



Article

Magnetic TiO₂/CoFe₂O₄ Photocatalysts for Degradation of Organic Dyes and Pharmaceuticals without Oxidants

Islam Ibrahim ^{1,*}, George V. Belessiotis ², Ahmed Mourtada Elseman ³, Mohamed Mokhtar Mohamed ^{4,5}, Yatao Ren ^{6,7,*}, Tarek M. Salama ¹ and Mahmoud Basseem I. Mohamed ¹

¹ Department of Chemistry, Faculty of Science, Al-Azhar University, Cairo 11884, Egypt

² Chemical Engineering Department, National Technical University of Athens NTUA, 15780 Athens, Greece

³ Electronic and Magnetic Materials Department, Advanced Materials Institute, Central Metallurgical Research and Development Institute, Cairo 11421, Egypt

⁴ Egypt-Japan University of Science and Technology, Borg El Arab, Alexandria 21934, Egypt

⁵ Chemistry Department, Faculty of Science, Benha University, Benha 13518, Egypt

⁶ Harbin Institute of Technology, School of Energy Science and Engineering, Harbin 150001, China

⁷ Faculty of Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK

* Correspondence: i.ibrahim@inn.demokritos.gr (I.I.); yatao.ren@nottingham.ac.uk (Y.R.)

Abstract: In the current study, CoFe₂O₄ and TiO₂ nanoparticles were primarily made using the sol-gel method, and subsequently, the hybrid magnetic composites of TiO₂ loaded with CoFe₂O₄ (5–15 percent *w/w*) were made using a hydrothermal procedure. X-ray diffraction (XRD), Fourier transform infrared (FTIR) and Raman spectroscopy, ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS), scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HRTEM) were all used to thoroughly characterize the materials. Additionally, the zero-charge point (ZCP) determination, the examination of the pore structure by nitrogen adsorption, and an evaluation of magnetic properties were performed. Six organic dye pollutants were selected to evaluate the performance of the synthesized nanocomposites toward photocatalytic degradation, including methylene blue (MB), methyl orange (MO), crystal violet (CV), acridine orange (AO), rhodamine B (RhB), and rhodamine 6G (R-6G). Photodegradation of tetracycline (TL), a model pharmaceutical pollutant, was also studied under UV and visible light. The composites exhibited a high degradation performance in all cases without using any oxidants. The photocatalytic degradation of tetracycline revealed that the CoFe₂O₄/TiO₂ (5% *w/w*) composite exhibited a higher photocatalytic activity than either pure TiO₂ or CoFe₂O₄, and thus attained 75.31% and 50.4% degradation efficiency under UV and visible light, respectively. Trapping experiments were conducted to investigate the photodegradation mechanism, which revealed that holes and super oxide radicals were the most active species in the photodegradation process. Finally, due to the inherent magnetic attributes of the composites, their easy removal from the treated solution via a simple magnet became possible.

Keywords: TiO₂ composite; visible light; tetracycline; photocatalytic oxidation; magnetic composite



Citation: Ibrahim, I.; Belessiotis, G.V.; Elseman, A.M.; Mohamed, M.M.; Ren, Y.; Salama, T.M.; Mohamed, M.B.I. Magnetic TiO₂/CoFe₂O₄ Photocatalysts for Degradation of Organic Dyes and Pharmaceuticals without Oxidants. *Nanomaterials* **2022**, *12*, 3290. <https://doi.org/10.3390/nano12193290>

Academic Editor: Vincenzo Vaiano

Received: 15 August 2022

Accepted: 17 September 2022

Published: 21 September 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

As a result of the use of dyes for coloring by the textile, plastics, and other industries, the amount of organic dye pollution has increased [1]. Industrial dyes are one of the most prominent water pollutants [2]. Some of the most infamous of these organic dye pollutants (ODP) include: (a) Methylene Blue (MB), known for its toxicity, carcinogenic nature, and non-biodegradability [2], (b) Crystal Violet (CV), which can cause issues from permanent eye injuries to respiratory or kidney failure [3], (c) Methyl Orange (MO), an azo dye that is mutagenic and carcinogenic and has a limited biodegradability [4], (d) Acridine Orange (AO), a cell-permeable toxic dye with mutagenic potential [5], (e) Rhodamine B (RhB), a dye which poses a threat for the respiratory tract and skin with carcinogenic and neurotoxic potential [6] and (f) Rhodamine 6G (R-6G), another dye of the rhodamine

family, which presents similar dangers [7]. The chemical structures of the selected six ODP are shown in Figure 1. Pharmaceutical ingredients are another major source of pollutants. They are considered a significant threat to humans' endocrine, reproductive, and cognitive systems [8]. One such pharmaceutical pollutant is the antibiotic Tetracycline (TL), which often finds its way into the environment, and can accumulate in water due to its high hydrophilicity and cause numerous problems in ecosystems and humans [9]. While numerous methods have been developed to deal with ODP, many of these methods require extra processes, since byproducts are frequently present.

Glossary			
Characterization Methods		Pollutants	
XRD	X-ray Diffraction	ODP	Organic Dye Pollutants
FT-IR	Fourier Transform Infrared	MB	Methylene Blue
UV-vis DRS	Ultraviolet-Visible Diffuse Reflectance Spectroscopy	MO	Methyl Orange
SEM	Scanning Electron Microscopy	CV	Crystal Violet
HR-TEM	High-Resolution Transmission Electron Microscopy	AO	Acridine Orange
ZCP	Zero Charge Point	RhB	Rhodamine B
		R-6G	Rhodamine 6G
		TL	Tetracycline

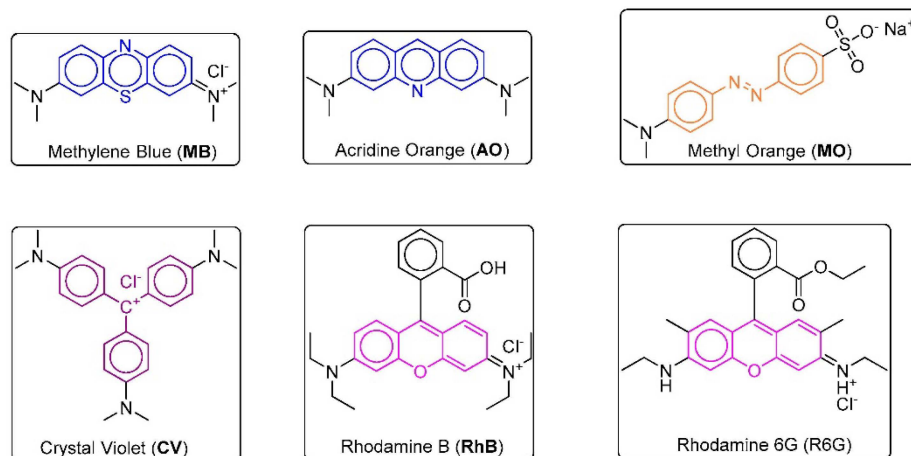


Figure 1. The structures of selected ODP.

Photocatalysis is an affordable green water treatment technology, which has the potential to be very efficient in the decomposition of the ODP [10,11], as the photo-oxidation of dyes, for example, can result in their mineralization into simpler species without toxicity [2]. Especially prevalent is the use of composite photocatalytic materials [12,13]. With a conscious choice of individual materials, a composite can be comprised of components that complement each other, leading to enhanced performance and utility. The most well-known photocatalyst is titanium dioxide (TiO₂) [14,15], especially its anatase phase, due to its high stability and outstanding photocatalytic performance under ultraviolet (UV) light. However, it has significant drawbacks regarding its wide band gap, which renders

it photocatalytically active only under UV light, and its fast charge pair recombination impairs its photocatalytic performance. Thus, the formation of composites with TiO_2 evolved into a common strategy, since it can rectify its weaknesses [1]. The formation of such a photocatalytic heterojunction can enhance factors such as charge separation, thereby enhancing photocatalytic performance [15,16]. Magnetic materials, on the other hand, have several interesting properties [17–19], and their combination with TiO_2 is promising [20,21], as the added magnetic properties offer increased utility for the composite: In magnetic composites, after the photocatalytic treatment of a solution is completed, the photocatalyst can be easily removed with a simple magnet, which facilitates its re-usability [22,23]. Spinel ferrites are a prominent family of magnetic ferrite materials with an AFe_2O_4 structure (A = divalent cation), characterized by a high saturation magnetization, among other favorable features [24]. Thus, the combination of TiO_2 with a spinel ferrite material appears especially promising. This work presents a complete overview of the TiO_2 /spinel ferrite nanocomposites with an extensive evaluation of their photocatalytic capabilities against several of the more well-known organic pollutants. It also presents the potential of the nanocomposites for recyclable usage, taking advantage of their magnetic retrieval ability, thereby highlighting the extensive capacities of the TiO_2 /spinel ferrite nanocomposites.

In this work, a hydrothermal process was employed to synthesize composites comprised of the CoFe_2O_4 -loaded TiO_2 . To optimize the composite compositions, three weight percentage ratios of CoFe_2O_4 to TiO_2 corresponding to 5, 10, and 15% *w/w* were synthesized. A complete characterization of the composites against the starting materials was undertaken via XRD, FTIR, Raman, UV–vis DRS, SEM, and HR-TEM. The structure analysis verified the successful formation of the $\text{CoFe}_2\text{O}_4/\text{TiO}_2$ hybrid nanocomposites. The photocatalytic performances of the hybrid composites were evaluated in the degradation of six different ODP under UV light and the degradation of tetracycline (TL) under UV and visible light.

2. Experimental Methods

2.1. Materials

The materials used in this research work are presented below. From Acros Organics: Absolute ethanol ($\geq 99\%$), ferric nitrate ($\geq 99\%$), titanium (IV), n-butoxide ($\geq 99\%$), benzoquinone, oxalic acid ($\geq 98\%$), and tetracycline ($\geq 99\%$). From Sigma-Aldrich: glacial acetic acid ($\geq 98\%$). From Chem-Lab: cobalt nitrate ($\geq 99\%$), HCl. From Sigma-Aldrich: Methylene Blue, Methyl Orange, Crystal Violet, Acridine Orange, Rhodamine B, and Rhodamine 6G were purchased.

2.2. Material Preparation

2.2.1. Synthesis of TiO_2 Nanoparticles

The sol-gel method was utilized for the preparation of titanium dioxide nanopowder [25,26]. In a typical process, a solution of 10 mL of Ti (IV) n-butoxide and 40 mL absolute ethanol (A) and a solution of 4 mL DI H_2O , 2 mL acetic acid, 10 mL absolute ethanol along with HCl (10% *wt/wt*) for pH adjustment to ~ 2 (B) were mixed by the dropwise addition of (B) to (A) and stirring (1 h). A yellow translucent gel was formed 3 h after the end of the stirring and after drying overnight at 100°C ; yellow crystallites were formed, which produced a white powder after grinding. Finally, this powder was calcinated (300°C for 1 h and 450°C for 2 h), producing our nano- TiO_2 sample (T).

2.2.2. Synthesis of CoFe_2O_4

The cobalt ferrite was also prepared via a sol-gel technique [11]. A total of 1.9 g of oxalic acid (complexing agent) was slowly added to a mixture of cobalt nitrate (0.01 moles) and ferric nitrate (0.02 moles), under stirring (1 h). After evaporation (80°C under stirring), the samples were dried (110°C , 24 h) and annealed (1000°C , 2 h).

2.2.3. Synthesis of CoFe₂O₄/TiO₂ Composites

For the preparation of the final composites, a hydrothermal method was adopted [11]. Samples with three different *w/w* % concentrations of CoFe₂O₄ to TiO₂ were prepared by varying the initial quantity of CoFe₂O₄ in the process: 0.05 (5% *w/w*), 0.1 (10% *w/w*), and 0.15 (15% *w/w*) g of CoFe₂O₄ was ultrasonically treated in 100 mL of deionized water (2 h) before the adding of 0.95, 0.9, and 0.85 g of TiO₂, respectively. A total of 10 g of urea was also added as a combustion fuel. After further ultrasonication (1 h), each solution was put in a 300 mL stainless steel autoclave coated with Teflon, where they were heated (200 °C, 12 h) before the natural cooling of the autoclave (room temperature). After washing and drying, we acquired the TC5, TC10, and TC15 samples, each with an index signifying its % *w/w* of CoFe₂O₄ (C) and TiO₂ (T).

2.3. Characterization of Samples

For the characterization of the prepared photocatalysts, we utilized X-ray diffraction (XRD, D8-ADVANCE), FTIR (Perkin Elmer Spectrum 100 Spectrometer) and micro Raman (Jobin-Yvon LabRam) vibrational spectroscopy, SEM (Jeol JSM 7401F FieldEmission), HR-TEM (high-resolution JEOL JEM-2100 LaB6), UV-Vis (Hitachi U-4100) spectroscopy, Magnetic measurements were performed via a VSM (9600-1 LDJ, Lake Shore, Columbus, OH, USA) instrument. Textural characterization of the samples was carried out by the N₂ adsorption-desorption at −196 °C. Prior the measurements, the samples were outgassed at 200 °C for 48 h. The Brunauer–Emmett–Teller (BET) equation was applied to determine the specific surface area (*S*_{BET}). The BJH method was applied to the desorption branch of the N₂ isotherms to obtain the meso-pore volume (*V*_{meso}) and cumulative surface area (*S*_{BJH}) of the mesopores. A batch technique was utilized for the determination of zero charge point (ZCP) using six beakers, each containing 0.1 M KCl (12.5 mL) with an assumed initial pH value of 4–12 using 0.1 M HCl or KOH [27]. After adding a standard quantity of a photocatalyst to each beaker, stirring for 24 h until the pH was at equilibrium, the sample was removed by filtration. The ZCP values were determined by graphing the final pH of the solution against the initial pH.

A total of 5 mg of the photocatalyst was added to an ODP or TL solution (50 mL, 10 ppm) to evaluate its photocatalytic degradation performance. After stirring for 1 h in dark conditions (adsorption-desorption equilibrium), the solution was illuminated (Osram L BLUE UVA 15 W/78 lamps), and 4-daylight Sylvania,—F15W/53-765-T8 (450–710 nm) lamps in a photoreactor box. The progress of the photocatalytic degradation was evaluated at standard time intervals by measuring the absorption peak of each dye solution through UV-Visible spectroscopy. The characteristic absorption peaks for the six ODP are: MB (664 nm), CV (585 nm), MO (464 nm), AO (490 nm), RhB (553 nm), Rh6G (526 nm), and (357 nm) for the TL solution. Finally, to study the active species responsible for the photocatalytic degradation, scavenger tests were performed by repeating the above process in the presence of a scavenger (for each studied species) in the solution: KI (h⁺ quencher), BQ (O₂[−] quencher), KBrO₃ (e[−] quencher), and IPA (OH[•] quencher) [14].

3. Results and Discussion

3.1. Structural Analysis

In terms of a crystal structure analysis, all samples were analyzed with XRD and the resulting patterns are shown in Figure 2. For TiO₂, the expected diffraction peaks and the corresponding Miller indices appear at 2θ of 25.8° (101), 36.9° (103), 37.8° (004), 38.5° (112), 48.0° (200), 53.8° (105), 55.0° (211), 62.8° (204), 68.7° (116), and 70.3° (220), verifying the presence of the pure anatase TiO₂ (I4₁/amd (141) space group, JCPDS Card number 21-1272) [28]. For CoFe₂O₄, the peaks at 2θ of 18.2° (111), 30.0° (220), 35.4° (311), 37.0° (222), 43.0° (400), 53.4° (422), 56.9° (511) and 62.5° (440) correspond to spinel ferrite with a cubic symmetry (Fd-3m (227) space group, and the JCPDS Card no. 22-1086) [24] were depicted. The diffraction patterns for the TC5, TC10, and TC15 hybrid nanocomposites present peaks that correspond to both starting CoFe₂O₄ and TiO₂ materials, signifying the good chemical hybridization of the

two oxides. Following the insertion of CoFe_2O_4 , a considerable decrease in the (101) anatase peak intensities was measured, demonstrating a strong interaction between the components constituting the composites, notably the TC10 sample.

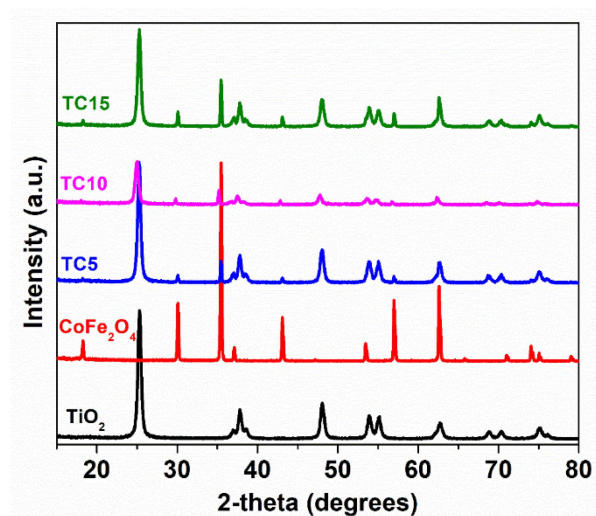


Figure 2. XRD patterns of the synthesized photocatalysts.

Vibrational spectroscopy, via Raman [29,30] and FT-IR measurements [31], was also utilized to study the samples' constitution and crystallinity. The corresponding analyses are presented in Figure 3.

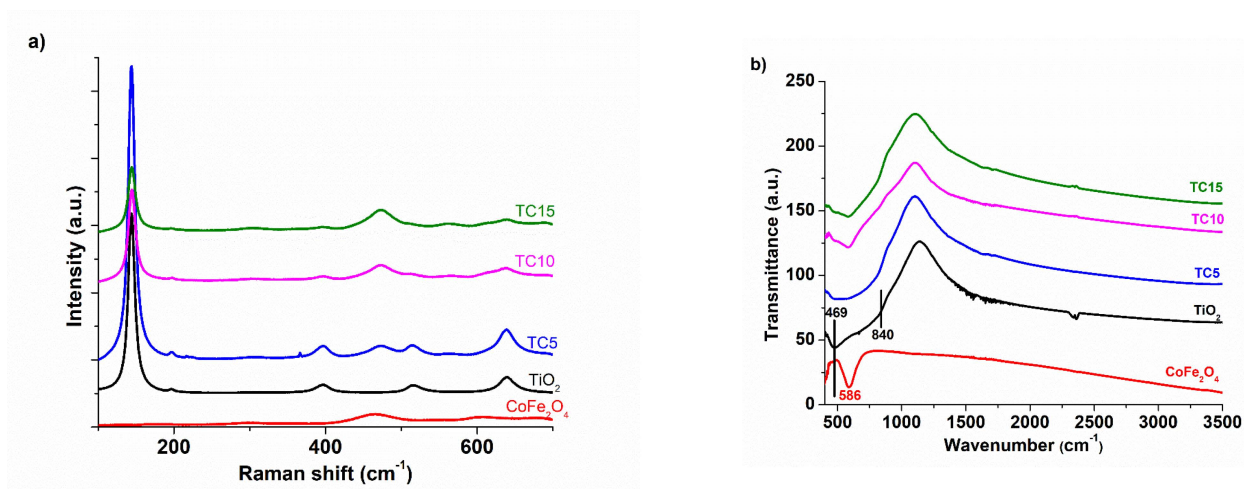


Figure 3. Vibrational spectrograms: (a) Micro-Raman and (b) FT-IR of synthesized photocatalysts.

Concerning Raman spectroscopy, (Figure 3a): For the TiO_2 sample, we observed the Raman active modes at 141 cm^{-1} (E_g), 196 cm^{-1} (E_g), 394 cm^{-1} (B_{1g}), 513 cm^{-1} ($A_{1g} + B_{1g}$), and, lastly, 640 cm^{-1} (E_g) [32], verifying the anatase- TiO_2 crystallization. For the CoFe_2O_4 sample, its characteristic bands appear at 175 cm^{-1} (T_{2g}), 295 cm^{-1} (E_g), 468 cm^{-1} (T_{2g}), and 613 cm^{-1} (T_{2g}) [33]. As for the composite materials, the characteristic peaks of the individual components appear in the final materials, proposing the amalgamation of the two components forming the composites. In the FT-IR spectra (Figure 3b), TiO_2 exhibits a broad absorption band ($\sim 469\text{--}840\text{ cm}^{-1}$) related to Ti-O-Ti vibration bonds [34], while CoFe_2O_4 exhibits a peak at $\sim 469\text{ cm}^{-1}$ (stretching vibration in Fe(III)-O^{2-}) and another peak at $\sim 586\text{ cm}^{-1}$ (stretching vibration in Co(II)-O^{2-}) [35]. Thus, a broad absorption at $\sim 462\text{--}580\text{ cm}^{-1}$ appears in the final composites. Thus, the proper merging of TiO_2 and CoFe_2O_4 is verified from either type of vibrational spectroscopy analysis.

3.2. Morphological Analysis

SEM and TEM microscopy were employed to assess the morphology of the synthesized samples concerning the starting components (Figure 4). While TiO_2 nanoparticles (NPs) appear distinct, there is an agglomeration of CoFe_2O_4 nanoparticles, since there are magnetic forces between them [21], making CoFe_2O_4 nanostructures significantly larger than TiO_2 NPs (TiO_2 NPs are under 20 nm, while CoFe_2O_4 clusters are over 120 nm in size). The SEM picture of TC10 (Figure 4c), which depicts the final composites, demonstrates how the CoFe_2O_4 nanostructures' surfaces have been suitably ornamented with TiO_2 NPs. As observed by the TEM picture (Figure 4d), titania has actually been dispersed over the grains of the ferrite material.

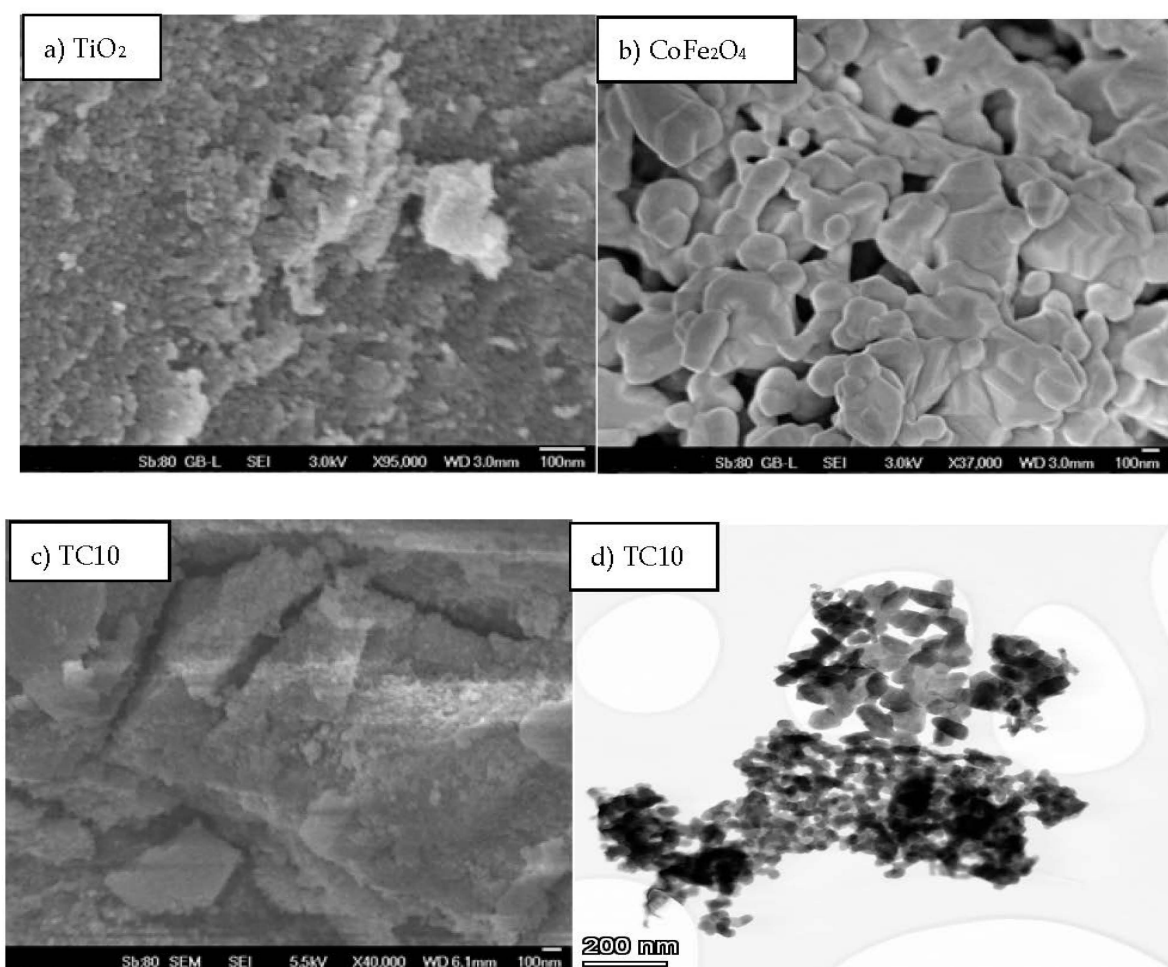


Figure 4. Microscopy-based analyses of the samples with SEM at 100 nm (a–c) and with TEM at 200 nm (d).

3.3. Surface Analysis

N_2 adsorption-desorption isotherms and pore-size distribution plots for each sample have been shown in Figures 5 and 6 to determine the samples' surface area and porosity.

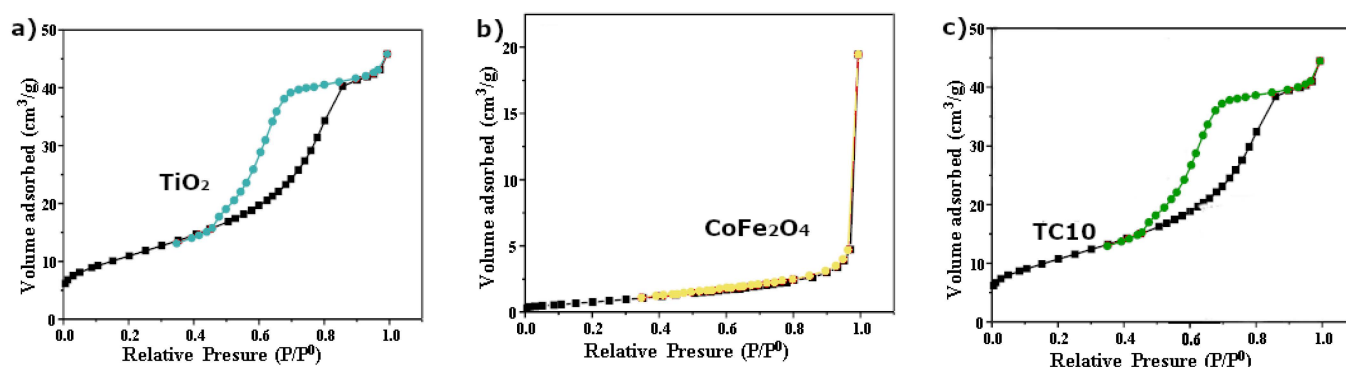


Figure 5. N₂ adsorption-desorption isotherm plot of TiO₂ (a), CoFe₂O₄ (b) and TC10 (c).

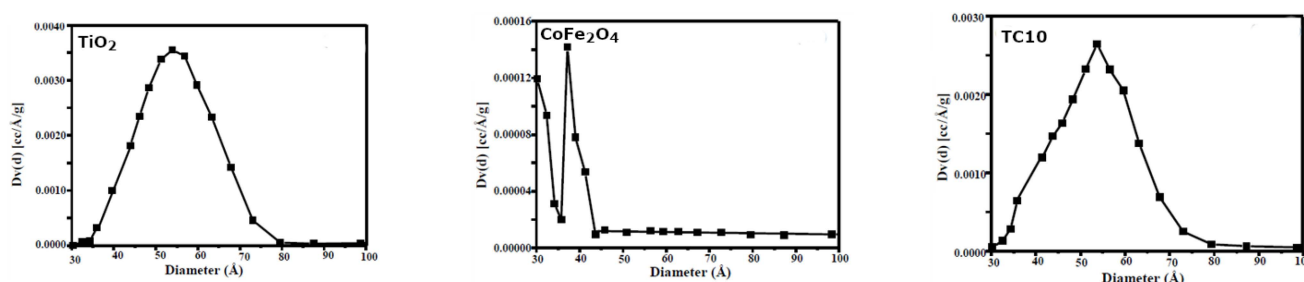


Figure 6. Pore size distribution curves of TiO₂, CoFe₂O₄, and TC10.

A Type IV isotherm corresponding hysteresis loop is presented by the base-TiO₂ sample (Figure 5a), signifying mesoporous materials [36], while there is no hysteresis loop present for CoFe₂O₄ (Figure 5b), signifying the type III isotherm [37]. The type IV isotherm is also representative of the composite materials (Figure 5c), meaning they are mesoporous. The specific surface values (m²/g) for the samples were: TiO₂ (40), CoFe₂O₄ (3.2), TC5 (39.1), TC10 (38.2), and TC15 (37). There was a slight decrease in the BET surface area value when going from TiO₂ to the TiO₂/CoFe₂O₄ composites due to the low value in the case of the ferrite. Pore size distribution reveals no significant differences for the unimodal type of pore presented, either from the mother TiO₂ or the composite TC10, with a pore maximized at around 52 Å compared to the bimodal type of pores depicted for CoFe₂O₄ at 30 and 40 Å. This demonstrates how the composites maintain their mesoporosity sequence. Regarding the surface chemistry of the samples, the zero charge point (ZCP) evaluation (Figure 7) took place for samples TiO₂ (4.45), CoFe₂O₄ (6.95) and TCX (x-5,10,15) (4.9) samples. At solution pH > ZCP pH, the photocatalyst can favor the adsorption of positively charged pollutants such as the positively charged MB [38], (with negatively charged contaminants being favored in the opposite case) [39]. Thus, at a higher solution pH (negatively charged surface), there can be increased pollutant adsorption of dyes such as MB [40] onto the TCX surface.

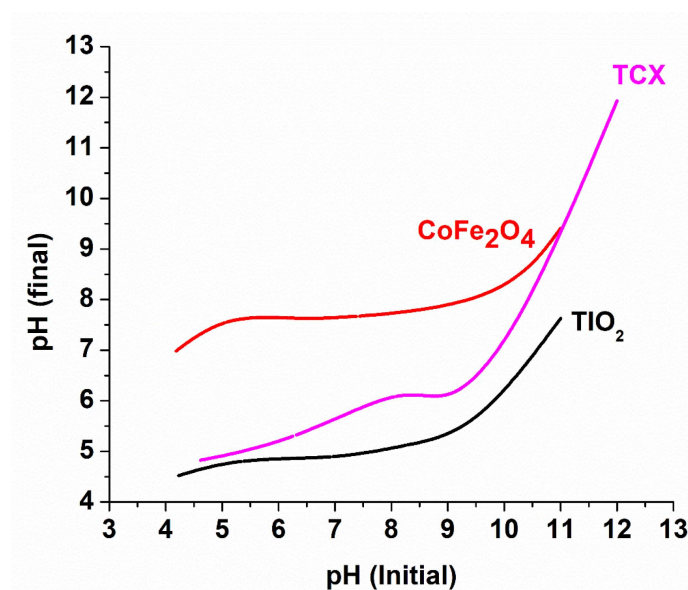


Figure 7. pH_{Initial} vs. pH_{final} curves for ZCP determination.

3.4. Optical Analysis

To learn more about the photocatalysts' optical characteristics, UV-vis spectroscopy was employed (Figure 8). The band gaps for TiO₂ (3.1 eV), CoFe₂O₄ (1.37 eV), TC5 (3.18 eV), TC10 (3.16 eV), TC15 (3.07 eV) were calculated via the Kubelka-Munk equation and the Tauc plots (derived from diffuse reflectance spectra) (Figure 8a). As for the absorption spectra (Figure 8b), the absorption edge for TiO₂ is located near 400 nm, as expected [41], while the spinel ferrite absorbs significantly in the visible region [37]. As a result, the composite materials have enhanced absorption in the visible range.

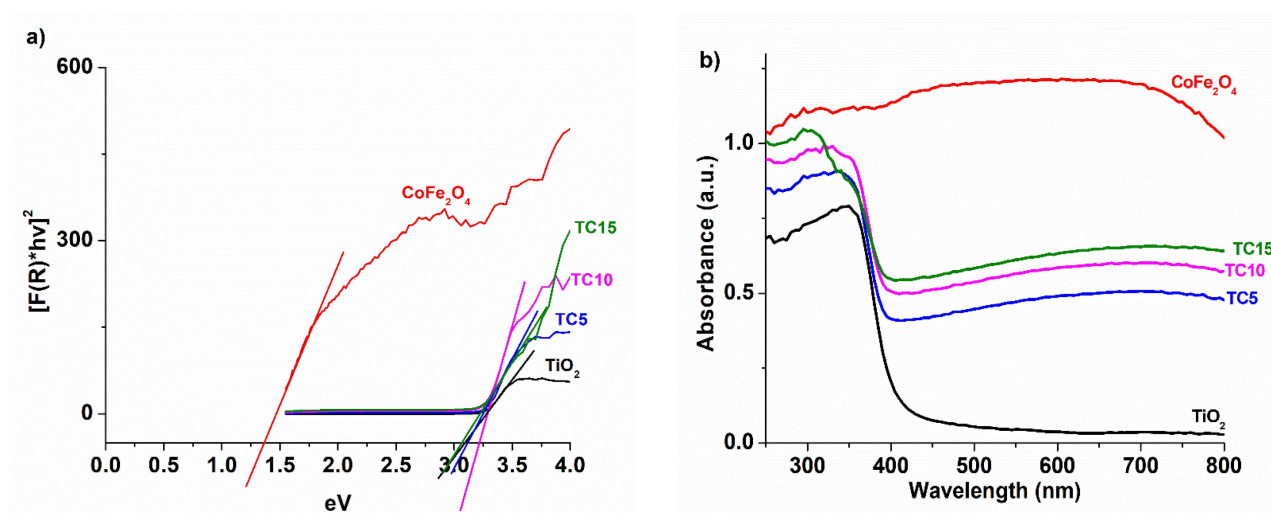


Figure 8. Tauc plots of the prepared photocatalysts (a), along with the relevant absorbance spectra (b).

3.5. Magnetization Analysis

The value of saturation magnetization (M_s) is important for a photocatalyst as it signifies its capability for magnetic removal from a treated solution. The magnetization curves of all magnetic samples are presented in Figure 9.

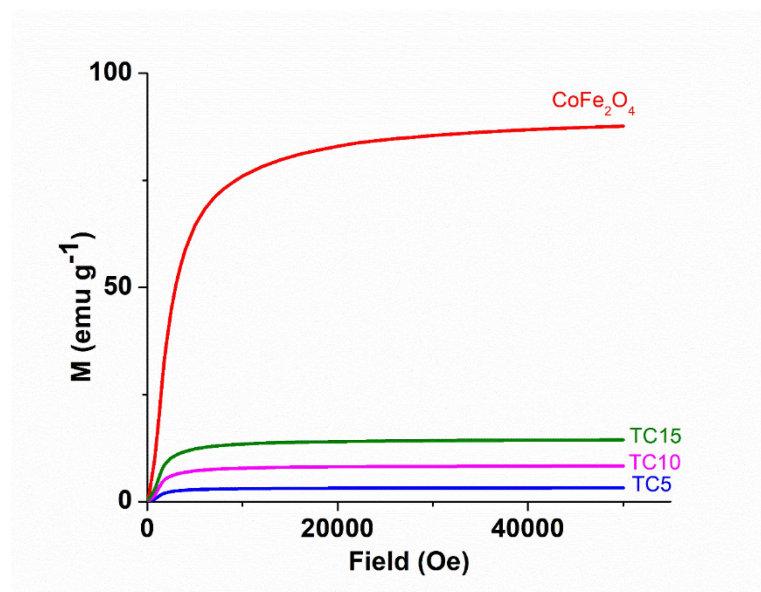


Figure 9. Magnetization curves of CoFe_2O_4 and the TCX composites.

As expected, the composites of magnetic CoFe_2O_4 and non-magnetic TiO_2 have significantly less M_s (emu/g) values than the pure spinel ferrite: CoFe_2O_4 (87.6), TC5 (3.1), TC10 (8.4), and TC15 (14.2). Furthermore, it comes as no surprise that composites with a greater percentage of magnetic spinel content present higher M_s values. This decrease, however, does not impair the capability of the magnetic composites to be easily removed from a solution through simple magnetic means (e.g., a magnetic bar).

3.6. Photocatalytic Oxidation Activity

3.6.1. Photocatalytic Degradation of ODP under UV Light

Under UV light irradiation, the photocatalytic oxidation performance of the produced materials was evaluated against six organic dyes (Figure 10). The TCX composites exhibit higher dye degradation efficiencies than either starting material in all cases. This efficiency is due to increased charge carrier separation at the $\text{TiO}_2/\text{CoFe}_2\text{O}_4$ contact, which enhances the electron lifetime for TCX samples [42].

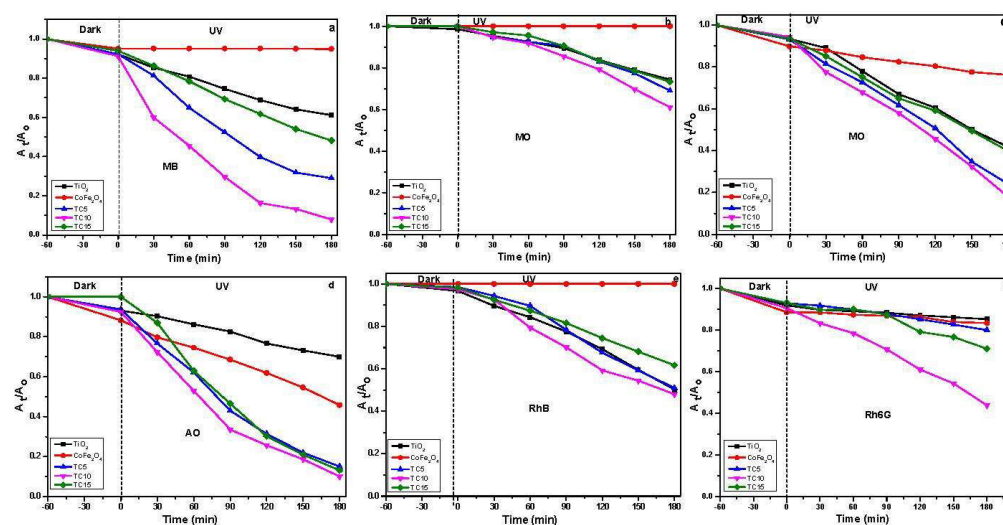


Figure 10. Photocatalytic oxidative degradation of (a) Methylene Blue (MB), (b) Methyl Orange (MO), (c) Crystal Violet (CV), (d) Acridine Orange (AO), and (e) Rhodamine B (RhB and (f) Rhodamine 6G, under UV irradiation by the prepared samples.

3.6.2. Photocatalytic Degradation of TL under UV and Visible Light

The photocatalytic oxidation of TL over TiO_2 , CoFe_2O_4 , TC5, TC10, and TC15 was evaluated under UV and visible light illumination (Figure 11a,b). It is obvious that the cobalt ferrite (CF) present in the TC nanocomposite maintains and slightly enhances the photocatalytic activity of titanium dioxide under both UV and visible light. The highest TL photocatalytic oxidation was observed for TC10, which was 75.31% at 180 min under UV illumination and 50.4% at 180 min under visible light illumination. Pure titania and cobalt ferrite, on the other hand, exhibit minor photocatalytic efficiency when compared to $\text{TiO}_2/\text{CoFe}_2\text{O}_4$ composites. This means that cobalt ferrite is crucial in enhancing the photocatalytic oxidation process. The high photocatalytic oxidation of the TC composites, particularly the TC10 sample, can be attributed to the presence of ferrites nanoparticles, which can improve light absorption and ensure more efficient charge separation.

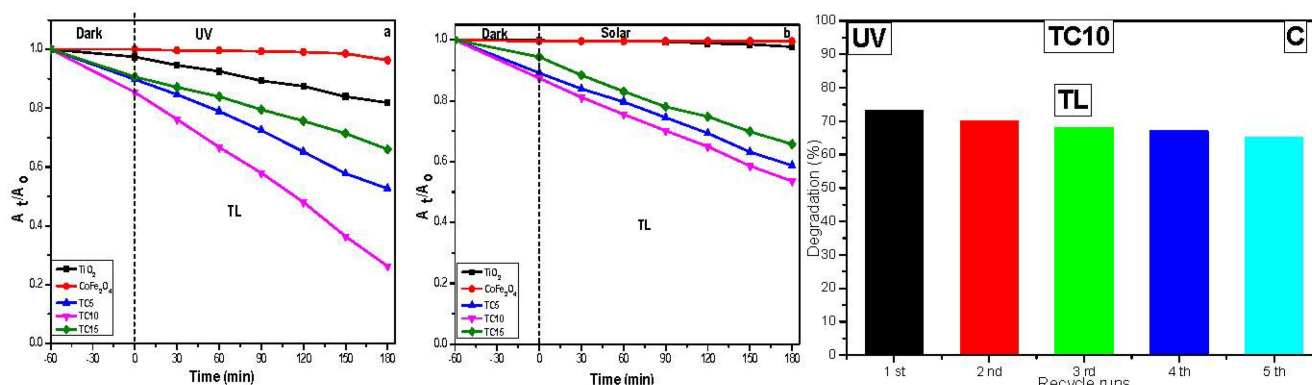


Figure 11. Photocatalytic oxidative degradation of tetracycline under (a) UV, (b) visible light irradiation using the prepared photocatalysts and (c) Reusability tests for the degradation efficiency of TL under UV for 5 subsequent cycles.

We performed recyclability experiments to verify the stability and reusability of the TC10 toward the TL photodegradation. Each time, the TC10 catalyst was collected and recovered, and then used in a cyclic batch. This procedure was conducted five times, with the final degradation efficiency recorded each time (Figure 11c). The TL degradation efficiency decreases slightly as the recycling test progresses, from ~75% in the first cycle to 65% in the final. As a result, we may consider this test to be indicative of the TC10 photocatalyst stability and reusability in the TL degradation.

Additionally, the synergistic interaction between TiO_2 and CoFe_2O_4 in TC10 was the optimal compared to the rest of the composites as depicted in XRD, optical, vibrational, and TEM analysis. Trapping experiments with scavengers were carried out under UV light to elucidate the photocatalytic oxidation mechanism for the TL and to detect the reactive species (Figure 12). There was no change in the oxidation process when IPA (hydroxyl radical scavenger), and KBrO_3 (electron scavenger) were added. In contrast, BQ (superoxide radical anion scavenger) had a noticeable effect, whereas the KI (hole scavenger) addition resulted in the photocatalytic oxidation reaction being blocked. Thus, holes were the prime motivator, followed by oxygen peroxide radicals as the main active species in the photocatalytic oxidation process (as observed in the graphical abstract).

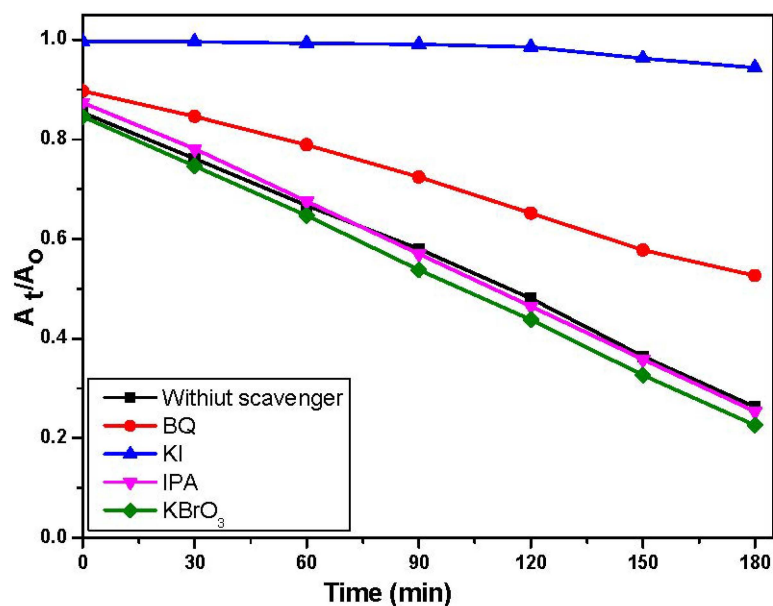


Figure 12. Scavengers' effects on TL oxidation efficiency using the TC10 composite under UV irradiation.

The dispersion of ferrites over TiO_2 , keeping the mesoporous nature and good visible light absorption, in addition to the broad-spectrum range of the catalysts, which allowed them to absorb UV and solar radiation without the help of oxidizing agents, were further causes for the improved photocatalytic activities.

For all dyes, significant degradation efficiency is achieved by the TCX samples: MB (over 95%), MO (45%), CV (over 83%), AO (over 91%), RhB (58%), Rh6G (56%), as will be shown in Figure 13. Among TCX samples, judging by overall performance, the best sample is TC10 (10% *w/w* CoFe_2O_4). It means that, the addition of CoFe_2O_4 has a volcano effect: it improves photocatalytic experiments up to an optimum (sample TC10), while a higher or lower amount decreases photocatalytic reactions.

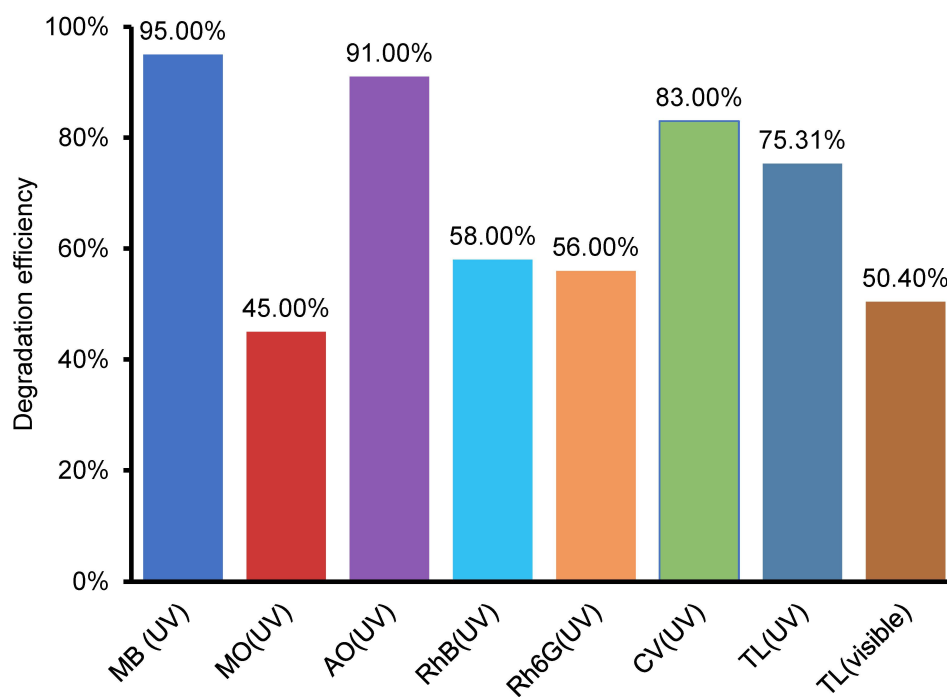


Figure 13. Significant degradation efficiency of all dyes and TL.

4. Conclusions

In this study, hybrid nanocomposites comprised of CoFe_2O_4 loaded into TiO_2 (5–15% w/w) were synthesized, characterized, and evaluated in the photocatalytic oxidation of six different organic dye pollutants under UV light and meanwhile under UV and visible light in the degradation of tetracycline. Characterization by XRD, FTIR, and Raman spectroscopy verified the fruitful construction of the $\text{CoFe}_2\text{O}_4/\text{TiO}_2$ hybrid nanocomposites. The optical analysis revealed enhanced light absorption by the $\text{CoFe}_2\text{O}_4/\text{TiO}_2$ nanocomposites compared to pure TiO_2 . In terms of oxidation/removal efficiencies under UV and visible light, $\text{CoFe}_2\text{O}_4/\text{TiO}_2$ (10% w/w) outperformed the other tested hybrid nanocomposites in the tested six organic azo dyes and the antibiotic tetracycline in the absence of any oxidant. The main reason for the observed behavior was the improved photo-charge carrier separation at the interfaces of $\text{TiO}_2/\text{CoFe}_2\text{O}_4$ nanocomposites, which is necessary for boosting photocatalytic activity. As long as the primary holes of the reactive species are present, the photocatalytic oxidation can be occurred. As a result, the $\text{CoFe}_2\text{O}_4/\text{TiO}_2$ catalyst substantially increased the oxidative photocatalytic activity. Finally, the $\text{CoFe}_2\text{O}_4/\text{TiO}_2$ powder is capable of easily being retrieved from the treated solution with a magnetic means as to its magnetic characteristics.

Author Contributions: Conceptualization, I.I.; methodology, I.I. and G.V.B.; validation, A.M.E., M.M.M. and T.M.S.; formal analysis, M.B.I.M. and I.I.; investigation, I.I. and M.M.M.; resources, I.I. and Y.R.; writing—original draft, I.I.; writing—review and editing, G.V.B., Y.R. and T.M.S.; visualization, T.M.S.; supervision, M.M.M. and T.M.S.; project administration, I.I., M.M.M. and T.M.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ali, I.; Kim, J.-O. Visible-light-assisted photocatalytic activity of bismuth- TiO_2 nanotube composites for chromium reduction and dye degradation. *Chemosphere* **2018**, *207*, 285–292. [[CrossRef](#)] [[PubMed](#)]
2. Khan, I.; Saeed, K.; Zekker, I.; Zhang, B.; Hendi, A.H.; Ahmad, A.; Ahmad, S.; Zada, N.; Ahmad, H.; Shah, L.A.; et al. Review on Methylene Blue: Its Properties, Uses, Toxicity and Photodegradation. *Water* **2022**, *14*, 242. [[CrossRef](#)]
3. Mittal, A.; Mittal, J.; Malviya, A.; Kaur, D.; Gupta, V. Adsorption of hazardous dye crystal violet from wastewater by waste materials. *J. Colloid Interface Sci.* **2009**, *343*, 463–473. [[CrossRef](#)] [[PubMed](#)]
4. Dutta, S.K.; Amin, K.; Ahmed, J.; Elias, M.; Mahiuddin, M. Removal of toxic methyl orange by a cost-free and eco-friendly adsorbent: Mechanism, phytotoxicity, thermodynamics, and kinetics. *S. Afr. J. Chem. Eng.* **2022**, *40*, 195–208. [[CrossRef](#)]
5. Chandrika, K.; Chaudhary, A.; Mareedu, T.; Sirisha, U.; Vangalapati, M. Adsorptive removal of acridine orange dye by green tea/copper-activated carbon nanoparticles (Gt/Cu-AC np). *Mater. Today Proc.* **2021**, *44*, 2283–2289. [[CrossRef](#)]
6. Ahmad, M.; Rehman, W.; Khan, M.M.; Qureshi, M.T.; Gul, A.; Haq, S.; Ullah, R.; Rab, A.; Mena, F. Phytogenic fabrication of ZnO and gold decorated ZnO nanoparticles for photocatalytic degradation of Rhodamine B. *J. Environ. Chem. Eng.* **2021**, *9*, 104725. [[CrossRef](#)]
7. Pal, U.; Sandoval, A.; Madrid, S.I.U.; Corro, G.; Sharma, V.; Mohanty, P. Mixed titanium, silicon, and aluminum oxide nanostructures as novel adsorbent for removal of rhodamine 6G and methylene blue as cationic dyes from aqueous solution. *Chemosphere* **2016**, *163*, 142–152. [[CrossRef](#)] [[PubMed](#)]
8. Shenoy, S.; Ahmed, S.; Lo, I.M.; Singh, S.; Sridharan, K. Rapid sonochemical synthesis of copper doped ZnO grafted on graphene as a multi-component hierarchically structured visible-light-driven photocatalyst. *Mater. Res. Bull.* **2021**, *140*, 111290. [[CrossRef](#)]
9. Huyen, N.T.K.; Pham, T.-D.; Cam, N.T.D.; Van Quan, P.; Van Noi, N.; Hanh, N.T.; Tung, M.H.T.; Dao, V.-D. Fabrication of titanium doped BiVO_4 as a novel visible light driven photocatalyst for degradation of residual tetracycline pollutant. *Ceram. Int.* **2021**, *47*, 34253–34259. [[CrossRef](#)]
10. Ibrahim, I.; Belessiotis, G.V.; Arfanis, M.K.; Athanasekou, C.; Philippopoulos, A.I.; Mitsopoulou, C.A.; Romanos, G.E.; Falaras, P. Surfactant Effects on the Synthesis of Redox Bifunctional V_2O_5 Photocatalysts. *Materials* **2020**, *13*, 4665. [[CrossRef](#)]
11. Mohamed, M.M.; Ibrahim, I.; Salama, T.M. Rational design of manganese ferrite-graphene hybrid photocatalysts: Efficient water splitting and effective elimination of organic pollutants. *Appl. Catal. A Gen.* **2016**, *524*, 182–191. [[CrossRef](#)]
12. Belessiotis, G.V.; Kontos, A.G. Plasmonic silver (Ag)-based photocatalysts for H_2 production and CO_2 conversion: Review, analysis and perspectives. *Renew. Energy* **2022**, *195*, 497–515. [[CrossRef](#)]

13. Liao, G.; Li, C.; Liu, S.-Y.; Fang, B.; Yang, H. Emerging frontiers of Z-scheme photocatalytic systems. *Trends Chem.* **2021**, *4*, 111–127. [\[CrossRef\]](#)
14. Ibrahim, I.; Athanasekou, C.; Manolis, G.; Kaltzoglou, A.; Nasikas, N.K.; Katsaros, F.; Devlin, E.; Kontos, A.G.; Falaras, P. Photocatalysis as an advanced reduction process (ARP): The reduction of 4-nitrophenol using titania nanotubes-ferrite nanocomposites. *J. Hazard. Mater.* **2018**, *372*, 37–44. [\[CrossRef\]](#)
15. Ibrahim, I.; Belessiotis, G.V.; Antoniadou, M.; Kaltzoglou, A.; Sakellis, E.; Katsaros, F.; Sygellou, L.; Arfanis, M.K.; Salama, T.M.; Falaras, P. Silver decorated TiO₂/g-C₃N₄ bifunctional nanocomposites for photocatalytic elimination of water pollutants under UV and artificial solar light. *Results Eng.* **2022**, *14*, 100470. [\[CrossRef\]](#)
16. Sridharan, K.; Shenoy, S.; Kumar, S.; Terashima, C.; Fujishima, A.; Pitchaimuthu, S. Advanced Two-Dimensional Heterojunction Photocatalysts of Stoichiometric and Non-Stoichiometric Bismuth Oxyhalides with Graphitic Carbon Nitride for Sustainable Energy and Environmental Applications. *Catalysts* **2021**, *11*, 426. [\[CrossRef\]](#)
17. Abdel-Khalek, E.; Ibrahim, I.; Salama, T.M.; Elseman, A.M.; Mohamed, M.M. Structural, optical, dielectric and magnetic properties of Bi_{1-x}La_xFeO₃ nanoparticles. *J. Magn. Magn. Mater.* **2018**, *465*, 309–315. [\[CrossRef\]](#)
18. Abdel-Khalek, E.K.; Ibrahim, I.; Salama, T.M. Dielectric anomaly in the microwave region and exchange bias effect in LaFeO₃ nanoparticles at room temperature. *Ferroelectrics* **2019**, *550*, 210–219. [\[CrossRef\]](#)
19. Abdel-Khalek, E.K.; Ibrahim, I.; Salama, T.M.; Elseman, A. Study of the optical, dielectric and magnetic properties of the Bi_{0.75}La_{0.25}FeO₃ sample. *Ferroelectrics* **2020**, *558*, 150–164. [\[CrossRef\]](#)
20. Liu, H.; Zhang, Z.-G.; Wang, X.-X.; Nie, G.-D.; Zhang, J.; Zhang, S.-X.; Cao, N.; Yan, S.-Y.; Long, Y.-Z. Highly flexible Fe₂O₃/TiO₂ composite nanofibers for photocatalysis and ultraviolet detection. *J. Phys. Chem. Solids* **2018**, *121*, 236–246. [\[CrossRef\]](#)
21. Sohail, M.; Xue, H.; Jiao, Q.; Li, H.; Khan, K.; Wang, S.; Feng, C.; Zhao, Y. Synthesis of well-dispersed TiO₂/CNTs@CoFe₂O₄ nanocomposites and their photocatalytic properties. *Mater. Res. Bull.* **2018**, *101*, 83–89. [\[CrossRef\]](#)
22. Wu, P.-F.; Xue, Q.; Wang, T.-Y.; Li, S.-J.; Li, G.-P.; Xue, G.-L. A PW₁₂/Ag functionalized mesoporous silica-coated magnetic Fe₃O₄ core-shell composite as an efficient and recyclable photocatalyst. *Dalton Trans.* **2020**, *50*, 578–586. [\[CrossRef\]](#)
23. Belessiotis, G.V.; Falaras, P.P.; Ibrahim, I.; Kontos, A.G. Magnetic Metal Oxide-Based Photocatalysts with Integrated Silver for Water Treatment. *Materials* **2022**, *15*, 4629. [\[CrossRef\]](#)
24. Ibrahim, I.; Ali, I.O.; Salama, T.M.; Bahgat, A.; Mohamed, M.M. Synthesis of magnetically recyclable spinel ferrite (MFe₂O₄, M = Zn, Co, Mn) nanocrystals engineered by sol gel-hydrothermal technology: High catalytic performances for nitroarenes reduction. *Appl. Catal. B Environ.* **2016**, *181*, 389–402. [\[CrossRef\]](#)
25. Belessiotis, G.V.; Papadokostaki, K.G.; Favvas, E.P.; Efthimiadou, E.K.; Karellas, S. Preparation and investigation of distinct and shape stable paraffin/SiO₂ composite PCM nanospheres. *Energy Convers. Manag.* **2018**, *168*, 382–394. [\[CrossRef\]](#)
26. Ye, T.; Chen, W.; Xu, H.; Geng, N.; Cai, Y. Preparation of TiO₂/graphene composite with appropriate N-doping ratio for humic acid removal. *J. Mater. Sci.* **2017**, *53*, 613–625. [\[CrossRef\]](#)
27. Abdelhaleem, A.; Chu, W. Photodegradation of 4-chlorophenoxyacetic acid under visible LED activated N-doped TiO₂ and the mechanism of stepwise rate increment of the reused catalyst. *J. Hazard. Mater.* **2017**, *338*, 491–501. [\[CrossRef\]](#)
28. Attia, Y.A.; Altalhi, T.A. Low-cost synthesis of titanium dioxide anatase nanoclusters as advanced materials for hydrogen photoproduction. *Res. Chem. Intermed.* **2017**, *43*, 4051–4062. [\[CrossRef\]](#)
29. Belessiotis, G.; Arfanis, M.; Kaltzoglou, A.; Likodimos, V.; Raptis, Y.; Falaras, P.; Kontos, A. Temperature effects on the vibrational properties of the Cs₂SnX₆ ‘defect’ perovskites (X = I, Br, Cl). *Mater. Chem. Phys.* **2021**, *267*, 124679. [\[CrossRef\]](#)
30. Belessiotis, G.; Arfanis, M.; Kaltzoglou, A.; Likodimos, V.; Raptis, Y.; Falaras, P.; Kontos, A. Temperature dependence of the vibrational and emission spectra in the 0D vacancy-ordered Cs₂SnI₆ perovskite. *Mater. Today Proc.* **2022**. [\[CrossRef\]](#)
31. Stathopoulos, N.; Belessiotis, G.; Oikonomou, P.; Papanicolaou, E. Experimental investigation of thermal degradation of phase change materials for medium-temperature thermal energy storage and tightness during cycling inside metal spheres. *J. Energy Storage* **2020**, *31*, 101618. [\[CrossRef\]](#)
32. Arabatzis, I.; Antonaraki, S.; Stergiopoulos, T.; Hiskia, A.; Papaconstantinou, E.; Bernard, M.; Falaras, P. Preparation, characterization and photocatalytic activity of nanocrystalline thin film TiO₂ catalysts towards 3,5-dichlorophenol degradation. *J. Photochem. Photobiol. A Chem.* **2002**, *149*, 237–245. [\[CrossRef\]](#)
33. Bhowmik, R.; Kazhugasalamoorthy, S.; Sinha, A. Role of initial heat treatment of the ferrite component on magnetic properties in the composite of ferrimagnetic Co_{1.75}Fe_{1.25}O₄ ferrite and non-magnetic BaTiO₃ oxide. *J. Magn. Magn. Mater.* **2017**, *444*, 451–466. [\[CrossRef\]](#)
34. Ali, T.; Ahmed, A.; Alam, U.; Uddin, I.; Tripathi, P.; Muneer, M. Enhanced photocatalytic and antibacterial activities of Ag-doped TiO₂ nanoparticles under visible light. *Mater. Chem. Phys.* **2018**, *212*, 325–335. [\[CrossRef\]](#)
35. Abroushan, E.; Farhadi, S.; Zabardasti, A. Ag₃PO₄/CoFe₂O₄ magnetic nanocomposite: Synthesis, characterization and applications in catalytic reduction of nitrophenols and sunlight-assisted photocatalytic degradation of organic dye pollutants. *RSC Adv.* **2017**, *7*, 18293–18304. [\[CrossRef\]](#)
36. Hernández-Gordillo, A.; Arroyo, M.; Zanella, R.; Rodríguez-González, V. Photoconversion of 4-nitrophenol in the presence of hydrazine with AgNPs-TiO₂ nanoparticles prepared by the sol-gel method. *J. Hazard. Mater.* **2014**, *268*, 84–91. [\[CrossRef\]](#)
37. Chen, X.; Zhao, Q.; Li, X.; Wang, D. Enhanced photocatalytic activity of degrading short chain chlorinated paraffins over reduced graphene oxide/CoFe₂O₄/Ag nanocomposite. *J. Colloid Interface Sci.* **2016**, *479*, 89–97. [\[CrossRef\]](#)

38. Gao, Y.; Wong, K.Y.; Ahiabu, A.; Serpe, M.J. Sequential and controlled release of small molecules from poly(N-isopropylacrylamide) microgel-based reservoir devices. *J. Mater. Chem. B* **2016**, *4*, 5144–5150. [[CrossRef](#)]
39. Shen, X. 10—Molecularly Imprinted Photocatalysts. In *Molecularly Imprinted Catalysts*; Elsevier: Amsterdam, The Netherlands, 2016; pp. 211–228. [[CrossRef](#)]
40. Boumediene, M.; Benaïssa, H.; George, B.; Molina, S.; Merlin, A. Effects of pH and ionic strength on methylene blue removal from synthetic aqueous solutions by sorption onto orange peel and desorption study. *J. Mater. Environ. Sci.* **2018**, *9*, 1700–1711. [[CrossRef](#)]
41. Chiang, L.-F.; Doong, R.-A. Enhanced photocatalytic degradation of sulfamethoxazole by visible-light-sensitive TiO₂ with low Cu addition. *Sep. Purif. Technol.* **2015**, *156*, 1003–1010. [[CrossRef](#)]
42. Ghosh, B.K.; Moitra, D.; Chandel, M.; Ghosh, N.N. Preparation of TiO₂/Cobalt Ferrite/Reduced Graphene Oxide Nanocomposite Based Magnetically Separable Catalyst with Improved Photocatalytic Activity. *J. Nanosci. Nanotechnol.* **2017**, *17*, 4694–4703. [[CrossRef](#)]