

## Article

# Degradation of Malachite Green Dye by Solar Irradiation Assisted by TiO<sub>2</sub> Biogenic Nanoparticles Using *Vaccinium corymbosum* Extract

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**Abstract:** The green synthesis of metal oxide nanoparticles (NPs) offers an alternative to chemical procedures, which can be harmful to human health due to exposure to hazardous substances and harsh synthesis conditions. The following work synthesized titanium dioxide nanoparticles (TiO<sub>2</sub> NPs) using a green synthesis method. As a precursor, food-grade TiO<sub>2</sub> was used with blueberry extract. This approach makes the process safer, cheaper, and simpler, requiring minimal effort to achieve effective TiO<sub>2</sub> NP synthesis. The TiO<sub>2</sub> NP characterization was performed by solid-state techniques, such as Ultraviolet-visible (UV-Vis) spectroscopy, X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). According to the XRD diffractograms, TiO<sub>2</sub> NPs were obtained in the anatase phase with incidence peaks of 25.28 (101). TEM confirmed their pseudo-spherical shape with an average size of 170 nm. The 3.2 eV bandgap of TiO<sub>2</sub> NPs enables UV absorption, making them ideal for efficient photocatalytic degradation under sunlight. On the other hand, the photocatalytic activity of TiO<sub>2</sub> NPs was examined using malachite green (MG) dye as a pollutant model under direct sunlight. After 30 min, a degradation of 94% was achieved. The kinetic analysis identified parabolic diffusion and modified-Freundlich kinetics as primary mechanisms, emphasizing diffusion and adsorption in electron transfer. The main reactive oxygen species (ROS) involved in the photodegradation of MG dye were h<sup>+</sup> and OH<sup>•</sup>.

**Keywords:** eco-friendly nanotechnology; TiO<sub>2</sub> NPs; green synthesis; photocatalytic degradation; environmental remediation

## 1. Introduction

In the last decade, there has been an increase in the green synthesis of metal oxide nanoparticles (NPs) with a particular interest in titanium dioxide nanoparticles (TiO<sub>2</sub> NPs), an eco-friendly approach to producing nanomaterials with diverse applications, particularly in photocatalysis [1,2]. Utilizing non-toxic reagents or natural resources such as blueberry

(*Vaccinium corymbosum*) extracts ensures minimal environmental impact while repurposing byproducts from local markets. In this study, blueberries that failed quality control were repurposed as a source of raw material for TiO<sub>2</sub> NP synthesis, reducing food waste and promoting sustainability in material synthesis [3,4]. In that sense, food-grade TiO<sub>2</sub> is often used as a whitening agent in paints, cosmetics, and food products. Known as E171 in Europe and INS171 in North America, it is incorporated into various foods, including dairy products, baked goods, and confectionery products [5]. TiO<sub>2</sub> is acknowledged for having slight toxicity [6].

Aside from TiO<sub>2</sub>, relevance in food applications aligns with its environmental impact, notably in treating industrial wastewater with dye contaminants. Anatase TiO<sub>2</sub>, a widely studied photocatalyst, is valued for its inertness, durability, mechanical toughness, photocatalytic activity, cost-effectiveness, and ease of use. Its synthesis has attracted attention due to its effectiveness in degrading toxic substances in water and air exposed to UV and visible light [2]. The wastewater discharged from textile, printing, manufacturing, and various industrial sectors, including dye pollutants, poses significant risks to the ecosystem and health care. The pigments and dyes in wastewater hinder the photosynthetic reaction of aquatic flora by blocking direct sunlight [7]. The contaminants from organic dyes are very toxic and can lead to human diseases and environmental harm. The green crystalline compound, malachite green (MG), possesses a high solubility in water and is often utilized as a pigment in sectors such as textiles, paper, and cosmetics. However, even at low concentrations, it has mutagenic and genotoxic effects, poisoning aquatic life and biological systems. Recent studies have highlighted its detrimental effects on reproductive and propagative systems [8–10]. The US Food and Drug Administration (FDA) has classified certain substances as Class II for health hazards, indicating their carcinogenic potential. Despite being banned due to these significant risks, the production of these substances continues, leading to ongoing environmental damage. Addressing MG impact is urgent, with efforts concentrated on mitigating its toxic effects. This discrepancy underscores the importance of developing eco-friendly methods, such as employing photocatalytic TiO<sub>2</sub> NPs, for its degradation [11].

TiO<sub>2</sub> NPs synthesized through various green methods have demonstrated remarkable efficacy in degrading multiple dyes, including methylene blue (MB), methyl orange (MO), crystal violet, acid blue 113, rhodamine B (RhB), and RG-19 dye. For instance, MB degradation was notably achieved using jasmine flower extract, resulting in a peak efficiency of 92% after 120 min of radiation exposure [12]. *Aloe vera* extract acted as a natural capping agent, achieving 94% degradation of MB within the same timeframe under UV radiation [13]. Complete degradation of MB was observed within 60 min with TiO<sub>2</sub> NPs synthesized using *Calotropis gigantea* extract [14]. Similarly, TiO<sub>2</sub> NPs synthesized with mulberry (*Morus alba*) extract achieved 96% degradation of MB under ultraviolet illumination within 120 min [15]. In contrast, TiO<sub>2</sub> NPs synthesized via green methods using extracts such as *Phyllanthus niruri* and *Tinospora cordifolia* exhibited high efficiency in degrading MO and Acid Blue 113, achieving 99.5% [16] and 94.43% [17] degradation, respectively, within specific timeframes. For RhB, more than 90% degradation was achieved within just 80 min using *Citrus limetta* extract [18]. Moreover, TiO<sub>2</sub> NPs synthesized with *Lagenaria siceraria* extract exhibited exceptional photocatalytic activity, removing 98.88% of RG-19 dye in just 60 min [19]. These findings underscore the potential of TiO<sub>2</sub> NPs synthesized via green methods for environmentally friendly dye degradation applications.

Few studies have specifically explored the oxidation of MG on TiO<sub>2</sub> NP surfaces under direct sunlight exposure, revealing that oxidative degradation and byproducts are poorly addressed, particularly their effect on MG discoloration and reduction on TiO<sub>2</sub> NPs. In wastewater treatment, photocatalytic degradation stands out for its simplicity, speed, and cost-effectiveness compared to other methods [20]. Semiconductor materials, which can destroy organic contaminants through redox processes, are increasingly important in this field. Photocatalytic efficiency depends on the excitation of electrons induced by photon absorption. In the photocatalytic oxidation process, the degradation of pollutants

occurs through the combined action of an oxidizing agent, a high-energy radiation source, and a semiconductor photocatalyst [11,14]. Ultraviolet (UV) radiation activates the TiO<sub>2</sub> NPs, producing hydroxyl radicals (OH•), oxidants capable of breaking down organic compounds. Electron-photo hole (e<sup>−</sup>/h<sup>+</sup>) pairs develop in the photocatalyst upon light exposure. When the energy provided by the light is equal to or greater than the bandgap energy of TiO<sub>2</sub> NPs, these e<sup>−</sup>/h<sup>+</sup> pairs stimulate the formation of reactive species such as OH• and superoxide (O<sub>2</sub><sup>−</sup>). These radicals are directly involved in the oxidation process to decompose contaminants [13,16].

Furthermore, TiO<sub>2</sub> NPs synthesized via green synthesis have demonstrated efficacy in degrading MG dye, expanding their applicability in treating textile industry wastewater. These results and the findings for other dyes discussed previously underscore the broad utility of green-synthesized TiO<sub>2</sub> NPs in wastewater remediation [21].

This research aims to investigate the efficacy of TiO<sub>2</sub> NPs synthesized using *V. corymbosum* extract in photocatalyzing the sunlight-driven degradation of MG dye. The characterization of TiO<sub>2</sub> NPs was performed using solid-state techniques such as Ultraviolet-visible (UV-Vis) spectroscopy, X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). This photocatalytic process shows promise for converting the dye into harmless substances. Understanding the mechanisms of these TiO<sub>2</sub> NPs could lead to the development of sustainable methods for treating wastewater and environmental cleanup.

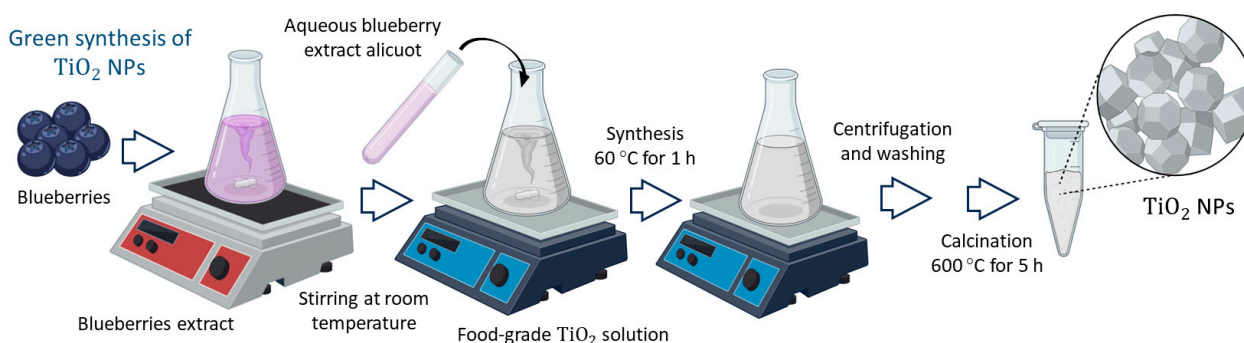
## 2. Materials and Methods

### 2.1. Precursors

Food-grade TiO<sub>2</sub> (Alday Ingredientes, Puebla, Mexico) was used as a precursor of TiO<sub>2</sub> NPs, and MG (analytical grade ≥ 90%) purchased from Sigma-Aldrich was used as a pollutant model. The fresh blueberry fruits were gathered as byproducts from a local market in the metropolitan zone of Guadalajara, Mexico. All reactions were carried out in deionized water.

### 2.2. Preparation of the Blueberry (*Vaccinium corymbosum*) Extract

The aqueous extract was prepared by boiling 1.0 g of chopped freeze-dried blueberries in 100 mL of water at 90 °C for 10 min under constant stirring (Figure 1). After cooling, the extract was centrifuged (10,000 rpm, 15 min) at room temperature. Subsequently, the extract was filtered. The filtered extract was stored in a dark glass bottle at 4 °C to protect it from light for future use.



**Figure 1.** Schematic representation of the green synthesis protocol for TiO<sub>2</sub> NPs using blueberry (*Vaccinium corymbosum*) extract.

### 2.3. Green Synthesis of TiO<sub>2</sub> NPs

As depicted in Figure 1, 90 mL of  $1 \times 10^{-3}$  M food-grade TiO<sub>2</sub> solution was stirred for 2 h at room temperature. Then, 10 mL of the aqueous extract of blueberries was added under constant stirring at room temperature (25 °C). After 2 h, heat treatment was

performed at 60 °C for 1 h. Subsequently, the product was purified by centrifugation at 10,000 rpm for 15 min and washing several times with distilled water. Finally, the product was calcinated at 600 °C for 5 h.

#### 2.4. Characterization of TiO<sub>2</sub> NPs

The analysis of the crystalline structure of both precursor and calcined TiO<sub>2</sub> powders was carried out by XRD using an Empyrean diffractometer (PANalytical, Westborough, MA, USA). The analysis of the chemical species present in the calcined powders was performed by XPS, using a Sigma2 XPS and a Theta-probe (Thermo Fisher Scientific, East Grinstead, UK). The FTIR spectrum, in the range of 400–4000 cm<sup>−1</sup>, was obtained using a 400 FTIR spectrometer (Perkin Elmer, Waltham, MA, USA). The particle shape and size of TiO<sub>2</sub> NPs were evaluated by TEM using a JEM 1010 microscope (Jeol, Tokyo, Japan). Absorbance measurements of TiO<sub>2</sub> NPs were obtained by using a UV-Vis spectrophotometer (Cary-300 model, Varian, Australia) in the λ range of 190 to 800 nm. The band gap energy (E<sub>g</sub>) value was determined using the relation between the Kubelka–Munk function, F(R), and the relation between the F(R) curve and the absorption edge according to Equation (1) [22].

$$(F(R)h\nu)^2 = B(h\nu - E_g) \quad (1)$$

where F(R) is the Kubelka–Munk function, hν is the photon energy, E<sub>g</sub> is the band gap energy, and B is a constant characteristic of the material.

#### 2.5. Photocatalytic Malachite Green Dye Degradation

The photocatalytic activity of TiO<sub>2</sub> NPs was evaluated for photodegradation of aqueous solution of MG dye under solar light. The photocatalytic experiments were carried out on spring days between 11 a.m. and 2 p.m. on the rooftop of the Molecular Biology Laboratory of the Universidad de Guadalajara (20°39′25″ N, 103°19′31.2″ W), Mexico. Solar irradiation was measured using a Thorlabs powermeter measuring 117.6 mW/cm<sup>2</sup> in the ultraviolet range. Briefly, 5 mg of TiO<sub>2</sub> NPs was dispersed into 20 mL of an MG dye solution at 1 × 10<sup>−4</sup> M. The mixture was sonicated in the dark for 5 min and poured on a petri dish. Then, the solution was kept under solar irradiation, and aliquots of the mixture were withdrawn at specific intervals. The ambient temperature was about 28 ± 3 °C while conducting the experiments. The absorbance spectrum of each sample was measured using a spectrophotometer (NanoDrop 2000, Thermo Scientific, Waltham, MA, USA). The degradation percentage was obtained as described in the following Equation (2):

$$\% \text{Degradation} = (C_0 - C) / C_0 \times 100 = (A_0 - A) / A_0 \times 100 \quad (2)$$

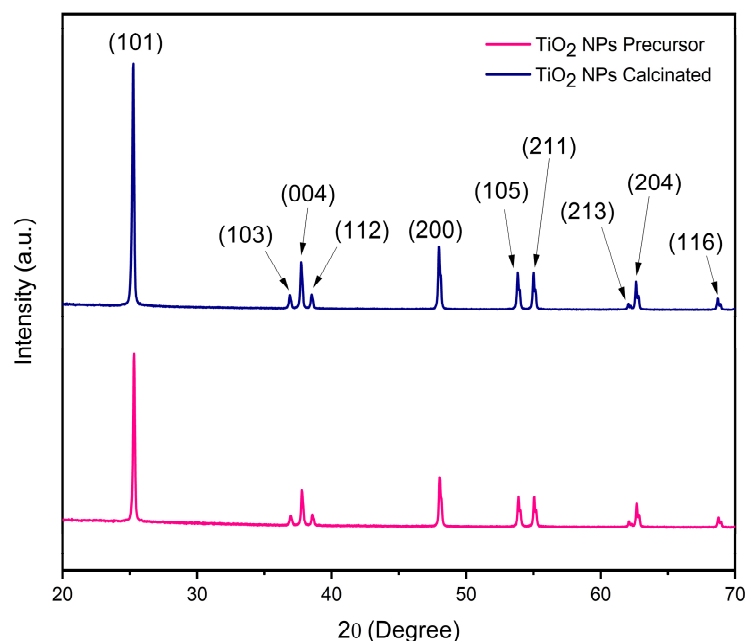
where C<sub>0</sub> and C are the MG dye concentrations at zero time and time t, respectively, and A<sub>0</sub> and A correspond to the absorbance values of the solution with the MG dye before and after exposure to light, respectively.

### 3. Results and Discussion

#### 3.1. Characterization

##### 3.1.1. XRD Analysis

Figure 2 shows the diffraction pattern of the precursor powders before and after being calcined at 600 °C. The analysis was conducted in the 2θ range from 20° to 70°. In both cases, the main diffraction peaks were located at 2θ = 25.5°, 35.5°, 44.5°, 52.5°, 57.5°, 66.5°, 68.5°, and 69.5°, which are associated with the anatase phase of TiO<sub>2</sub> (JCPDS file No. 21-1272). It should be noted that no peaks related to the rutile phase (JCPDS file No. 21-1276) or impurities related to organic compounds from the material synthesis were detected. Comparing the diffraction peaks of the precursor and calcined powders, an increase in the intensity of the peaks associated with the calcined powder was observed. This result suggests an increase in the crystallinity of the calcined powder.



**Figure 2.** XRD patterns of the precursor TiO<sub>2</sub> NP powders and the TiO<sub>2</sub> NP powders after calcination at 600 °C.

Additionally, the d-spacing, crystallite size, crystallinity, and dislocation density were obtained from the values recorded in the diffraction patterns of each powder (Table 1). Each value described above was obtained using Bragg's law (3), Debye–Scherrer Equation (4), and Equations (5) and (6), respectively. To obtain the d-spacing value, the peak with the highest intensity (101) was considered as a reference.

$$d = \frac{n\lambda}{2 \sin \theta} \quad (3)$$

$$D = \frac{(0.95)(\lambda)}{\beta \cos \theta} \quad (4)$$

$$\text{Crystallinity} = \frac{\text{Area}_{\text{Crystalline peaks}}}{\text{Area}_{\text{All peaks}}} \quad (5)$$

$$\delta = \frac{1}{D^2} \quad (6)$$

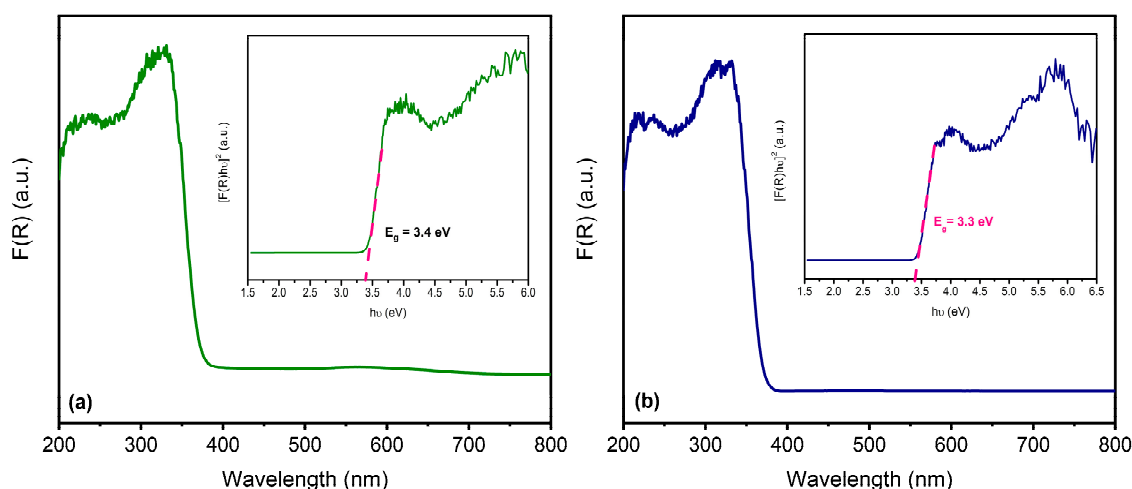
**Table 1.** Structural parameters of precursor and synthesized TiO<sub>2</sub> NPs.

| Powder                         | d-Spacing <sub>(101)</sub><br>(nm) | Crystallite Size<br>(nm) | Crystallinity<br>(%) | Dislocation<br>Density (nm) <sup>−2</sup> |
|--------------------------------|------------------------------------|--------------------------|----------------------|-------------------------------------------|
| Precursor                      | 0.3515                             | 54.12                    | 77.07                | $3.4141 \times 10^{-4}$                   |
| TiO <sub>2</sub> (synthesized) | 0.3522                             | 49.98                    | 88.01                | $4.0032 \times 10^{-4}$                   |

### 3.1.2. UV-Vis Spectroscopy

Figure 3 shows the UV-Vis spectrum of (a) precursor TiO<sub>2</sub> NPs (green line) and (b) TiO<sub>2</sub> NPs (blue line). As observed, the TiO<sub>2</sub> NP powders reveal a broad absorbance starting from 380 nm, making it a promising candidate for use as a photocatalyst in sunlight [18]. Additionally, the figure also shows the plotting  $[F(R)h\nu]^2$  vs  $(h\nu)$ , where the intersection of the dotted line with the x-axis gives the  $E_g$  value of 3.4 eV and 3.3 eV, respectively. A lower bandgap energy generally enhances the material's ability to absorb visible light, thereby increasing its efficiency in sunlight photocatalytic reactions. The small difference in

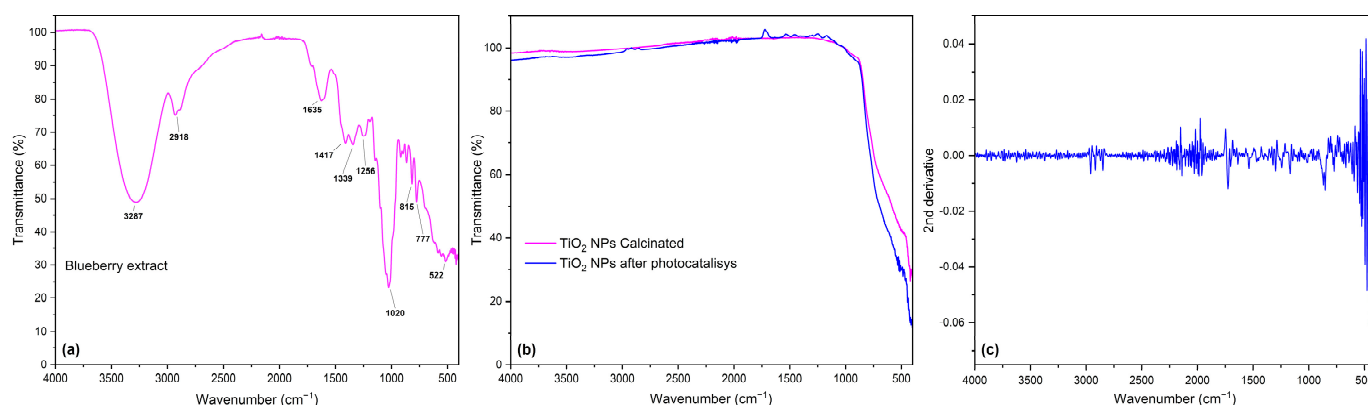
bandgap energies suggests that the synthesized TiO<sub>2</sub> NPs might have slightly improved photocatalytic properties compared to their precursor [23].



**Figure 3.** (a) UV-Vis spectra of precursor TiO<sub>2</sub> NPs, and (b) TiO<sub>2</sub> NPs. The inset of the figure shows the energy band gap plot.

### 3.1.3. FTIR Analysis

Figure 4a shows the IR spectrum of the blueberry extract, which was used as a precursor in the synthesis of TiO<sub>2</sub> NPs. As can be observed, the blueberry extract contains various functional groups, indicating the presence of polyphenols (including anthocyanins), flavonoids, organic acids, and carbohydrates. Key peaks include 3287 cm<sup>−1</sup> (O-H stretching, hydroxyl groups in polyphenols), 2918 cm<sup>−1</sup> (C-H stretching, CH<sub>2</sub> and CH<sub>3</sub> groups in fatty acids and sugars), 1635 cm<sup>−1</sup> (usually attributed to C=O stretching vibrations, indicative of flavonoids or other carbonyl-containing compounds), 1256 cm<sup>−1</sup> (C-O stretching, esters, or phenolic groups), 1020 cm<sup>−1</sup> (C-O and C-C stretching; this could be related to polysaccharides and alcohols), and 815 and 777 cm<sup>−1</sup> (aromatic C-H bending, aromatic rings) [24]. This fingerprint aligns with the known chemical composition of blueberries, highlighting their rich array of beneficial compounds. These peaks decrease in intensity in the FTIR spectrum of greener TiO<sub>2</sub> NPs, suggesting their involvement in TiO<sub>2</sub> NP formation [25].



**Figure 4.** FTIR spectra of the blueberry extract (a) and FTIR spectra (b) and second derivative (c) of TiO<sub>2</sub> NPs.

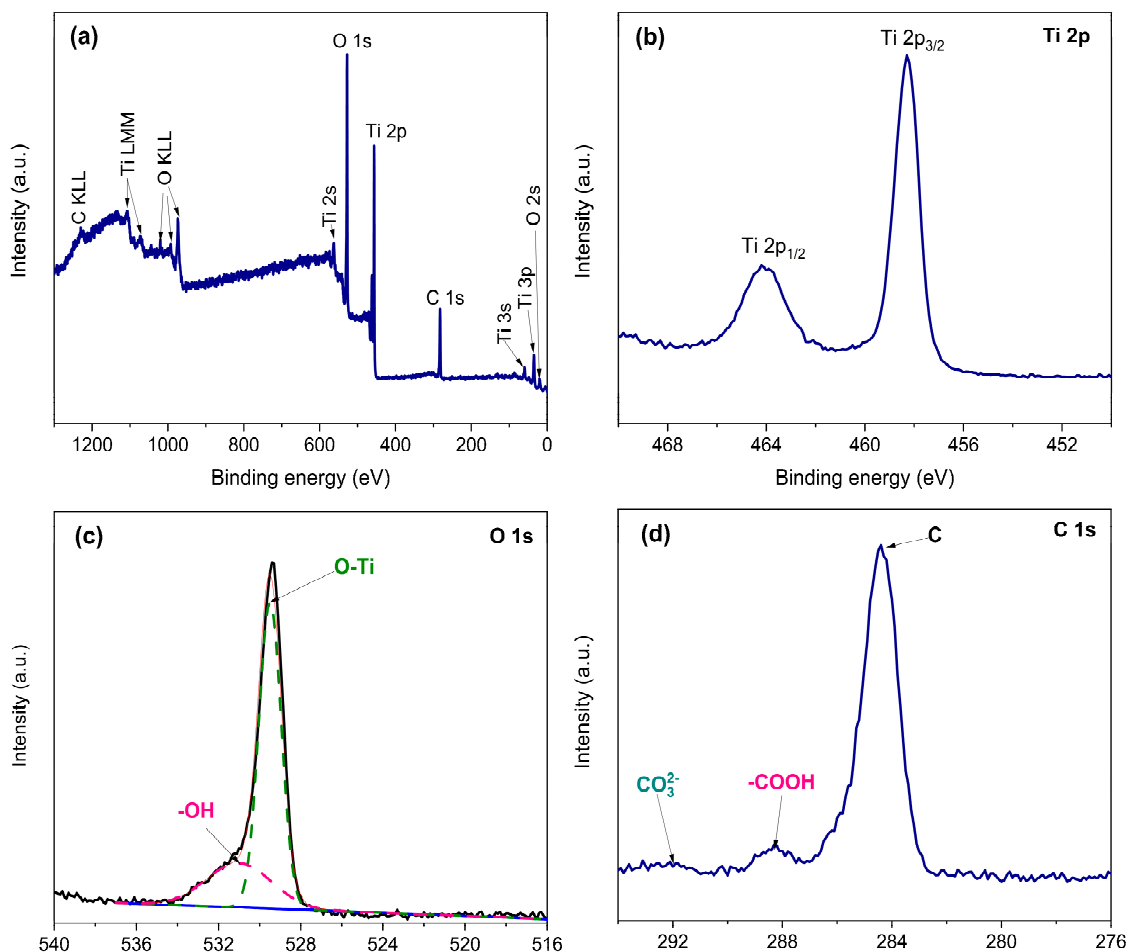
The blueberry extract contains polyphenols and flavonoids, which reduce and stabilize TiO<sub>2</sub> NPs, avoiding aggregation and managing their size and structure [4,12]. This stabilization is crucial for maintaining consistent particle size and increasing photocatalytic activity. Moreover, the extract's functional groups, such as carboxyl and hydroxyl, can functionalize TiO<sub>2</sub> NP surfaces, increasing their photocatalytic activity [15]. Using blueberry extract is consistent with ecologically friendly practices. Employing less hazardous substances produces more biocompatible TiO<sub>2</sub> NPs, making them suitable for environmental applications.

Additionally, the FTIR spectra of the TiO<sub>2</sub> NPs, before and after being used as a photocatalyst, were also obtained (Figure 4b). Both spectrums show similarities, particularly stretching vibrations observed below 1000 cm<sup>-1</sup>, related to Ti-O and Ti-O-Ti [26]. This indicates that no changes occurred in the crystalline structure of TiO<sub>2</sub> (anatase) after being used as a photocatalyst. It is also relevant that no bands associated with organic matter from the synthesis process were detected. Regarding the second derivative spectrum after the photocatalytic reaction (Figure 4c) of TiO<sub>2</sub> NPs, other chemical groups between 1500–1000 cm<sup>-1</sup> are highlighted, particularly the presence of CH<sub>2</sub> and CH<sub>3</sub> groups. However, the presence of these bands can also be associated with C-O stretching vibrations. In both cases, the chemical species described above can be related to fragments (moiety) of the MG dye molecule produced during its photodegradation [27].

These results reveal the effectiveness of the TiO<sub>2</sub> NPs produced by this green synthesis method in photodegrading the MG dye, suggesting their potential in environmental applications.

#### 3.1.4. XPS Analysis

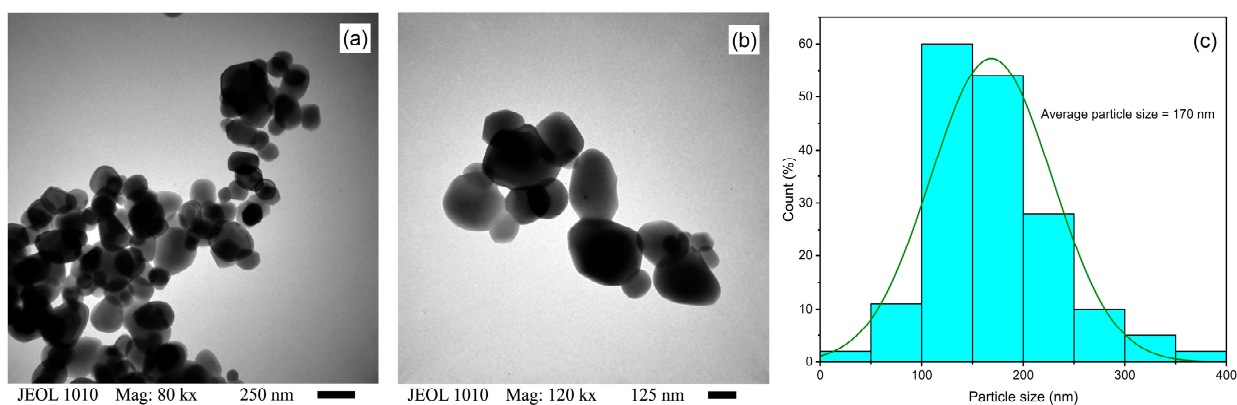
Figure 5a shows the XPS survey scan core levels of the synthesized TiO<sub>2</sub> powders after being calcined and of C 1s used as a reference. The latter was used as a reference to calibrate all binding energy positions. Figure 5b shows the Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> peaks centered at 458.3 and 464.1 eV, respectively. These binding energies confirm the presence of Ti<sup>4+</sup> in the TiO<sub>2</sub> NPs [28]. The O 1s XPS spectrum was deconvoluted into two Gaussians (Figure 5c). The Gaussian centered at around 530 eV was attributed to oxygen atoms bonded to titanium (O-Ti), while the second, centered at approximately 532 eV, was related to surface hydroxyl groups (-OH) [28]. The presence of -OH is usually related to the formation of defects on the TiO<sub>2</sub> surface, particularly oxygen vacancies [29,30]. However, the -OH can contribute to the photocatalytic activity of titanium dioxide because it promotes the formation of OH• [31]. The C 1s (Figure 5d) was also deconvoluted, obtaining three peaks. The main peak, at around 284.8 eV, was attributed to the adhesive used to fix the samples during XPS analysis. The peak at approximately 288 eV was attributed to carbon atoms in carboxyl groups (-COOH). The lower intensity peak located at 290 eV can be associated with forming carbonate species (CO<sub>3</sub><sup>2-</sup>) [28] on the surface of TiO<sub>2</sub> NPs. The presence of carbonate and carboxyl groups on the surface of the material is related to two factors: the adsorption of atmospheric CO<sub>2</sub> on the TiO<sub>2</sub> NP surface [32] and the thermal decomposition process of the precursors produced during the calcination of the powders. Nevertheless, both chemical species described above (-OH and -COOH) can contribute to the photocatalytic performance of the synthesized titanium dioxide. The -OH can serve as active sites for catalysis, while carboxyl groups may enhance the dispersion and stability of TiO<sub>2</sub> NPs in aqueous media [33,34].



**Figure 5.** Survey scan (a) and narrow scan of (b) Ti 2p, (c) O 1s, and (d) C 1s recorded from TiO<sub>2</sub> NPs.

### 3.1.5. TEM Analysis

The TEM images of the TiO<sub>2</sub> NP are depicted in Figure 6a,b. As can be observed, the images reveal a homogeneous formation of particles with pseudo-spherical geometry. This type of morphology can be associated with the green synthesis method used in this work, where thermal treatments contribute to obtaining this morphology [35,36]. Additionally, the size distribution of the TiO<sub>2</sub> NPs was obtained, as shown in Figure 6c. Their sizes were in the range of 100 to 250 nm. The average particle size was 170 nm. However, there were fewer particles below 100 nm.



**Figure 6.** TEM micrographs of TiO<sub>2</sub> at (a) 80,000 and (b) 120,000 magnifications. (c) Particle size distribution.

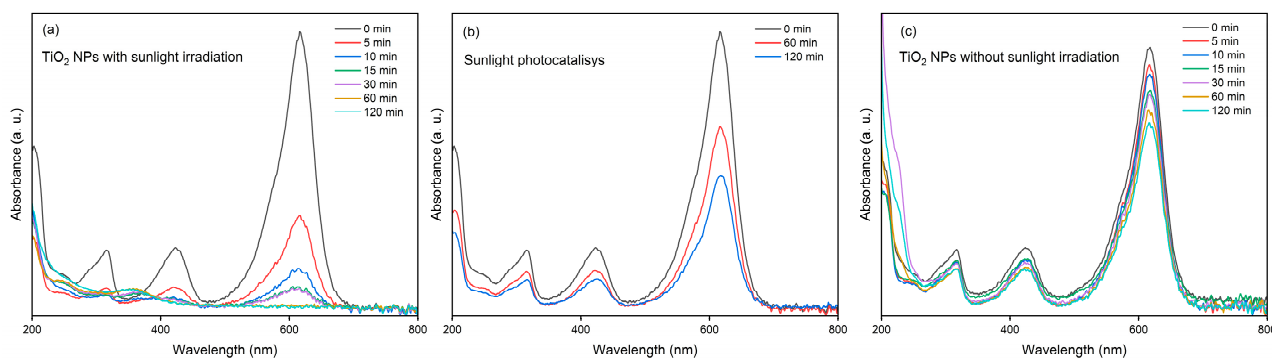
TiO<sub>2</sub> NPs with similar morphology have already been used as photocatalysts, reaching photocatalytic efficiencies greater than 60%, as described in Table 2. In photodegradation processes, the particle size of the photocatalysts can contribute to their photocatalytic activity, making the degradation process more efficient. This is because the separation of the charge carriers (h<sup>+</sup>, e<sup>−</sup>) occurs in a shorter time, contributing to the formation of reactive oxygen species (ROS) [37].

**Table 2.** Photocatalytic degradation of malachite green using TiO<sub>2</sub> NPs.

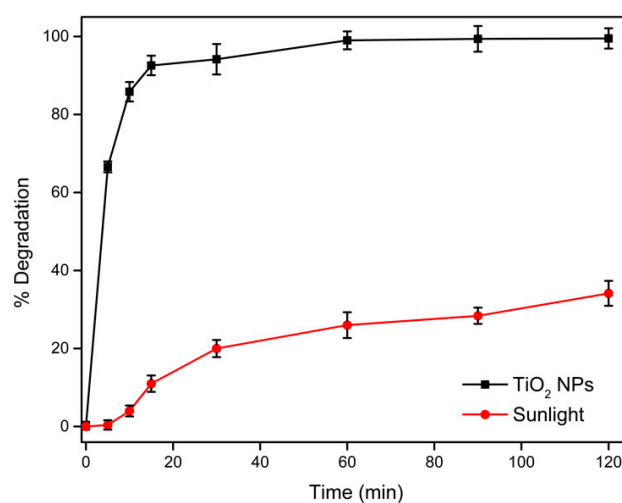
| Nanoparticle                       | Precursor                                                                                                                            | Synthesis Method                      | Shape/Size                   | Nanoparticle/<br>Dye Proportion                                                 | Conditions                                 | Degradation<br>Efficiency/Time      | Reference  |               |
|------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------|------------------------------|---------------------------------------------------------------------------------|--------------------------------------------|-------------------------------------|------------|---------------|
| TiO <sub>2</sub>                   | Titanium Hydroxide                                                                                                                   | Green synthesis                       | Spherical/<br>25–191 nm      | 80 µg/mL/<br>$1.098 \times 10^{-4}$ M                                           | Visible light                              | 83.48–86.28%/2 h<br>56.42%/24 h     | [36]       |               |
|                                    | TiO <sub>2</sub> P-25                                                                                                                | Directly added to the reaction system | Spherical/<br>20–30 nm       | 0.5 mg/mL/<br>$1.37 \times 10^{-4}$ M                                           | 15 W UV-365 nm irradiation                 | ~99%/4 h                            | [38]       |               |
|                                    |                                                                                                                                      |                                       | Spherical                    | 1.0 mg/mL/<br>$5.0 \times 10^{-4}$ M                                            | 18 W UV (330–400 nm) under oxic conditions | ~99%/1 h                            | [39]       |               |
|                                    | Titanium n-butoxide                                                                                                                  | TiO <sub>2</sub> , and NiO as dopant  | Hydrothermal                 | Spherical/<br>~600 nm                                                           | 0.8 mg/mL/<br>$1.0 \times 10^{-5}$ M       | UV irradiation (set at 175 W).      | ~99%/2 h   | [10]          |
| Ni-TiO <sub>2</sub>                | Spherical                                                                                                                            |                                       |                              | 1.2 mg/mL/<br>$6.86 \times 10^{-4}$ M                                           | Sunlight                                   | [40]                                |            |               |
| Co <sup>2+</sup> -TiO <sub>2</sub> | Titanium Isopropoxide and Co(NO <sub>3</sub> ) <sub>2</sub> , as dopant                                                              |                                       |                              | Spherical/<br>8–11 nm                                                           | 50 mg/mL/<br>$1.37 \times 10^{-4}$ M       | UV light                            | 61.16%     | 180 min       |
|                                    |                                                                                                                                      |                                       |                              | Visible light                                                                   | 74.32%                                     |                                     |            |               |
|                                    |                                                                                                                                      |                                       |                              |                                                                                 | Sunlight                                   | 82.30%                              |            |               |
| Fe-TiO <sub>2</sub>                | Titanium Isopropoxide and Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O, as dopant                                            |                                       | Spherical                    | 0.3 and 7%, iron doping levels in TiO <sub>2</sub> /<br>$1.37 \times 10^{-5}$ M | UV light                                   | ~76%/110 min                        | [41]       |               |
|                                    |                                                                                                                                      |                                       |                              |                                                                                 |                                            |                                     |            | Visible light |
| N/Na/Fe-TiO <sub>2</sub>           | Titanium Isopropoxide and NaNO <sub>3</sub> , NH <sub>4</sub> NO <sub>3</sub> , and FeCl <sub>3</sub> ·6H <sub>2</sub> O, as dopants | Hydrothermal-green synthesis          | Spherical/<br>6–16 nm        | 2.0 mg/mL/<br>$1.37 \times 10^{-1}$ M                                           | Visible light                              | 96.57%/25.83 min                    | [8]        |               |
| TiO <sub>2</sub>                   | Food-grade TiO <sub>2</sub>                                                                                                          | Green synthesis                       | Spherical/<br>average 170 nm | 250 µg/mL/<br>$1.0 \times 10^{-4}$ M                                            | Sunlight                                   | ~94%/30 min, and 100% within 60 min | This study |               |

### 3.2. Evaluation of Photocatalytic Activity of TiO<sub>2</sub> NPs in Malachite Green Dye Degradation

Figure 7a shows the UV-Vis absorbance spectra of the aliquots of the MG dye solution containing TiO<sub>2</sub> NPs after exposure to sunlight irradiation. The degradation percentage was calculated at 617 nm as a reference. As the exposure time increases in the presence of TiO<sub>2</sub> NPs, the intensity of the characteristic absorption peak diminishes. In the first 30 min, 94% degradation of the dye was achieved. After 60 min, the degradation increased to 100% (Figure 8). Additionally, the contribution of sunlight in the photodegradation process of the MG dye was evaluated. Thus, a solution of this dye without TiO<sub>2</sub> NPs was used. Figure 7b shows the absorbance spectra of the aliquots extracted from this solution at different time intervals. The degradation percentage was determined after 180 min, being 34% (Figure 8). Based on the results, it is inferred that sunlight contributes to the photodegradation process of the MG dye, which is negligible.



**Figure 7.** UV-Vis absorbance spectrum of malachite green dye solution with (a) and without (b)  $\text{TiO}_2$  NPs after exposure to sunlight irradiation and (c) with  $\text{TiO}_2$  NPs in absence of sunlight.



**Figure 8.** Percentage degradation of malachite green dye with and without  $\text{TiO}_2$  NPs under sunlight irradiation.

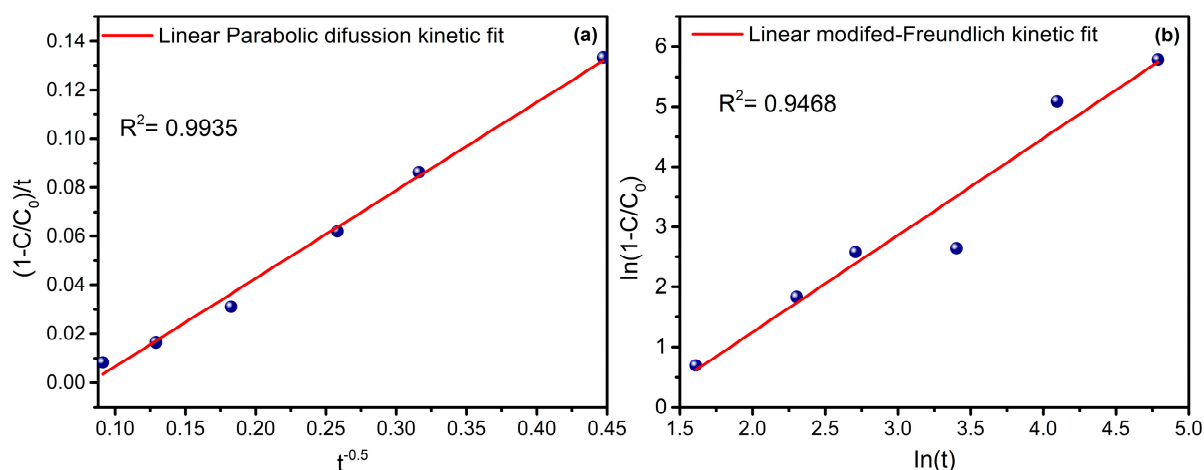
Derived from the absorption spectra, it suggests that the degradation of this dye occurs due to the cleavage of C-N bonds within the molecule of MG dye. The proposed mechanism for the photocatalytic degradation of MG by  $\text{TiO}_2$  NPs involves several sequential and concurrent processes. Amigun et al. [8] suggested that during the photocatalytic degradation of MG, several reactions took place, including hydroxylation, demethylation, oxidation, deamination, and the disruption of the benzene ring structure due to cleavage. The photodegradation mechanism supported the proposed pathway previously studied by Ju et al. [37]. Initially, MG undergoes N-demethylation, producing intermediates. Simultaneously, the  $\text{OH}^\bullet$  generated in the system added to the MG molecule, forming hydroxylated products. Additionally, the central carbon atom of the MG structure undergoes cleavage, leading to the breakdown of the conjugated chromophore structure. This is followed by the removal of benzene rings and the opening of phenyl rings [27].

In contrast, the spectrum depicted in Figure 7c shows minimal changes in absorbance over time when the MG dye is exposed to  $\text{TiO}_2$  NPs without sunlight irradiation. This result stresses the importance of sunlight in activating the photocatalytic properties of  $\text{TiO}_2$  NPs for effective MG dye breaking down. Without direct sunlight irradiation, the  $\text{TiO}_2$  NPs do not generate the necessary ROS, and as a result, there is little to no degradation of the dye. The slight decrease in absorbance observed might be attributed to the adsorption of the dye molecules onto the surface of the  $\text{TiO}_2$  NPs rather than actual degradation. Adsorption occurs when the dye molecules interact with the surface of the  $\text{TiO}_2$  NPs, leading to a reduction in the concentration of free dye in the solution, but this effect is minimal compared to the degradation achieved with sunlight [16]. The comparison in

Figure 7 between (b) and (c) illustrates that while sunlight alone can cause some degree of photodegradation, the presence of TiO<sub>2</sub> NPs greatly amplifies this effect. TiO<sub>2</sub> NPs show minimal activity without sunlight, indicating that their photocatalytic properties largely depend on light-induced activation.

To compare the degradation capability achieved with the TiO<sub>2</sub> NPs synthesized in this work, Table 2 shows some of the photocatalytic efficiencies of TiO<sub>2</sub> NPs synthesized by various methods used to degrade the MG dye. Based on Table 2, it is observed that metal-doped variants like Ni-TiO<sub>2</sub> and Co<sup>2+</sup>-TiO<sub>2</sub> NPs show degradation efficiencies from approximately 61.16% to 82.30% over 180 min under sunlight. With the TiO<sub>2</sub> NPs synthesized in this work, degradation of more than 94% in 30 min using sunlight was obtained. This photocatalytic efficiency is higher than that achieved with many TiO<sub>2</sub> NPs shown in Table 2. Furthermore, the TiO<sub>2</sub> NPs obtained are easy to synthesize and non-toxic and do not use precursors that harm health or the environment.

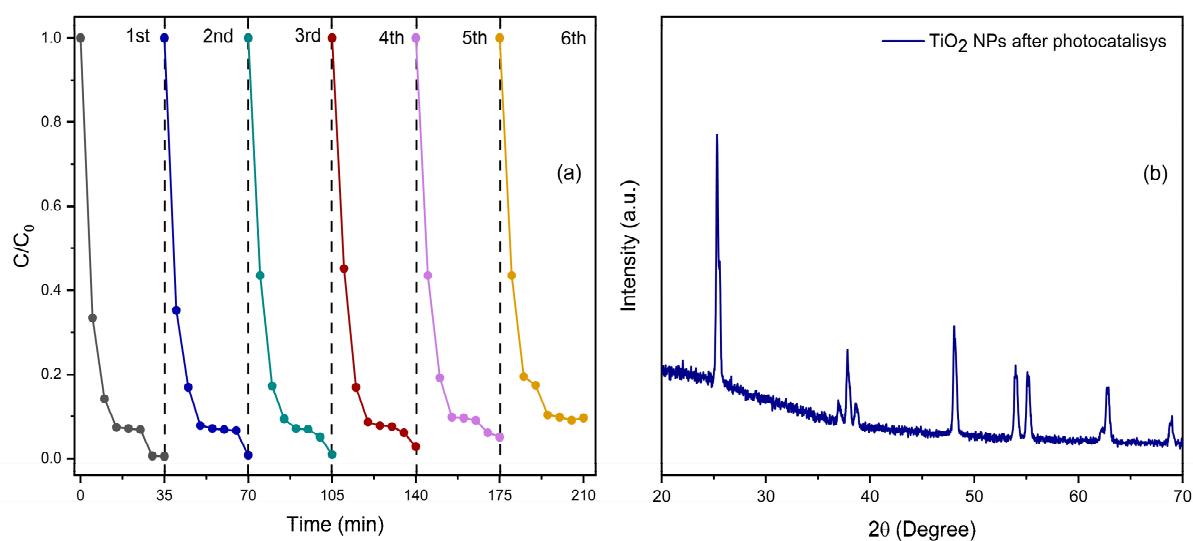
Additionally, a kinetic model that supports the photodegradation process of the MG dye was proposed. Zero-order, pseudo-first-order, modified-Freundlich, and parabolic diffusion kinetics were considered. After using the kinetic models proposed above, a linear fit was applied to the data obtained from each. The coefficients of determination ( $R^2$ ) were 0.2801, 0.8298, 0.9468, and 0.9935, respectively. Based on the  $R^2$  values, it is evident that the kinetic models that best adjusted to the photodegradation process of MG dye were parabolic diffusion and modified-Freundlich, as shown in Figure 9. In these kinetic models, electron transfer is controlled by the diffusion and adsorption of the dye molecules from the solution to the active sites of the photocatalyst.



**Figure 9.** Linear fit corresponds to the (a) parabolic diffusion, and (b) modified-Freundlich kinetics using 5 mg of TiO<sub>2</sub> NPs.

### 3.3. Reusability Test

To warrant the reusability of the photocatalyst, minimizing costs while still achieving long-lasting and efficient photocatalytic outcomes in removing dye pollutants is essential. Figure 10a shows the reusability test of TiO<sub>2</sub> NPs. As observed, the degradation efficiency remains relatively high across all cycles. However, there is a noticeable increase in the time required to achieve the same reduction in dye concentration as the cycles progress. The analysis reveals that, while the TiO<sub>2</sub> NPs maintain high degradation efficiency (around 99%) for the first two cycles, there is a noteworthy decrease in efficiency, dropping to around 80% by the fifth and sixth cycles. The reduction in photocatalytic activity may be influenced by the absorption of moieties from the MG dye molecule, which can decrease the formation of active sites [42]. The corresponding XRD patterns were registered to investigate the structure of TiO<sub>2</sub> NPs after the photocatalytic reaction cycles (Figure 10b). Secondary phases in the material bulk were not observed. This indicates that its crystalline structure does not alter even when utilized as a photocatalyst.

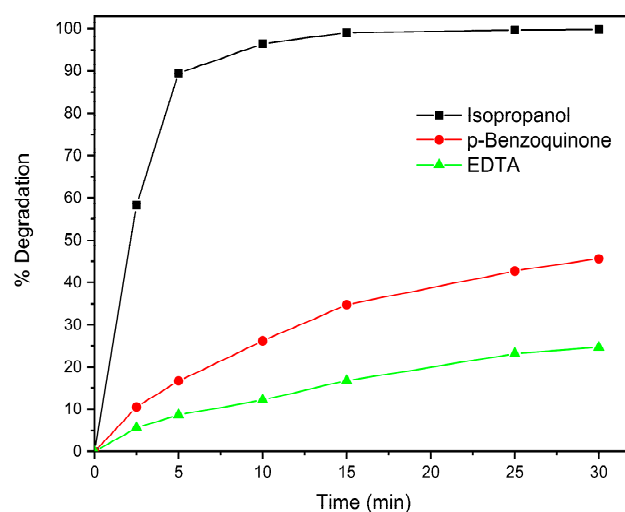


**Figure 10.** (a) Cycling test of photocatalytic degradation under sunlight irradiation of malachite green aqueous solution in presence of TiO<sub>2</sub> NPs and (b) diffraction pattern of TiO<sub>2</sub> NPs after being used as photocatalysts.

### 3.4. Scavenger Test

To assess the contribution of the key ROS involved in the photodegradation of MG dye, disodium ethylenediamine tetraacetic acid (EDTA), isopropyl alcohol, and p-benzoquinone were selected as scavengers of  $h^+$ ,  $OH^\bullet$ , and  $O_2^-$ , respectively. In this experimental setup,  $5 \times 10^{-3}$  M of each scavenger was added to three 20 mL MG dye solutions, each containing 5 mg of TiO<sub>2</sub> NPs as the photocatalyst. Other conditions were consistent with the above photocatalytic experiments.

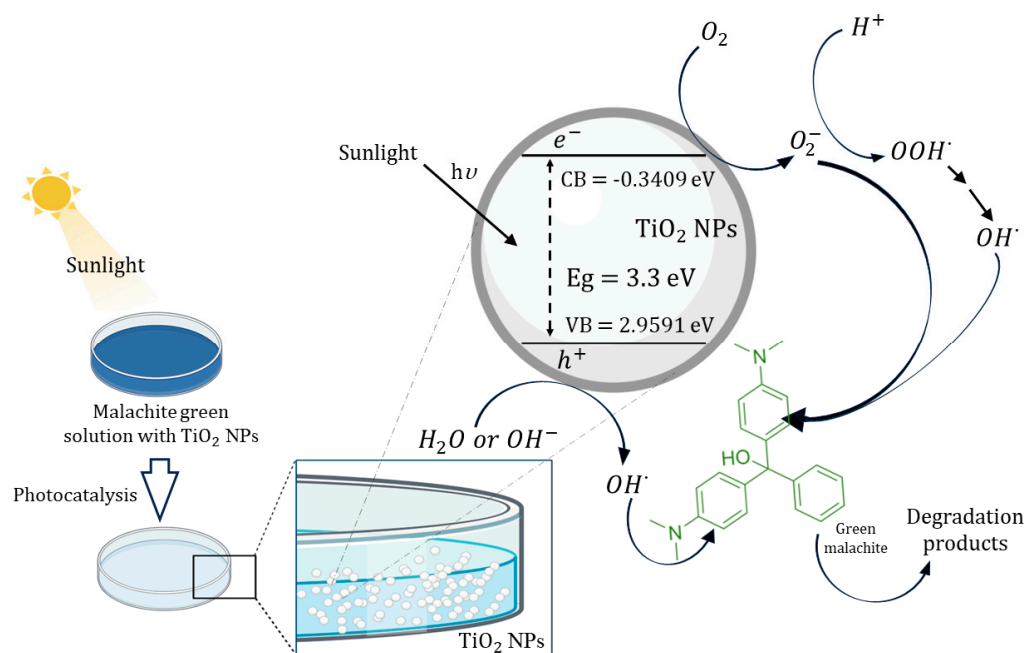
Figure 11 shows the graphical results of this test. As observed, the main ROS involved in the photodegradation process were  $h^+$  and  $OH^\bullet$ , and the least involved was  $O_2^-$ .



**Figure 11.** Assessment of scavengers' effect on the sunlight-induced photodegradation of MG dye, utilizing TiO<sub>2</sub> NPs as the photocatalyst.

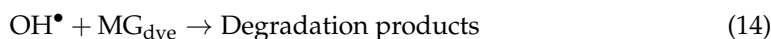
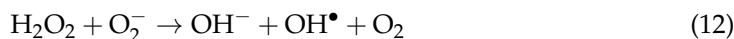
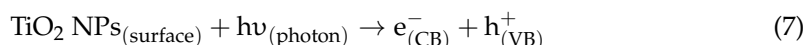
### 3.5. Mechanism of Photodegradation

Based on the results obtained from the tests with scavengers, a mechanism for the photodegradation of the MG dye was proposed (Figure 12). This mechanism involves several steps and is based on generating an  $e^-/h^+$  pair upon exposure to sunlight irradiation, which causes the generation of ROS [10,38].



**Figure 12.** The photocatalytic degradation process of the MG dye using TiO<sub>2</sub> NPs as the photocatalyst when exposed to solar irradiation.

The proposed mechanism is discussed in detail as follows: When TiO<sub>2</sub> NPs are exposed to photons with energy equal to or greater than their bandgap, electrons (e<sup>−</sup>) are excited from the valence band (VB) to the conduction band (CB) (Equation (7)). The photoexcited electrons in the CB can react with oxygen molecules adsorbed on the surface of the TiO<sub>2</sub> NPs, forming O<sub>2</sub><sup>−</sup> (Equation (8)). In turn, this radical promotes the formation of other ROS, particularly hydroperoxyl (OOH•) and OH• (Equations (9) and (10)). On the other hand, the h<sup>+</sup> in the valence band reacts with the water molecule (H<sub>2</sub>O) and -OH, forming OH• (Equations (9) and (13)). The generated OH• are highly reactive and can attack the MG dye molecules, breaking down their chemical bonds into degradation products (Equation (14)).



In order to clarify the photodegradation mechanism shown in Figure 12, the VB and CB potentials of TiO<sub>2</sub> NPs were obtained. For this, the following empirical equations were used:

$$E_{\text{CB}} = X - E_e - 0.5E_g \quad (15)$$

$$E_{\text{VB}} = E_{\text{CB}} + E_g \quad (16)$$

where  $E_{\text{CB}}$  and  $E_{\text{VB}}$  correspond to the potential values of the VB and CB, respectively. Also,  $X$  and  $E_e$  represent the electronegativity of the compound and the energy of free electrons vs. hydrogen (4.5 eV), respectively.

To quantify the electronegativity of TiO<sub>2</sub>, the following equation was used:

$$X = \left[ \chi(A)^a \chi(B)^b \right]^{\frac{1}{a+b}} \quad (17)$$

where a and b represent the number of titanium and oxygen atoms in TiO<sub>2</sub>, respectively. The electronegativity values of each atom were obtained from those recorded in another study [43].

Finally, the obtained values for X, EVB, and ECB were 5.8091, 2.9591, and −0.3409 eV, respectively. Where a and b are the number of atoms in the compounds.

#### 4. Conclusions

The green synthesis of TiO<sub>2</sub> NPs proposed in this work using non-toxic food-grade TiO<sub>2</sub> and blueberry extract proved cost-effective and aligned with sustainable practices. The TiO<sub>2</sub> NPs obtained by this method were characterized by XRD, FTIR, XPS, and TEM, confirming the successful formation of the anatase phase with a pseudo-spherical morphology. These TiO<sub>2</sub> NPs demonstrated remarkable photocatalytic activity, achieving approximately 94% degradation of MG dye within 30 min under direct sunlight and complete degradation within 60 min. The high photocatalytic efficiency was attributed to the generation of ROS, particularly h<sup>+</sup> and OH<sup>•</sup>. No changes were observed in the crystalline structure of the material after being used as a photocatalyst.

Although various synthesis methods have been used to obtain TiO<sub>2</sub> NPs, the green method proposed in this work considerably improves the photocatalytic activity of TiO<sub>2</sub> NPs. It is also completely environmentally friendly and could be considered an alternative to improve the photocatalytic activity of other semiconductor oxides. This eco-friendly nature makes it especially appealing for medical and environmental applications, stating its potential as a long-term solution in many areas. However, challenges still exist, including controlling the size and shape of NPs, ensuring uniformity, and expanding manufacturing processes. It will be crucial to address these problems if green synthesis techniques are to be widely used in industrial settings and maintain their status as a practical and environmentally responsible choice for producing NPs.

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