

Review On The Biosynthesis Of Composite TiO₂ - Inorganic/Metal Oxide (Fe₂O₃): Photocatalytic And Antibacterial Purpose Of Wastewater Treatment

Jaffner Anak Johngika¹, Zawati Harun²

¹Universiti Tun Hussein Onn Malaysia, 86400, Parit Raja, Johor, MALAYSIA

²Advanced Manufacturing Material Centre (AMMC),
University Tun Hussein Onn Malaysia, 86400, Parit Raja, Johor, MALAYSIA

*Corresponding Author Designation

DOI: <https://doi.org/10.30880/rpmme.2023.04.01.058>

Received 15 July 2022; Accepted 26 January 2023; Available online 1 June 2023

Abstract: Photocatalytic process has the ability of to degrade or reduce toxicity substance by chemical reaction and producing non-hazardous gasses to the environment has attract many researchers to apply this technology in treating waste water problem recently. There are many methods to synthesize the composite TiO₂-Fe₂O₃, such as hydrothermal, sol-gel and ultrasonic impregnation methods, which will be described in this study for the comparison of which composite would have the highest rate of photocatalytic activity based on its synthesizing technique. In this research, the review of synthesized composite mixture of TiO₂-Fe₂O₃ will be investigated towards photocatalytic and antibacterial application. The analysis and comparison will be conducted based on phase analysis (XRD), Field Emission Scanning Electron Microscopy, FTIR analysis and UV-vis diffuse reflectance spectroscopy. Thus, the study will focus on the properties and performance analysis of composite inorganic particles in eliminating the mixture of organic pollution specifically for waste water treatment.

Keywords: Photocatalytic, Sol-gel, Synthesize, TiO₂-Fe₂O₃, Antibacterial Application, Phase Analysis (XRD), Field Emission Scanning Electron Microscopy, FTIR Analysis, UV-vis, Organic Pollution, Waste Water Treatment

1. Introduction

Recent technology has shown the potential of using nanoparticles from metal oxide and inorganic materials in degrading chemical substances such as dyes, oily waste, paint via photocatalytic process that has shown better effect towards conserving environment as its offer green technology approach. The ability of photocatalytic process to degrade or reduce toxicity substance by chemical reaction and producing non-hazardous gasses to the environment has attract many researchers to apply this technology in treating waste water problem recently (Ameta et al., 2018).

In this present work, the composite mixture between TiO_2 and Fe_2O_3 will be investigated towards photocatalytic and antibacterial application (Noh et al., 2016). Combination of this synthesized composite with biosynthesis technique will be considered as this will provide and offer much better green approach of waste water treatment by minimizing the toxic secondary waste product as well as minimizing the chemical usage in their synthesizing technique.

1.1 Significant of Study

The review will propose the most significant approach with a suitable processing-controlled parameter in producing composite TiO_2 and Fe_2O_3 nanoparticles that can perform effectively in photocatalytic process and as an antibacterial agent. It is also expected that the composite mixture of particles will show antibacterial properties and the synthesized of particles itself would offer an environmental-friendly technique, that satisfy the green-technology requirement.

2. Materials and Methods

There is various processing for synthesizing such as chemical and physical techniques may be used for manufacturing of TiO_2 - Fe_2O_3 products such as sol-gel procedure, sonochemical system, electrochemical deposition, self-assembly caused by evaporation, atomic layer deposition (ALD), mechanochemical synthesis and techniques of hydrothermal production.

Since sol-gel method seems to be a promising method for synthesizing TiO_2 - Fe_2O_3 with different properties and outcome for the best result of photocatalytic activity, it is safe to say that it is the best approach for this review of research papers.

2.1 Materials

Titanium dioxide (TiO_2) had already generally been known amongst the most effective photocatalysts for the reduction of environmental contamination as well as the generation of hydrogen through photocatalysis via water by sunlight irradiation. TiO_2 is ecologically safe and is therefore deemed to be a "green" catalyst. TiO_2 coatings tend to also have self-cleaning characteristics where TiO_2 reacts with the water whenever it is subjected to sunlight to produce hydroxyl radicals, that breaks down surface adsorbed organic molecules including bacteria (Dariani et al., 2016). Iron oxide would be a metal oxide transition that seems to have various stoichiometric as well as crystalline structures, along with wustite (FeO), hematite (Fe_2O_3), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and magnetite (Fe_3O_4). This is a good potential photoelectrochemical (PEC) water separating photoanode substance. The photocatalytic efficiency of $\alpha\text{-Fe}_2\text{O}_3$, however, remains restricted by conditions such as strong charge recombination for holes and electrons, short diffusion spans of holes (2-4 nm) including weak conductivity, leading to both weak efficiencies and greater requirements for photo-assisted water oxidation state (Singh et al., 2019). Inside the Ti sponge, the cause of oxygen toxicity is primarily the TiOCl_2 pollutant found in the raw resources, TiCl_4 (Song et al., 2014). Because TiCl_4 interacts towards humidity intensely which generates TiOCl_2 and HCl , as such an impurity, it often comprises several quantities of TiOCl_2 . The TiOCl_2 material contained inside this TiCl_4 must be quantified, because TiOCl_2 influences the consistency of the Ti sponge where oxygen has a major hardness effect. For its infrared characteristic spectrum line, TiOCl_2 can be measured by infrared spectroscopy. The weak alkali solution was also aqueous ammonia. Whenever it dissolves inside of an aqueous ammonia solution, CO_2 reacts with both ammonia and hydroxyl ions. At temperatures from 5 to 50 C, the densities of ammonia solutions with dissimilar concentrations would be evaluated utilizing both an apycnometer as well as an Anton Paar Stabinger Viscometer SVM 3000 (Kang et al., 2019).

2.2 Methods

The nanocomposites were synthesised utilising 20 mL TiOCl_2 , however in order to produce composites with different Fe-to-Ti ratios, each feed intake quantity of iron salts varied $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ($\text{Fe}^{3+}:\text{Fe}^{2+} = 1:2$) had been initially applied and stirred at ambient temperature in distilled water. For all the synthesis tests, their ratio among Fe^{3+} and Fe^{2+} was held at 1:2. Table 2.1 provides the exact sum of TiOCl_2 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ used throughout the synthesis of each specimen (Supporting information). The mixture was then applied to the TiOCl_2 solution in the beaker then mixed for 30 minutes (Abbas et al., 2016).

Its pH was about 1 and 2 of that initial solution consisting Ti and Fe precursors. Ammonia solution was then applied progressively. The final pH of 9 was retained. Slurry was aged for 4 hours at 80°C and then required to rest for 12 hours with soft stirring in ambient temperature. Throughout the oxidation of Fe_3O_4 to Fe_2O_3 , ageing improves. This same product sample was treated with abundant amounts of ethanol and water. That powdered substance was dried for 24 hours in the 80°C thermal oven. That dried samples were then calcinated separately for 2 hours inside a box furnace for 3 various temperatures at 400°C , 600°C and 800°C to investigate the influence of the calcination temperature upon this property of the specimen. The heating rate was $5^\circ\text{C}/\text{minute}$ and was heated in an atmospheric pressure environment. For the research of the impact of chemical proportions on the physical, morphological, optical and photochemical properties of binary oxide composite nanomaterials, the volume of Fe_2O_3 in TiO_2 was retained at 2%, 5%, 8 percent, 15%, 25% and 35% for various samples.

Table 2.1: $\text{TiO}_2\text{-Fe}_2\text{O}_3$ Composite's Structural and Textural Properties.

Sample name	Amount of Fe_2O_3 designed (wt%)	Amount of Fe_2O_3 by XRF (wt%)	Amount of TiO_2 by XRF (wt%)	Ti/Fe weight ratio by EDX	Crystallite size (nm)	Amount of rutile in TiO_2 (%)
Ti-600	0	0	100	-	21.5	-
TiFe2-600	2	2	98	82.8	14.5	-
TiFe5-600	5	5	95	33.6	11.8	-
TiFe8-600	8	8.11	91.89	18.6	14.5	-
TiFe15-600	15	15.1	84.9	10.5	12.7	-
TiFe25-600	25	25.5	74.5	5.1	30.7	36%
TiFe35-600	35	33.88	66.12	3.2	62.1	73%

For the 2, 5%, 8 percent, 15%, 25% and 35% Fe_2O_3 inside this composite matrix, those materials obtained were called TiFe2, TiFe5, TiFe8, TiFe15, TiFe25 and TiFe35. Iron salts are never applied to the TiOCl_2 solution to produce an un-doped pure titania. The remaining of the process will be exactly the same as synthesizing composites with TiFe. TiFeX-calcination temperature was called the calcined samples; whereby X is the Fe_2O_3 's percentage inside this composite. For instance, $\text{TiO}_2\text{-Fe}_2\text{O}_3$ composite was designated as TiFe5-600 with 5wt percent Fe_2O_3 and calcinated at 600°C . Synthesized composites were labelled by adding '-As' that after specimen's name (Abbas et al., 2016)

X-ray diffraction (XRD) technology was used to analyze the crystal structure of the formulated $\text{TiO}_2\text{-Fe}_2\text{O}_3$ composites. Figure 2.2 shows the XRD-6000, Shimadzu X-ray Diffractor (Abbas et al., 2016). The field emission scanning electron microscopy machine analyzed the morphology of such materials collected under various conditions. In order to test the bonding pattern of such synthesized materials using the FTIR Spectrometer, Fourier transform infrared spectroscopy has been used for analysis. In order to characterize the presence of particular chemical groups in materials, FTIR spectroscopy is used. With FTIR spectroscopy, the structure of chemical reactions as well as the identification of unstable compounds are studied. A diffuse reflectance distribution (DRS) of a synthesised composite materials has been measured by the UV-Vis spectrophotometer. A particularly

useful technique to describe the local titanium atmosphere in titanosilicates is UV-vis diffuse reflectance spectroscopy (DRS). To contrast the photocatalytic behavior of TiO₂-Fe₂O₃ nanocomposites, a photochemical reaction for such removal of methylene blue was included. That depletion activity of methylene blue dye throughout the existence of TiO₂-Fe₂O₃ photocatalysts while irradiation was then reported as a feature of time in minute.

2.3 Results and Discussion

The analysis of titanium dioxide and iron (III) oxide, as well as the efficiency of Photocatalytic action, will be addressed in this section. And as per the previous study, experiment, and journal, the result is obtained. Numerous findings can also be correlated thanks to the experimental substance and treatment.

There were 7 authors chosen for comparison which is (Cheng et al., 2017), (Abbas et al., 2016), (Mirmasoomi et al., 2017), (M. Ahmadi Golsefidi *, F. Abbasi , M. Abrodi, Z. Abbasi, 2016), (Zhu et al., 2015), (Mohamed et al., 2017) and (Subramonian et al., 2017) which is using different synthesis method of hydrothermal, sol-gel, ultrasonic-assisted impregnation method, sonochemical-assisted method, electrochemical deposition, deposition-self-assembly technique and mechanochemical milling respectively. The purpose of this comparison is to gather different synthesis methods, come out with the best synthesis method and compare the varied parameters for the chosen methods with few other authors with the same method.

Research	Technique	Targeted Characteristic for Comparison
Author	Method	Percentage of output synthesized
(Cheng et al., 2017)	Hydrothermal	High
(Abbas et al., 2016)	Sol-gel	High
(Mirmasoomi et al., 2017)	Ultrasonic-assisted impregnation method	High
(M. Ahmadi Golsefidi *, F. Abbasi , M. Abrodi, Z. Abbasi, 2016)	Sonochemical-assisted method	Mediocre
(Zhu et al., 2015)	Electrochemical deposition	Moderate
(Mohamed et al., 2017)	Deposition-self assembly technique	Weak
(Subramonian et al., 2017)	Mechanochemical milling	High

Table 3.1 presents general comparison on different technique of composite TiO₂ synthesis. As can be observed from the table, the hydrothermal, Sol-gel, Ultrasonic-assisted impregnation method and Mechanochemical milling show the higher possibility in getting higher composite. Among this technique Sol-gel has reported the easiest, quick and good technique in synthesizing TiO₂ particles composite, as reported by other studies (Abbas et al., 2016). In fact, sol-gel also is one of the preferred techniques in synthesizing other inorganic particles since it gives better purity and more stable composite particles as reported elsewhere by the other researcher (Razani et al., 2017). Even though this technique involved chemical routes with higher toxicity materials but the potential output is quite

optimum with higher output possibility has made this technique to be used among researcher (Bouziani et al., 2020).

Table 3.2 presents specific comparison of composite TiO₂'s synthesis. Although the level of purity of the composite is pure for all five of the authors, it may be comparable through the differences in temperature of calcination which may affect the result of the photocatalysis. In this case, the author: (Abbas et al., 2016), (Razani et al., 2017), (Bouziani et al., 2020), (Koohestani, 2019), and (Pang et al., 2016) has come out with different calcination temperature of 600, 550, 500, 450 and 200°C respectively.

Table 3.2: Specific Comparison

Research	Varied Parameters: Sol-Gel	Targeted Characteristic for Comparison
Author	Temperature, °C (Calcination)	Level of Purity
(Nadir Abbas, 2016)	600	Pure
(Afini Razani, 2017)	550	Pure
(Bouziani A, 2020)	500	Pure
(Hassan Koohestani, 2019)	450	Pure
(Yean Ling Pang, 2015)	200	Pure

Table 3.3 presents the method of Sol-Gel which explains briefly about the parameters, characteristic including performance. Each author has their own reaction or reduction medium used for their very own experiments.

Table 3.3: Methods Sol-Gel: Parameters/Characteristic/Performance

Research	Vary Parameters (Significant)	Characteristic	Performance
Author/ Year	Temperature, °C	Reaction/ Reduction Medium	Level of Purity Particle Morphology Band Gap
(Abbas et al., 2016)	600	Titanium Oxychloride (TiOCl ₂)	Pure ✓ ✓
(Razani et al., 2017)	550	Ethanollic iron (III) nitrate nonahydrate with 0.1 mol/dm ³ ethanollic titanium tert-butoxide solution	Pure ✓ ✓
(Bouziani et al., 2020)	500	Iron III nitrate nonahydrate (FeN ₃ O ₉ . 9H ₂ O), titanium tetra-isopropoxide (TTIP, 97%), acetic acid (CH ₃ COOH, 99.78%) and ethanol (C ₂ H ₅ OH, 99.5%)	Pure ✓ ✓

(Koohestani, 2019)	450	Distilled water (85 cc), HCl (6 cc) and 2-propanol (6 cc)	Pure	✓	✓
(Pang et al., 2016)	200	FeCl ₂ · 4H ₂ O and NaOH	Pure	✓	✓

The main focus for all of this comparison amongst the author would be the band gap for each of their published paper. The recorded data of parameters of TiO₂-Fe₂O₃ composites obtained from few journals entitled Sol-gel Synthesis of TiO₂-Fe₂O₃ Systems: Effects of Fe₂O₃ Content and Their Photocatalytic Properties (Abbas et al., 2016), Sol-Gel Synthesis of Fe₂O₃-Doped TiO₂ for Optimized Photocatalytic Degradation of 2,4-Dichlorophenoxyacetic Acid (Razani et al., 2017), Synthesis of α-Fe₂O₃/TiO₂ Heterogeneous Composites by the Sol-gel Process and Their Photocatalytic Activity (Bouziani et al., 2020), Synthesis and Characterisation of TiO₂ nanoparticles/Fe₂O₃ Waste Chips Composite (Koohestani, 2019), and Synthesis, Characteristics and Sonocatalytic Activities of Calcined γ-TiO₂ and TiO₂ Nanotubes/ γ-TiO₂ Magnetic Catalysts in the Degradation of Orange G (Pang et al., 2016).

3.2 Photocatalytic Activity

3.2.1 Based on 600°C's Calcination Temperature

Figure 3.1 shows the deterioration of methylene blue dye throughout the presence of Ti-600, TiFe5-400, TiFe2-600, TiFe5-600, TiFe8-600, TiFe15-600, TiFe25-600, and TiFe35-600 photocatalysts as a time - dependent (min). It also demonstrates that all composite materials that have been produced have photocatalytic properties. Its reaction prepared by the addition of TiFe5-600 catalyst yielded the most methylene blue deterioration. Amongst these developed setups, TiFe8-600 was the second most successful catalyst. TiFe15-600, TiFe25-600, and TiFe35-600 have considerably lower photocatalytic effectiveness than TiFe5 and TiFe8. TiFe5, a substance containing 5% Fe₂O₃ doping in TiO₂, has been discovered to be the best catalyst compound amongst other. Figure 3.1 shows the deterioration curve for TiFe5-400 to show the influence of calcination temperature. TiFe5-400 likewise shown high degrading efficiency; however, TiFe5-600 photocatalytic performance was found to be superior than TiFe5-400's.

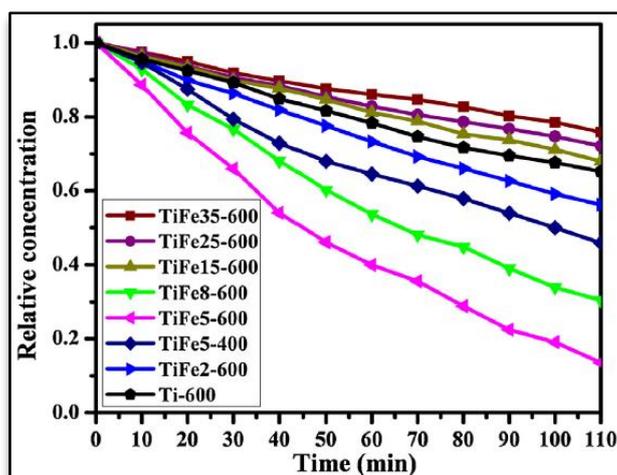


Figure 3.1: The Degradation of Methylene Blue Dye Solution by Photocatalysis

Figure 3.2 illustrates the plot of reaction time versus the logarithms of relative concentration of methylene blue dye solution (lnC₀/C). By all trials, the trends demonstrate a linear relationship between methylene blue dye solution and response time. Their reaction rate changes for each sample,

demonstrating that perhaps the catalytic activity for powdered materials is highly influenced by a variety of structural and chemical compositional characteristics. The reaction rates of 15%, 25%, and 35% iron oxide comprising catalysts were lower than the rate constants of 5% and 8% iron oxide comprising catalysts. The TiFe5 specimen had the greatest rate constant.

Each alteration in photocatalytic activity with Fe₂O₃ content proves that such quantity of Fe₂O₃ in blended oxides influences the crystallinity, particle size, porosity, and optical properties of TiO₂-Fe₂O₃ composites, which in turn affects the crystallinity, particle size, porosity, and optical properties of TiO₂-Fe₂O₃ composites. According to photocatalytic studies, the proportion of methylene blue dye adsorbed on catalyst surface was measured in adsorption-desorption equilibrium investigations. The greatest adsorption was found in TiFe5-600 and TiFe8-600, with 27% and 29%, respectively. Methylene blue dye adsorption was found to be 23%, 24%, 21%, 22%, and 24% on Ti-600, TiFe2-600, TiFe15-600, TiFe25-600, and TiFe35-600, respectively.

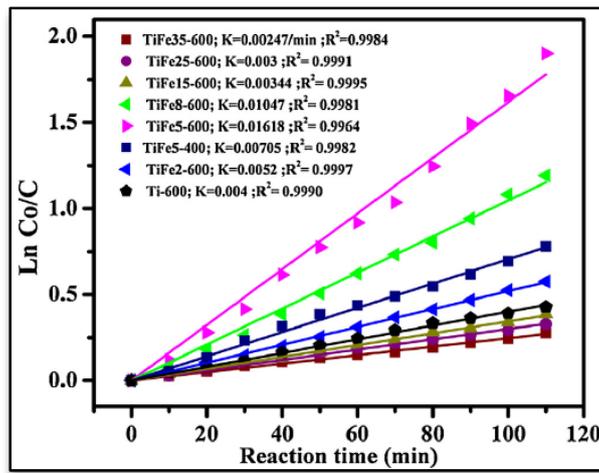


Figure 3.2: Linear Relationship Between Reaction Time and Logarithm of Relative Methylene Blue Concentration

3.2.2 Based on 550°C’s Calcination Temperature

The efficiency of Fe₂O₃-doped and undoped TiO₂ photocatalysts was tested, and thus the results are shown in Figure 3.3. Figure 3.4 shows the gradual degradation of 2,4-Dichlorophenoxyacetic acid by 0.05wt% Fe₂O₃ doped TiO₂ as a factor of irradiation time.

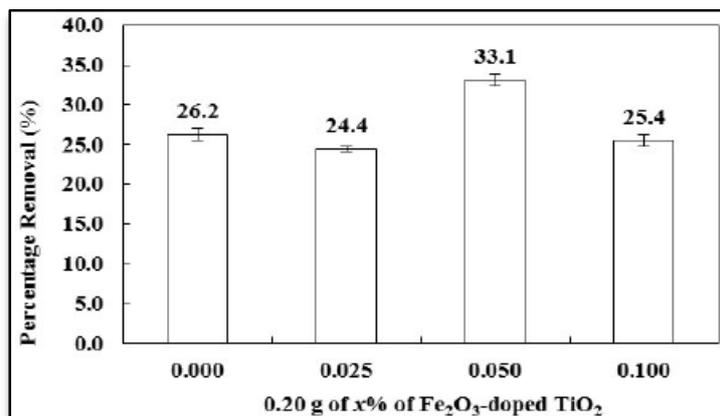


Figure 3.3: Percentage of 10 ppm 2,4-Dichlorophenoxyacetic Acid Degradation Using a 0.2 g/L Catalyst at pH 4.7.

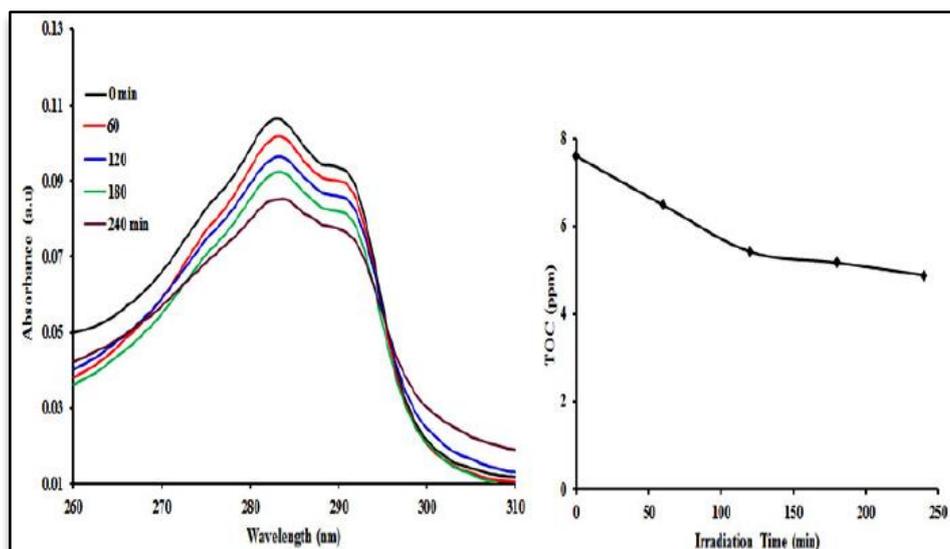


Figure 3.4: The Gradual Degradation of 2,4-Dichlorophenoxyacetic Acid as a Function of Irradiation Time Monitored via UV-vis Spectra and TOC Analysis

The Fe^{3+} ion, which functions as shallow trapping points for charge carriers and therefore separates the time of arrival of e^- and h^+ couples to the catalyst surface, could be due to the increased photocatalytic activity reported for the 0.05 wt% Fe_2O_3 doped TiO_2 . Meanwhile, the Fe^{3+} ion prevents photo-generated e^- and h^+ couples from recombining. The photo produced electron being trapped increases the usage efficiency of the photo generated e^- and h^+ couples by doping TiO_2 with an appropriate Fe^{3+} ion concentration. Greater Fe^{3+} dopant concentrations could function as recombination sites for photo-generated e^- and h^+ couples, lowering photo catalytic activity.

3.2.3 Based on 500°C's Calcination Temperature

Figure 3.5 depicts the absorption and photodegradation operations for the methylene blue solution which contains $\alpha-Fe_2O_3$ particles calcined at various temperatures in dark and sun-like light, respectively. Methylene blue absorption and photodegradation were found to be low in $\alpha-Fe_2O_3$ particles in experiments (3% and 8%, respectively).

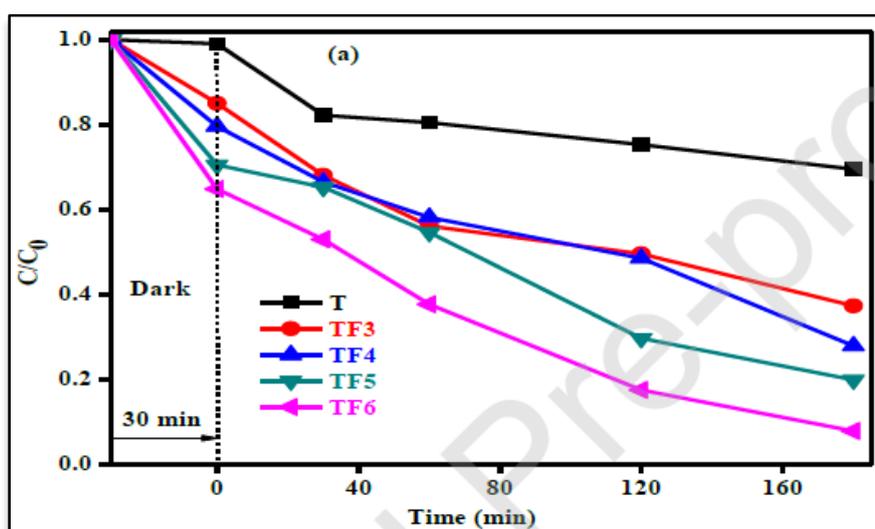


Figure 3.5: Conversion Plots for Photochemical Discoloration

Experimental conversion plots of methylene blue and phenol for the produced pristine TiO₂ powder are shown in Figure 3.6. After 180 minutes of sun-like light, both methylene blue and phenol show less than 30% conversion. While the calcination temperature of α-Fe₂O₃ powder increased, the photoactivity of that same composites increased. After 120 minutes of illumination, the greatest degradation rate for both methylene blue (92%) and Ph (52%) was observed for TF6.

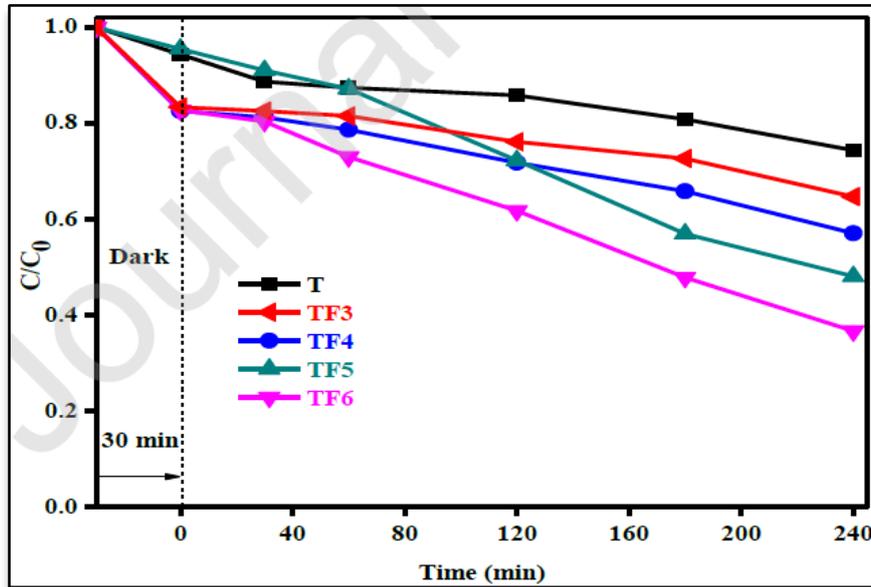


Figure 3.6: Conversion Plots for Photodegradation of Ph Under Sun-like Illumination.

Via first order rate kinetics, the reaction rates involving methylene blue and phenol for the chosen powders were determined. Table 3.9 summarizes the findings. The reaction rates appear to rise when α-Fe₂O₃ is integrated into TiO₂, as well as as the calcination temperature of α-Fe₂O₃ is raised. With both absorbents, an increase in TiO₂ photoactivity was found. By either methylene blue or phenol, its greatest photoactivity were achieved using TF6 composite. Regarding methylene blue and phenol, the photocatalytic reaction rates of the TF6 composite were 0.12 and 0.004 min⁻¹, respectively. Better crystallinity and successful interfacial contacts of α-Fe₂O₃ and TiO₂ are credited for the enhanced photocatalytic reaction rates. Each photodegradation pace of methylene blue and phenol was similarly impacted by the calcination temperature of a pristine α-Fe₂O₃ powder. Because the calcination temperature of a pristine α-Fe₂O₃ powder was raised, the photoactivity of the α-Fe₂O₃/TiO₂ composites improves. The findings back up the enhancement in crystallite size described earlier in this paper. Following 120 minutes of irradiation, the TF6 composites represents the highest photodegradation for both methylene blue (92%) and phenol (52%). That enhancement is due to improved visible light absorption efficiency, which leads to the production of photo-generated electrons enabling effective charge separation.

Table 3.9: Reaction Rates for Methylene Blue and Phenol for the Selected Powders.

Powder	K (min ⁻¹)	
	Methylene Blue	Phenol
T	0.0023	0.001
TF3	0.0045	0.0013
TF4	0.0056	0.0018

TF5	0.0076	0.0028
TF6	0.012	0.004

3.2.4 Based on 450°C's Calcination Temperature

Methylene orange is a model contaminant for photocatalytic degradation processes and is harmful to marine life. Figure 3.7 shows the deterioration of methylene orange pigment throughout the presence of TiO₂ and TiO₂/Fe₂O₃ mixtures as a function of frequency during irradiation. The inclusion of TiO₂ improved photocatalytic efficiency since pure TiO₂ only destroyed 74% of methylene orange in such a time period of 180 minutes, whereas Fe₂O₃ increased performance. The highest degrading efficiency was achieved when the operation was conducted out throughout the presence of TiO₂-10% Fe₂O₃, following whereby the efficiency decreased when the Fe₂O₃ percentage was increased.

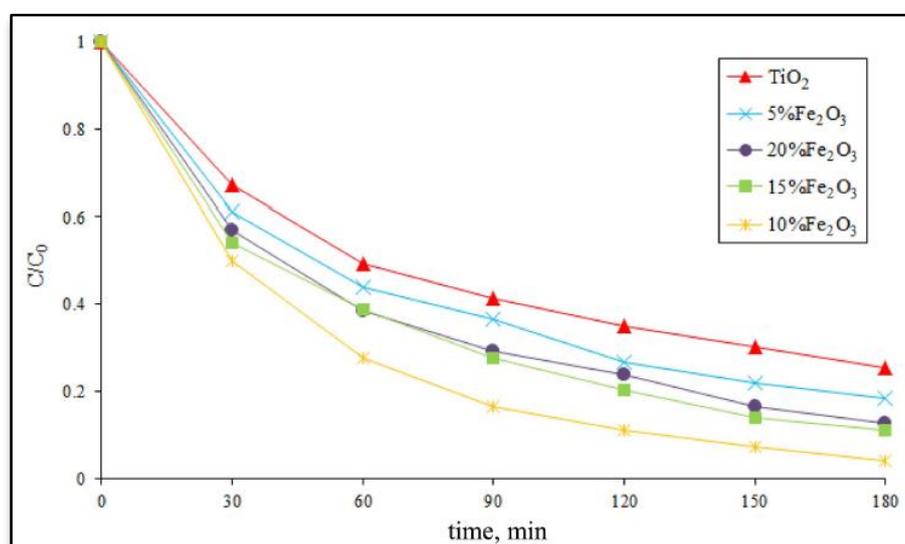


Figure 3.7: Degradation of Methylene Orange

TiO₂-10% Fe₂O₃ induced the most significant decrease of methylene orange, which was 96%. Upon 180 minutes of response time, the elimination data were acquired by UV-Vis and TOC analyses are listed in Table 3.10. TiO₂-10% Fe₂O₃ had the highest performance for methylene orange's deterioration under the same parameters.

Table 3.10: Removal Results Obtained by UV-Vis and TOC Measurements After the Reaction Time

Samples	UV-Vis,%	Rate constant, min ⁻¹
TiO₂	74	0.0084
TiO₂-5%Fe₂O₃	82	0.0103
TiO₂-10%Fe₂O₃	96	0.0182
TiO₂-15%Fe₂O₃	89	0.0131
TiO₂-20%Fe₂O₃	87	0.0121

3.2.5 Based on 200°C's Calcination Temperature

Table 3.11 shows that such calcination temperature as well as the inclusion of TiO₂ NTs inside this composite had an impact upon that specific surface area as well as mesoporous volume. As that the calcination temperature rises, the amount of porosity throughout the calcined γ -Fe₂O₃ sample reduced. Because tiny holes collapsed, its porosity volume decreased, indicating a development of big pores. Because of the decreased porosity, fewer nitrogen gas may be adsorbed upon that catalyst surface, resulting in a reduction on contact area. Its specific surface area dropped from 26.15 to 10.48 m²/g because as calcination temperature increased from 200 to 500°C, revealing that calcination of 500°C resulted in substantial material growth. Once the weight ratio of TiO₂ NTs/ γ -Fe₂O₃ composites were raised from 1:5 to 10:1, the total area of γ -Fe₂O₃ rose from 49.55 to 181.51 m²/g. Because γ -Fe₂O₃ calcined at 200°C seems to have a modest surface area and mesoporous volume (26.15 m²/g and 0.093 cm³/g, respectively), its inclusion throughout composites should result in a reduction in surface area as well as mesoporous volume compared to that of pure TiO₂ NTs.

Table 4.11: Catalytic properties of the calcined γ -Fe₂O₃ at various calcination temperatures and TiO₂ NTs/ γ -Fe₂O₃ composites at various compositions.

Samples	Indirect Band Gap Energy (eV)
γ -Fe ₂ O ₃ 100	1.90
γ -Fe ₂ O ₃ 200	1.99
γ -Fe ₂ O ₃ 300	1.75
γ -Fe ₂ O ₃ 500	1.85
Ti: Fe = 1: 5	2.80
Ti: Fe = 1: 1	2.85
Ti: Fe = 5: 1	3.02
Ti: Fe = 10: 1	3.05
TiO ₂ NTs	3.08

3.3 Comparison Amongst Catalyst by Different Author

All of their composite as a catalyst proves that photocatalysis can be done with their produced specimens which they proven that they have their own best specimens to prove it was a success. Therefore, as a review, the comparison amongst each author's best specimen would be differentiate accordingly with prove that supports the statement. The Specimen for each of the author's best product of catalyst is shown in Table 3.12.

Table 4.12: Best Specimens by Each Authors

Author	Calcination		Band Gap Energy (eV)
	Temperature (°C)	Best Specimen	
(Abbas et al., 2016)	600	TiFe25-600	1.87
(Razani et al., 2017)	550	0.025%Fe ₂ O ₃ – TiO ₂	3.10
(Bouziani et al., 2020)	500	TF5	2.62

(Koohestani, 2019)	450	TiO ₂ -10%Fe ₂ O ₃	2.72
(Pang et al., 2016)	200	Ti: Fe = 10: 1	3.05

For the specimen done by calcination temperature of 600°C (Abbas et al., 2016), In TiO₂-Fe₂O₃ nanocomposites, a 5% incorporation of Fe₂O₃ into TiO₂ is determined to become the optimal quantity for morphological and photocatalytic benefits. When compared with Ti-600, BET research revealed that TiFe5-600 has a higher surface area. Owing to its excellent characteristics, the TiFe5-600 sample had the greatest photocatalytic activity amongst those produced materials.

Calcination temperature that was done at 550°C (Razani et al., 2017), an optimal quantity of Fe₂O₃ which can be incorporated into TiO₂ photocatalyst to generate the greatest 2,4-DA elimination is 0.05 wt percent. With 10 ppm 2,4-DA solution, 1.0 g of 0.05wt% Fe₂O₃ doped TiO₂, plus pH 4, the optimal elimination of 48.64% was estimated using response surface techniques. At the temperature of 500°C for the calcination (Bouziani et al., 2020), during sun-like light, the α-Fe₂O₃ /TiO₂ composites demonstrate improved photocatalytic activity to destroy both methylene blue and phenol. As when the calcination temperature of such pristine α-Fe₂O₃ powder is elevated, these photoactivity of such α-Fe₂O₃ /TiO₂ mixtures for the photodegradation frequency of MB and Ph enhances as well.

When the temperature of the calcination is 450°C (Koohestani, 2019), This impact of Fe₂O₃ composition on methylene orange decolorization was investigated, and it was discovered that the higher the Fe₂O₃ concentration, the faster the methylene orange decolorization rate. As for the specimen that was calcined at 200°C (Pang et al., 2016), the sonocatalytic characteristics, stability, and magnetic separability so that as-synthesised TiO₂ NTs/γ-Fe₂O₃ composites are all good. Although, to make it excellent at achieving its band gap, the ratio for TiO₂ are required to be bigger than γ-Fe₂O₃ which therefore are quite obsolete as to be compared with the rest of the author. Based on the information discovered by those authors, the discovery is consistent with a recent research, where found that the sample containing 7 wt% Fe₂O₃ in TiO₂-Fe₂O₃ combinations had the best photocatalytic activity. The photocatalytic activity of TiFe5-600 was considered to be effective than TiFe5-400 (Abbas et al., 2016). Due to its limited oxidation capability, the semiconductor with a narrow band gap energy displayed low visible light photocatalytic performance (Pang et al., 2016). It is yet to be decided that the best method for this experiment is to have a calcination temperature 550°C and the amount of 0.025% Fe₂O₃ for a good catalyst.

4. Conclusion

The sol-gel method was successfully done to combine both catalysts into a desired photocatalyst with different properties as done by all five researchers. The inclusion of such an adequate quantity of Fe₂O₃ improves the crystalline structure morphology, surface area, porosity, and eventually photocatalytic activity as per according to research. Based on the results obtained by each author, different approach can be used to conduct the photocatalysis experiments. It is observed that when Fe₂O₃ were to be calcined at a high temperature around 550°C, the amount of calcined Fe₂O₃ should be around 0.025% to be synthesized with TiO₂ for an optimum and efficient catalyst. However, the biosynthesis of TiO₂-Fe₂O₃ can still be improve for a better catalyst for wastewater treatment in the future. For example, Higher temperature up until 550°C shall be used to calcine Fe₂O₃ at the optimum amount at around 0.025% wt before synthesized with TiO₂ for the best result of photocatalysis because when calcination temperature reaches 600°C or more, it tend to deteriorate the quality of the catalyst. Other than that, as the temperature of the calcination reduce, the amount of Fe₂O₃ shall be increase as done by one of the authors which uses 450°C and applying the amount of 10% wt Fe₂O₃ which absorb the most contaminants in the experiments. It is also important that when calcination temperature was decided to be lower such as one of the authors where uses the

temperature of 200°C, the ratio of TiO₂ to Fe₂O₃ shall be bigger for TiO₂ to produce the best and efficient catalyst.

Acknowledgement

The authors wish to thank to the Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia that has supported on the accomplishment of research activity.

References

- [1] Abbas, N., Shao, G. N., Haider, M. S., Imran, S. M., Park, S. S., & Kim, H. T. (2016). Sol–gel synthesis of TiO₂-Fe₂O₃ systems: Effects of Fe₂O₃ content and their photocatalytic properties. *Journal of Industrial and Engineering Chemistry*, 39, 112–120. <https://doi.org/10.1016/j.jiec.2016.05.015>
- [2] Ameta, R., Solanki, M. S., Benjamin, S., & Ameta, S. C. (2018). Photocatalysis. In *Advanced Oxidation Processes for Wastewater Treatment: Emerging Green Chemical Technology*. <https://doi.org/10.1016/B978-0-12-810499-6.00006-1>
- [3] Bouziani, A., Park, J., & Ozturk, A. (2020). Synthesis of α-Fe₂O₃/TiO₂ heterogeneous composites by the sol-gel process and their photocatalytic activity. *Journal of Photochemistry and Photobiology A: Chemistry*, 400, 112718. <https://doi.org/10.1016/j.jphotochem.2020.112718>
- [4] Cheng, G., Xu, F., Xiong, J., Wei, Y., Stadler, F. J., & Chen, R. (2017). A novel protocol to design TiO₂-Fe₂O₃ hybrids with effective charge separation efficiency for improved photocatalysis. *Advanced Powder Technology*, 28(2), 665–670. <https://doi.org/10.1016/j.apt.2016.12.004>
- [5] Dariani, R. S., Esmaili, A., Mortezaali, A., & Dehghanpour, S. (2016). Photocatalytic reaction and degradation of methylene blue on TiO₂ nano-sized particles. *Optik*. <https://doi.org/10.1016/j.ijleo.2016.04.026>
- [6] Kang, X., Liu, S., Dai, Z., He, Y., Song, X., & Tan, Z. (2019). Titanium dioxide: From engineering to applications. In *Catalysts* (Vol. 9, Issue 2). <https://doi.org/10.3390/catal9020191>
- [7] Koohestani, H. (2019). Synthesis and characterisation of TiO₂ nanoparticles/Fe₂O₃ waste chips composite. *Micro and Nano Letters*, 14(6), 678–682. <https://doi.org/10.1049/mnl.2018.5583>
- [8] M. Ahmadi Golsefidi *, F. Abbasi , M. Abrodi, Z. Abbasi, F. yazarlou. (2016). Synthesis, Characterization and Photocatalytic Activity of Fe₂O₃ -TiO₂ Nanoparticles and Nanocomposites. *J. Nanostructure*, 6(1), 64–69. <https://doi.org/10.7508/jns.2016.01.010>
- [9] Mirmasoomi, S. R., Mehdipour Ghazi, M., & Galedari, M. (2017). Photocatalytic degradation of diazinon under visible light using TiO₂/Fe₂O₃nanocomposite synthesized by ultrasonic-assisted impregnation method. *Separation and Purification Technology*, 175, 418–427. <https://doi.org/10.1016/j.seppur.2016.11.021>
- [10] Mohamed, M. M., Bayoumy, W. A., Goher, M. E., Abdo, M. H., & Mansour El-Ashkar, T. Y. (2017). Optimization of α-Fe₂O₃@Fe₃O₄ incorporated N-TiO₂ as super effective photocatalysts under visible light irradiation. *Applied Surface Science*, 412, 668–682. <https://doi.org/10.1016/j.apsusc.2017.03.200>
- [11] Noh, J., Yi, M., Hwang, S., Im, K. M., Yu, T., & Kim, J. (2016). A facile synthesis of rutile-rich titanium oxide nanoparticles using reverse micelle method and their photocatalytic applications. *Journal of Industrial and Engineering Chemistry*, 33, 369–373. <https://doi.org/10.1016/j.jiec.2015.10.020>
- [12] Pang, Y. L., Lim, S., Ong, H. C., & Chong, W. T. (2016). Synthesis, characteristics and sonocatalytic activities of calcined γ-Fe₂O₃ and TiO₂ nanotubes/γ-Fe₂O₃ magnetic catalysts in

the degradation of Orange G. *Ultrasonics Sonochemistry*, 29, 317–327.
<https://doi.org/10.1016/j.ultsonch.2015.10.003>

- [13] Razani, A., Abdullah, A. H., Fitrianto, A., Yusof, N. A., & Gaya, U. I. (2017). Sol-gel synthesis of Fe₂O₃-doped TiO₂ for optimized photocatalytic degradation of 2,4- dichlorophenoxyacetic acid. *Oriental Journal of Chemistry*, 33(4), 1959–1968. <https://doi.org/10.13005/ojc/330442>
- [14] Singh, P., Sharma, K., Hasija, V., Sharma, V., Sharma, S., Raizada, P., Singh, M., Saini, A. K., Hosseini-Bandegharai, A., & Thakur, V. K. (2019). Systematic review on applicability of magnetic iron oxides–integrated photocatalysts for degradation of organic pollutants in water. *Materials Today Chemistry*, 14, 100186. <https://doi.org/10.1016/j.mtchem.2019.08.005>
- [15] Song, G. L., Luo, Y. J., Li, J. Q., Li, Z. Bin, & Tan, H. (2014). Determination of titanium oxychloride in refined titanium tetrachloride by infrared spectroscopy. *Advanced Materials Research*, 997, 475–479. <https://doi.org/10.4028/www.scientific.net/AMR.997.475>
- [16] Subramonian, W., Wu, T. Y., & Chai, S. P. (2017). Photocatalytic degradation of industrial pulp and paper mill effluent using synthesized magnetic Fe₂O₃-TiO₂: Treatment efficiency and characterizations of reused photocatalyst. *Journal of Environmental Management*, 187, 298–310. <https://doi.org/10.1016/j.jenvman.2016.10.024>
- [17] Zhu, X., Cui, X., Che, Z., Jin, X., & Li, M. (2015). Thermal decomposition fabrication of Fe₂O₃ nanoparticle-sensitized TiO₂ nanotube arrays and their photoelectrochemical properties. *Journal of Nanoscience and Nanotechnology*, 15(12), 9717–9720. <https://doi.org/10.1166/jnn.2015.10310>