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Eco-Friendly TiO2 Nanoparticles: Harnessing Aloe Vera for Superior Photocatalytic Degradation of Methylene Blue

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Eco-Friendly TiO_2 Nanoparticles: Harnessing *Aloe Vera* for Superior Photocatalytic Degradation of Methylene Blue

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Abstract: In recent years; the contamination of aquatic environments by organic chemicals has become an increasing concern. To effectively remove toxic pollutants and biologically resistant compounds; a combination of advanced technologies must complement conventional methods. Indeed; among environmental pollutants; dyes such as methylene blue (MB); congo red and crystal violet persist in the environment because they are difficult to biodegrade. Advanced oxidation processes (AOPs) are widely employed to treat various types of wastewaters; often in conjunction with biological treatments. Among these technologies; heterogeneous photocatalysis stands out as one of the most extensively studied; with Titanium dioxide being the most researched photocatalyst due to its high photoactivity. In this study; Titanium dioxide nanoparticles (NPs) were synthesized using both a green method; leveraging the natural properties of Aloe vera leaf extract; and a conventional approach. The resulting NPs were thoroughly characterized using XRD; TEM; and ζ-potential analysis. Their photocatalytic performance was assessed by measuring the degradation of MB under UV light. The TiO_2 NPs synthesized via the green method demonstrated a degradation efficiency of (50 ± 3) % after 180 minutes; significantly higher than the (16 ± 3)% achieved by NPs synthesized through the conventional route. Moreover; the reaction rate constant for the green-synthesized TiO_2 NPs was found to be approximately five times greater than that of the conventionally synthesized NPs. These results open new scenario in the pollution removing strategy research

Keywords: green titanium dioxide nanoparticles; green synthesis; photocatalytic effects; Methylene Blue

1. Introduction

In recent years, the aquatic environment has been found to be contaminated by organic chemicals such as industrial chemicals, pharmaceuticals and consumer products [1]. These substances are only partially removed through conventional physical and biological wastewater treatment, necessitating the use of additional technologies are necessary to eliminate toxic pollutants and biologically recalcitrant compounds [2]. For instance, synthetic dyes, such as congo red, toluidine blue, crystal violet and methylene blue, are difficult to biodegrade, so they remain in the environment [3]. Advanced oxidation processes (AOPs) are widely employed for treating various types of wastewaters, often in conjunction with biological treatments [4]. AOPs facilitate the in-situ generation of strong oxidants that enable the oxidation of organic compounds [5]. Different AOPs utilize different mechanisms for organic destruction and can be classified into ozone-based, UV-based,

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catalytic (cAOP), physical (pAOP) and electrochemical (eAOP) AOPs [6]. Heterogeneous photocatalysis is the one of the most investigated AOP [7,8]. It involves the creation of electron-hole pairs through the absorption of photons with energy equal to or greater than the semiconductor bandgap [9]. If electron-hole recombination does not occur, these charge carriers can induce redox reaction with adsorbed species on the semiconductor surface, producing radical species such as hydroxyl radical, superoxide radical anions, and other reactive oxygen species that facilitate the degradation of pollutants [10]. Among several semiconductors, titanium dioxide (TiO_2) is the most thoroughly investigated due to its properties, such as its chemical and thermal stability, high photoactivity, cost-effectiveness, and low toxicity [11]. TiO_2 occurs in nature in four polymorphisms: anatase, rutile, both with a tetragonal crystal structure, brookite, with an orthorhombic geometry, and TiO_2(B), the monoclinic phase of titanium dioxide [12]. Anatase and rutile are the most commonly occurred forms [13], finding numerous applications including photocatalysis. The photocatalytic activity of TiO_2 depends on several factors, including phase structure, crystallite size, specific surface area and pore structure [14]. Anatase exhibits considerably higher photocatalytic activity then rutile [15]. Several strategies can be employed to obtain nanoparticles (NPs) of TiO_2 [16], including sol-gel, hydrothermal, and solvothermal methods. For instance, Collazzo et al. used the hydrothermal method with titanium tetraisopropoxide (TTIP) as precursor in order to obtain TiO_2 nanopowders with a crystallite size ranging from 9 to 17 nm, depending on the synthesis conditions such as temperature and reaction time [17]. Li et al. prepared nano-TiO_2 powders by sol–gel method using tetra-n-butyl-titanate as precursor, investigating different synthesis parameters such as calcination temperature and pH value, to control the grain size and microstructure of nano-TiO_2 powders [18]. Xu et al. synthesized nano-TiO_2 from Tetrabutyl titanate (n-TBT) [19], obtaining NPs with a homogeneous microstructure and a size of around 10–15 nm through a sol–gel process mediated in reverse microemulsion combined with a solvent thermal technique. Sadek et al. used TTIP to prepare TiO_2 nanopowders with a crystal size of 49.3 nm through the sol-gel method [20]. Currently, the growing use of NPs in various applications has stimulated the development of more inexpensive and sustainable synthesis approach. In particular, green approach [21], based on the use of natural source materials, allows for the elimination or reduction of chemical reagents and the generation of hazardous substances [22]. The green synthesis can be carried out by means of the use of plants and their extracts as well as the microbes, although the former is considered more stable [23]. Several part of the plant, such as flowers, roots, seeds, and leaves can be employed to prepare plant extracts, though leaves are more commonly used. Leaves are rich in biomolecules such as proteins, amino acids, terpenoids, flavonoids, saponins. These molecules are key elements in the synthesis of nanoparticles because they act as a reducing agents and capping agents, as stabilizer and redox mediators. Santhoshkumar et al. prepared TiO_2 NPs using $TiO(OH)_2$ as precursor and the aqueous extract of *Psidium guajava* leaves [24]. Ahmad et al. synthesized spherical TiO_2 NPs ranging from 20 to 70 nm using TTIP and *Mentha arvensis* leaves extract as precursor and reducing agent, respectively [25]. Saini et Kumar achieved the green synthesis of TiO_2 NPs, with an average crystallite size of 15.02 nm, by mixing the *Tinospora cordifolia* leaves extract to the precursor, TTIP [26]. Rao et al. prepared TiO_2 NPs with an estimated average particle size of 32 nm by using Titanium Chloride ($TiCl_4$) and *Aloe Vera* leaf extract [27]. In this context TiO_2 NPs have been synthesized via both a green route using *Aloe Vera* leaves extract and a conventional route. The properties of the obtained NPs were characterized by different techniques, specifically Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and ζ-potential measurements. Moreover, the photocatalytic activity of NPs was evaluated by the degradation of methylene blue (MB) under UV light. MB was chosen because it is a popular cationic dye frequently used for dyeing (clothes, paper and leathers) and in the textile industry [3] and it is harmful to human health above a certain concentration [28]. Additionally, the effect of the calcination temperature for TiO_2 NPs synthesized by the green route was investigated.

2. Materials and Methods

2.1. Reagents

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Titanium (IV) isopropoxide (TTIP, 97%), ethanol absolute (≥99.8%), 2-propanol (≥99.8%), nitric acid (HNO_3 65%), ultrapure water (produced by Barnstead Smart2Pure water purification system Thermo Scientific), methylene blue hydrate.

2.2. Synthesis of TiO_2 NPs

2.2.1. Conventional route for Synthesis of TiO_2 NPs (TiO_2-Chem NPs)

TiO_2 NPs was synthesized following the method described in [29] by sol-gel route. 1 mL of TTIP was slowly added to 5 mL of 25% (v/v) ethanol aqueous solution. The mixture was kept under stirring for 60 min, then the pH was adjusted to 2-3 by adding nitric acid and it was kept under stirring for 60 min. Afterwards, the mixture was dried in an oven using two steps: 120 °C for 120 min and then at 270 °C for 24 h. Finally, the obtained TiO_2 NPs were ground with a mortar. In Figure 1 (on the left) the flow chart of the synthesis process is shown.

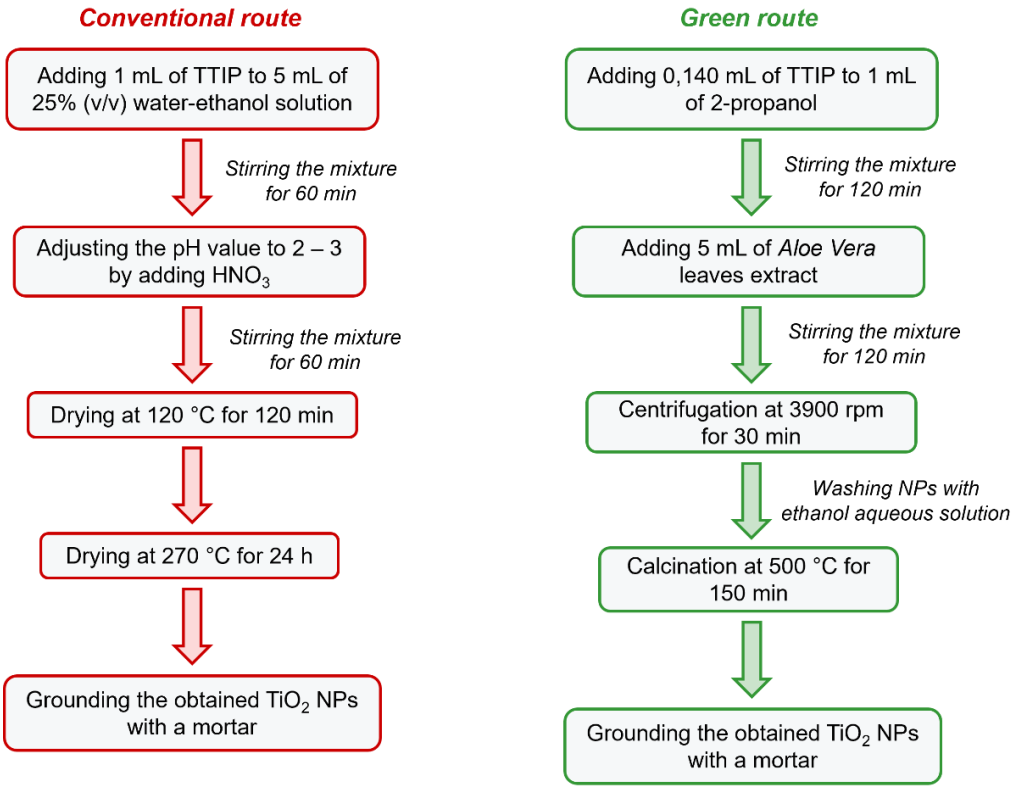

Figure 1. Flow charts concerning the synthesis of TiO_2 NPs: conventional route (on the left) and green route (on the right).

2.2.2. Green Synthesis of TiO_2 NPs (TiO_2-Green NPs)

Preparation of the Leaves Extract

Aloe vera leaves was separated from the gel and washed with ultrapure water. After drying at room temperature, they were cut into small pieces. Then, 25 g of leaves were transferred into a glass flask containing 250 mL of ultrapure water and the mixture was boiled at 100 °C for 20 min. After cooling, the mixture was filtered by Whatman filter.

Synthetic Procedure

0.140 mL of TTIP was slowly added to 1 mL of 2-propanol and the solution was kept under stirring for 120 min. Then, 5 mL of the *Aloe vera* leaves extract were slowly added to the solution and the obtained mixture was kept under stirring for 120 min. Afterwards, TiO_2 NPs were collected by centrifugation at 3900 rpm for 30 min. The collected NPs were washed 4-5 times with 50% (v/v) ethanol aqueous solution, then the TiO_2 NPs were calcined at 500 °C for 150 min. Lastly, the TiO_2 NPs were ground with a mortar. The flow chart the synthesis process is shown in Figure 1 (on the right).

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2.3. Characterization of TiO_2 NPs

2.3.1. Transmission Electron Microscopy (TEM) Analysis

TEM characterizations were performed by a JEOL JEM-1011 transmission electron microscope operating at 100 kV. For both synthesized TiO_2 NPs, samples were prepared by dropping a dilute suspension of TiO_2 NPs in ultrapure water on TEM grid and drying overnight at room temperature.

2.3.2. Zeta Potential Analysis

ζ-potential analysis was performed at 25 °C by Zetasizer Nano-ZS (Model ZEN3600, Malver Instruments Ltd., Malvern, UK) equipped with a HeNe laser working at 663 nm. Each suspension of TiO_2 NPs (0.4 mg/mL) in ultrapure water was prepared for the measurements.

2.3.3. X-Ray Diffraction (XRD) Analysis

X-ray diffraction analysis was performed in Bragg-Brentano reflection geometry using filtered Cu-Ka radiation. The X-ray diffraction data were collected at a scanning rate of 0.02 degrees per second in 2θ ranging from 20° to 80° by step scanning.

2.4. Assessment of Photocatalytic Activity

The photocatalytic activity of the synthesized TiO_2 NPs was evaluated by the degradation of MB in aqueous solution. With this aim, an UV irradiator (Figure 2), equipped with 2 UV lamps (8W, λ=365 nm) and a magnetic stirrer, was used. A suspension of the TiO_2 NPs with a concentration of 0.4 g/L was prepared in 5 mg/L methylene blue solution and it was homogenized by sonication for 60 s. The suspension was kept under stirring and under dark condition for 30 min to achieve the adsorption-desorption equilibrium, then it was exposed to UV light under stirring condition at a distance from the UV source of about 12.5 cm and samples were taken at different times: 0 min, 30 min, 60 min, 90 min, 120 min, 180 min. Afterwards, the collected samples were centrifuged in order to remove the nanoparticles and the absorption spectra of the samples were acquired by BioTek Synergy Mx multi-mode microplate reader. The absorption maximum at 664 nm was used in order to monitor the dye degradation over time.

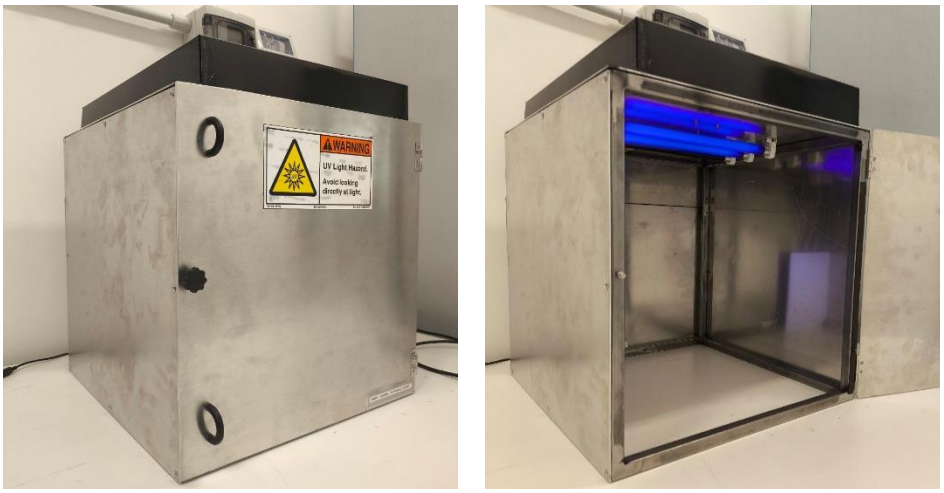

Figure 2. Pictures of the UV irradiator used for the photocatalysis experiments.

3. Results and Discussion

The findings of this study underscore the potential of green synthesis methods for TiO_2 NPs production in enhancing the efficiency of photocatalytic processes for environmental remediation. In particular we have focused on Methylene blue that is considered a potent pollutant due to several factors. Indeed, it is highly toxic to aquatic life, even at low concentrations, disrupting ecosystems by

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affecting the health and reproduction of various species [30]. Additionally, methylene blue is resistant to biodegradation, meaning it can persist in the environment for extended periods, leading to long-term contamination of water bodies [31]. It also absorbs strongly in the visible spectrum, which can block sunlight from penetrating the water, inhibiting photosynthesis in aquatic plants and algae, further disturbing the balance of aquatic ecosystems [3,32]. Moreover, methylene blue can enter the human food chain through contaminated water sources, posing health risks to humans and animals [33,34]. These characteristics make it a significant concern for environmental pollution. Titanium dioxide (TiO_2) nanoparticles are crucial in the photocatalysis of methylene blue due to their unique properties and effectiveness in breaking down organic pollutants [35,36]. TiO_2 exhibits exceptional photocatalytic activity when exposed to UV light. Its wide bandgap allows it to generate electron-hole pairs upon irradiation, which are essential for initiating the oxidation and reduction reactions necessary to degrade organic compounds like methylene blue [37,38]. Therefore, the synthetic processes required the use for toxic substances and time-consuming equipment's. Then, the development of environmentally friendly method to obtain TiO_2 NPs highly efficient is necessary in order to making it a safe option for treating wastewater without introducing additional harmful substances into the environment [21,39]. In our work we obtained TiO_2 NPs from a conventional route and green route using, in the last case *Aloe Vera* leaf extract. This plant is widely distributed in the Mediterranean region and is extensively used in the agricultural, biomedical, and cosmetic fields. In the latter case, in particular, the gel found in the leaves is a valuable material often used to produce skin and beauty lotions. On the other hand, the leaf epidermis, which is considered a waste product, contains high concentrations of vitamins, proteins, and polyphenols, and its extract can be used to produce TiO_2 NPs. The fito molecules enriched the extracts acting as reducing and capping agent [40,41]. Then, we proceed to achieve TiO_2 NPs from the two different routes described in the Materials section following the characterization of their physico-chemical properties. Firstly, we investigated about TEM analysis (Figure 3) showed that synthesized TiO_2 NPs showed an irregular shape as also reported in literature [42–44]. It was observed that the synthesized NPs had similar size. An average size of (12 ± 3) nm for the TiO_2-chem NPs and an average size of (12 ± 4) nm for the TiO_2-green NPs were estimated. However, aggregation phenomena were also observed, which were more evident in the case of TiO_2-green NPs probably due to the high concentration of organic compounds enriched the leaves extract.

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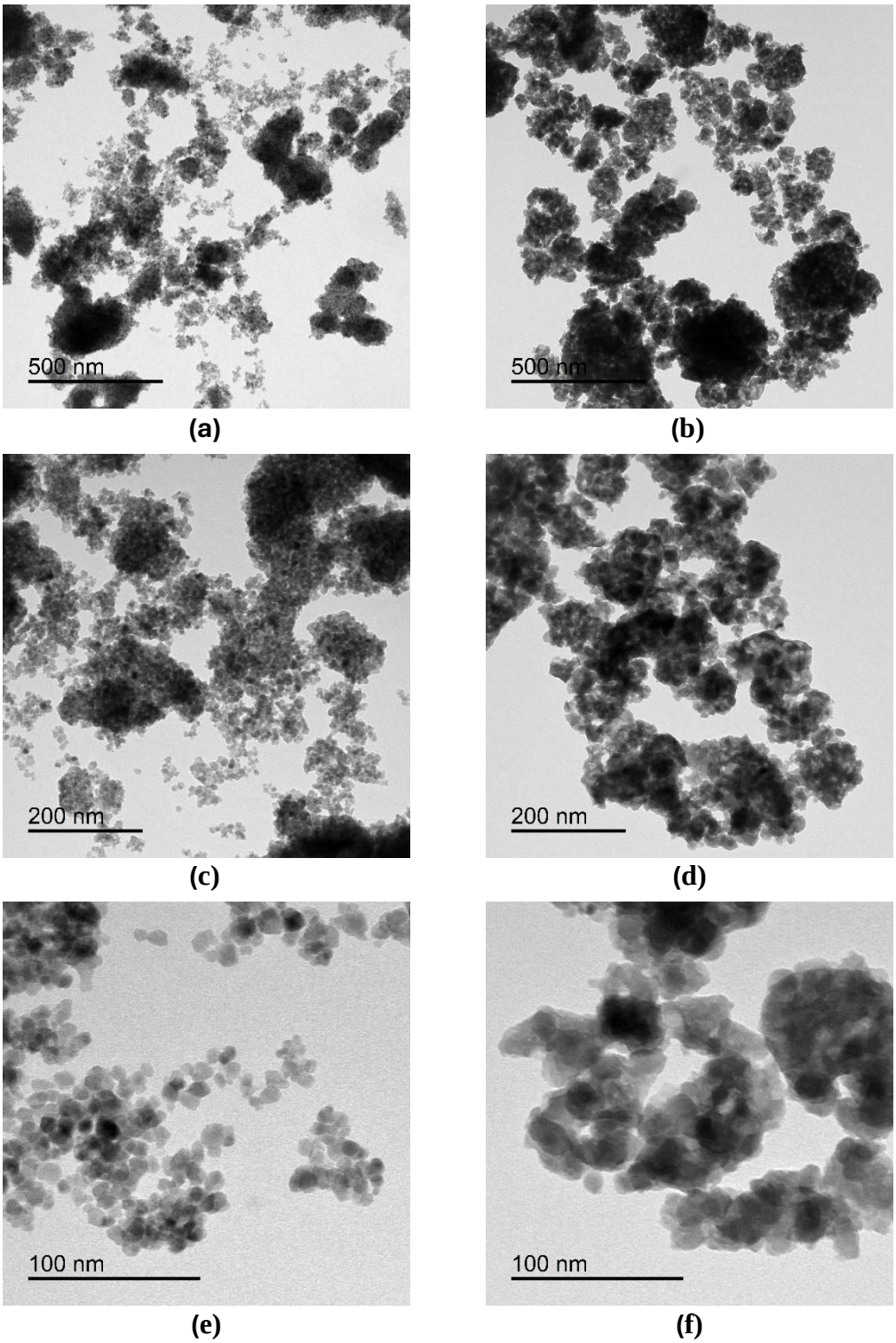

Figure 3. Representative TEM images of TiO_2-chem NPs on the left (a, c, e), TiO_2-green NPs on the right (b, d, f).

Both synthesized TiO_2 NPs showed a negative surface charge in ultrapure water at neutral pH. Z-potential values of (-18.2 ± 0.2) mV and (-28.4 ± 0.9) mV were observed for TiO_2-chem and TiO_2-green NPs, respectively. Therefore, adsorption of MB is expected to be favoured on the surface of the synthesized NPs, since MB is a cationic dye [45,46].

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The XRD pattern of the synthesized TiO_2 NPs (Figure 4) showed characteristic peaks of anatase for both TiO_2-chem and TiO_2-green NPs around the following 2θ values: 25.4° (101), 37.9° (004), 48.1°(200), 62.9°(204). Two small characteristic peaks of rutile phase, around 27.5° (110) and 36.2° (110) were observed only for the TiO_2-green NPs [47,48]. In addition, a small peak around 30.8° (121), that can be related to brookite phase [49], was also observed for both TiO_2 NPs. The anatase phase generally has higher photocatalytic performance than that of rutile due to a higher density of localized states and consequent surface-adsorbed hydroxyl radicals and lower recombination of photogenerated electrons and holes in anatase than in rutile [50].

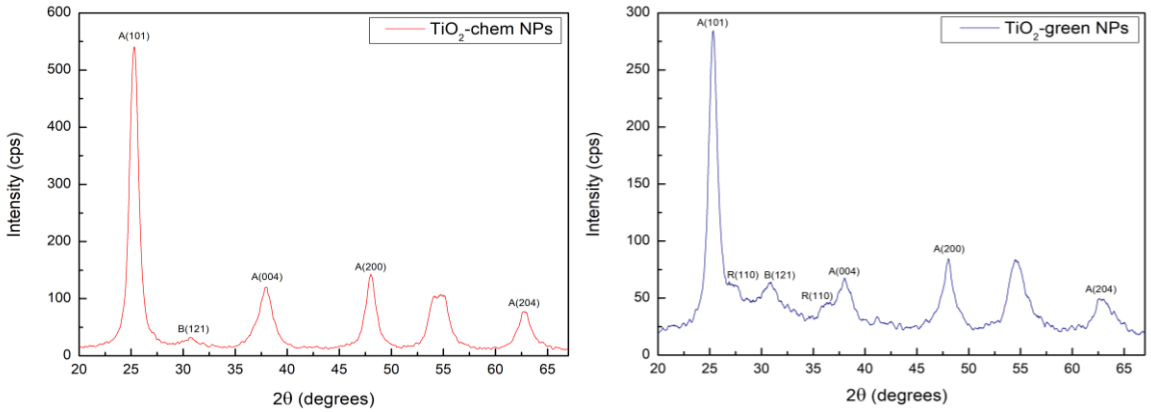

Figure 4. XRD pattern of TiO_2-chem NPs (on the left) and TiO_2-green NPs (on the right).

After the TiO_2 characterization, we perform the assessment of their photocatalytic activity. The photocatalytic activity of the synthesized TiO_2 NPs was evaluated by the degradation of MB in aqueous solution under UV light (Figure 5, upper image). As shown in lower image of Figure 5, it was found that the kinetics of the photocatalytic degradation follow a pseudo-first-order model (equation 1):

$$ln\left(\frac{C_t}{C_0}\right) = -k \cdot t$$

where C_t is the concentration of MB at time t, C_0 is the concentration of MB at time $t = 0$ and k is the reaction rate constant. The reaction rate constant for TiO_2-green NPs was about 5 times higher than that for TiO_2-chem NPs. As shown in Table 1, the reaction rate constants were 0.004 min^{-1} and 0.0008 min^{-1} for TiO_2-green and TiO_2-chem NPs, respectively. The degradation efficiency was calculated using the following equation 2:

$$Degradation\ efficiency(\%) = \left(\frac{C_0 - C_t}{C_0}\right) \cdot 100$$

where C_0 is the concentration of MB at time $t = 0$ and C_t is the concentration of MB at time t.

As shown in Table 1, the TiO_2-green NPs showed higher efficiency for MB degradation than the TiO_2-chem NPs. In fact, the degradation efficiency values obtained after 180 min were (50 ± 3) % and (16 ± 3) % for TiO_2-green and TiO_2-chem NPs, respectively.

The higher negative ζ-potential value of TiO_2-green NPs, compared with TiO_2-chem NPs, may suggests an improvement in the adsorption of cationic organic pollutants leading to an enhancement of photocatalytic efficiency [51]. Moreover, the small rutile content found for TiO_2-green NPs may indicate that the enhancement of the photocatalytic activity may also be due to charge transfer effects in mixed phase TiO_2 (anatase/rutile) that improve the charge separation of photogenerated carries [52,53].

Table 1. Degradation values after 180 min and reaction rate constants for TiO2 NPs synthesized by green route (TiO2-green NPs) and by conventional route (TiO2-chem NPs).

Catalyst	Degradation after 180 min	*K*
TiO_2-green NPs	(50 ± 3) %	0.004 min^{-1}
TiO_2-chem NPs	(16 ± 3) %	0.0008 min^{-1}

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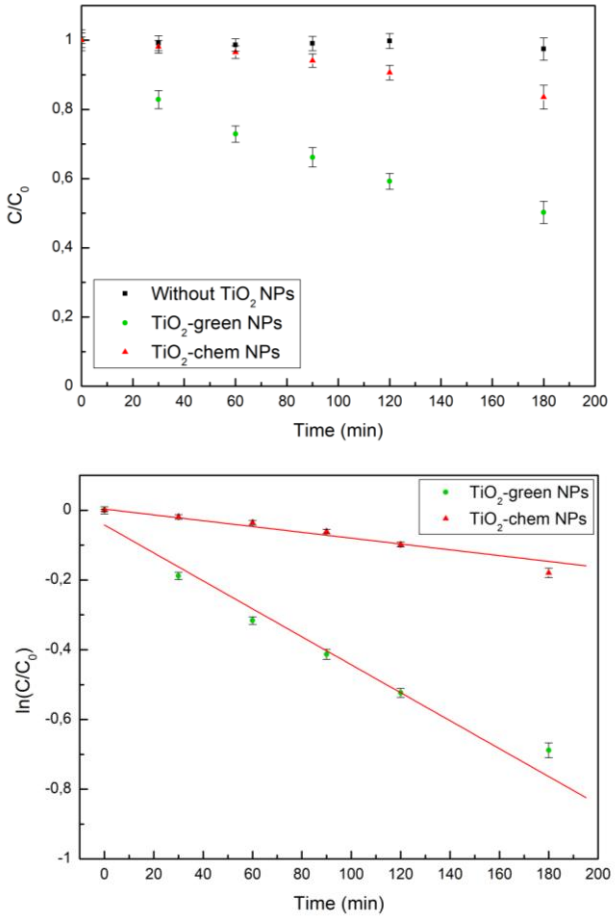

Figure 5. Photocatalytic degradation of MB as a function of time under UV light (upper image) and pseudo first-order kinetics (lower image). The slope of the fitted lines gave the values of the reaction rate constants: 0.004 min^{-1} (R^2= 0.97) for TiO_2-green NPs (green circles) and 0.0008 min^{-1} (R^2= 0.95) for TiO_2-chem NPs (red triangles).

The effect of calcination temperature on TiO_2-green NPs was also analyzed by the evaluation of the photocatalytic activity of the synthesized NPs. As shown in Figure 6, it was observed that the TiO_2-green NPs calcined at 500 °C showed higher degradation efficiency than the TiO_2 NPs calcined at 400° C. This can be due to the residual organic material on the surface of NPs calcined at 400 °C. The degradation efficiency values obtained after 180 min were (50 ± 3) % for the TiO_2 NPs calcined at 500 °C and (10 ± 4) % for the TiO_2 NPs calcined at 400 °C. A fine white powder was obtained by calcination process at 500 °C, whereas a gray powder with large grains was observed for TiO2 NPs calcined at 400° C, maybe due to residual carbon from organic compounds of the leaves extract. The excess of residual carbon material on the surface of NPs calcined at 400 °C can cover part of the photocatalyst, leading to an impediment of light access and reactants access to the photocatalyst surface [54], resulting in a decreased photocatalytic efficiency.

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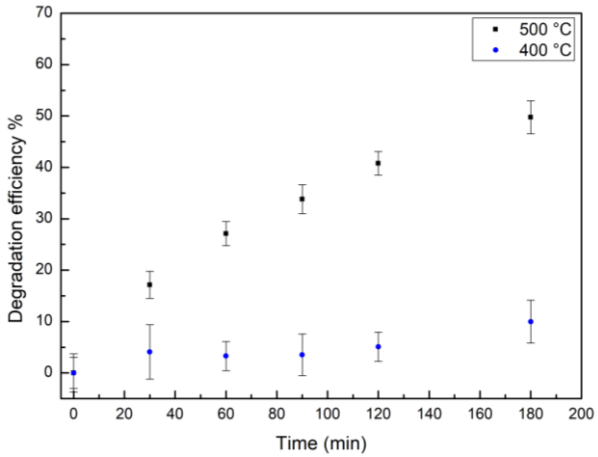

Figure 6. Photocatalytic degradation of MB under UV light: degradation efficiency as a function of time using TiO2-green NPs calcined at 500 °C (black squares) and calcined at 400 °C (blue circles).

4. Conclusions

In this work, TiO_2 NPs were synthesized, and their photocatalytic activity was evaluated by the degradation of MB in aqueous solution, under UV light. TiO_2 NPs were synthesized by means of two approaches using TTIP as precursor: a green route exploiting the properties of *Aloe vera* leaves extract and a conventional synthesis. Both types of TiO_2 NPs showed irregular shape and aggregation phenomena. The TiO_2-green NPs showed characteristic peaks of anatase phase, two small characteristic peaks of rutile phase and a small peak that can be related to brookite phase, whereas TiO_2-chem NPs showed only characteristic peaks of anatase phase and a small peak that can be related to brookite phase. ζ-potential analysis showed that both synthesized TiO_2 NPs had a negative surface charge with a higher negative value of TiO_2-green NPs compared with TiO_2-chem NPs. Concerning the evaluation of the photocatalytic activity by the degradation of MB in aqueous solution, the reaction rate constant for TiO_2-green NPs was about 5 times higher than that for TiO_2-chem NPs. In fact, the degradation efficiency values obtained after 180 min were (50 ± 3)% for TiO_2-green NPs and (16 ± 3)% for TiO_2-chem NPs. The high photocatalytic activity exhibited by TiO_2-green NPs compared with TiO_2-chem NPs may be due to a higher negative surface charge. This can improve the adsorption of cationic organic pollutants and may be due to charge transfer effects in mixed phase TiO_2 (anatase/rutile) that enhance the charge separation of photogenerated carries.

Data Availability Statement: The data presented in this study are available in this article.

Conflicts of Interest: There are no conflicts to declare.

Author Contributions: V.D.M and Mf.C Conceptualization, Methodology, Supervision, data analysis, editing draft of manuscript; A.D.L synthesized the nanomaterials, A.D.B and A.D.L. methodology, writing original manuscript; R.D.C. methodology and data analysis; M.C methodology; RR funding and supervision.

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