**Characterization and methylene blue photodegradation efficiency of   
chitosan mediation in coupling MgFe2O4-TiO2   
at various calcination temperatures and times**

**Thieu Quang Quoc Viet1,2,3,4, Doan Ba Thinh1,2,3, Che Quang Cong1,2,3, Le Minh Huong1,2,3,   
Nguyen Duy Hai1,2,3, Nguyen Minh Dat1,2,3, Nguyen Thanh Hoai Nam1,2,3, Nguyen Thi Huong Giang1,2,3, Tong Hoang Lin1,2,3, Le Pham Minh Triet3,5, Mai Thanh Phong2,3, and Nguyen Huu Hieu1,2,3\***

*1VNU-HCM, Key Laboratory of Chemical Engineering and Petroleum Processing (CEPP), Ho Chi Minh City University of Technology (HCMUT), 268 Ly Thuong Kiet Street, District 10, Ho Chi Minh City, Vietnam*

*2Faculty of Chemical Engineering, Ho Chi Minh City University of Technology (HCMUT), 268 Ly Thuong Kiet Street, District 10, Ho Chi Minh City, Vietnam*

*3Vietnam National University Ho Chi Minh City (VNU-HCM), Linh Trung Ward, Thu Duc Ciy, Ho Chi Minh City, Vietnam*

*4College of Engineering Technology, Can Tho University, 3/2 Street, Xuan Khanh, Ninh Kieu, Can Tho City, Vietnam*

*5University of Science, 227 Nguyen Van Cu, District 5, Ho Chi Minh City, Vietnam*

**\***Corresponding author, e-mail: [nhhieubk@hcmut.edu.vn](mailto:nhhieubk@hcmut.edu.vn)

**Abstract**

Herein, the coupling ferrite MgFe2O4-TiO2 (MFO-TiO2) was fabricated by the hydrothermal-prior to the calcination process with chitosan was utilized as a particle stabilizer and studied within photocatalysis toward methylene blue (MB) in water sources. The fabrication process was investigated via calcination temperature and time while the as-prepared materials were characterized by modern analysis methods such as X-ray diffraction, Raman microscopy, Scanning electron microscopy energy-dispersive X-ray spectroscopy, Brunauer-Emmett-Teller specific surface area, and thermal gravimetric analysis. The characterization and photodegradation efficiency results revealed a just sufficient thermal treatment of 2 h exposure in 800 oC for an outstanding structural-morphological analysis via nearly complete photo-treatment with the organic matter. The obtained results also emphasized the usage of oxygen radicals joined in MB degradation whereas H2O2 played a decisive role in Fenton-assisted photodegradation of the coupling material. Indeed, the research shows a prominent and economical procedure on a mass scale to prepare the ferrite TiO2 coupling material as an impressive photocatalyst for dealing with organic contaminants in wastewater treatment.

**Keywords:** MgFe2O4, TiO2, chitosan, methylene blue, photocatalyst.

**1. Introduction**

Photocatalysis, in which light energy is used to drive pairs of chemical reactions, has gained an era of wide interest and met great attention for its benefits. In recent years, the application of nanotechnology in this field has been widely used for the degradation of organic pollutants [1]. Because of its high efficiency, low operating cost, simple design, and eco-friendly products, photocatalysis is proved to be superior to other conventional methods in wastewater treatment. Regarding photocatalysts, TiO2 is known as an outstanding semiconductor for photo-treatment processes due to its non-toxicity, high photoactivity, low cost, and chemical stability [2]. Nevertheless, the limitations have restricted its potentiality in practical usages, including vast re-combination of excited charge (e–) – hole (h+) concurring the process as well as the quite large bandgap (3.2 and 3.0 eV for anatase and rutile phase, respectively) due to the light irradiation capacity under only ultraviolet range [3]. Therefore, TiO2 coupling with other metallic oxides to narrow the bandgap energy and control the charge conveyance is vitally crucial to cope with those issues [2,4,5].

On the other hand, ferrite particles are stated to be ferromagnetic in nature with remarkably low bandgap energy owing to the virtue of their lattices [6]. Spinel ferrites (XFe2O4 where X relates to metal within valency of 2), particularly, hold up paramount photocatalytic properties under visible irradiation region [7]. Moreover, the recycling capacity after treatment processes characterized by the super-magnetic property of ferrite molecules has highlighted the impressive and maintainable treatment solution against trace organic pollutants in aquatic media [3]. Therefore, the doping of spinel ferrite into the TiO2 matrix can diminish the overall bandgap energy of the semiconducting composite, which facilitates the transportation of excited electrons and holes toward TiO2 active sites to initiate the photo-oxidation series [8]. Up-to-date, magnesium ferrite (MgFe2O4-MFO) has dragged the attention of researchers in different fields such as magnetic materials and photocatalytic applications thanks to its small bandgap (~ 2 eV) and low toxicity via less sensitivity in leaching under photo-treatment [9,10]. The increase in ferrite structural stability and assisting magnetic properties were reasonably raised for the introduction of the addition of the Mg2+ ion [11,12], making it become a good candidate for combining with TiO2 nanoparticles for photocatalytic enhancement.

However, the aggregation of the as-mentioned binary form to relatively high cluster size can easily occur would reduce the active face for attaching the pollutants and exciting under UV control. Therefore, the interest in the method of loading oxide nanoparticles into a polymer matrixhas been widely possessed to deal with this drawback [13]. In particular, chitosan, a deacetylated derivative of chitin, has beenreported as a sufficient medium for nanoparticle synthesis due to its hydrophilic, biodegradable, and biocompatible properties [14]. The presence of active amino groups and cross-linking ability that endows for attachment to oxygen particles of coupling oxide makes chitosan a synergetic reducing and stabilizing agent in forming the material. The numerous electrostatic interactions formed via the long-chain carbohydrate unit also facilitate the favorable shape for the ferrite titania with an immerse degree of crystallinity [15,16]. Furthermore, the hydroxyl groups in chitosan can access the hydrogen bonding with co-metallic hydroxide production during the precipitation step, whilst uniformly dispersing it through the polymer chains [14]. The calcination process afterward (600 – 900 oC) has played a vital role in coupling by Ti–O–Fe bonding formation, crystalizing, as well as affirming the appropriate size of the MFO-TiO2 with a high degree of purity [8].

In this research, MFO-TiO2 was fabricated by agitating-assisted hydrothermal route using chitosan as a stabilizing agent. The influences of annealing temperature and time on the crystallinity and structure of the nanocomposite are also investigated, as shown in Scheme 1. The produced materials then experimentally underwent photodegradation proceeding with a well-known organic dye, methylene blue (MB), and assigned within kinetic studies. The photocatalytic mechanism of the material was also studied in the presence of other radical scavengers.

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| **Scheme 1.** Synthesis process and utilization of MFO-TiO2 as a photocatalyst for MB degradation |

**2. Experimental**

**2.1. Materials and chemicals**

Graphite (particle size < 20 µm), chitosan (from shrimp shells, wt. 190–375 kDa, practical grade), 1,4-Benzoquinone (C6H4O2–BQ), and titanium (IV) isopropoxide (TIP, (C12H28O4Ti)) were purchased from Sigma Aldrich Co. Ltd, USA. Ethanol (C2H6O–EtOH), magnesium nitrate (Mg(NO3)2.6H2O), ferrite nitrate (Fe(NO3)3.9H2O), acetic acid (C2H4O2), sulfuric acid (H2SO4), phosphoric acid (H3PO4), potassium permanganate (KMnO4), hydrogen peroxide (H2O2), ammonium hydroxide (NH4OH), disodium ethylenediamine-tetraacetate (EDTA), and isopropanol (IPA, C3H8O) were purchased from Xilong Scientific Co. Ltd, China and used without further purification.

**2.2. Synthesis of MgFe2O4**–**TiO2**

The fabrication of ferrite and ferrite coupling material was performed in a pressurized stirring reactor. Briefly, 1.28 g magnesium and 4.04 g ferric salt (Fe3+:Mg2+ ratio of 2:1) in 50 mL of chitosan solution (1 g/L) were added into the mixture containing 1 mL acetic acid with 50 mL EtOH and 1 mL TIP within gradual stirring for 30 min under ambient atmosphere. Then, the mixture was adjusted to pH 11 by NH4OH 30 % solution before being heated to 90 oC under vigorous stirring for 2 h. The residue was then separated, centrifuged, washed, dried at 80 oC for 6 h, and finally, calcinated. The TiO2 and MgFe2O4 samples for reference were performed in the same route, but without adding their corresponding precursors. The composite materials were conducted with seven calcination temperatures for 2 h from 300 to 900 oC (delta temp. of 100 oC). The appropriate samples were chosen for investigating calcination time, including 1, 2, 3, 4, and 6 h.

**2.3. Characterization of materials**

X-ray diffraction (XRD) was measured by Advanced X8, Bruker (λX = 0,154 nm) with CuKα irradiation in the range of 5 ~ 80 °. Raman spectra were conducted with a LabRam micro-Raman system at an excitation wavelength of 632 nm (He-Ne laser). Scanning electron microscopy (SEM) (Hitachi S-4800, Japan) was used to investigate the morphological term of the ferrite coupling. Elemental analysis was identified in sequence using energy-dispersive X-ray spectroscopy (EDS) (Jeol – JMS 6490, Japan). Brunauer Emmett-Teller (BET) specific surface area and pore volume were determined by nitrogen adsorption using TriStar II 3020 V1.03 analyzers, Micromeritics Instrument Corporation. Thermal gravimetric analysis (TGA) was conducted using TGA Q500 V20.10 Build 36.

**2.4. Photocatalysis activity**

An MB stock solution (20 mg/L) was prepared and stored in the fridge before utilization. The photo-treatment started with 100 mL of MB solution substituted with 80 mg catalyst. The mixture was stirred in the dark for 10 min, then added 2 mL H2O2 before being exposed to UV light (TUV 215mm 11W, Philips). A portion of the sample was taken at a regular time interval of 10 min, filtered, and quantified under UV-vis spectroscopy at the wavelength of 665 nm. The photodegradation mechanism was investigated by adding free-radical scavengers (BQ, EDA, and ISP) to the reaction mixture. The yield and kinetic reaction rate for the photocatalysis were recognized via Equations (1) and (2), respectively:

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|  | (1) |
|  | (2) |

where and (mg/L) are respective the initial and final concentration of MB after the irradiation time t (min), and k is the rate constant.

**3. Results and discussion**

**3.1. Effect of calcination temperature**

Figure 1 reveals the overall impact of calcination temperature on crystallinity via the photocatalytic properties of the MFO-TiO2 materials. Accordingly, the higher the temperature was controlled (from 500 oC and above), the more excluding interference observed in the material patterns (Figure 1a), indicating that the complete decomposition has played the role of forming and stabilizing metal oxides at those points. However, at 500 °C, the breakout of chitosan matrix to CO and CO2 occurred widely on the material surface, the water splitting to produce bare oxides (TiO2, MgO, FeO, and Fe2O3) along with the crystallite growth to form coupling oxide phase (MgFe2O4 and MgFe2O4-TiO2) might cause a high tendency to reach each other of those particles. This phenomenon facilitated the solid-solid phase reaction among the crystalline phases. In addition, the temperature is also considered to be the main factor leading to the splitting of hydroxides followed by atomic and crystallite migration in the matrix to form the composite. Those statements were well-accordance with Figure 2, whereas regarding an increment of temperature from 300 to 400 oC, there observed a reduction in large patches of material corresponding to presented metallic hydroxide and chitosan stick together. At 500 oC, the polymer medium for loading metal oxide seems to disappear, however, the agglomeration that reduces the XRD intensities derived from the as-mentioned thermal sintering process still occurs. Interestingly, at calcination temperatures of 600 – 900 oC, the highly-clarified intensities of the XRD pattern suggest that the optimization of ferrite oxide formation-coupling oxide and enhanced thermal sintering process driven by temperature has led to a spreading larger crystal to the desired dimension and impressive crystallographic phase[17].

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| **Figure 1.** (a) XRD patterns; (b) Elimination yield and (c) Kinetic studies  for MB photodegradation of MFO-TiO2 at various calcination temperatures |

More specifically, regarding Figure 1a, at 300 oC, the material held up the TiO2 in rutile (at peaks 36.2 and 54.4 o) and brookite phases were obtained from the initial hydrothermal before the calcination process while traces of Fe2O3 and FeO existed revealed the primary growth of them from Fe precursor. From 400 to 600 oC, the oxidation process continues in an oxygen-rich calcination environment, converting mostly amount of FeO to Fe2O3 phase while still no characteristic peaks of TiO2 anatase phase were detected in those patterns. The peak at 35.5 o indicates the presence of MgFe2O4 at a temperature range of 300 – 500 oC, nevertheless, the lower amount at the initial has been overlapped by the Fe2O3 phase in the matrix. At 700 oC, the formation of MgFe2O4 in the composite is more prominent corresponding to (220), (331), and (440) facets by 2θ of 18.1 and 32.4, and 62.5 o, respectively. Besides, the anatase phase appears at the peaks 25.3, 37.5, 54.1, and 62.0 o accordance with the (101), (004), (200), (105), and (204) planes, respectively. When the material was heated to 800 – 900 oC, most TiO2 and MgFe2O4 crystalline phases were both detected, suggestive of the complete forming and coupling of those to composite with intense crystallinity [3].

Furthermore, in terms of Figure 1b and c, the degradation efficiency and kinetic analysis of the composite are illustrated, respectively. As can be observed, in 60 min, the dye-eliminating yield of ferrite MgFe2O4-TiO2 generally escalates with an increase in temperature. This phenomenon can be attributed to the fact that higher temperatures would lead to the higher kinetic energy of reactant molecules, in other words, higher collision velocities, which results in promoting the reaction rates and their corresponding dye-removing efficiencies. Thus, the kinetic figure expresses an excellent linear relationship between and t, indicating the validity of the pseudo-first-order reaction model [1]. Accordingly, the lower the parameter of was obtained, the lower the residual concentration of dye existing in the solution after the reaction was left, as a result, an enhanced reaction yield is acquired. The kinetic results are also well-accordance with the aforementioned degrading efficiency outcomes. In conclusion, increasing the calcination temperature generally promotes decomposition as well as more effective forms and stabilizes the particles, leading to better photocatalysis performances expressed via the examinations of elimination yield and kinetic studies.

As stated, the accumulated outcomes are relatively consistent with SEM images in Figure 2. In detail, as the temperature rises, the particles are more uniformly and visibly formed with a size of 100 – 200 nm. However, a too-high temperature (900 oC) results in a backward trend: the small-sized molecule with a relatively high surface area aiding in thermal migration achieved a great tendency to re-bound among the solid phase. Yet the agglomeration at this point did not occur vastly due to the complete decomposition of hydroxide to oxide, the rise in molecular size is inevitable. Conclusively, 800 oC is a suitable breakpoint for completing the composite fabrication.

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| **Figure 2.** SEM images of MgFe2O4-TiO2 at various calcination temperatures |

The thermal analysis of the material in the oxygen-rich media (Figure 3a) has clarified the mediate loss via the phase change of the base oxide for coupling. The first weight loss of ~ 3.6 and 2.4 % for the aforesaid ferrites up to 150 oC was attributed to the dehydration and the removal of trace organic matter on the material surface. Once the temperature reached 213 and 274 oC occurring with 2 exothermally downward peaks at thermogram, there witnessed a significant reduction of the mass that is well-indexed to the chitosan decomposition (up to ~ 7 %) as described by XRD and SEM images above. At this stage, the formation of the basal oxide was stated to be approximately completed and ready for initiating another, once the temperature reached above 350 oC. In the next steps (400 – 500 oC), the small change in mass is well responding to the final removal of the trace organic maters and polymer, the disintegration of incompletely unhydrolyzed TIP via the vast transformation of precursor hydroxides to their oxides. At 650 oC, while the mass curve remained unchanged, the thermogram exhibited an endothermal upwards peak that indicates a crystallization and phase change among those oxides to ferrite and its coupling with TiO2. That was also appropriate with fully-clear XRD patterns of the material after 700 oC and above calcination treatment. Finally, those residuals and coupling ferrites were stably formed due to the insignificant weight loss at 700 – 800 oC, attributing to the mass of 83.97 % as compared to the initial. Interestingly, in the inert environment (Figure 3b), the same trend was observed likewise in the previous investigation, confirming the as-mentioned stages in the formation pathway of ferrite and its coupling with TiO2 [16].

As noted earlier, a sufficient increment of calcination temperature is vitally crucial to enhance the active phase and catalytic surface area for photocatalysis towards organic dye in water. In Figure 1b, their witness a dramatic increase in elimination yield of ~ 99.6 % once the temperature is controlled to 800 oC. However, at   
900 oC, the aggregation of the oxide particle with larger sizing indicates a slight reduction in yield, affirming the less sorption of MB via the penetration of light to the active phase. Specifically, the restricted adsorption of MB onto the material at both 500 and 900 oC after 10 min has marked the polymer support via pore collapse (for the former) and the over-growth of the crystal (for the latter) accelerated by the thermal treatment. Additionally, this tendency can be also explained by the presence of different polymorphs in the resulting materials. In particular, the increase in calcination temperature to 800 oC efficaciously promotes the brookite-to-anatase transformation. Moreover, the anatase phase of TiO2 possesses a structure of indirect band gap, which endows a longer duration of recombination of electron and hole pairs when compared to the direct bandgap structure of rutile and brookite phases, thereby enhancing the photocatalysis performance of the fabricated materials [17]. Furthermore, the anatase TiO2 also shows superior photodegradation effects thanks to the smaller size and the lower effective mass of electron and hole pairs that effectively increase the rate of charge transfer. Contrarily, it has also been reported that the further rise in calcination temperature to above 900 oC may potentially stimulate the formation of larger crystallite size of rutile phase from the anatase, which exhibits the direct bandgap structure, leading to the gradual attenuation in the photodegradation efficiency [18]. Besides, from Table 1, the photocatalytic degradation of MB by MgFe2O4-TiO2 was in good match with the pseudo-first-order kinetic with a high correlation coefficient. The rate constant of calcinated materials at 700 oC has the highest value (0.0854 min-1), but with 800 oC treatment, there was no significant change in this value. Therefore, aligned with structural analysis, the ideal calcination temperature to optimize photodegradation performance was further confirmed at 800 oC and matched with the explanations above.

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| **Figure 3.** TGA and DTA curves of MFO-TiO2 in (a) oxygen-rich and (b) inert gas environment |

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| **Table 1.** The kinetic parameters of MFO-TiO2 at various calcination temperatures | | |
| **Calcination temperatures (oC)** | **Rate constant k (min-1)** | **Correlation coefficient R2** |
| 300 | 0.0380 | 0.9954 |
| 400 | 0.0426 | 0.9967 |
| 500 | 0.0504 | 0.9912 |
| 600 | 0.0568 | 0.9836 |
| 700 | 0.0854 | 0.9839 |
| 800 | 0.0848 | 0.9836 |
| 900 | 0.0737 | 0.9977 |

The band gap energy of the material at different calcination temperatures can be determined based on the linear relationship of (ahν)2 and hν, as indicated in Table 2. As can be witnessed from the results, the increase in the calcination temperature from 300 to 800 oC significantly decreases the bandgap energy from 2.91 to 1.78 eV, which can be attributed to the gradual generation of the rutile phase during the calcination process. The bandgap energies of all samples are also higher than that of the pristine TiO2. This can be ascribed to the participation of the ferrite structure with low band gap energy, as well as the support of the polymer matrix of the chitosan, which is responsible for the good degree of crystallinity and the stability of the material thanks to the strong interaction with long-chain carbohydrate. The results are also consistent with the aforesaid analysis of the fluctuation trends in the XRD patterns.

**Table 2.** Bandgap energy of the MFO-TiO2 at various calcination temperatures

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| **No.** | **Calcination temperatures (oC)** | **Bandgaps (eV)** |
| 1 | 300 | 2.91 |
| 2 | 400 | 2.08 |
| 3 | 500 | 2.07 |
| 4 | 600 | 1.92 |
| 5 | 700 | 1.84 |
| 6 | 800 | 1.82 |
| 7 | 900 | 1.78 |

Table 3 indicates a significant diminish in surface area and the porous dimension of the material once controlling calcinate temperature from 80 to 800 oC. This was well-attributed to the vast thermal decomposition of the chitosan carrier that inherently provides the bounding platform for metallic hydroxide and preformed TiO2, the Ti octahedral structure, formation onto polymer matrix [2]. The higher heat treatment has owned a role in accelerating the matrix breakage and pore collapse, therefore, initiating the seed conveyance via phase interaction to ferrite and its coupling with TiO2. The results were well-match to all previous statements.

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| **Table 3.** Surface area and pore volume of MFO-TiO2 with two calcination stages | | | | |
| **Temperatures (oC)** | **BET surface areas (m2/g)** | **Langmuir surface areas (m2/g)** | **Pore volume  (10-3 cm3/g)** | **Pore size**c **(nm)** |
| 80 | 56.1164 | 339.5031 | 62.0640a | 4.4239 |
| 800 | 0.0848 | 0.9836 | 1.5150b | 1.3859 |
| aSingle point adsorption total pore volume of pores less than 1.6279 nm width at P/P0 = 0.0770  bSingle point adsorption total pore volume of pores less than 1.6852 nm width at P/P0 = 0.0881  cAdsorption average pore width (4V/A by BET) | | | | |

**3.2. Effect of calcination time**

Figure 4 reveals the impact of calcination time on crystallinity via the photocatalytic properties of the MFO-TiO2 materials. The above statement emphasizes the existence of the rutile and brookite TiO2 phase of the material at the beginning of the thermal treatment process, proved by Raman peaks of 230 and 612 cm–1 corresponding to the symmetries of B1g and A1g whilst 413 and 665 cm–1 belong to the symmetries of B2g and A1g active modes, respectively [18,19]. Enlargement of treating time witnesses an increase in Raman scattering of those characteristic bands, affirming the thermal driving force for vast decomposition of chitosan matrix and assisted phase transformation in those oxides. The latter was intensely solidified by the presence of TiO2 anatase phase just clearly after 3 – 4 h of calcination (at 362, 497, and 618 cm–1 matching up with B1g, A1g, and Eg stretching mode, respectively) while the detection of it at one-hour-calcination was considerable [19]. Particularly, the accumulation of Eg mode of anatase and A1g mode of rutile phase have resulted in a superior signal of that band in Raman spectra [20]. Likewise, MgFe2O4 also appeared at the initial stage of the process, but with a small amount presented, three Raman lattice vibrations at 210, 610, and 820 cm–1 assigned to two F2g and A1g were undetectable [8,21]. Turning to 4 h of treatment, the enhancement in those bands indicates a good interaction among those bare oxides to form their ferrite and coupling ferrite likewise the temperature effect. The chitosan substitution has played a vital role in dispersing and stabilizing appropriate sizing (Figure 5) so that the thermal collision among the phases occurs efficiently in long-term treatment. Interestingly, the strong Raman peak at 297 cm–1 was owned by Eg symmetry phonon modes of the hematite Fe2O3 phase, suggesting the formation of its ferrite with Mg precursor and/or the unreactive oxide remaining in the crystal structure [22].

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| **Figure 4.** (a) Raman spectra; (b) Elimination yield and (c) Kinetic studies  for MB photodegradation of MFO-TiO2 with different calcination times |

Interestingly, the calcination temperature shows less effect on the photodegradation of MB as 99 % of the pigment was eliminated with the two-hour-treated material whereas, with others, the yields did not change significantly in the range of 98.2 – 99.5 % (Figure 4b). This proposes an effective fabrication pathway for the coupling ferrite with a desirable active phase and sufficient sizing. Besides, the highest sorption yield after 10 min in the dark observed in MgFe2O4-TiO2 within two-hour-treatment has facilitated the photocatalysis of the organic matter. Similar to the temperature effect, the relative aggregation of the oxides vastly resulted from the structural change before the chitosan decomposition and/or the crystalline growth that loses the catalytic surface area [4]. Regarding Figure 4c, the photocatalytic degradation of MB due to the calcination time is also visibly well-accordant with the pseudo-first-order. With good structural, topological characteristics, and photo-treatment, 2 h is considered an appropriate treatment time for ferrite preparation, yet its rate constant is lower than that of material treated with larger times. The use of suitable calcination time not only ensures the efficiency of the catalysis but also proposes an economical aspect in timing and energy usage. It both reduces the cost of the process and increases its practical use in photo treatment for mass scale [23].

The aforementioned statements are well-supported by the change in the composition and size of the oxide particles formed upon increasing the annealing temperature from 1 to 4 hours in the SEM images and EDS spectra as shown in Figures 5 and 6, respectively. Prolonged time exposure to high temperature has become the main agent for the decomposition of chitosan carriers through significant changes in C and O element composition, the dehydration from metallic hydroxide to oxide, via the conveyance of the base oxide to each other to form the ferrite and its coupling with TiO2. As shown in Figures 3a and 5b, enhanced time in thermal treatment might lead to a gradual increase in the Ti content for TiO2 (~ 20 wt.%) with a higher degree of anatase phase while the Fe content in the composite approaches almost 50% as a major component for the ferrite molecules due to the decrease in the total of presenting atoms [17]. The sufficient long-term treatment also ends up in relative nano-sizing of 99.46 ± 2.5 nm for the material.

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| **Figure 5.** SEM images of MgFe2O4-TiO2 with different calcination times and its distribution of particle sizes |

Moreover, the EDS figures of the material are incredibly well-remained after 4 h of treatment with no significant differences in the number of peaks and their intensities [24]. As mentioned above, the element analysis of the ferrite MgFe2O4-TiO2 also illustrates the particular changes in the mass composition of the composite after each calcination period. In general, it can be witnessed that the wt.% of C, O, and Mg diminished over time while the other two metallic figures of Ti and Fe tended to increase when the calcination duration rises. These obtained phenomena can also be assigned to the decomposition of chitosan and the additional generation of ferrite and coupling ferrite compounds as the treating time escalates, which is further well-accordant with the results of the Raman spectra.

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| **Figure 6.** (a) EDS spectra and (b) Element analysis of MgFe2O4-TiO2 with different calcination times |

In addition, as expressed in Table 4, the photo-elimination of MB using MgFe2O4-TiO2 is relatively consistent with the pseudo-first-order model with a high correlation coefficient for all four durations, similar to the influences of the reaction temperatures. The rate constant of the one-hour-calcinated composite held up the lowest value (0.0393 min-1), but four samples indicate approximately similar rate constants with excellent correlation coefficients. Particularly, the figure for 2 h is noticeably achieved at 0.0638 min-1 and R2 = 0.9981, which is the most accurate in the examinations. In conclusion, the suitable calcination time to conduct the photo-treatment was selected at the previously mentioned 2 h.

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| **Table 4.** The kinetic parameters of material with different calcination times | | | |
| **Temperatures (oC)** | **Time (h)** | **Rate constant k (min-1)** | **Correlation coefficient R2** |
| 80 | 6 | 0.0393 | 0.9894 |
| 800 | 1 | 0.0646 | 0.9982 |
| 800 | 2 | 0.0847 | 0.9799 |
| 800 | 3 | 0.0651 | 0.9953 |
| 800 | 4 | 0.0689 | 0.9919 |

**3.3. Photocatalytic mechanism**

As shown in Figure 7, three scavengers, BQ, EDTA, and IPA, were studied within MgFe2O4-TiO2 under photo-treatment MB to confirm the assistance of oxygen radical. The use of IPA, on the other hand, has noticed a yield of 48.86 % due to the increase in •OH radical reservoirs, similar to those obtained without a scavenger. In contrast, the reduction in radicals caused by the replacement of BQ and EDTA has hampered their photodegradation. The results show that •O2 and •OH radicals play a crucial role in the photodegradation process. Under UV light, those radicals were formed by the reaction of induced charge and hole to water and dissolved oxygen molecules in media. The coupling of ferrite to TiO2 has increased transportation through the ferrite matrix and then to the dye pollutants. Furthermore, H2O2 under light irradiation might act as a reservoir for •OH radicals and aided-in Fenton reaction with Fe-component in the coupling ferrite [8]. For the oxidation pathway, initially, those radicals with highly electrophilic properties might join in reaction with cationic sulfur, in advance to break down the N and/or S-heterocyclic compounds [25]. Then, the chain or ring cleavage of those intermediates might occur due to the presence of the radicals. Finally, the resultants of the aforementioned reactions are further mineralized into docile and harmless substances like H2O and CO2 [26].

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| **Figure 7.** (a) Influences of scavenging agents on the photocatalytic activity of MFO-TiO2 toward MB and  (b) Photodegradation mechanism of MFO-TiO2 for MB. |

**4. Conclusions**

In this study, a green media, chitosan, has been applied as an assistant in coupling ferrite MgFe2O4-TiO2 under hydrothermal-prior to calcination treatment. The results indicated that calcination temperature and time both efficaciously affect the photocatalysis performance of the resulting material due to the transformation of phases of the TiO2. Moreover, the XRD results also revealed that the combination of the anatase, rutile, and brookite phases can effectively contribute to the variation of the photodegradation performance of the fabricated material. The suitable condition for the latter has been thoroughly conducted to obtain the catalytic product with promising structural and morphological characterization. A near complete removal of methyelene blue (99.53%) was achieved when the coupling ferrite MgFe2O4-TiO2, obtained with the calcination temperature and time of 800 oC and 2 h respectively, was utilized.Conclusively, the results suggest a certain preparation procedure for this catalyst to propose an outstanding photo-treatment performance of organic matters from an aqueous medium.

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