

Photocatalytic Degradation of Brilliant Green Dye using B-TiO₂ under Visible Light Irradiation

Phephile Ngwenya*, Fisseha A. Bezza, Shepherd M. Tichapondwa, Evans M. N. Chirwa

Water Utilisation and Environmental Engineering Division, Department of Chemical Engineering, University of Pretoria, Pretoria 0002.

u16252642@tuks.co.za

The presence of dyes in aquatic environments is a subject of concern owing to their significant toxicity and potential for bioaccumulation. Consequently, it is imperative to eliminate these dyes from wastewater treatment effluents prior to environmental discharge. This requirement aligns with Sustainable Development Goal (SDG) 6, targets 6.1, 6.3, and 6.6, as well as SDG 3, target 3.9. To date, variant advanced oxidation remediation techniques have been explored, with TiO₂ photocatalysis emerging as an efficient and sustainable option due to its strong oxidative capabilities. However, the dependence of the process on ultraviolet (UV) light irradiation constrains application due to the related energy demands. Overcoming all the inadequacies of pristine TiO₂, hydrogenated black TiO₂ (B-TiO₂) has a narrower bandgap of approximately 1.5 eV, augmented light absorption efficiency in the visible and infrared spectra, and consequently enhanced photocatalytic performance. Thus, the motivation of the present study was to successfully synthesize B-TiO₂ nanoparticles by the chemical reduction of TiO₂ using NaBH₄ during calcination. The success of the synthesis process was confirmed by X-ray diffraction patterns which showed crystal planes of the anatase and rutile TiO₂ phases in the synthesized nanoparticles, while scanning electron microscopy (SEM) imagery established the morphology to be near spherical. Energy-dispersive X-ray spectrometry (EDS) showed a variation in the Ti to oxygen ration indicating successful B-TiO₂ formation. The synthesized semiconductor photocatalyst had degradation efficiencies as high as 99% within a 30-minute visible light exposure at a pH of 5.8 and a catalyst loading of 0.1 g/L. Surmounting the performance of other TiO₂-based photocatalysts used for the photocatalytic degradation of BG under similar conditions. Therefore, substantiating the practicality of the catalyst for dye degradation under visible light irradiation.

1. Introduction

Industrial wastewater ranks among the principal contributors to environmental pollution. Given the substantial effluent volumes, its intricate composition, and the number of industries involved, wastewater treatment in this sector is thus regarded as a critical issue for environmental protection (Xu et al., 2020). The pollutants found in industrial wastewater encompass dyes, heavy metals, pesticides, herbicides, pharmaceuticals, personal care products (PPCPs), and other aromatic compounds (Rathi et al., 2021). These pollutants are predominantly toxic to both humans and the environment. Therefore, it is crucial to eliminate them from wastewater before the effluent is released into receiving water bodies.

In particular, brilliant green (BG) dye, commonly utilized in the textile, paper, leather, cosmetic, and other industries for producing coloured compounds, induces allergic reactions in the human body, causes eye irritation, and may even result in blindness (Romzi et al., 2020). Upon ingestion, it adversely affects the liver and kidneys, potentially leading to organ failure and further has the capacity to cause cancer, due to its toxic nature (Gul et al., 2023). Numerous researchers have emphasized the urgent need for the efficient and sustainable elimination of these contaminants from the environment to mitigate potential adverse effects on both human and ecological health.

The exclusive use of conventional wastewater treatment processes is insufficient to eliminate toxic compounds from textile dye wastewater, as indicated by the presence of pigmented water in the environment (Pan et al.,

2017). In contrast, advanced oxidation processes (AOPs) can achieve complete reduction and mineralization of contaminants, thereby being considered more feasible for oxidizing persistent organic pollutants into non-toxic products (Liu et al., 2020). Thus, these processes play a vital role in the treatment of water and wastewater. Among AOP treatment technologies, titanium dioxide (TiO₂) based photocatalysis has been extensively applied for the elimination of organic micropollutants due to its advantages of photostability, affordability, nontoxicity, and high pollutant removal efficiency (Bayan et al., 2021). Despite these advantages, TiO₂ has its limitations, notably the wide band gap (3.2 eV) of anatase-crystalline TiO₂, which restricts its photocatalytic activity to UV irradiation (Liu et al., 2024). This is significant given that UV light constitutes approximately 4% of the solar energy spectrum, whereas visible light, is more abundant, constituting approximately 46% (Arora et al., 2022). Moreover, TiO₂ exhibits low photo-quantum efficiency, resulting from the short diffusion length of photoinduced electron-hole pairs. Consequently, these characteristics significantly limit the application of TiO₂ as a photocatalyst.

Discovered by Chen et al. (2011), B-TiO₂ ameliorates the limitations associated with TiO₂, thus rendering it superior to pristine TiO₂. This superiority of B-TiO₂ is attributed to its narrower band gap and extensive solar absorption across the ultraviolet-visible near infrared spectrum (Bezza et al., 2023). Additionally, B-TiO₂ possesses charge carrier-trapping sites within its disordered surface layer, which inhibit premature charge carrier recombination and enhance its photocatalytic activity (Naldoni et al., 2019). When compared to pristine TiO₂, B-TiO₂ nanoparticles exhibit superior thermal stability within the temperature range of 350–600 °C (Imparato et al., 2021). To the authors' knowledge, existing literature does not address the photocatalytic degradation of BG using B-TiO₂ as a catalyst. Consequently, the present study documents the synthesis, characterization, and performance of B-TiO₂ nanoparticles as a catalyst for the degradation of BG dye.

2. Experimental

2.1 Materials

Titanium oxide (Degussa P25) (> 98%), sodium boron hydride (NaBH₄) (> 98%) were purchased from Sigma-Aldrich-Merck (Darmstadt, Germany). Deionized water, obtained from an Elga Purelab Flex 3 Water Purifier, was employed as the solvent for all experiments conducted in the study.

2.2 Synthesis

B-TiO₂ was synthesized by reducing commercial P25 (80% anatase and 20% rutile) using sodium boron hydride (NaBH₄, 98%) at room temperature. The employed methodology represents a slight modification of the method described by Tan et al., (2014). In this investigation, 4 g of TiO₂ nanoparticles and 1.5 g of NaBH₄ were thoroughly mixed, ground and subsequently placed in a porcelain boat and calcined at 300 °C for 3 h in a N₂ rich environment. The resultant product was then cooled, washed several times with deionized water and finally dried at 60 °C for 24 h.

2.3 Characterization

The structural properties of the synthesized nanoparticles were characterized by obtaining, X-ray diffraction (XRD) patterns using a Rigaku Ultima IV X-ray diffractometer (Tokyo, Japan) equipped with Cu-K α radiation (λ = 0.154056 nm) at 40 kV and 30 mA over the 2θ range of 0 to 80°. The surface morphologies of the synthesized B-TiO₂ were determined using Scanning Electron Microscopy (SEM) (Zeiss Ultra Plus). Elemental analysis of the synthesized B-TiO₂ was carried out by Energy Dispersive X-ray Spectrometry (EDS) using the same instrument. For the two analyses, sample preparation entailed dispersing the nanoparticles on carbon tape fixed to a microscopy stub, then coating them by carbon sputter under an argon rich atmosphere. The broadband-diffused solar absorption performance of both B-TiO₂ and Degussa were investigated across a wavelength range of 250–900 nm employing an Ultraviolet-Visible Reflectance (UV-Vis DRS) spectrophotometer (U-3900 Hitachi, Japan). The interfacial interactions within the synthesized nanoparticles were analysed using a Field Emission Transmission Electron Microscopy (JEOL JEM-2100F TEM). Here, the samples were first dispersed in ethanol, then the mixture was sonicated for 15 min and finally drop-casted on the TEM grids. Further, to ascertain the specific surface area and the textural characteristics of the synthesized nanoparticles, Brunauer-Emmett-Teller (BET) analysis was carried out using a Micrometrics Tristar 3000. Lastly, BG dye degradation was monitored using an UV-Vis spectrophotometer (VWR UV_1600PC, California, USA).

2.4 Photocatalytic performance

The photocatalytic performance of B-TiO₂ was assessed for its efficacy in degrading BG dye under visible light exposure within a photochemical reactor equipped with a 450 W xenon lamp, which incorporates a cut-off filter of 420 nm., purchased from Lelesil Innovative System, India. 100 mg of B-TiO₂ nanoparticles were deposited in 100 ml of 10 ppm BG dye solution. The resultant solutions were continuously stirred by a magnetic stirrer in the

dark for 30 min to attain optimal BG dye photocatalyst adsorption and desorption equilibrium. Thereafter, the emulsions were subjected to continuous illumination under visible light for 30 min, while the temperature in the reactor was maintained at a range of 22 – 30 °C.

For the analysis, 2 ml aliquots of the solution were collected at intervals of 5 minutes. These samples underwent centrifugation to effectively segregate the photocatalysts from the solution, then analysed using UV–visible spectroscopy, with measurements taken at an absorbance of 624 nm to determine the degree of BG dye degradation. Equation 1 below, was applied to calculate the removal efficiency.

$$\text{Removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

3. Results and discussion

3.1 Characterization

3.1.1 Crystallinity and phase composition

Figure 1 illustrates the crystalline phase and composition of both Degussa and the synthesized material, displaying diffraction peaks corresponding to the (101), (004), (200), (105), (211), (204), (116), (220), and (215) planes of the anatase crystalline structure (JCPDS card no. 21-1272). Diffraction peaks associated with the (110), (101), and (111) crystal planes of the rutile phase (JCPDS no. 21-1276) were also observed, indicating that Degussa comprises a mixture of anatase and rutile polymorphs. The observed peaks demonstrate that, akin to Degussa, B-TiO₂ exhibits substantial crystallinity, with a prominent peak occurring within the 2θ range of 25 – 30°, indicating the pre-eminence of the anatase crystalline phase in both materials. Consistent with the observations of Nawaz et al. (2022), no crystalline phase transformation was detected in the synthesized material, irrespective of the reduction by NaBH₄.

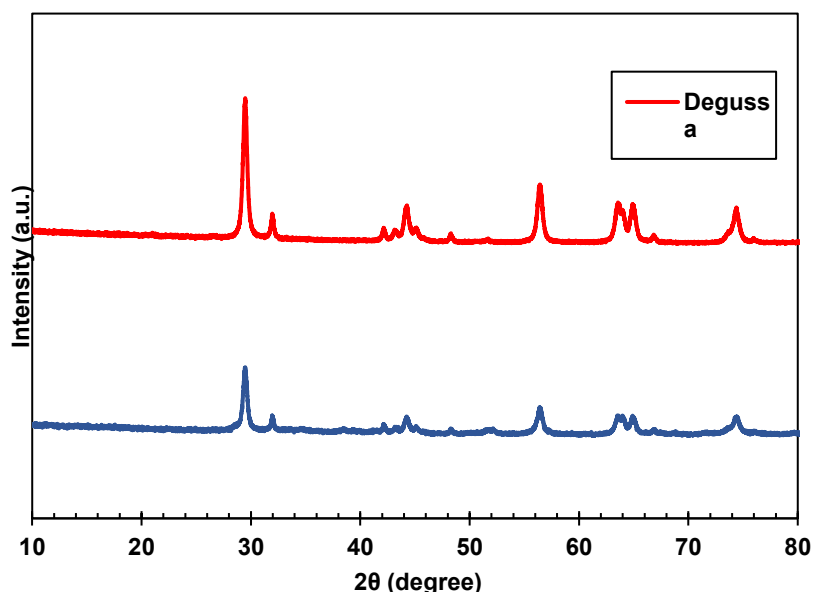


Figure 1: XRD pattern for Degussa and B-TiO₂.

3.1.2 Elemental composition

Analysis carried out using EDS revealed the elemental composition for both Degussa and B-TiO₂ as illustrated in Figure 2. The analysis inferred that the O:Ti ratio for the Degussa sample was approximately 1.2, which reduced to 0.68 in the B-TiO₂ sample. This observation is in alignment with the alteration in the oxidation state of TiO₂ from +4 to +3, accompanied by the generation of oxygen vacancies, which transpires when TiO₂ undergoes reduction by NaBH₄. A comparable phenomenon was documented in an investigation conducted by Andronic et al., (2022), where the O:Ti ratio decreased from 1.7 to 1.6 and 1.4 as the TiO₂:NaBH₄ ratio was varied in the sequence of 4:1, 2:1, and 1:1, respectively. These findings further suggest the emergence of superoxide phases within the B-TiO₂ sample, thereby enhancing its potential for photodegradation.

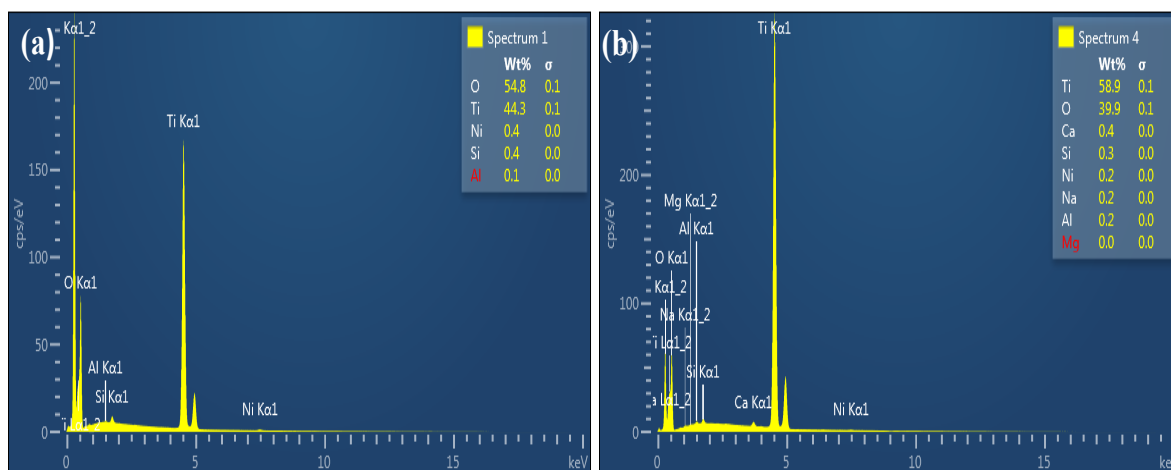


Figure 2: EDS spectra of (a) Degussa and (b) B-TiO₂ detailing the sum spectrum of O and Ti in the two samples.

3.1.3 Surface characterisation

The microstructure of the nanoparticles was evaluated utilizing SEM. This examination (Figure 3) revealed a relatively uniform size distribution of granular formations characteristic of TiO₂ nanoparticles. B-TiO₂ synthesized via NaBH₄ reduction of TiO₂ does not modify the size nor shape of the nanoparticles. However, this treatment primarily modifies the electronic structure and surface chemistry of the synthesized material, facilitating the formation of oxygen vacancies and surface defects, thus enhancing the visible-light activity of B-TiO₂ while preserving its fundamental structural characteristics (Rajaraman et al., 2023). Consequently, both materials maintain the distinctive nanostructured morphology of Degussa, resulting in comparable spherical agglomerated shapes with a relatively uniform size distribution observed in both pristine TiO₂ and B-TiO₂. These morphological similarities imply that the photocatalytic disparities between the two materials are predominantly influenced by electronic modifications rather than alterations in the physical structure.

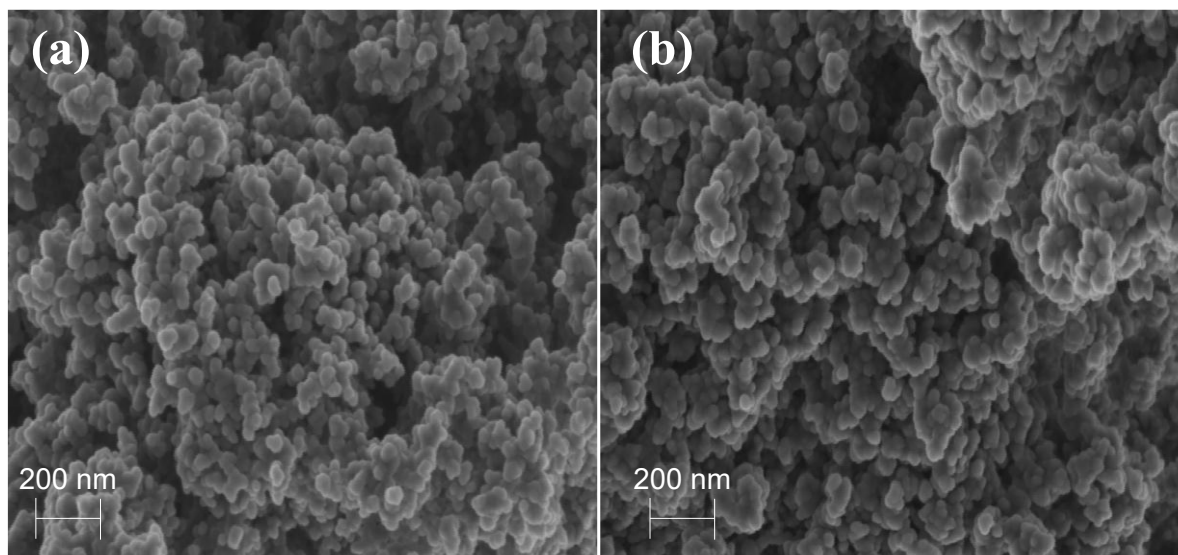


Figure 3: SEM images of (a) Degussa and (b) B-TiO₂.

3.2 Photocatalytic performance

The degradation potential of both the synthesized photocatalyst and Degussa was examined on BG dye under visible light irradiation. Adsorption and photolysis experiments were also conducted, yielding degradation efficiencies of 46% and 20% respectively, while after 30 minutes of visible light illumination, Degussa achieved a degradation efficiency of 77% (Figure 4). Although numerous literature sources suggest that the degradation of organic pollutants by Degussa is only feasible under UV irradiation, this study demonstrates that Degussa achieved a degradation efficiency of approximately 80% under visible light irradiation. This efficiency may be

ascribed two mechanisms: firstly, the rutile component of the photocatalyst possesses a lower band gap, thereby allowing for greater absorption of the solar spectrum. Secondly, this charge transfer facilitates a more pronounced spatial separation of the photogenerated holes and electrons. This results in enhanced charge separation compared to pure anatase, which subsequently diminishes recombination and thereby augments the efficiency of Degussa (Pan et al., 2019).

Exhibiting the highest photocatalytic degradation efficiency, B-TiO₂ demonstrated superior performance, achieving a 99% degradation of BG dye under similar conditions. The enhanced degradation efficiency of B-TiO₂ can be credited to the presence of Ti³⁺ interstitial defects, which facilitate increased visible light absorption and charge carrier separation, while simultaneously reducing electron-hole pair recombination, akin to Degussa. Furthermore, when compared to Degussa, the prior mentioned Ti³⁺ interstitial defects and oxygen vacancies in B-TiO₂, along with an augmented surface area and porosity, enhance the interaction between dye molecules and the photocatalyst. Collectively, these characteristics render B-TiO₂ an ideal photocatalyst for treating dye-contaminated wastewater.

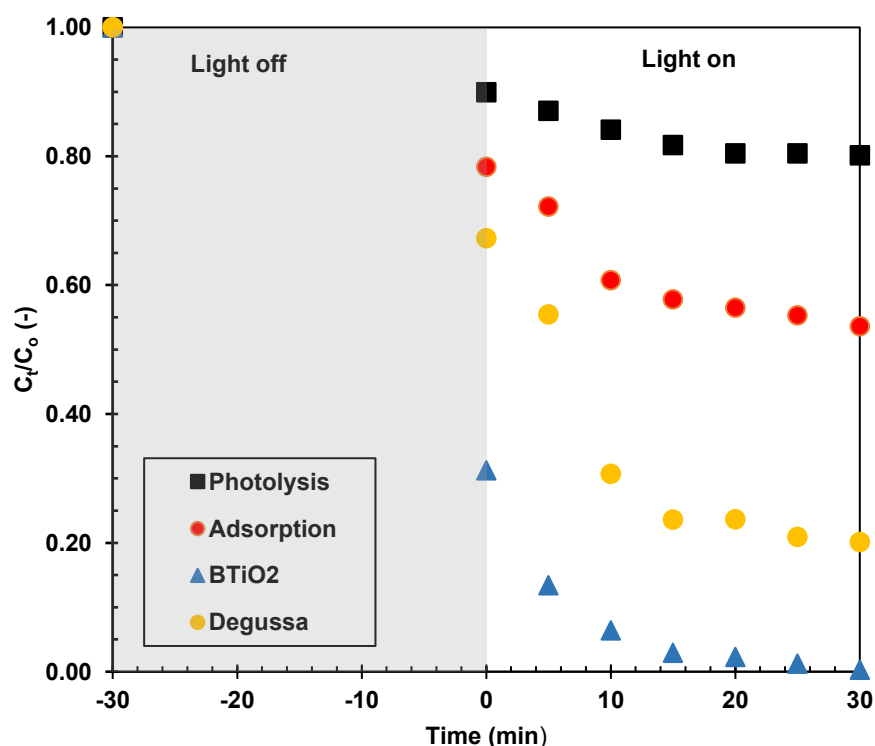


Figure 4: Degradation of BG dye by adsorption, photolysis and photocatalysis under visible light irradiation.

4. Conclusions

The study successfully synthesized B-TiO₂ nanoparticles via the chemical reduction of TiO₂ by NaBH₄ achieved by calcination at 300 °C. Comprehensive characterization affirmed the formation of oxygen vacancies and Ti³⁺ defects, which enhanced the photocatalytic properties of the material. The synthesized B-TiO₂ demonstrated superior photocatalytic performance in comparison to commercial Degussa, accomplishing a noteworthy 99% degradation efficiency of BG dye within 30 minutes of visible light exposure. This performance is ascribed to the enhanced light absorption across the visible spectrum, efficient charge carrier separation, and an increased surface area of the catalyst. The results underscore the potential of B-TiO₂ as a proficient, sustainable photocatalyst for the remediation of dye-contaminated wastewater, addressing significant environmental challenges and contributing to the achievement of Sustainable Development Goals 6 and 3. Future research endeavors might explore the scalability of this approach and its applicability to a wider range of contaminants under real-world conditions.

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