ($k_1 = 4.65 \times 10^{-3} \text{ min}^{-1}$), confirming that the optimum catalyst composition strongly depends on the physicochemical characteristics of the target pollutant.

The AICc analysis confirmed that the BMG model provided the best description of the Tartrazine degradation kinetics for all twelve catalysts. The strongest distinction among the models was observed for F2Z2-400, for which the ΔAICc values reached 31.84 for PFO and 25.48 for PSO. Pronounced differences were also obtained for T-300 ($\Delta\text{AICc} = 7.33$ and 16.53), F10Z2-200 ($\Delta\text{AICc} = 11.30$ and 8.54), and F10Z2-400 ($\Delta\text{AICc} = 11.04$ and 7.52 for PFO and PSO, respectively). These results confirm that the BMG model provided the best overall representation of the Tartrazine degradation profiles. Its excellent agreement with the experimental data, particularly for F2Z2-400 (adjusted $R^2 = 0.999$) and F10Z2-400 (adjusted $R^2 = 0.986$), indicates that the model effectively captured the changes in degradation rate occurring throughout the photocatalytic treatment.

For cheese whey, the COD-removal kinetics were considerably slower than the degradation kinetics observed for the azo dyes, consistent with the greater compositional complexity of this real wastewater. The PFO kinetic constants ranged from 0.907×10^{-3} to $2.320 \times 10^{-3} \text{ min}^{-1}$, approximately two orders of magnitude lower than those obtained for Red 40. These lower values reflect the greater resistance of the organic constituents of cheese whey to photocatalytic oxidation. Despite the slower reaction rates, the BMG model again provided excellent fitting quality for most catalysts, with adjusted R^2 values reaching 0.999 for T-300 and 0.989 for F10Z2-400.

Model selection based on AICc confirmed that the BMG model provided the best description of the cheese-whey COD-removal kinetics for all twelve catalysts. Its superiority was particularly pronounced for T-300, for which the ΔAICc values of the PFO and PSO models were 18.35 and 13.82, respectively. Similarly, substantial differences were observed for F10Z10-200 ($\Delta\text{AICc} = 16.60$ for PFO and 15.77 for PSO), F10Z2-200 ($\Delta\text{AICc} = 15.53$ and 14.20), and F10Z10-400 ($\Delta\text{AICc} = 14.75$ and 13.14, respectively). These results demonstrate that the BMG model described the experimental cheese-whey COD-removal profiles more accurately than the PFO and PSO models.

The highest PFO kinetic constant ($k_1 = 2.320 \times 10^{-3} \text{ min}^{-1}$) was obtained for F10Z10-400, in agreement with its superior COD removal efficiency of 41.01%, confirming that this catalyst promoted the fastest COD-removal kinetics among the evaluated materials. The relatively high m values obtained for cheese whey compared with those obtained for the dye solutions further indicate a slower initial degradation stage, which is consistent with the heterogeneous composition of the effluent and the oxidation of multiple classes of organic compounds through different reaction pathways [33,70].

Overall, the consistently lowest AICc values obtained for the BMG model across the three investigated matrices confirm its selection as the most appropriate model for describing the experimental degradation and COD-removal profiles. The AICc analysis therefore supports the kinetic interpretation based on the adjusted R^2 values and standard deviations and confirms the superior fitting performance of the BMG model under the investigated photocatalytic conditions.

2.2.6. Conceptual Photodegradation Mechanism

The photocatalytic performance of the synthesized materials appears to result from the combined influence of crystalline phase composition, textural properties, surface chemistry, and catalyst–pollutant interactions. Based on the characterization results, photocatalytic experiments, kinetic analyses, and previous literature, a conceptual degradation scheme for Red 40, Tartrazine, and cheese whey is presented in Figure 4. Although heterogeneous photocatalysis generally involves photon absorption, charge-carrier generation, and the possible formation of reactive oxygen species (ROS), the relevant degradation pathways and most favorable catalyst compositions may vary according to the physicochemical characteristics of the target pollutant. For the Red 40 and Tartrazine systems, this interpretation is additionally informed by the reactive-species scavenging results reported in Table S7.

Upon irradiation, TiO_2 -based catalysts absorb photons with sufficient energy to promote electrons from the valence band to the conduction band, thereby generating electron–hole pairs [67]. These charge carriers may migrate to the catalyst surface, where they can react with adsorbed oxygen, water, and surface hydroxyl groups to generate ROS, including hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\text{O}_2\bullet^-$) [65]. The efficiency of these processes is influenced by the structural, textural, and surface properties of the catalyst [33]. The XRD results showed that calcination at 400 °C increased crystallinity while preserving anatase as the predominant TiO_2 phase. Fe/Zn modification altered the crystalline phase assemblage, with hematite and rutile becoming detectable as the Fe content increased [68]. Nitrogen physisorption showed that calcination and metal loading modified the textural properties of the materials, whereas the pH_{PZC} measurements indicated substantial changes in their surface-charge behavior. These properties may influence charge-carrier dynamics, the availability of accessible surface sites, and catalyst–pollutant interactions. However, their individual contributions to photocatalytic activity cannot be distinguished conclusively from the present dataset [33].

Previous studies on heterogeneous photocatalysts have emphasized the importance of deliberately engineered interfaces in promoting spatial charge separation and interfacial

electron transfer. Host–guest coupling in porphyrinic metal–organic frameworks, Zn–O–W interfacial electron bridges in $\text{WO}_{3-x}/\text{ZnCdS}$ heterojunctions, and S-scheme $\text{Zn}_2\text{In}_2\text{S}_5/\text{CdS}$ heterostructures have been reported to improve photocatalytic performance by regulating charge-transfer pathways and suppressing charge-carrier recombination [76–78]. Although these systems involve different photocatalysts and target reactions from those investigated in the present study, they provide useful mechanistic context for considering how phase junctions and interfacial interactions could affect photocatalytic behavior. For the present Fe/Zn-modified TiO_2 materials, however, such interpretations remain hypothetical because direct charge-carrier measurements were not performed.

Accordingly, the scheme presented in Figure 4 should be interpreted as a conceptual representation supported by the scavenging responses for the two dye systems and by previous literature. The marked suppression caused by IPA and p-BQ provides indirect experimental evidence that $\bullet\text{OH}$ and $\text{O}_2\bullet^-$ participate in dye discoloration, with $\bullet\text{OH}$ showing the strongest relative contribution, while the smaller AO effect supports a contribution from h^+ . However, EPR spin-trapping, oxidation-state-resolved analyses, and direct charge-carrier measurements, including photoluminescence, time-resolved photoluminescence, transient photocurrent, and electrochemical impedance spectroscopy, were not performed. Consequently, the scavenging results do not directly identify the reactive species, confirm $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycling, demonstrate changes in electron–hole recombination, or establish the sequence of elementary charge-transfer reactions. The proposed charge-transfer pathways therefore remain mechanistic hypotheses, whereas the relative involvement of $\bullet\text{OH}$, $\text{O}_2\bullet^-$, and h^+ in the selected dye systems is supported indirectly by the scavenging experiments.

The degradation of Red 40 is proposed to involve oxidative attack by reactive species generated at the catalyst surface (Figure 4a). F10Z2-400 achieved nearly complete discoloration and the highest COD removal among the catalysts evaluated for this dye, together with favorable kinetic parameters. These results are consistent with a favorable combination of crystalline phases, textural properties, and surface characteristics, although they do not directly demonstrate changes in charge-carrier generation or recombination. Structurally, F10Z2-400 consists predominantly of anatase, with smaller fractions of rutile and hematite. Interfaces among these phases could facilitate interfacial charge transfer and increase the probability that photogenerated charge carriers participate in surface reactions before recombination [79]. Nevertheless, this proposed function requires confirmation through photoluminescence, photocurrent, or electrochemical measurements. The 65.41% inhibition caused by IPA, compared with 44.66% for p-BQ and 25.67% for AO, supports $\bullet\text{OH}$ as the principal reactive species involved in chromophore destruction, while $\text{O}_2\bullet^-$ and h^+ also contribute to the process.

According to literature-based pathways, oxidative cleavage of the azo bond ($-\text{N}=\text{N}-$) disrupts the conjugated structure responsible for the characteristic red coloration of Red 40. The resulting aromatic transformation products may subsequently undergo hydroxylation, ring-opening, and further oxidation reactions, producing lower-molecular-weight oxygenated compounds [80]. The substantially higher discoloration than COD removal indicates that chromophore destruction occurred more readily than complete oxidation of the dye and its transformation products. Therefore, the 77.02% COD removal obtained with F10Z2-400 suggests considerable but incomplete oxidation rather than complete mineralization. Identification of the transformation products would require chromatographic and mass-spectrometric analyses.

A different activity trend was observed for Tartrazine (Figure 4b). Although similar reactive species may participate in its oxidation, T-400 exhibited the highest photocatalytic activity. This result suggests that Tartrazine degradation benefited from the properties of the highly crystalline, predominantly anatase TiO_2 support rather than from Fe/Zn

modification. The XRD results showed that T-400 consisted of anatase and brookite without detectable Fe- or Zn-containing phases. In contrast, increasing the Fe content promoted the formation of additional crystalline phases that, although associated with improved Red 40 degradation, did not improve Tartrazine removal. The scavenging results nevertheless revealed the same reactive-species hierarchy observed for Red 40: IPA produced 72.24% inhibition, followed by p-BQ (43.99%) and AO (21.91%), supporting a predominant role of $\bullet\text{OH}$ in Tartrazine discoloration.

This pollutant-dependent behavior indicates that catalyst–pollutant interactions play an important role in determining photocatalytic performance [33]. Tartrazine contains sulfonate groups and a pyrazole ring and therefore differs from Red 40 in its molecular structure, adsorption behavior, and susceptibility to oxidative attack. Consequently, the structural and surface changes associated with Fe/Zn modification do not necessarily result in greater Tartrazine degradation. This finding demonstrates that the effects of catalyst modification are pollutant-specific rather than universal [81].

The photocatalytic treatment of cheese whey (Figure 4c) is considerably more complex because this effluent contains a heterogeneous mixture of proteins, lactose, lipids, peptides, and other dissolved organic compounds [70]. Unlike azo-dye discoloration, which can occur rapidly through chromophore cleavage, cheese-whey treatment requires the simultaneous oxidation of several classes of organic compounds with different structures and reactivities. Under these conditions, surface accessibility and interactions between the organic constituents and the catalyst may strongly influence the observed oxidation kinetics [82].

F10Z10-400 provided the highest COD removal among the catalysts evaluated for cheese whey. This result may be related to the combined effects of its textural properties, crystalline phase composition, and surface-charge behavior. The pH_{PZC} of F10Z10-400 was 6.39, slightly higher than the initial pH of the cheese-whey effluent (6.02), indicating that its surface was expected to be weakly positively charged under the reaction conditions. This surface state could favor interactions with negatively charged or anionic organic moieties present in the effluent. However, because adsorption, molecular speciation, and surface interactions were not directly quantified, this explanation should be regarded as a hypothesis rather than a demonstrated adsorption mechanism [71].

Reactive species generated during irradiation may attack peptide bonds, carbohydrates, lipid chains, and other organic components, producing smaller and more oxidized transformation products [82]. Nevertheless, the COD removal of 41.01% indicates partial oxidation of the cheese-whey matrix rather than complete degradation or mineralization. The observed performance of F10Z10-400 is therefore consistent with favorable interactions between its physicochemical properties and the complex effluent matrix, but the individual reaction pathways cannot be established without identifying the reactive species and transformation products.

Overall, the proposed scheme indicates that the photocatalytic performance of the Fe/Zn-modified TiO_2 materials cannot be attributed to a single physicochemical property. Instead, the observed activity trends appear to result from the combined effects of crystalline phase composition, crystallinity, textural properties, surface charge, and catalyst–pollutant interactions [67]. The most favorable catalyst composition consequently depends on the chemical characteristics and complexity of the treated matrix. F10Z2-400 provided the best performance for Red 40, T-400 was the most effective catalyst for Tartrazine, and F10Z10-400 achieved the highest COD removal from cheese whey. These findings show that the design of TiO_2 -based photocatalysts should be tailored to the target wastewater rather than directed toward a supposedly universal catalyst composition. The proposed charge-transfer pathways and degradation intermediates remain incompletely resolved because they were

not directly characterized. For the selected Red 40 and Tartrazine systems, the scavenging responses provide indirect experimental support for the participation of $\bullet\text{OH}$, $\text{O}_2\bullet^-$, and h^+ , although the charge-transfer sequence and the reactive species involved in cheese-whey oxidation remain unresolved.

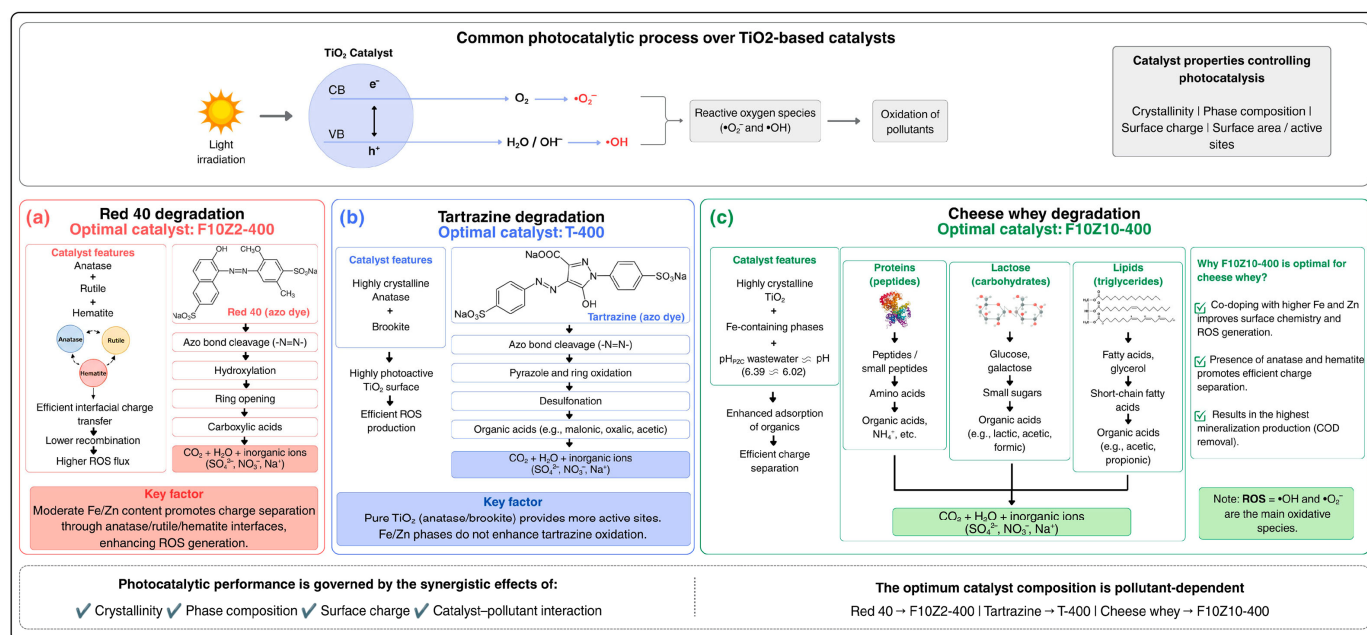


Figure 4. Conceptual scheme of the possible photocatalytic degradation pathways: (a) Red 40, (b) Tartrazine, and (c) cheese whey. The scavenging experiments provide indirect support for the participation of $\bullet\text{OH}$, $\text{O}_2\bullet^-$, and h^+ in dye discoloration; the proposed charge-transfer steps, degradation intermediates, and cheese-whey pathways remain literature-based.

2.3. Statistical Modeling and Optimization

2.3.1. Optimization of Operating Conditions Using Response Surface Methodology

Response Surface Methodology (RSM) was employed to evaluate the combined effects of calcination temperature (A), Fe loading (B), and Zn loading (C) on the photocatalytic performance of the synthesized catalysts and to establish the optimum synthesis conditions for the degradation of Red 40, Tartrazine, and cheese whey. The statistical significance of the quadratic models was assessed by analysis of variance (ANOVA), while the corresponding response surface plots are presented in Figure 5 and Figure S5.

The ANOVA results (Table 5) indicate that the quadratic models were statistically significant for all evaluated responses ($p < 0.05$), demonstrating that the investigated synthesis variables explained a significant proportion of the observed variation within the experimental domain. Among these variables, calcination temperature exhibited the largest statistical effect on all responses, as indicated by its comparatively high F-values. This influence was particularly pronounced for Tartrazine COD removal, for which the temperature term made the largest statistical contribution. These results are consistent with the characterization data, which showed that calcination temperature was associated with substantial changes in crystallinity, crystalline phase composition, textural properties, and surface acid–base behavior.

Nevertheless, the statistical importance of calcination temperature does not identify a single physicochemical cause for the observed activity trends. Calcination simultaneously affects crystallinity; the relative fractions of anatase, rutile, brookite, and hematite; surface area and pore structure; surface hydroxylation and acid–base properties; and potentially the distribution of Fe- and Zn-containing species. Therefore, the F-value associated with

calcination temperature represents the aggregate influence of these interrelated changes and should not be interpreted as evidence that any individual material property independently controls photocatalytic performance.

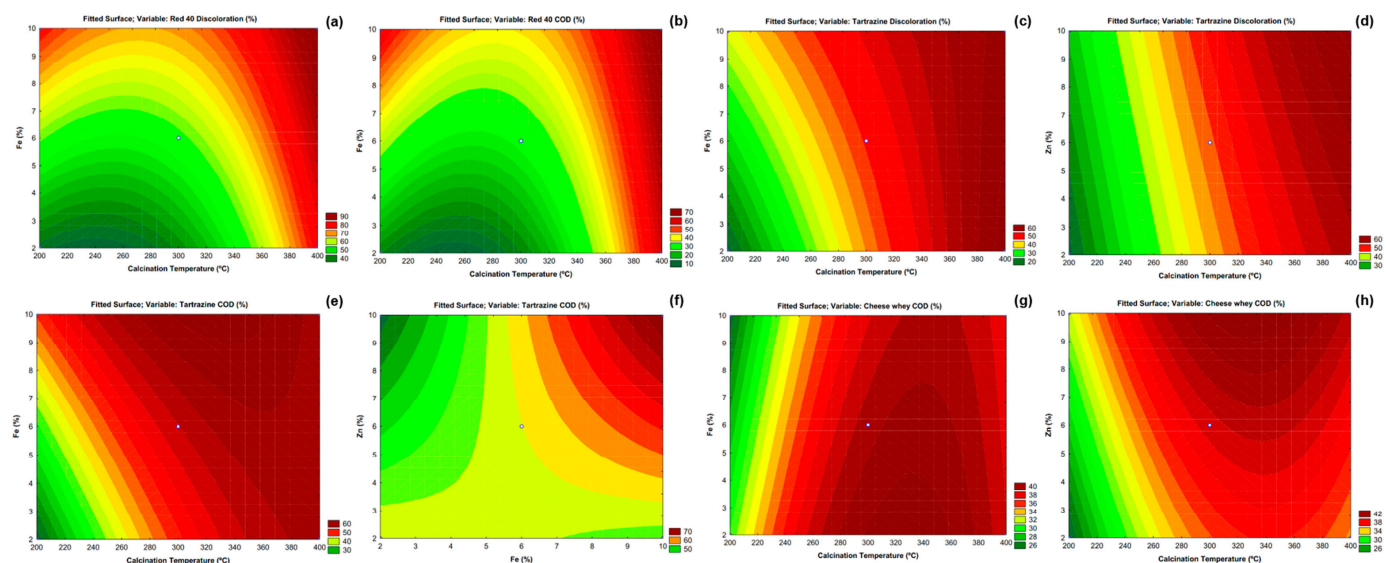


Figure 5. Contour Plot of the Response Surface Model: (a) Red 40 discoloration (Temperature $\times$ Fe); (b) Red 40 COD (Temperature $\times$ Fe); (c) Tartrazine discoloration (Temperature $\times$ Fe); (d) Tartrazine discoloration (Temperature $\times$ Zn) (e) Tartrazine COD (Temperature $\times$ Fe); (f) Tartrazine COD (Fe $\times$ Zn); (g) Cheese whey COD (Temperature $\times$ Fe); (h) Cheese whey COD (Temperature $\times$ Zn).

The Fe loading also exerted a significant influence on several photocatalytic responses, particularly for Red 40 discoloration and COD removal. The significant positive contribution of Fe indicates that increasing its concentration enhances photocatalytic activity within the investigated experimental domain. This behavior agrees with the XRD results, which demonstrated the gradual formation of hematite with increasing Fe loading, as well as with the photocatalytic experiments, where catalysts containing higher Fe contents exhibited superior Red 40 degradation. In contrast, the influence of Fe on Tartrazine discoloration and cheese whey COD removal was less pronounced, indicating that the beneficial effect of Fe strongly depends on the nature of the target pollutant.

Compared with calcination temperature and Fe loading, Zn loading exhibited a smaller individual contribution to most responses. Nevertheless, Zn significantly affected cheese whey COD removal and participated in several interaction terms, demonstrating that its influence is primarily associated with modifying the combined effect of the synthesis variables rather than acting independently. This observation is consistent with the structural characterization, where no crystalline Zn-containing phases were detected by XRD, suggesting that Zn remains highly dispersed or incorporated into the TiO₂ lattice while modifying the catalyst surface rather than its crystalline structure.

The estimated regression coefficients (Table S6) provide additional insight into the direction and magnitude of the effects identified by ANOVA. For Red 40 COD removal, Fe exhibited the largest positive linear coefficients, confirming that increasing Fe loading favors both discoloration and COD removal. Conversely, Zn produced comparatively smaller coefficients, reinforcing its secondary role in controlling photocatalytic activity. The quadratic coefficients associated with calcination temperature further indicate the existence of nonlinear behavior, suggesting that catalyst performance increases markedly at higher calcination temperatures within the investigated range. For Tartrazine, the regression coefficients reveal that Zn alone exerts a negative influence on both discoloration and COD removal, whereas the positive Fe $\times$ Zn interaction term indicates that the effect of one

factor depends on the level of the other within the investigated design. This statistical interaction does not demonstrate a physicochemical synergy between Fe and Zn. In the case of cheese whey, positive coefficients associated with calcination temperature and Zn loading indicate that both variables contribute favorably to COD removal, while excessive Fe loading tends to reduce catalyst performance.

The interaction effects identified by ANOVA further demonstrate that catalyst performance results from the combined influence of the synthesis variables rather than from isolated factors. Significant temperature $\times$ Fe and Fe $\times$ Zn interactions were observed for several responses, indicating that the effect of one synthesis parameter depends on the level of the others. This behavior is clearly illustrated by the three-dimensional response surfaces (Figure 5 and Figure S5), which exhibit well-defined nonlinear regions. The response surfaces reveal that distinct optimum synthesis conditions are required depending on the target pollutant. For Red 40, the maximum photocatalytic performance is obtained at high calcination temperature combined with high Fe and low Zn contents, corresponding to the experimentally identified catalyst F10Z2-400. In contrast, the response surfaces for Tartrazine indicate a different optimum region, reflecting the distinct degradation mechanism of this dye compared with Red 40. Likewise, cheese whey COD removal is favored by catalysts containing relatively high Zn contents, emphasizing the greater importance of surface chemistry during the oxidation of complex organic matrices. These observations demonstrate that catalyst optimization is intrinsically pollutant-dependent and confirm that no single catalyst composition provides the highest activity for all wastewater types.

The standardized Pareto charts (Figure S4) further corroborate the ANOVA results by ranking the effects of the synthesis variables according to their statistical significance. Calcination temperature consistently exhibited the largest standardized effects for all photocatalytic responses, followed by Fe loading, whereas Zn loading and the interaction terms showed comparatively smaller but still significant contributions depending on the evaluated pollutant. These results further confirm that calcination temperature is the dominant synthesis parameter governing photocatalytic activity.

2.3.2. Model Validation and Predictive Performance

The predictive capability of the developed response surface models was evaluated by comparing the predicted optimum responses with the corresponding experimental values obtained under the optimized synthesis conditions (Table 6). Overall, the quadratic models exhibited excellent goodness of fit, with coefficients of determination (R^2) ranging from 0.960 to 0.997 and adjusted coefficients (R^2_{adj}) between 0.865 and 0.990, indicating that the models explain most of the experimental variability and accurately describe the relationship between the synthesis parameters and the photocatalytic responses.

The highest predictive performance was obtained for Red 40 discoloration and COD removal, which presented R^2 values close to 0.99 and validation errors below 4%. Similarly, the model developed for Tartrazine discoloration exhibited satisfactory predictive capability, with a validation error of only 5.83%. Although slightly larger deviations were observed for Tartrazine COD removal (10.88%) and cheese whey COD removal (15.87%), these responses still exhibited high coefficients of determination, demonstrating that the models adequately represent the experimental behavior despite the greater complexity associated with the degradation of heterogeneous organic matrices.

The reliability of the developed models is further demonstrated by the observed $\times$ predicted plots shown in Figure S6. For all responses, the experimental data are closely distributed around the reference line, indicating good agreement between measured and predicted values. The smallest deviations are observed for Red 40 discoloration and Red 40 COD removal (Figure S6a,b), confirming the excellent predictive performance

of the corresponding regression models. Likewise, the models developed for Tartrazine discoloration and COD removal (Figure S6c,d) also exhibit a satisfactory distribution of the experimental points around the reference line, although a slightly greater dispersion is evident, particularly for COD removal, in agreement with the larger validation error obtained for this response. Among the investigated systems, cheese whey COD removal (Figure S6e) exhibits the largest scatter around the reference line. However, the deviations remain randomly distributed, with no systematic tendency toward overestimation or underestimation, indicating that the regression model adequately captures the experimental variability. The greater dispersion observed for cheese whey is expected considering the heterogeneous composition of this effluent, which contains proteins, carbohydrates, lipids, and other organic constituents that undergo multiple simultaneous oxidation pathways during photocatalysis [70].

The optimum synthesis conditions predicted by the response surface models were generally consistent with the experimental observations (Table 6). For Red 40 COD removal, the model identified 10 wt.% Fe, 2 wt.% Zn, and a calcination temperature of 400 °C as the optimum synthesis conditions, corresponding to the experimentally best-performing catalyst, F10Z2-400. Comparable agreement was observed for the other responses, indicating that the models were able to identify favorable regions of photocatalytic activity within the investigated experimental domain. Differences between the predicted optimum conditions and the experimentally evaluated formulations are expected because the response surfaces estimate continuous optimum from the fitted quadratic equations, whereas the experimental design includes only discrete combinations of factor levels.

The validation error of 15.87% obtained for cheese-whey COD removal was higher than those obtained for the synthetic dye solutions, indicating greater uncertainty in the corresponding model predictions. This difference may reasonably be associated with the heterogeneous nature of cheese whey, whose composition and COD can vary because of differences in the relative proportions and distribution of proteins, lactose, lipids, peptides, and suspended organic matter among experimental aliquots. Accordingly, this model should be interpreted primarily as a screening and optimization tool within the investigated experimental domain rather than as a robust predictor for extrapolation or scale-up. Because the available validation dataset contained a limited number of independent observations, reliable prediction intervals could not be determined. Additional validation using independent cheese-whey samples would therefore be required to characterize the predictive uncertainty more accurately.

Overall, the statistical analysis demonstrates that RSM is a useful tool for relating synthesis parameters to photocatalytic performance and identifying favorable experimental conditions within the investigated domain. The coefficients of determination, the general agreement between predicted and experimental responses, the proximity of most observed-versus-predicted values to the identity line, and the distribution of residuals around zero support the adequacy of the fitted models for screening purposes. Nevertheless, the higher validation error obtained for cheese-whey COD removal limits claims regarding predictive accuracy for this response. Calcination temperature exhibited the largest statistical effect on the measured responses, whereas the effects of Fe and Zn loading depended on the target pollutant and their interactions with the other synthesis variables. These findings highlight the value of multivariate optimization for developing Fe/Zn-modified TiO₂ photocatalysts tailored to specific wastewater matrices, while emphasizing the need for additional independent validation before extrapolation to other conditions or larger treatment scales.

Table 5. Analysis of Variance (ANOVA) of the Fitted Response Surface Model.

Source ¹	df	Red 40 Discoloration (%)				Red 40 COD (%)				Tartrazine Discoloration (%)				Tartrazine COD (%)				Cheese Whey COD (%)			
		SS	MS	F	<i>p</i>	SS	MS	F	<i>p</i>	SS	MS	F	<i>p</i>	SS	MS	F	<i>p</i>	SS	MS	F	<i>p</i>
A	1	1782.6	1782.6	73.64	0.013	1987.0	1987.0	113.2	0.002	2194.9	2194.9	44.12	0.007	1064.7	1064.7	460.4	0.000	213.2	213.2	31.78	0.011
A ²	1	619.8	619.8	38.40	0.008	1227.0	1227.0	69.94	0.004	21.86	21.86	0.440	0.555	158.4	158.4	68.51	0.004	117.5	117.5	17.51	0.149
B	1	1609.7	1609.7	66.50	0.014	1410.3	1410.3	80.38	0.003	147.0	147.0	2.950	0.184	336.3	336.3	145.4	0.001	21.78	21.78	3.250	0.169
C	1	40.14	40.14	1.658	0.326	9.720	9.720	0.550	0.511	77.44	77.44	1.560	0.301	18.33	18.33	7.930	0.067	106.0	106.0	15.80	0.028
A × B	1	244.4	244.4	10.09	0.086	427.8	427.8	24.38	0.057	243.87	243.87	4.900	0.114	325.5	325.5	140.8	0.001	11.52	11.52	1.720	0.281
A × C	1	95.63	95.63	3.950	0.185	152.2	152.2	8.680	0.060	1.420	1.420	0.030	0.877	0.260	0.260	0.110	0.758	4.560	4.560	0.680	0.470
B × C	1	99.12	99.12	4.094	0.180	85.81	85.81	4.890	0.114	1189.0	1189.0	23.90	0.016	510.6	510.6	220.8	0.001	3.001	3.001	0.450	0.551
Error	3	48.41	16.14			52.64	17.55			149.2	49.75			6.940	2.310			20.13	6.710		
Lack-of-fit	1	48.12	48.12	311.8	0.003	51.21	51.21	71.71	0.014	147.1	147.1	140.9	0.007	4.910	4.910	4.860	0.158	19.53	19.53	65.34	0.015
Total	10	4539.9				5352.6				4024.7				2421.0				497.7			

¹ A—Calcination temperature; B—Fe content; C—Zn content; df = degree of freedom; SS = sum of squares; MS = mean square.

Table 6. Regression models, goodness-of-fit statistics, and optimum synthesis conditions obtained from the 2³ factorial design.

Response	Regression Model ¹	R ²	R ² _{adj}	Fe (%)	Zn (%)	Calcination Temperature (°C)	Predicted Response (%)	Experimental Response (%)	Error (%)
Red 40 discoloration	$D = 111.3 - 0.727 \times A + 6.370 \times B + 0.710 \times C + 0.002 \times A^2 - 0.014 \times A \times B - 0.009 \times A \times C + 0.220 \times B \times C$	0.989	0.950	10	2	400	97.40	99.85	2.520
Red 40 degradation (COD)	$COD = 129.6 - 1.090 \times A + 7.580 \times B + 1.770 \times C + 0.002 \times A^2 - 0.018 \times A \times B - 0.011 \times A \times C + 0.204 \times B \times C$	0.990	0.967	10	2	400	74.49	77.02	3.400
Tartrazine discoloration	$D = -42.00 + 0.445 \times A + 0.640 \times B - 3.480 \times C - 0.001 \times A^2 - 0.014 \times A \times B - 0.001 \times A \times C + 0.762 \times B \times C$	0.963	0.876	10	10	400	73.62	77.91	5.830
Tartrazine degradation (COD)	$COD = -77.60 + 0.720 \times A + 3.409 \times B - 2.753 \times C - 0.001 \times A^2 - 0.016 \times A \times B + 0.001 \times A \times C + 0.499 \times B \times C$	0.997	0.990	10	10	330	72.43	64.55	10.88
Cheese whey degradation (COD)	$COD = -44.10 + 0.485 \times A - 1.083 \times B + 1.706 \times C - 0.001 \times A^2 + 0.003 \times A \times B - 0.002 \times A \times C - 0.038 \times B \times C$	0.960	0.865	2	10	320	46.05	38.74	15.87

¹ A—Calcination temperature; B—Fe content; C—Zn content; D—discoloration reduction; COD—COD reduction.

3. Limitations and Future Perspectives

The present study demonstrates that Fe/Zn modification and calcination temperature influence the physicochemical properties and photocatalytic performance of TiO₂ synthesized by the sol–gel method. The combination of catalyst characterization, kinetic modeling, and response surface methodology (RSM) enabled the comparative evaluation of the synthesized materials and the identification of favorable formulations for treating synthetic food dyes and real cheese-whey effluent under the irradiation conditions evaluated. Nevertheless, several aspects require further investigation before these materials can be considered for large-scale wastewater-treatment applications.

First, although XRD, SEM/EDS, nitrogen physisorption, and pH_{PZC} analyses provided valuable information on the structural, textural, elemental, and surface properties of the catalysts, the chemical states and locations of the Fe and Zn species could not be conclusively determined. The absence of secondary crystalline phases in the XRD patterns does not demonstrate addition of these elements into the TiO₂ lattice, as highly dispersed, amorphous, or sub-detection-limit surface species could produce similar results. Techniques such as X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and local

structural analysis would help distinguish lattice addition from surface dispersion and provide further information on oxidation states, defect formation, and oxygen vacancies.

The photocatalytic trends observed in this study do not provide direct evidence of changes in electron–hole recombination or interfacial charge-transfer kinetics. Because photoluminescence, time-resolved photoluminescence, transient photocurrent, and electrochemical impedance measurements were not performed, the effects of Fe and Zn loading on charge-carrier dynamics cannot be conclusively established. Therefore, charge-transfer explanations discussed herein are literature-supported hypotheses proposed to rationalize the experimental activity trends rather than experimentally demonstrated mechanisms.

UV–Vis diffuse reflectance spectroscopy (DRS) was not performed in the present study. Consequently, possible changes in the optical absorption edge and band-gap energy associated with Fe/Zn modification cannot be established experimentally from the current dataset. Photocatalytic activity under natural sunlight alone does not demonstrate visible-light activation because the incident radiation contains both ultraviolet and visible components. Therefore, statements concerning electronic-structure modification, band-gap narrowing, or enhanced visible-light absorption should be considered hypotheses based on previous literature. Future studies should include DRS measurements and appropriate band-gap analysis to characterize the optical response of the synthesized materials.

Second, the photocatalytic experiments were conducted under batch conditions using model dye solutions and cheese whey collected from a single dairy-processing facility. Although cheese whey represents a complex real effluent, its composition can vary depending on milk origin, cheese type, processing conditions, and seasonal fluctuations. Additional studies involving effluents from different sources, continuous-flow photoreactors, and larger treatment volumes are therefore required to evaluate the robustness and scalability of the materials under practical operating conditions. Although all catalyst–pollutant conditions were evaluated in three independent photocatalytic batch experiments and the results are reported as mean $\pm$ standard deviation ($n = 3$), the number of replicates was limited. Additional experiments using independently prepared catalyst batches and a larger number of photocatalytic replicates would further strengthen the uncertainty estimates and the assessment of synthesis-to-synthesis reproducibility.

Catalyst-reuse cycles and quantitative Fe and Zn leaching measurements were not performed. Therefore, retention of photocatalytic activity over repeated use, structural stability under the reaction conditions, and the extent of metal release into treated effluent remain unknown. The present results should be regarded as proof-of-concept activity data rather than evidence of practical durability or environmental safety. Future application-oriented studies should combine multiple reuse cycles with post-reaction characterization and ICP-OES or ICP-MS analysis of Fe and Zn in the liquid phase.

Catalyst durability is another important consideration. Although the present study identified favorable synthesis conditions for each target pollutant within the investigated experimental domain, catalyst reuse, long-term structural stability, resistance to photocorrosion, and Fe and Zn leaching were not evaluated. Consequently, retention of photocatalytic activity over repeated cycles and the potential release of metals into the treated effluent remain unknown. Reuse experiments combined with post-reaction characterization and quantitative leaching analyses by ICP-OES or ICP-MS will be essential for evaluating catalyst lifetime and environmental safety, particularly in applications involving food-industry effluents.

Reactive-species scavenging experiments provided indirect evidence for the participation of hydroxyl radicals, superoxide radicals, and photogenerated holes in the discoloration of Red 40 by F10Z2-400 and Tartrazine by T-400. However, the tests were restricted to the best-performing dye–catalyst combinations and cannot be extrapolated quantitatively to

all catalysts or to cheese-whey COD removal. Moreover, scavenger inhibition does not constitute direct detection of the reactive species. Future studies combining EPR spin-trapping measurements with chromatographic and mass-spectrometric identification of transformation products would help confirm the proposed pathways, determine whether the reactive-species hierarchy changes with catalyst composition, and evaluate changes in effluent toxicity.

Although RSM identified favorable combinations of calcination temperature, Fe content, and Zn content within the investigated domain, the statistical models should be interpreted primarily as screening tools rather than as robust predictors for extrapolation or scale-up. This caution is particularly important for cheese-whey COD removal, for which the validation error reached 15.87%, and for responses exhibiting significant lack of fit. Future experimental designs could incorporate additional factors, including catalyst dosage, initial pollutant concentration, solution pH, irradiation intensity, and reaction time, together with additional independent replicates and external validation experiments. Such an approach would support the development of more reliable predictive models for different industrial wastewater matrices.

Overall, the results provide proof-of-concept evidence for the use of sol-gel-derived Fe/Zn-modified TiO₂ photocatalysts in the treatment of food-industry effluents. However, Fe/Zn modification did not universally improve TiO₂ performance: the most favorable catalyst depended on the pollutant and matrix evaluated. Future research integrating advanced spectroscopic characterization, charge-carrier analysis, catalyst-reuse and leaching assessments, degradation-product identification, toxicity evaluation, and pilot-scale continuous operation will be necessary to determine whether these materials can support robust, safe, and sustainable wastewater-treatment applications.

4. Materials and Methods

4.1. Materials

Titanium (IV) isopropoxide (TTIP, ≥97%), zinc chloride (ZnCl₂, ≥97%), iron(III) chloride hexahydrate (FeCl₃·6H₂O, ≥99%), sodium hydroxide (NaOH, ≥97%), ethanol (≥99.5%), nitric acid (HNO₃, ≥65%), hydrochloric acid (HCl, ≥37%), Red 40 dye (≥85%), and Tartrazine dye (≥85%) were purchased from Merck Sigma-Aldrich (St. Louis, MO, USA). All reagents were of analytical grade and used as received without further purification. Ultrapure Milli-Q® water (18.2 MΩ·cm resistivity) was used as the solvent throughout the synthesis procedures. Cheese whey was obtained from a dairy facility located in northern Paraná State, Brazil, and collected during the production of Minas Frescal cheese at the curd-cutting stage of milk coagulation. After collection, the whey was filtered through cheesecloth to remove residual particulate matter generated during the cheesemaking process. Analytical-grade isopropyl alcohol (IPA), p-benzoquinone (p-BQ), and ammonium oxalate (AO) were used as reactive-species scavengers.

4.2. Synthesis and Preparation of the Fe/Zn/TiO₂ Catalysts

The TiO₂ support and Fe/Zn-modified TiO₂ photocatalysts were synthesized by the sol-gel method following the procedure described by Castro et al. (2020) [28], using a molar ratio of H₂O:Ti precursor:HNO₃ = 2.4:1:0.08. TTIP was employed as the Ti precursor, while iron(III) chloride hexahydrate (FeCl₃·6H₂O) and zinc chloride (ZnCl₂) were used as the Fe and Zn precursors, respectively. Ethanol, ultrapure Milli-Q® water (Direct-Q® 3 UV, Millipore, Billerica, MA, USA) (18.2 MΩ·cm), and nitric acid served as the solvent, hydrolysis agent, and acid catalyst, respectively.

The synthesis was carried out using two precursor solutions. The first solution consisted of TTIP dissolved in ethanol under a N₂ atmosphere to prevent premature hydrolysis

of the alkoxide. The second solution contained ultrapure water, nitric acid, ethanol, and the appropriate amounts of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and ZnCl_2 according to the desired catalyst composition. This solution was stirred for 5 min before being slowly added to the alkoxide solution under continuous nitrogen flow. Rapid hydrolysis and condensation reactions occurred upon mixing, leading to gel formation within approximately 15 s. The resulting gel was then aged overnight at room temperature to promote further polycondensation and network stabilization.

For the TiO_2 support, the aged gel was washed three times daily for four consecutive days using a 1:1 ($v v^{-1}$) water–acetone mixture to remove residual reagents and organic by-products. In contrast, the Fe/Zn-modified gels were not subjected to the washing step to minimize metal leaching and preserve the nominal metal loading. Subsequently, all materials were dried using a rotary evaporator at 40–90 °C for 1 h, followed by vacuum drying ($\approx 10^{-3}$ atm) at 80 °C for 8 h.

The dried xerogels were finally calcined in air at 200, 300, or 400 °C for 5 h using a controlled heating program to promote crystallization while minimizing particle sintering. The resulting materials were designated according to their nominal Fe and Zn contents and calcination temperature (e.g., F2Z2-400, F10Z2-400, and F10Z10-400).

To investigate the influence of the synthesis parameters on photocatalytic performance, a 2^3 factorial experimental design was employed to evaluate the effects of calcination temperature, Fe loading, and Zn loading on the photodegradation efficiency of Red 40, Tartrazine, and cheese whey. The central point was performed in triplicate to estimate the experimental error and ensure the statistical reliability of the developed models. The coded and actual levels of the independent variables are presented in Table 7. In addition, TiO_2 support samples calcined at 200, 300, and 400 °C were synthesized and evaluated as control catalysts to compare the photocatalytic performance of the Fe/Zn-modified formulations with that of the TiO_2 supports.

Table 7. Control variables considered in the 2^3 factorial design and experiments for Fe/Zn/ TiO_2 catalyst synthesis.

Experiment Codes	Catalysts	Codified Variables			Non-Codified Variables		
		X_1	X_2	X_3	Calcination Temperature (°C)	Fe (%)	Zn (%)
T-NC	TiO_2	-	-	-	-	-	-
T-200		-1	-	-	200	-	-
T-300		0	-	-	300	-	-
T-400		+1	-	-	400	-	-
F2Z2-NC	$\text{Fe}_2\%/\text{Zn}_2\%/\text{TiO}_2$	-	-1	-1	-	2	2
F2Z2-200		-1	-1	-1	200	2	2
F2Z2-400		+1	-1	-1	400	2	2
F2Z10-NC	$\text{Fe}_2\%/\text{Zn}_{10\%}/\text{TiO}_2$	-	-1	+1	-	2	10
F2Z10-200		-1	-1	+1	200	2	10
F2Z10-400		+1	-1	+1	400	2	10
F6Z6-NC	$\text{Fe}_6\%/\text{Zn}_6\%/\text{TiO}_2$	-	0	0	-	6	6
F6Z6-300		0	0	0	300	6	6

Table 7. Cont.

Experiment Codes	Catalysts	Codified Variables			Non-Codified Variables		
		X ₁	X ₂	X ₃	Calcination Temperature (°C)	Fe (%)	Zn (%)
F10Z2-NC	Fe _{10%} /Zn _{2%} /TiO ₂	-	+1	-1	-	10	2
F10Z2-200		-1	+1	-1	200	10	2
F10Z2-400		+1	+1	-1	400	10	2
F10Z10-NC	Fe _{10%} /Zn _{10%} /TiO ₂	-	+1	+1	-	10	10
F10Z10-200		-1	+1	+1	200	10	10
F10Z10-400		+1	+1	+1	400	10	10

4.3. Characterization of the Fe/Zn/TiO₂ Catalysts

The synthesized photocatalysts were characterized to evaluate their textural, morphological, structural, surface, and chemical properties.

Nitrogen adsorption–desorption isotherms were recorded at 77 K using a NOVA 2000e sorption analyzer (Quantachrome Instruments, Boynton Beach, FL, USA). Prior to analysis, the samples were degassed under vacuum to remove physically adsorbed species. The specific surface area (S_{bet}) was determined using the Brunauer–Emmett–Teller (BET) method, whereas the total pore volume (V_p) and average pore diameter (d_p) were calculated from the adsorption branch of the isotherms.

The morphology and elemental composition of the catalysts were examined by scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM/EDS) using a VEGA3 microscope (TESCAN, Brno, Czech Republic).

The crystalline structure of the materials was investigated by X-ray diffraction (XRD) using a XRD-6000 diffractometer (Shimadzu Corporation, Kyoto, Japan) equipped with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) and operated at 30 kV and 20 mA. Diffraction patterns were collected over the selected 2θ range at a scanning rate of 2° min^{-1} . Phase identification was performed by comparison with the International Centre for Diffraction Data (ICDD) Powder Diffraction File (PDF-4+) database. Quantitative phase analysis was carried out by Rietveld refinement using the GSAS-II software (revision 4576) package, allowing the determination of the crystalline phase composition, lattice parameters, and refinement quality indicators (R_p , R_{wp} , and χ^2).

The surface charge properties of the catalysts were evaluated by determining the point of zero charge (pH_{PZC}) using the pH drift method [33,50]. Briefly, 50 mg of catalyst was dispersed in 50 mL of aqueous solutions with initial pH values adjusted between 2 and 12. The suspensions were stirred at room temperature for 24 h, after which the final pH was measured. The pH_{PZC} was determined from the intersection of the initial and final pH values.

4.4. Photocatalytic Assays

The photocatalytic activity of the synthesized catalysts was evaluated under natural sunlight and artificial irradiation using the experimental setups illustrated in Figure 6a,b, respectively. In both configurations, the reactions were carried out in a batch reactor consisting of a 250 mL borosilicate glass beaker placed on a magnetic stirrer to ensure continuous suspension and homogeneous dispersion of the photocatalyst.

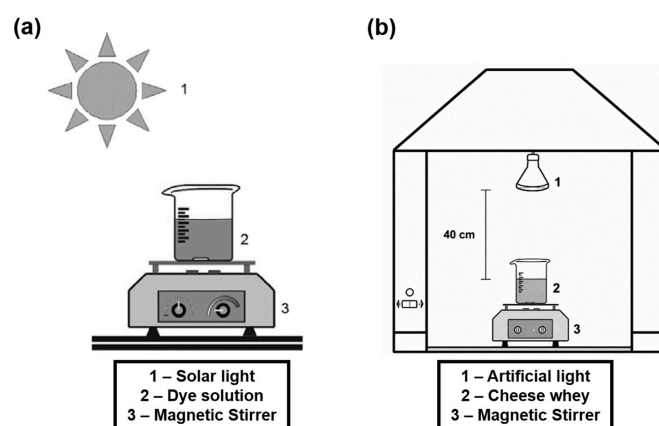


Figure 6. Schematic diagram of the photocatalytic apparatus for food effluent degradation: (a) Sun light-assisted, (b) Artificial light-assisted.

Prior to the photocatalytic assays, adsorption experiments were performed to evaluate the removal of Red 40 and Tartrazine in the absence of light. The experiments were conducted under the same operating conditions as the photocatalytic tests, except that the suspensions were maintained in the dark for 30 min to establish adsorption–desorption equilibrium. In addition, photolysis experiments were carried out under natural sunlight without the photocatalyst for 120 min to assess the intrinsic photosensitivity of the dyes.

The photocatalytic degradation of Red 40 and Tartrazine was performed under natural sunlight (Figure 6a). Each experiment employed 150 mL of an aqueous dye solution (10 mg L^{-1} , $\text{pH} = 4$) containing 50 mg of photocatalyst. Each photocatalytic assay was performed in three independent experimental replicates ($n = 3$). The suspensions were irradiated for 120 min, and aliquots were collected at 0, 30, 60, 90, and 120 min. Immediately after sampling, the suspensions were vacuum-filtered through cellulose ester membranes (47 mm diameter, $0.45 \mu\text{m}$ pore size) to remove catalyst particles and stored under refrigeration until analysis. Photocatalytic performance was evaluated in terms of discoloration by UV–Vis spectrophotometry and mineralization by COD removal.

The sunlight-driven experiments were conducted between 5 and 7 January 2026, from 11:00 a.m. to 1:00 p.m., corresponding to a period of high solar irradiance. Incident solar radiation was monitored using a LI-200 radiometer (SIMEPAR, Curitiba, PR, Brazil), operating in the 390–1100 nm wavelength range. The average solar irradiance ranged from 1055.3 to 1095.0 W m^{-2} . The experiments were performed under clear-sky conditions, with ambient temperatures ranging from 28 to 31°C .

The discoloration of the dye solutions was monitored using a UV–Vis spectrophotometer (Drawell, Model EEQ9011I UV-B, Chongqing, China). Absorbance was measured at the characteristic wavelengths of each dye (Table S1), and the corresponding concentrations were determined from previously established calibration curves. The discoloration efficiency was calculated according to Equation (S1). Mineralization was assessed by determining the COD at the end of the photocatalytic process following the procedures described in the Standard Methods for the Examination of Water and Wastewater [83].

The photocatalytic treatment of cheese whey wastewater was carried out under artificial irradiation using the setup shown in Figure 6b. The reactions were performed under the same batch configuration described above, employing 150 mL of cheese whey at its original pH of 6.02 and 50 mg of photocatalyst under continuous magnetic stirring. Each photocatalytic assay was performed in three independent experimental replicates ($n = 3$). Irradiation was provided by a 250 W mercury vapor lamp, which served as the UV–visible light source throughout the experiments. The suspensions were irradiated for 4 h, and aliquots were collected at 0, 1, 2, 3, and 4 h. Each sample was immediately vacuum-filtered

through 0.45 μm cellulose ester membranes (47 mm diameter) to remove catalyst particles and stored under refrigeration until analysis. Photocatalytic performance was evaluated based on COD removal, which was used as an indicator of the mineralization of the organic constituents present in cheese whey wastewater, following the Standard Methods for the Examination of Water and Wastewater [83]. The use of artificial irradiation provided stable and reproducible operating conditions, minimizing fluctuations in light intensity and enabling a reliable assessment of photocatalytic activity. In addition, photolysis experiments were carried out under UV-light without the photocatalyst for 4 h to assess the intrinsic photosensitivity of the cheese whey.

Reactive-Species Scavenging Experiments

Reactive-species scavenging experiments were performed to evaluate the relative contributions of hydroxyl radicals ($\bullet\text{OH}$), superoxide radicals ($\text{O}_2\bullet^-$), and photogenerated holes (h^+) to the discoloration of Red 40 and Tartrazine. The experiments were conducted using the best-performing catalyst for each dye, namely F10Z2-400 for Red 40 and T-400 for Tartrazine, under the same operating conditions employed in the photocatalytic assays described in Section 4.4.

For each experiment, 50 mg of photocatalyst was dispersed in 150 mL of an aqueous dye solution with an initial concentration of 10 mg L^{-1} . Isopropyl alcohol (IPA), p-benzoquinone (p-BQ), and ammonium oxalate (AO) were separately added to the reaction medium at a final concentration of 1.0 mmol L^{-1} to act as scavengers of $\bullet\text{OH}$, $\text{O}_2\bullet^-$, and h^+ , respectively [62]. A control experiment without a scavenger was performed under otherwise identical conditions. After scavenger addition, the solution pH was readjusted to the value used in the original photocatalytic experiments. For both dye systems, the adjusted reaction pH was 4.0.

The suspensions were maintained under continuous magnetic stirring and irradiated under natural sunlight for 120 min. To minimize variations in solar irradiance, the control and scavenger-containing experiments were conducted simultaneously using parallel reactors. Incident solar irradiance and ambient temperature were monitored throughout the experiments. Aliquots were collected at 0, 30, 60, 90, and 120 min and immediately vacuum-filtered through cellulose ester membranes with a pore size of 0.45 μm to remove the photocatalyst particles.

The residual dye concentrations were determined by UV–Vis spectrophotometry at the characteristic wavelength of each dye, as specified in Table S1. Before the photocatalytic experiments, UV–Vis spectra of solutions containing each scavenger were recorded to verify the absence of relevant spectral interference at the analytical wavelengths. Scavenger-containing blanks without photocatalyst were also analyzed under irradiation to evaluate possible direct effects of the scavengers on dye discoloration.

All conditions were evaluated in three independent batch experiments ($n = 3$), and the results were expressed as mean $\pm$ standard deviation. The inhibition caused by each scavenger was calculated according to Equation (1).

$$\text{Inhibition (\%)} = \frac{D_{\text{control}} - D_{\text{scavenger}}}{D_{\text{control}}} \times 100 \quad (1)$$

where (D_{control}) is the discoloration efficiency obtained without a scavenger and ($D_{\text{scavenger}}$) is the discoloration efficiency obtained in the presence of the corresponding scavenger. A greater inhibition percentage was interpreted as evidence of a greater contribution of the associated reactive species to dye discoloration. Differences among treatments were evaluated by one-way analysis of variance followed by Tukey's test at ($p \leq 0.05$).

The scavenging experiments were restricted to the synthetic dye solutions because the addition of organic scavengers would interfere with chemical oxygen demand measurements in the cheese-whey matrix. Consequently, no specific reactive species or degradation pathway was assigned to cheese-whey COD removal.

4.5. Photocatalytic Kinetics

To evaluate the kinetics of the photodiscoloration and photodegradation of Red 40, Tartrazine, and cheese whey, three kinetic models were employed: the pseudo-first-order (PFO) model (Equation (S2)), the pseudo-second-order (PSO) model (Equation (S3)), and the Behnajady–Modirshahla–Ghanbery (BMG) model (Equation (S4)).

4.6. Statistical Analysis

The experimental data were statistically analyzed by analysis of variance (ANOVA) to identify the significant effects of the synthesis variables and their interactions. Mean comparisons were performed using Tukey's post hoc test at a significance level of $p \leq 0.05$. The photocatalytic responses, expressed as discoloration and chemical oxygen demand (COD) removal percentages, were modeled using Response Surface Methodology (RSM) based on a second-order polynomial equation (Equation (S9)). The significance of the regression coefficients was evaluated by ANOVA ($p \leq 0.05$), and the optimum operating conditions were determined using the Simplex optimization method. All statistical analyses were performed using STATISTICA® software (version 7, TIBCO Software Inc., Palo Alto, CA, USA).

5. Conclusions

Fe/Zn-modified TiO₂ photocatalysts were synthesized by the sol–gel method, and the effects of Fe loading, Zn loading, and calcination temperature on their physicochemical properties and photocatalytic performance were systematically evaluated using a 2³ factorial experimental design. Nitrogen physisorption indicated mesoporous structures with type IV isotherms, while SEM/EDS confirmed the presence and relatively homogeneous micrometric distribution of Fe and Zn within the analyzed particles. XRD and Rietveld refinement showed that lower metal loadings were associated with anatase as the only detectable crystalline phase, whereas increasing Fe loading promoted the formation of hematite and rutile. No crystalline Zn-containing secondary phases were detected. However, these results do not establish the lattice addition of Fe or Zn. The Fe/Zn-modified materials also generally exhibited higher pH_{PZC} values than the TiO₂ supports, demonstrating that metal loading and calcination temperature influenced their surface acid–base properties.

Photocatalytic performance was strongly dependent on the target pollutant. Under natural sunlight, F10Z2-400 exhibited the highest activity toward Red 40, achieving 99.85% discoloration and 77.02% COD removal. In contrast, the TiO₂ support calcined at 400 °C (T-400) provided the best performance for Tartrazine, reaching 86.25% discoloration and 87.61% COD removal. For cheese whey treated under artificial irradiation, F10Z10-400 achieved the highest COD removal, reaching 41.01% after 4 h. These distinct trends demonstrate that Fe/Zn modification did not universally improve TiO₂ photocatalytic performance and that the most favorable formulation depended on the pollutant and treatment matrix.

Control experiments confirmed that non-photocatalytic processes made only minor contributions to pollutant removal. Dye adsorption and direct photolysis resulted in low discoloration efficiencies, while catalyst-free irradiation of cheese whey produced only 2.87% COD removal. These findings support the conclusion that the removal efficiencies

observed in the presence of the catalysts resulted predominantly from heterogeneous photocatalysis. Among the kinetic models evaluated, the Behnejady–Modirshahla–Ghanbary model provided the best overall description of the degradation profiles for Red 40, Tartrazine, and cheese whey, capturing the nonlinear decrease in the apparent reaction rate over time.

Reactive-species scavenging provided further evidence regarding the dye-discoloration pathways. For Red 40, IPA, p-BQ, and AO caused inhibitions of 65.41%, 44.66%, and 25.67%, respectively; for Tartrazine, the corresponding inhibitions were 72.24%, 43.99%, and 21.91%. The common inhibition order supports $\bullet\text{OH}$ as the predominant reactive species in both selected dye–catalyst systems, followed by $\text{O}_2\bullet^-$ and h^+ , while remaining an indirect mechanistic assessment that requires confirmation by direct spectroscopic detection.

Response Surface Methodology enabled the effects of the investigated synthesis variables to be assessed within the experimental domain. Calcination temperature was generally the most influential variable, whereas the effects of Fe and Zn loading depended on the target pollutant and their statistical interactions with the other synthesis variables. The resulting models were useful for screening synthesis conditions and identifying favorable catalyst formulations. Nevertheless, they should not be considered validated predictors for extrapolation or scale-up without additional independent experiments.

Catalyst-reuse cycles and quantitative Fe and Zn leaching measurements were not performed. Consequently, the retention of photocatalytic activity during repeated use, structural stability under the reaction conditions, and the extent of metal release into the treated effluent remain unknown. The present results should therefore be regarded as proof-of-concept activity data rather than evidence of practical durability, environmental safety, or readiness for full-scale application. Future application-oriented studies should combine multiple reuse cycles with post-reaction characterization and ICP-OES or ICP-MS measurements of Fe and Zn in the liquid phase.

Overall, the results demonstrate that Fe and Zn loading and calcination temperature produced composition- and pollutant-dependent changes in the properties and photocatalytic performance of TiO_2 . Because matched Fe-only and Zn-only catalysts were not included, the study does not establish a true Fe–Zn synergistic effect. Instead, the findings support pollutant-specific optimization within the experimental domain investigated: F10Z2-400 was the most effective formulation for Red 40, the T-400 TiO_2 support was the most effective catalyst for Tartrazine, and F10Z10-400 provided the highest COD removal from cheese whey. These results provide a basis for the further development of TiO_2 -based photocatalysts for food-industry wastewater treatment while clearly identifying the additional stability, safety, mechanism, and scale-up assessments required for practical application.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/inorganics14090234/s1>, Figure S1. N_2 adsorption–desorption isotherms at 77 K; Figure S2. SEM-EDS elemental mapping of the catalysts calcined at 400 °C, except 6%Fe/6%Zn/ TiO_2 calcined at 300 °C; Figure S3. Rietveld refinement of the XRD patterns; Figure S4. Pareto chart of the Response Surface Model; Figure S5. Response surface contour plots of the Response Surface Model; Figure S6. Observed vs. Predicted values plots of the Response Surface Model; Table S1. Physical-chemical properties of the food effluent; Table S2. XRD phase composition of the catalysts calcined; Table S3. Rietveld refinement parameters of the catalysts; Table S4. Exploratory Pearson correlation coefficients (r) for the catalysts; Table S5. Kinetic parameters of the synthesized catalysts for the treatment of food-industry effluents; Table S6. Estimated Regression Coefficients of the Fitted Model; Table S7. Effect of reactive-species scavengers on the photocatalytic discoloration of Red 40 and Tartrazine under solar irradiation.

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