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CELLULOSE TITANIUM-DIOXIDE COMPOSITES FOR MALACHITE GREEN DYE PHOTODEGRADATION

by

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Requirements for the Award of the Degree of Master of Science in Chemistry of BIUST

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ABSTRACT

Textile industries largely contribute to water pollution by releasing their waste into streams, rivers, and other water bodies. With the rise in technology, researchers are discovering more ways of reducing water pollution in the environment. This research was aimed at extracting cellulose from a unique local plant source, *Colophospermum mopane* leaves. The process involved sodium hydroxide treatment, bleaching, and several washes to get the white fluffy cellulose. The cellulose was further used as a support material in making the cellulose-titanium dioxide composites which were synthesized using the hydrothermal method. Composites with 1-4% TiO₂ catalyst loading were made. X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FTIR) techniques were used. XRD results showed that *Colophospermum mopane* extracted cellulose to be semi-crystalline with crystallite size of 1.36 nm. The patterns of the titanium dioxide matched that of anatase which is known to be photoactive. Infrared spectroscopy mainly showed cellulose functional groups. The morphology of the fibers appeared smooth and with an average diameter of 1 μm. TGA revealed that the titanium dioxide-cellulose composites were thermally stable up to 360 °C. Titanium dioxide particles with average size of 100 nm were observed. Amongst the different catalyst compositions, the composite with 2% catalyst loading (Cell-TiO₂-2) was found to be the most effective. The photo-degradability under ultra-violet and solar irradiation indicated that photodegradation under sunlight using the Cell-TiO₂-2 catalyst, was higher than that done under UV light giving rise to percent degradations of 98.88 and 98.92% for that of solar, without adsorption contribution. Several scavengers were tested for their effectiveness in quenching the photoactivity. The presence of benzoquinone hindered the contribution effect of O²⁻ radicals in the photocatalytic mechanism. The Cell-TiO₂-2 was found to be still photoactive even after 4 cycles, thereafter reached plateaus. Adsorption played a role in the decolorization of the MG dye and cellulose proved to be a highly adsorptive material hence improving the catalytic effect of the composite. The kinetics of the photoactivity indicated a pseudo first-order reaction. The bandgap of 3.47 eV was recorded which provides the precise extent for the degradation process to occur. The results provided established the suitability of *Colophospermum mopane* as an active catalyst support.

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LIST OF ABBREVIATIONS

QD	Quantum Dot
AOP	Advanced Oxidation Process
UV	Ultra-Violet
VB	Valence Band
CB	Conduction Band
NPs	Nanoparticles
ACF	Activated Carbon Fibres
MB	Methylene Blue
CNC	Cellulose Nanocrystals
CNF	Cellulose Nano-fibrils
CPD	Critical Point Drying
XRD	X-Ray Diffraction
PAE	Polyamide-amine-epichlorohydrin
MFC	Micro-Fibrillated Cellulose
MG	Malachite Green
FWHM	Full Width at Half Maximum
FESEM	Field Emission Scanning Electron Microscopy
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
UV-VIS	Ultra-Violet Visible spectrum
Co	Initial concentration
C	Final concentration
CI	Crystallinity Index
TiO ₂	Titanium dioxide
Cell-	Cellulose-
Cell-TiO ₂ -2	Composite mixture of cellulose and titanium dioxide at 2% concentration
MO	Methyl Orange
EDTA	Ethylenediaminetetraacetic acid
TBA	Tert-Butyl alcohol
BQ	p-Benzoquinone

1.0 INTRODUCTION

1.1 Background of the Study

Global environmental issues such as pollution, destruction, depleting natural energy resources and insufficient clean water are persistent challenges faced today. Contributing to harmonious, ecologically clean and safe sustainable technologies development should be our aim as scientists. Consequently, photocatalysis can be harnessed for sustainable, nonhazardous, and economically viable technologies, therefore it is a viable means for pollution control. Photocatalytic activities make the titanium dioxide appealing to a wide range of industrial applications such as in environmental purification, gas sensing, dielectric ceramics, pigments, high efficiency dye-sensitized solar cells, cosmetics, inorganic membranes, and catalysis [1]. Furthermore, nano-sized TiO_2 has been reported for photocatalysis in wastewater treatment and for UV screening in cosmetics, plastic, silicone resins and lacquers, wherein nano-sized TiO_2 impart desirable transparency [2]. Many research studies have been conducted on synthesis of nanosized TiO_2 with different morphologies such as nano-spheres, nanostructured thin films, nanotubes, nanowires, nanofibers, and meso-porous structures [1]. Besides, to improve the photocatalytic activity of TiO_2 , the crystalline phase, crystal size, and specific surface area (small size and high crystallinity of nanoparticles) have been evaluated [2]. The preparation methods of photocatalysts have been studied in order to achieve uniform nano-crystalline powder structures. These include; sono-chemical, co-precipitation, sol-gel, micro-emulsion, combustion synthesis, hydrothermal, solvothermal, tartaric acid-assisted gel strategy, polyacrylamide gel, ferrioxalate, molten salt, and polymeric precursor. Nevertheless, a number of these procedures have some drawbacks, e.g. solid-state reaction procedure necessitates sample treatment at high temperatures more than $800\text{ }^\circ\text{C}$ in order to synthesize single-phase crystals. Attaining uniform nano-particles by some listed chemical methods seems impossible. However, they can be achieved using the hydrothermal or microwave technique making it the most significant method of achieving nano-sized single-phase crystal structures and homogenous particles at less than $250\text{ }^\circ\text{C}$. Consequently, the effect of morphology, particles size and how it influences photocatalysis of contaminants under ultra violet and visible light is more pronounced when using these chemical methods[3].

Various visible light-driven photocatalysts such as m-BiVO₄/t-BiVO₄, Ag₂O/Ag₂CO₃ and BiOI/BiOBr have been developed for H₂ production and decomposition of organic pollutants. Unfortunately, these materials suffer from high recombination rates and limited delocalized conductivity, absorbing visible light at wavelengths less than 450 nm and having a small surface area that reduces photocatalytic activity. To overcome these problems, photovoltaic materials have been modified using quantum dots to increase surface area, which in turn absorbs light thereby enhancing its photocatalytic performance [6].

Quantum dots are also called colloidal semiconductors, which are zero-dimensional nanostructures. QDs have a nano-scale dimension of less than 20 nm, forming an inorganic core surrounded by an outer organic layer. They have received enormous research interest due to their excellent photocatalytic properties and their applications in photocatalysis, sensing, light-emitting diodes, energy storage devices, bio-imaging, and solar cells. Quantum dots are primarily used as photocatalysts to remove waste organic matter from water, remove toxic gases, and produce hydrogen from water and break down H₂S. The properties of QDs can be adjusted by doping or modifying the surface with different functionalities. Due to the quantum size effect, the large surface area degrades the properties of excitons, increasing electron and hole access to the surface. This makes the oxidation and reduction processes efficient. The band gap increases when photogenerated charges rapidly diffuse to the surface of the quantum dot.

Apart from dye degradation, photocatalysis has other applications. The potential for photo-electro-catalysis (a branch in photocatalysis), based on heterogeneous photocatalysts and semiconductors, has attracted a lot of attention for solar energy and harvesting for its storage, solving the energy crisis. Photoelectro-chemical cells are considered beneficial with the potential of consuming wastes and transforming sunlight into useful energy types through degradation of organic wastes. It was noted that the photocatalytic activity is significantly influenced by the applied potential, more precisely that the reactivity is increased several times by applying an external bias voltage. Illuminated TiO₂ electrodes are reported to be useful for the splitting of water molecules and hydrogen production. Bhunia and Dutta explained the reaction mechanism and noted several semiconductors and their maximum potential [5].

Advanced oxidation process (AOP) as described by Hendri et al., [26], is a water treatment scientific knowledge for the removal of organic pollutants that are untreatable by

conventional methods. These pollutants have high chemical stability or low biodegradability. Photocatalysis based AOP using semiconductor material has become a promising method for degrading the pollutant. One of the semiconductor materials that can be used as photocatalyst is titanium dioxide (TiO_2). According to Byrne *et al.*, advanced oxidation technologies (AOTs) are proving to be an effective waste water treatment with the ability to degrade numerous organic microbes and pollutants on a wide scale. It is an encouraging method of eradicating water pollution problems. Notwithstanding recent research into other photocatalysts e.g. ZnO , ZnS , Semiconductor-Graphene composites, perovskites, MoS_2 , WO_3 and Fe_2O_3 , TiO_2 remains the most prevalent photocatalyst owing to its affordability, nontoxicity and high oxidizing ability. Additionally, the ability to immobilize the photocatalyst on a number of surfaces and scaling it up for water treatment makes it the more favorable semiconductor. [17]. TiO_2 /cellulose hybrids possess unique qualities that make them widely used as photocatalysts of dangerous organic compounds and several environmental pollutants. The synergistic effects from the physical or chemical interactions between the organic and inorganic components play an important role in its photocatalytic ability. TiO_2 has noticeable mechanical and UV- shielding properties useful in the formation of films and also applicable in the synthesis of transition-metal carbide materials or for antibacterial use. Preparation of TiO_2 hybrids containing biological components or synthetic polymers via sol-gel route is an area of interest to many researchers. Researchers prepare TiO_2 hybrids containing biological components or synthetic polymers via a sol-gel route which has been a rising study [141].

Natarajan *et al.*, emphasized the important characteristics that an efficient photocatalyst should possess. First characteristic is the maximum absorption efficiency and band gap; for example, TiO_2 absorbs UV light region. Therefore, several approaches have been proposed to adapt its band gap to the visible range or to provide a secondary absorber to inject carriers into its conduction band. Secondly, the efficient separation of holes and electrons without controlled recombination dependent on the presence of electronic structures and external or internal electric fields, crystal structures, shapes, etc for the catalyst under investigation. Thirdly, the redox levels of the invading substrate and the band alignment of the photocatalytic material, or the acceleration of the reaction species is within the heterogeneous phase. Fourth, the media chemical stabilization to avoid photo-corrosion of photovoltaic. In some cases, a hole scavenger or co-catalysts are used to keep the substance in check [8].

A composite material is one which is manufactured from two or more fundamental materials. These constituent materials have particularly different chemical or physical properties and are fused to create a material with properties unlike the individual elements. Cellulose-TiO₂ composite is an example of such composite. Composites of two different photocatalysts have also recently gained interest. Forming hetero-junctions between the photocatalysts allow the increase of charge separation which is important in the degradation rate. With the aid of the hetero-junctions, energy adsorbed by the first catalyst is transferred to the second resulting in enlarged charge separation [17]. Formation of composites with other semiconductor materials such as TiO₂ and core/shell nanostructures, improves stability, charge separation, photocatalytic efficiency of QD [7].

Also, cellulose fiber is the most abundant, biodegradable, low cost and environmentally friendly biopolymer and is the major component of paper products. Many uses of cellulose are known with one famously used in papermaking and as reinforcements. Consequently, cellulose-titanium dioxide hybrids hold abundant organic and inorganic interactions with another hence making it plausible to be used in industrial applications. Titanium dioxide can be introduced into the cellulosic material by either coating or grafting. Qisi Yu *et al.*, have used supercritical carbon dioxide to synthesize the hybrid composite [10]. The chemical interaction between cellulose and titanium dioxide particles is explained by Martakov *et al.*, [11]. Their study also showed that doping cellulose composite with inorganic materials adjust their thermal, electrical, optical, rheological and mechanical properties providing the optimum photoactivity required. The extraction of cellulose from these natural fibers is done through a series of chemical and mechanical processes. This research uses a new source from *Colophospermum mopane* leaves which is indigenous to the southern African environment and most importantly, it is abundant in Botswana.

Malachite green dye was originally manufactured as a yarn tint for silk, stationery, acrylic and pelt industries. It is a prevalent triphenylmethane compound acting as a food and hair coloring. Because of its negative effects on the environment, it is necessary to degrade this dye into harmless end-products using a cellulose-TiO₂ composite photocatalyst and light source.

1.2 Statement of the Problem

One of the goals of the United Nations is that all people will have access to clean drinking water by the year 2030 through the attainment of Sustainable Development Goal 6, which

is about clean water and sanitation. Ensuring availability and sustainable management of water and hygiene for all is the Sustainable Development Goal 6. By the year 2030, 8 targets are to be achieved, measuring the progress by 11 indicators. The six targets include; (i) cheap and safe drinking water, (ii) eliminate open-defecation (iii) dispense access to sanitation and hygiene (iv) expand water quality, waste-water management and safe reuse (v) advance water-use efficiency and widen water supplies (vi) protect and restore water related ecosystems [142]. However, one of the impurities of concern are the colorants which are industrial wastes. Industrial waste such as liquid waste contaminated with paper or textile dye residues is one of the environmental problems. Different methods have been used to overcome this problem.

Numerous studies have concentrated on using diverse treatment methods to decolorize industrial waste-water. Unfortunately, most of these methods are practically difficult. In recent studies, different systems were used, such as, ozonation, $\text{H}_2\text{O}_2/\text{UV}$, photo-Fenton electrocoagulation, sonolysis, gamma radiolysis, biological and combined anaerobic–photocatalytic treatment. Disadvantages associated with the methods are that: Ozonation is not preferred due to its high cost of equipment and because ozone is irritable and possibly toxic. The efficiency of the H_2O_2 method strongly depends on the type of oxidant used. Coagulation and flocculation process produces a sludge which is toxic and leading to a new pollution that needs to be treated. Sonolysis has low mineralization efficiency and high energy consumption. Gamma radiolysis is also an expensive method of water treatment. Biological treatment requires an optimum environment to be created in order to attain maximum catalytic ability. The main goal is to synthesize a composite material that has high adsorptive qualities, heightened photocatalytic activity, increased response to visible light, lower charge carrier recombination and a suitable band gap. Hence, the need for the application of cellulose-titanium dioxide composites for malachite green dye photodegradation.

1.3 Aim and Objectives of the Study

1.3.1 Aim

The study aimed at the photodegradation of malachite green dye by cellulose-titanium dioxide composites.

1.3.2 Objectives

The specific objectives for the study were;

1. To extract cellulose from *Colophospermum mopane* (mopane) leaves and further synthesize cellulose-titanium photocatalysts
2. To characterize the cellulose-titanium dioxide composites
3. To evaluate the photocatalytic activity of the cellulose-titanium photocatalysts under UV and solar irradiation
4. To study the effect of temperature, catalyst loading, and radicals on photodegradation as well as kinetics rate of reaction and recyclability.

1.4 Research Questions

1. Can cellulose be extracted from *Colophospermum mopane*?
2. Does cellulose-titanium catalyst have the ability to photodegrade malachite green dye?
3. Do the composites show photocatalytic activity under UV and solar irradiation?
4. Do temperature, catalyst loading, radicals, kinetics rate of reaction and recyclability have effects on photodegradation?

1.5 Scope of the Study

In this research; extraction of cellulose from *Colophospermum Mopane* (mopane) leaves, characterization and composition of the cellulose, and its application in photocatalysis of malachite green dye were covered.

1.6 Significance of the Study

The research will play a distinctive role in providing beneficial information to industry and academia on the applications of composited cellulose extracted from *Colophospermum mopane* (mopane) leaves in the photocatalysis of malachite green. The outcome of the study will promote the use of mopane leaves as a raw material for industrial production of photocatalytic materials and other potential products for foreign exchange. This will also encourage conservation of the plant for multipurpose uses. The exploitation of the leaves in

this study will add to the database of researches related to plants' application in green chemistry.

2.0 LITERATURE REVIEW

2.1 Background of Photocatalysis

The inexhaustible, clean, safe and abundant energy of the sun is harnessed for sustainable technologies using the process of photocatalysis[12,13]. In addition to dyes and crude oil, degradable toxins like pharmaceutical waste and pesticides are disintegrated this way[13]. It is beneficially used to recycle huge amounts of treated water in textile factories enhancing the method of water conservation [14]. However, the technology works in such a way that the energy provided meets the activation requirements for a lot of chemical reactions that are either difficult or impossible to occur under normal conditions. For instance, organic toxins' decomposition is challenging and reduction of carbon dioxide is nearly impossible to conduct on its own [15].

Qu and Duan [16] explained how photocatalysis is inspired by photosynthesis. In 1901, scientists looked into new ways of using energy from photons to power mechanisms without using heat and this was enthused by the study of nature. Plants produce energy aided by the sun in the process of photosynthesis. How the energy is harvested and transferred brought about the innovation of photocatalysis and with the replacement of leaves, photocatalysts were created to function as the harvester and transferee of the electrons from one point to another. Consequently, both reactions use the vitality from photons to power chemical reactions. In plants, the energy converts carbon dioxide and water forming carbohydrates. This energy is studied to know how it solves environmental problems. For example, converting toxins into harmless molecules.

Byrne *et al.*, detailed the photocatalytic reaction mechanism of a typical advanced oxidation technique. The reaction starts with the bombardment of photons from a light source (which could be an ultra-violet radiation) with the semiconductor elements. Electrons on the photocatalyst surface are excited in the valence band (VB) by the photons. If the energy is greater than the band gap, the electron gets excited into the conduction band (CB). Once absorbed, there is a formation of a positive hole in the VB. The excited electron in the CB reacts with O_2 to give superoxide (O_2^-) and hydroperoxide ions (HO_2^-). Reactive oxygen species are further used to degrade contaminants into water (H_2O) and carbon dioxide (CO_2). Secondary degradation steps are able to correspondingly be carried out by the superoxides. Simultaneously, the positive hole allows water to be oxidized in the VB. Hydroxyl radicals

(OH⁻) are formed along with hydrogen ions (H⁺). The OH⁻ reacts with the impurities creating water (H₂O) and carbon dioxide (CO₂) [17]. Figure 2.1 below diagrammatically explains the process with titanium dioxide as the semiconductor material.

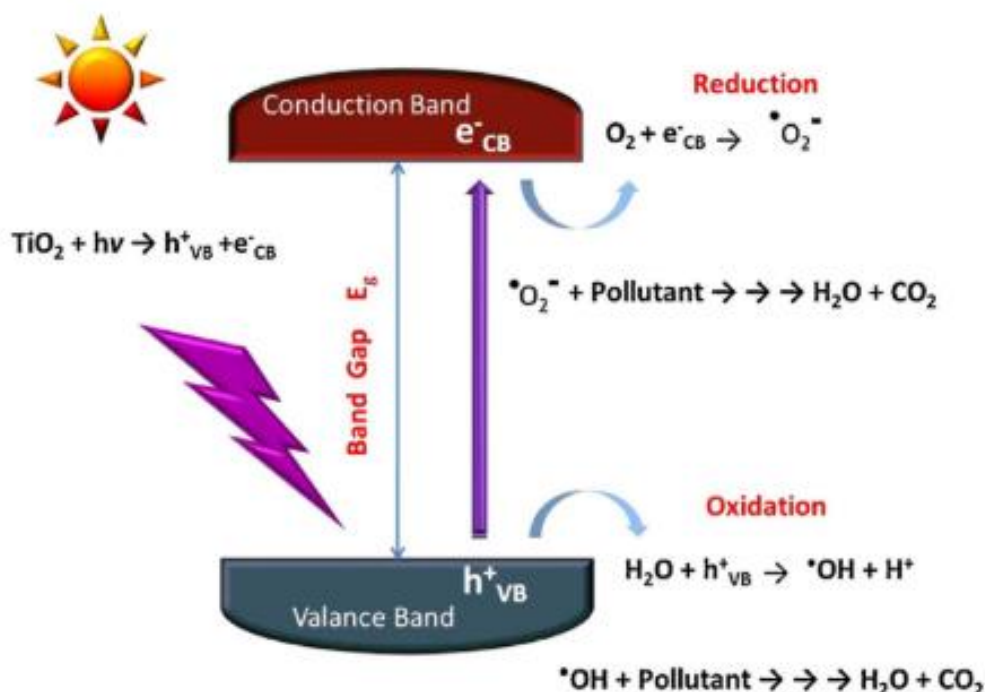


Figure 2.1: Mechanism of photocatalysis. Reprinted with permission from ref [17].

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2.1.1 Photocatalysts

Photocatalysts are materials used in the process of photocatalysis to speed up chemical reactions. Such a material has the ability to absorb light and excite electrons to a higher energy level than its band gap. It then provides the energy to the reactant hence catalyzing the chemical reaction. They can also be referred to as semiconductors [21].

The breakthrough in this focus has opened up so many doors for material scientists to study the photocatalysts available and ways of improvement. Photocatalysts based on semiconductors have attained a lot of attention because of their application in to solving both energy and ecological issues. Their applications range from the process of thermocatalysis, separation, purification and solar cells [21].

In 1911, ZnO displayed photo activity by bleaching Prussian blue pigment in the presence of light. Further discoveries were made like the ability of the material to reduce Ag⁺ to Ag

was possible. Some years later, TiO_2 and Nb_2O_5 were found to be the driving force of the photocatalysis, converting AuCl_3 to Au and AgNO_3 to Ag. Interests about the ecological impact of large industrial companies date back to 1968 which has encouraged researchers to discover new renewable energy sources resulting deeper studies of photocatalysis [15]. The characteristics of a good photocatalyst is in its large surface area and keeping thus, researchers identify and construct materials that suit the criteria [22].

2.1.2 Examples of Photocatalysts

Many articles have been published on studying different photocatalysts, which includes; zinc oxide (ZnO) [23], titanium dioxide (TiO_2), niobium(V) oxide (Nb_2O_5) [24], zinc sulphide (ZnS).

Zinc oxide photocatalyst is described to be an economical, non-toxic material and is commended for its efficiency in the absorption across a large division of solar spectrum [25] [4] and has been tested for its degradative property. Hendri *et al.* synthesized the material using flame spray pyrolysis method and applied it in the degradation of amaranth dye resulting in a degradation efficiency of 95.3% in 75 min [26]. Furthermore, different authors tested its degradability against dibenzothiophene [27] and microcystin-LR pollutant [28], both found the result to be 97% effective. As good as ZnO could be, it has limiting factors that elevate TiO_2 as a better catalyst. Having chemical instability in alkaline and acidic aqueous medium as well as its level of insufficiency disqualifies it as a future material [29].

Zuzzanna *et al.*, decided to test the photo activity of ZnO and TiO_2 against Congo red dye, it was concluded that ZnO was more photoactive in that experiment [30]. However, its application in sunscreens has called a major concern as skins are being damaged and hence another drawback [30]. Apart from that, ZnO thin film is reported to be useful in the applications of solar cells. Its properties include: transparency, high electron mobility and environmental stability [31]. The material provides a good buffer layer for high efficiency inverted polymer cells.

Yun Zhao *et al.*, [32] reviewed the nanostructured Nb_2O_5 catalyst. This material is used to speed up peculiar acid reactions, photo-catalytic and redox reactions. Among its other oxidation states, Nb_2O_5 is the most stable and the most studied catalyst. Currently, niobium pentoxide is applied in electrochromics, catalysis, gas sensing and in photo-electrodes. It is known for its strong acidity and stability in aqueous medium making it suitable for photodegradation of organic pollutants. The preparation method mostly used is that of the

sol-gel. In addition, Nb_2O_5 can be fashioned into nanotubes, nanowires, nanofibers, nanobelts and nanorods. Yun and his team aimed at tailoring oxide material with controlled structures and morphologies [24]. Nonetheless, understanding the structures does not match up to the forceful search for applications. An additional advantage of Nb_2O_5 is that when tested against indigo carmine dye, it proved to be recyclable [24]. Some other studies have described the photo activity of Nb_2O_5 hybrid catalyst. Silva *et al.* studied the degradability of yellow neutracyl and dark blue neutracyl and applying Nb_2O_5 alone showed less than 35% catalysis. However, when doped with silver, the percent degradation shot up to 99% [33].

As an example of a metal-sulphide semiconductor, zinc sulphide catalyst has also been looked at severally. It was mentioned that ZnS has rapid reconstruction of electron – hole pairs by photo-excitation and very negative potential of excited electrons. Therefore, it is particularly used in photo-reduction of CO_2 , production of H_2 from water, photo-transformation of various organic substrates and treatment of wastewater. The major setback of the material is that it is expensive, hard to recover and recycle [34]. Mostly, ZnS is used in the evolution of H_2 from aqueous solutions [19][35]. However, after testing the photo-electro catalytic ability of $\text{CdS/ZnS} - \text{TiO}_2$, it was reported that the material acted as a visible light sensitizer of titanium dioxide which also assisted the separation of electron-hole pairs formed by UV excitation of the catalysts. A maximum hydrogen production rate was achieved in this experiment [36]. ZnS does not portray outstanding photo degradability [36], however, when doped with reduced graphene oxide composite [37], nickel sulphide [38], cobalt [39] and cadmium sulphide, CdS [40], there is a level of improvement in the photo activity but not as compared to TiO_2 .

Other semiconductor materials include: graphene as a functional composite material with unique properties and its low cost advantage [41]. Graphite oxides used in catalyzing H_2 production from water [42]. Bismuth oxy chloride, BiOCl , has been shown to be able to photo degrade methyl orange at a better rate than TiO_2 P25 [43]. Metal oxides of vanadium, iron (i) oxide, iron (ii) Fe_2O_3 , chromium, molybdenum and gold as well as Strontium (SrNbO_3) degraded methylene blue dye under UV light [44] and silver Ag_2MoO_4 which was said to be stable under visible light [45] etc. Mxenes, also known as transition metal carbides. They have been reported to be rising photocatalysts for the splitting of water. The material achieved good optical absorbance within the wavelength range of 300- 500 nm, comprising of the UV-Vis region [46].

A 1972 review by Steinbach pointed out the direct relationship between photons and valence electrons of a semiconductor by means of photo sorption, photoelectron emission, the influence of wavelength and light irradiance in photocatalytic reactions. Fujishima and Honda made a discovery that evolved photocatalysis after successfully photolyzing water electrochemically with the help of an illuminated titanium dioxide (TiO_2) and dark platinum electrode. Since then, the heterogeneous catalyst, TiO_2 was termed the “workhorse among other photocatalysts”. The exponential growth of TiO_2 had begun in the 1980s, contributing to so many fields, and is continuing till date [21].

2.2 TiO_2 Photocatalyst

2.2.1 Importance of the Catalyst

Titanium dioxide has been a innovatory material with many applications ranging from photovoltaic, semiconductors, cancer treatments, environmental purification to textiles, [47-49]. Its existence is in 3 states, brookite, anatase and rutile. Rutile and anatase are the most commercially used. René and Myrtill demonstrated that the rutile crystal might be the thermodynamically more stable form of titanium dioxide but anatase has the sturdiest photoactive characteristic [50]. The chemical structure of titanium plays a role in its industrial application. Nanoparticles (NPs) are used as UV-filters in sunscreens and paints, used as photo catalysts and semiconductors and is also used as water and air treatment [50-53][10]. TiO_2 is chemically stable, absorbing at UV-VIS wavelengths and possesses a high potential to break molecular bonds leading to degradation [13].

An important step in photoreaction is the formation of electron-hole pairs, which require energy to bridge the band gap between the conduction and the valence bands [32]. Below summarize the photocatalytic processes by Zhao *et al.*, :

- a) Dye is adsorbed onto the TiO_2 surface as an alcoholate species in the dark
- b) Adsorbed species are activated by transferring electrons to the conduction band, reducing Ti^{4+} to Ti^{3+} and leaving a hole in the alcoholate
- c) Alkenyl radicals are formed and converted to a carbonyl compound.
- d) The product is desorbed
- e) Oxidation of Ti^{3+} sites occur by reaction with molecular oxygen.

The rate determining step is the desorption of the formed products [15]. Based on the synergistic effect, excited state electrons from the cellulose molecule can be introduced into

the conduction band of TiO₂ and reacted with oxygen to form superoxide anion. Similarly, holes ($h\nu\beta^+$) formed in the valence band react with water molecules to form hydroxyl radicals ($\bullet\text{OH}$). Oxidation and degradation of organic molecules is enhanced by both the holes and hydroxyl radicals. [54] The reactions involved in the photocatalytic mechanism of the cellulose-titanium surface are shown below [17]:



Through this, the process of recombining electron hole pairs is inhibited hence improving charge separation and photocatalyst stability. As a result, there has been a significant increase in the photo-catalysis of organic pollutants under sunlight radiation [17].

Table 2.1: Summary of reported photocatalysts and their efficiencies

Author and year	Photocatalysts/pollutant degraded	Efficiency
Guo et al., (2012) [143]	TiO ₂ -nanosheet arrays on carbon fibers for photocatalytic degradation of methyl orange	92%
Banisharif et al., (2015) [144]	Fe ₂ O ₃ -doped TiO ₂ photocatalyst for the degradation of trichloroethylene in air under UV and visible light	97%
Meena et al., (2016) [145]	Modified ZnO nanomaterials for degradation of malachite green	94%

Jian et al., (2010) [119]	TiO ₂ immobilized in cellulose matrix for photocatalytic degradation of phenol under weak UV light irradiation	95%
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2.2.2 Degradability by TiO₂

Photocatalysis is reported to be the new technology for controlling environmental pollution. However, this technology has limited practical use due to its low efficiency and insufficient absorption capacity of light rays when used for photo-degradation. Various techniques have been adopted and demonstrated to overcome these limitations with some useful results. Lately, scientists have developed TiO₂ nano-structures doped with various metal and non-metal ions to strengthen the properties of TiO₂. Such modulation can proficiently advance the photocatalytic properties of TiO₂ nanostructures. Advantageous properties of the catalyst include its rare physicochemical properties, low cost, wider band gap, high stability, chemically inert, non-toxicity and biocompatibility [55].

Alexandre *et al.*, [24] tested the photo activity of several catalysts by degrading indigo carmine dye. It was found that 100% degradation was achieved by TiO₂ in 20 minutes, ZnO in 45 minutes and Nb₂O₅ in 90 minutes. This proves how fast TiO₂ is in photocatalysis as compared to the other two.

Silva *et al.*, [22], reported that nanoscale anatase TiO₂ escalates the catalysts' competence due to its large surface area. The degradability was tested using methylene blue under ultra violet and solar irradiation. It was recorded that the Nb₂O₅-doped material proved to be more efficient than ordinary TiO₂. The paper further explained the important role of a photocatalyst having a large surface area in a catalytic reaction is the absorption of more light offering more reaction centers and adsorption sites. The character of Nb₂O₅-TiO₂ catalyst behavior under the sun displayed poor results compared to the experiment conducted using UV light. TiO₂ catalyst was also tested against acid green 16 leather dye degradability [56]. In another experiment, acid brown 14 dye was degraded by both ZnO and TiO₂. Using visible light, TiO₂ differ in comparison to ZnO because of its low sunlight absorption [56].

Free catalysts, those unbound to a surface, were used in the past for water treatment but the isolation and reusability of the ultrafine catalyst is costly and tedious. Catalysts fixation on firm substrates came about as a solution. Wang *et al.*, reported that the use of an extensible and penetrable organic matrix during photocatalysis showed an enhanced performance on the treatment of multiform organic contaminants having good recycling and easy recovery benefits [54].

Work has been done to immobilize TiO₂ using biological and chemical methods. Enzymes have been attached onto the surface of the catalyst and simple materials like paper, films and corks [54] have also been used. Combining a photocatalyst and a support material is referred to as a composite.

2.3 Composite Materials

Composite materials are a mixture of two materials where the properties of both the individual precursor's releases strength, flexibility, light weight and durability which is embedded into the new material thereby increasing the strength-to-weight ratio. A strong bond is created between the strong stiff reinforcement and the weaker, less stiff matrix. This composition is usually made between fibers and particles or platelets [57]. Heterogeneous photocatalysts with multiple components combine the pros of different components to overcome the cons of single component photocatalysts [16]. Existing types of composites include glass-fibers supported aluminum, carbon-fiber polymer, porous glass, silica nanoparticles, nano-porous gold, and chitosan [58]. Other types of composites embrace the properties of metal, ceramics, and carbon nanotubes.

Engineering and material science takes advantage of this technique and they are very popular in industries like automotive, aeronautics, catalysis, sustainable energy, water treatment and pharmaceuticals [59]. There are usually 3 phases embedded in composite materials. Matrix phase (continuous phase), filler/reinforcement (surrounded by matrix) and the interface phase (with different structures and properties from the 2 other phases) [60].

The synergy of hybrid materials were studied for infrastructural applications looking at their physical properties. It was revealed that weak hydrogen bonds, in its complexity, was used to create a tougher cement. Navid Sakhavand explained that with the right hydrogen bonding mix in a polymer and cement complexes, hard, durable and pliable infrastructure material can be synthesized [61]. This shows the importance of hydrogen bonds and in their different quantities contribute to the materials contribution as a whole.

2.3.1 Hybrid Photocatalysts

Hybrid photocatalysts, as reported appear to be the solution to improving photocatalysis. A review on ZnO highlighted the problem of the ZnO catalyst such as its wide band gap and immense recombination of photo generated charge transporters which reduce the efficiency as a whole. The authors proposed to modify the electron band structure by hybridizing it with a material having a narrower band gap. It was proven that the wavelength for absorption had moved to the visible-region in the spectrum. A number of materials with narrow band gap are: metals, metal oxides, carbon –based and polymeric based composites [62]. But the key is not to bring the band gap so low because small band gap photocatalysts experience inadequate photoactivity and poor reproducibility [56].

Interestingly, Eduardo *et al.*, studied the photoactive nanostructures based on clays incorporating TiO₂ and ZnO nanoparticle. Noticing that clays were easy to manipulate and that it provides stable electronic, magnetic and photoactive properties, they are considered to be excellent platforms for developing nanostructured functional materials. With the aim of proving clays to be the ideal support material, they went on to test the photo activity of TiO₂, ZnO and TiO₂-ZnO against pharmaceutical pollutants. The following photodegradation sequence was documented: TiO₂-ZnO-clay > TiO₂-ZnO > TiO₂ > ZnO. In addition to demonstrating that a support material like clay contributes to the efficiency of photocatalysis, TiO₂ is still a better semiconductor [63].

2.3.2 Support Materials

Apart from metal oxides, carbon fibers have been viewed upon as a unique material with a less researched ability to be explored. Carbon nanofibers, cellulose-based paper, activated carbon fiber are just a few and the use of support materials which are highly advantageous with easy recovery and good recyclability alleviating the problems of powder filtration [1]. The wide band gap in TiO₂ limits activation to radiate energy larger than 3.2 eV and the rapid recombination speed of photo-generated electron/hole pairs. In addition, a big band gaps impedes the photoactivity under visible light, sunlight. Compositing a photocatalyst lowers the band gap in turn increasing the reactivity [54].

Pingfeng Fu *et al.*, [65] looked at activated carbon fibers as a proficient support material for TiO₂. The article aimed at introducing a new method for the preparation of activated carbon

fibers (ACFs) support, with focus of increasing photoactivity of the catalyst by combining the adsorptive characteristic of the fiber and the catalytic ability of anatase-type TiO₂ material in the decomposition of methylene blue dye (MB). Molecular adsorption-desorption technique was used in the synthetic process. Successfully, the new technique provides adequate photodegradation on a 3-Dimensional environment that cannot be achieved on a 2D surface like glass, ceramic or silica gel. ACFs are highly porous materials with a large pore volume and adsorption capacity, fast rates of adsorption and desorption processes. With the layer of TiO₂ roughly surfaced on the support, substrates easily adsorb onto the solid. Hydroxyl groups on the catalyst's exterior can be accredited to the adsorption reaction of H₂O and formation of Ti-OH as shown by the equation below:



Electron-donating –OH groups for photo generated H⁺ is oxidized into hydroxyl radicals attacking a majority of biological toxins. The paper concluded that the merged power from the adsorption effect from ACFs and the photocatalysis by TiO₂ gave peculiar photodegradation of MB dye with a 99.1% efficiency. The setback of this method was that at high temperatures, the crystallinity of the anatase peaks reduced and were replaced by rutile hence lowering the performance along the way.

Wenxi *et al.*, [66] proposed to grow nanosheets on substrates in the form of an ordered film free of clusters. Pointing out that the TiO₂ photo-activity is influenced by dimension, structure, crystallinity and the exposure intensity of reactive crystal faces, synthesizing a film free from agglomerates could enhance the activity. Carbon fibers are described to be flexible, conductive and stable in corrosive environment. They have a large surface area with heat and fatigue resistance which qualifies as a good support material. 92% decomposition of methyl orange dye was reached by the use of the TiO₂/nanosheets/carbon fibers composite under UV light for 50 minutes. The transfer of electrons between TiO₂ and carbon reduces the photo-induced charge carriers' recombination and prolonged the electron life. The 3-D hybrid structure was commended for its ability to capture light rays from all directions and is suitable to be applied in areas of high fraction of light reflection. Carbon fibers made an impact in the photo activity of TiO₂ and have potential to be explored deeper.

Other support materials like clay, silicon and carbon fibers displayed issues which needed to be resolved. Issues like expense to produce, non-biocompatibility, recyclability strains, lack of reusability or that they are ineffective [52] are key points to the technological

advancement. In addition, immobilization efforts on materials such as zeolite and stainless steel substrates failed to succeed due to the low surface areas inhibiting TiO_2 from completely being immobilized [67].

2.4 Cellulose

2.4.1 Background of Cellulose

The research study on biodegradable materials have heightened as their demand for application has increased [68]. The most lavish source of these materials is cellulose as they are derived from plants and their residue. This is considered one of the most abundant renewable resource on earth. It remains a major raw material for paper, food, pharmaceutical, textile, energy, and composite industries owing to its environmental friendliness. This is because, biomass, which is the main source of cellulose is cheap, readily available and renewable. Carbon-based compounds made in the chemical industry are obtained from petroleum. Over the years, the cost has risen with a deteriorating oil supply has resulted in industries searching for possible routes to solvents, chemicals and fuels production from biomass instead [69]. Like any other material, cellulose has four building blocks which are known as nanocrystals, nanowhiskers, nanofibrils and nanofibers. These have become hot topics in research due to the large potential and promising employments they hold in green chemistry [70].

Nano-cellulose has been known to have broad applications for example, cellulose nanocrystals (CNCs) have been used for photonic applications to obtain lustrous films with defined optical properties. CNCs and cellulose nano fibrils (CNFs) make optically transparent self-contained solar cells films which are seen daily on cellphone screens. Nano cellulose is useful for chiral nematic organization material, optical properties, gas barrier, water sorption, and mechanical properties. CNC are used in the production of foams and aerogels for food and electronic packaging, including solvent exchange/critical point drying (CPD) and freeze drying. Nanocellulose, including CNC and CNF, is widely used as a filler in thermoplastic polymeric matrix to create green, cheap, long-lasting nano-composites. It is also an encouraging biomaterial for medicinal uses i.e. tissue regeneration due to its good biocompatibility and low toxicity [71]. Just like crystalline cellulose has its various applications, amorphous cellulose has its own applications.

Michael Loelovitch successfully managed to synthesize amorphous cellulose and characterize it [72]. It was discovered that even with the low crystallinity and shapelessness, it was converted to glucose through hydrolyzation by cellulolytic enzymes. The gel-like paste that was formed exhibited thickening properties (high viscosity) and also had the ability to immobilize proteolytic enzymes and other therapeutically active substances. This discovery made it possible to use amorphous nanoparticles as a precursor in making cosmetic and skin care products that can easily clean wounds and remove dead cells without affecting the healthy ones.

Over 150 years ago, it was reported that Anselm Payen isolated and extracted cellulose from green plants for its catalytic potentials [73]. Consequently, this is known as the primary build-up of plants though it can be found in bacteria, algae and fungi. Mostly found in the cell walls of stalks, stems trunks and leaves of plants, it's fibrous, water-insoluble and tough. It has been reported that cellulose has 6 polymorphs, cellulose (I, II, III₁, III₁₁, IV₁ and IV₁₁). Cellulose I (native cellulose) is found in bacteria (I α) and plants (I β). Cellulose (I α), bacterial cellulose, is reported forms a cellulose fibrils network that have diameters of microfibrils within 2–4 nm and are less than 100 nm wide [74]. Cellulose II is obtained through either regeneration or mercerization of Cellulose I. Polymorphs III₁ and III₁₁ are synthesized via reversible processes from cellulose I and II respectively. Cellulose IV₁ and IV₁₁ are derived by applying heat to cellulose III₁ and III₁₁ accordingly. Each of these polymorphs have their unique characteristics and are used differently [75]. The first crystalline structure of the material was reported by Carl von Nageli which was then verified using x-ray crystallography [76]. Cellulose I α and β have crystalline structures of triclinic and monoclinic respectively [77]. Figure 2.2 illustrates the typical structure of cellulose I β conformation that is found in plants, which is the expected allomorph from this research.

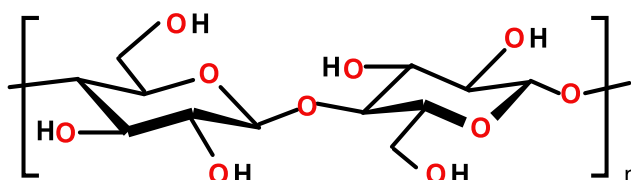


Figure 2.2: Chair conformation of an unbraided homopolysaccharide composed of β -D-glucopyranose units linked by (1, 4) glycosidic bonds

Park *et al.*, studied the crystallinity of cellulose and reported that XRD patterns of cellulose are insufficient in the extractions of crystal lattice data because of the small cellulose crystallite size, which was 5 nm. A significant portion of cellulose is amorphous with the crystallite structure being deficient. Crystallinity index is used to describe the relative amount of crystalline material, for example amorphous is shown as less ordered and crystalline is shown as ordered [77]. Using the XRD height method as developed by Segal *et al.*, gives the most accurate CI result as compared to XRD amorphous subtraction, XRD peak deconvolution and NMR C4 peak separation.

Cellulose composite is reported to be allured by the eco-friendliness of the materials produced [78]. The mechanical properties indicated its ability to compete with aluminum and glass fibers revealing the relatively high modulus. When it comes to specific stiffness, it happens to be among the best natural fibers. The paper reported that natural fibers are also use for composite materials. Bio-composites are less hazardous to handle and need less energy during processing. They are aimed to replace petroleum-derived polymers since their application runs from structural to biomedical. More so, they can be used to eliminate the chemical incompatibilities between reinforcements and matrix phases. The eco-friendliness of composite depends on the materials involved, processing methods and the corresponding energy needed. The good mechanical properties permit it to be applied as a replacement of bone and cartilage in biomedical devices. The quality of cellulose as a fiber-reinforcement material plays a major role in the future.

2.4.2 Studies on cellulose as a support reinforcement materials

Research has been done focusing on cellulose as a matrix and how to improve the photocatalytic activity of the cellulose- titanium dioxide composites.

Reusable photocatalytic TiO_2 -Cellulose nanofiber films were studied [79]. It was agreed that both cellulose nanocrystals and cellulose nanofibers have physiochemical properties. Being flexible, hydrophilic biopolymers, they can easily be molded into films of different shapes and sizes. Their readily functionalized surface makes it a good matrix. The paper aimed to process and design TiO_2 -CNF films that can be applied over the entire solar spectrum and used to degrade methylene blue dye. Solar irradiation for one hour without

pre-soaking resulted in the degradation efficiency of 60%. However, when doped with gold and silver (Au-TiO₂-CNF and Ag-TiO₂-CNF), the percentage shot up to 75%. While testing the absorbability, there was an initial concentration drop similar to the result when irradiated. This means that adsorption contributes to the photo activity of the composites. Repeating the experiment 4 to 5 times, the reusability showed more degradability potentials. The films can be cleaned off dye by simply soaking in water for 10 min. Though the efficiency of TiO₂-CNF film did not display a high percentage in their experiment, they reported that further investigations on the time factor e.g. increasing the time of irradiation, could have shown a better result. Nevertheless, CNF is still an encouraging matrix material that is a lot easier to handle.

Recently, water-resistant cellulose doped in TiO₂ was studied for its photo activity. The authors of the article referenced [52], explained that the basic understanding of the retention, dispersion and aggregation of nanoparticles for the regulated photocatalysis is lacking. As a contribution to knowledge from their paper, polyamide-amine- epichlorohydrin (PAE) was used as an adhesive between micro fibrillated cellulose (MFC) and titanium dioxide (TiO₂) resulting in a water-resistant material. As a proposed solution to the aggregation, their aim was to disperse TiO₂ NPs in an MFC network with meticulous retention, scattering and agglomeration, while maintaining the wet strength of the produced composites. The photocatalytic activity was monitored by degrading methyl orange dye. MFC-PAE showed no photocatalytic activity except for adsorption which took 2 hours under visible light in order to attain equilibrium. For this reason, all the sample were kept in the dark for 2 hours to adsorb the MO molecules completely before exposure to UV light. The network of PAE proved to strongly retain the nanoparticles and prevent leaching. An optimum composite ratio was derived, above the ratio, photo activity was levelled off.

2.4.3 Sources of cellulose

As already stated, cellulose is a material that comes from different sources. Research studies shows the isolation of cellulose from a number of sources over the years. Yandan and his team successfully extracted cellulose from the lotus leaves characterizing the cellulose fibers as potential candidates for future research [80].

Velvet leaves [81] are another interesting source of cellulose that was studied and it too is classified as weed. They are currently used to manufacture ropes, bags and cordages in North America. The paper aimed to study the properties, structure and composition of the cellulose fibers in comparison to other sources. It was reported with evidence that the mechanical properties make the leaves compliant and a prospective source of cellulose.

With the aim to add to the knowledge base, Narenda *et al.*, [82] decided to look at cellulose extracted from sorghum leaves and stem. Apart from it being an edible crop and applicable in the pulp industry, the wonder of it being used as a source of fiber was the question. With intense processing and characterization, it was concluded that the cellulose fibers extracted are comparable to known sources and could be even more efficient in terms of stress and strain than that gotten from cotton.

Other reported sources of cellulose include; cotton [83], rice straw [84], caraua fibers [74], a crop in Indonesia known as *Gigantochloa scortechinii* [85], black leaf, palm leaf [86], tropical water hyacinth [87] and Palm kernel cake [88] just to name a few. The highlights of cellulose extraction are described efficiently with various methods by Esraa Mohammed [86]. According to our knowledge, little or no studies have been done on *Colophospermum mopane*.

Cellulose extracted from varying sources results in diversity of dimensions, morphologies, and degree of crystallinity. All these are dependent on the initial biological source and the processing conditions. This research uses a new source from *Colophospermum mopane* leaves which is indigenous to the Southern African environment and prone to valorization. Unlike glass fibers and other fillers, natural fibers are less hazardous, biodegradable and use less energy during production [89].

There are so many cellulose extraction methods that have been reported and extensive research have been done because of the complexity of plant cell walls [86][88-89]. Cellulose nanofibers can be extracted by three process types namely: mechanical treatments (grinding / milling), chemical treatments (TEMPO oxidation), or a combination of chemical and mechanical treatments [71]. For this research, the latter method is used. Chemical and mechanical treatments are needed to dissolve lignin, hemicellulose and non-cellulosic materials. The role of lignin in plants is to retain water in fibers, stiffens the plant enable it to withstand gravity and wind, and lastly to protect the plant from biological attack.

Hemicellulose is known to be the glue between cellulose and lignin [91]. In order to attain pure cellulose, these two compounds need to be eliminated. Amongst the abovementioned extraction processes, the method selected for this research consisted of acid hydrolysis, chlorination, alkaline extraction and bleaching of the fibers. This method was chosen due to its environmental friendliness, economic reservations and energy-saving advantage.

2.5 *Colophospermum mopane* as Cellulose Source

2.5.1 Current Uses of Mopane Tree

In rural areas, it was cited by Makhado *et al.*, [92] that 80% of the locals use fuel wood as a main source for cooking and heating. Mopane tree wood is preferred because it releases less smoke when dry, has high energy content and is durable. 7.8 kg of wood is for cooking per meal/day would suffice a family of 7 indicating its value in villages. Women craft the branches into sweeping grass and use it to thatch roofs [93].

Additionally, the wood is used to build houses and fences because of its termite-resisting capability. Mopane timber is also widely utilized in the construction of the traditional huts, kraals and grain store [9]. The distinguished red color makes it a wonderful woodwork for the floors. Internationally, it is known as the “Rhodesian ironwood” and is used as an adorning wood on ornaments or sculptures. Furthermore, it is applied to construct musical instruments for example the woodwind or the clarinets [94].

Apart from some articles highlighting the nutritional value of mopane leaves, leaf phenology and the use of mopane leaves to heal wounds, there is very little physical research done on it. During autumn, the leaves fall off from the trees and cause a mess to the surroundings as they are blown around which end up blocking sewers, causing pollution to the surroundings and keeping it untidy. Residents rake and burn them which is also another environmental danger releasing dangerous gases into the atmosphere. A solution has been proposed to convert this natural resource into a value-added product of higher value. This research aims to broaden the application of mopane leaves by tailoring the extracted cellulose into a catalysts’ support material.

2.6 Textile Dyes

2.6.1 Dyes

Industrial waste water, contains a variety of pollutants, dyes being one of them. The color-inducing groups they contain aids with the intensification of color [58]. Dobner and Fisher made an aniline-based dye (a triphenylmethane salt) and derived its name from the minerals colour, hue. Malachite green (MG) dye is used for the dyeing of silk, wool, leather food and hair. The green crystals give a maximum absorbance of 616.9 nm. it is also applied as an acid-base indicator, used to kill parasites, mould and fungi in fish tanks [95].

2.6.2 Reported Dye Removal

Having explained the importance of dye-removal, there are techniques that are already in practice. Guahui Li *et al.*, [58], listed a number of approaches: Ion exchange, coagulation-flocculation, physical-chemical decolouration, adsorption, oxidation and biological methods.

Enzymes are used in the biological treatment of wastewater with 3 common ones being catalase and superoxide dismutase [96], and laccase. Li *et al.*, wrote an article looking at laccase-immobilized bacterial cellulose composited with TiO₂ in order to degrade red X-3B dye. Lacasse is a multi-copper oxidase derived from plants and fungi has the ability to catalyze the degradation of phenolic groups without co-forming toxicants. Immobilization of enzymes on materials with high surface areas adds benefit to the degradation process by reducing the period of oxidation which in turn avoids the polymerization of reaction products. Titanium dioxide, having a high surface area was selected as the matrix [58]. The large number of hydroxyl groups on the TiO₂ surface expedites covalent coupling with the enzymes maximizing the efficiency of photo-biocatalytic dye degradation. Radicals formed during UV irradiation causes the photocatalytic reaction between TiO₂ and the molecules adsorbed on the surface with a positive effect from the high surface area to volume ratio [97]. It was pointed out that TiO₂/UV photocatalysis is non-toxic, operational and green for waste water treatment. The problem faced by TiO₂ agglomeration was overcome by compositing it with bacterial cellulose. This natural biopolymer was produced from *Komagataeibacter xylinus* having a fiber diameter of 40–70 nm (good surface area-to-volume ratio), super-hydrophilicity and great wet mechanical strength giving it a positive

advantage to act as titanium support. By the sol-gel synthetic method, TiO_2 sol was adsorbed by the hydroxyl binding sites of fibrous cellulose network onto the surface [98]. Bacterial cellulose membranes are reported to be an effective enzyme carrier in photocatalysis compared to free laccase. Studying the photodegradability, it was noticed that the performance was 40% less than the performance from cellulosic nanofiber.

Organic dyes such as xanthenes, flavins, ruthenium complexes, and colloidal scatterings of nanomaterials for example carbon nitrides, quantum and carbon dots have been used to develop photosensitizers to effect transfer of excited electrons to enzymes for redox biocatalysis has been researched about. Natural dyes mentioned as photosensitizers include the extracts of black rice, Rose xanthine, paprika, seaweed and flowers of *Erythrina variegata* [96]. However, the straightway inoculation of electrons from the photocatalyst to the enzyme core has to explored in depth [96].

Song *et al.*, published an article describing the biodegradation of malachite green dye by *Pseudomonas veronii*. Although bio-catalytic degradation could be an efficient method of water treatment, only a selected bacteria species are able to grow malachite green (MG) whereas the rest died out. The degradation efficiency of the isolated bacterial strain reached 92.2% within 4 days. The microorganism was said to perform well under acidic or neutral conditions [99].

Another paper by Raval *et al.*, [100] sheds light on the dye and its different treatment techniques testing the dye removal using only adsorption by various adsorbents. The authors describe dyes to be chemical compounds, usually organic, that attach onto the fabrics' surface changing the color. Approximately half of them are classified as azo dyes which are the largest group of synthetic colorants used in textile industries. Recorded treatment techniques include; biodegradation, decolorization, photo active degradation, photocatalytic degradation and coagulation-flocculation. Activated carbon fibers were mentioned as good adsorbents alongside zeolites, clays, nanocomposite and biopolymers.

An attempt to remove MG dye using a polyester known as P(3HB) as an adsorbent agent investigated [101]. The electro spun film exhibited great adsorption capacity. The film was further improved by doping it with TiO_2 photocatalyst to form a dual-type treatment system employing adsorption and photocatalyst decomposition. Complete decolorization of MG in 45 min under visible light was reported.

ZnO/TiO₂ [102] and TiO₂/WO₃ [103] composites were used to degrade MG dye under UV irradiation. ZnO nanoparticles were used for photocatalysts of MG dye. The photocatalyst was synthesized using co-precipitation method. The degradation process was carried out under different energy source; microwave, ultrasonic and solar irradiation. It was reported that sono chemical treatment was the most effective, (99.3%). This technique has its drawbacks such as high expense and maintenance. In places where solar energy is plentiful, sunlight irradiation is recommended as an energy source proving to be 97.7%. This method can be easily applied to effluent treatment plants industries.

Cu/ZnO nanocomposite were also used to degrade MG dye by Modwi *et al.*, doping Cu in Zn was done with the aim of lowering the band gap by creating lattice defects in turn increasing the visible light absorption. Mostly, it was highlighted that crystallinity, crystal planes, surface areas and surface properties play a role in the photocatalytic activity. The authors noted that this catalyst was less photo-active towards MG dye as compared to other Cu-doped composites [104].

Wang *et al.*, successfully degraded MG dye in seawater using a hybrid of ZnO nanorods grown in a 3D graphene oxide/nickel foam. Apart from MG dye being a colorant, it was used in the past as a fungicide in fisheries. Along the way, the dye resulted in promoting tumors being toxic to the aquatic life. The article studied the complete mineralization of organic colorants in brine. Three materials were synthesized with ZnO-NF, RGO-NF and ZnO-RGO-NF using hydrothermal method to grow the ZnO nanorods. It was reported that the photodegradability was highest using ZnO-RGO-NF under UV light compared to the other photocatalysts [1]. The reaction followed pseudo-first order with a fast rate of 0.06 min⁻¹. Silva *et al.*, affirmed that titanium dioxide catalyst has proven its ability to degrade dyes like alizarin S, congo red, crocein orange G, methyl red and methylene blue (MB) under UV light [22].

3.0 MATERIALS AND METHODOLOGY

3.0 Introduction

This chapter gives an overview of the materials, methods and procedures used for the synthetic process of cellulose-titanium composites at different concentrations. Also explained are the techniques used for the sample analysis and finally the photocatalytic activity. The characterization determined the crystallinity, functional groups, hydrogen bonding, morphology, thermal stability and optical properties of the materials. Thereafter, the photoactivity of the catalysts were tested by degrading malachite green dye over a fixed time period. The photocatalytic performance was studied under UV and solar light irradiation. The kinetic study and recyclability experimental setup are explained.

3.1 Chemicals and Materials

Two sets of reagents and apparatus were used for the experimental processes of cellulose extraction and photocatalyst synthesis as listed below.

3.1.1 Cellulose extraction

Colophospermum mopane leaves (locally collected in Palapye, Botswana), Sodium hydroxide pellets, NaOH; (99.99% Sigma Aldrich, Germany), Sodium hypochlorite (NaOCl); (10% w/v. Sigma Aldrich, Germany), Glacial acetic acid (CH₃COOH); (99.97% Sigma Aldrich, Germany), Nitric acid, HNO₃; (90% Sigma Aldrich, Germany), Ethanol; (99.9% Sigma Aldrich, Germany), and De-ionized water.

3.1.2 Cellulose-titanium dioxide composites

Titanium isopropoxide, TTIP; (99.9% Sigma Aldrich), Acetone, C₃H₆O; (95% Sigma Aldrich), Teflon-Lined stainless-steel autoclave reactor; (200 mL Sigma Aldrich) and Malachite green dye. The XRD Diffractometer used was a Bruker D8 to attain the intensity and 2 θ angle readings from the samples. Bruker Vertex 70v FT-IR was the spectrophotometer used to derive the transmittance and wavenumbers reflected by the materials. The microscopic images were captured by JEOL JSM 7100F field emission scanning electron microscope (FESEM) at different magnitudes. Mettler Toledo TGA/DSC measured the %weight of the samples at increasing temperature. Absorbance and wavelength of the samples were measured using UV–Vis spectrophotometer (Thermo Scientific™ Evolution 201).

3.2 Collection and Extraction of Cellulose from *Colophospermum mopane* leaves

A bucket of fresh mopane leaves was collected from the neighborhood and left to dry for a week. The leaves were then ground with a blender into smaller fibers. About 5 g of the fibers were heated in 150 mL of 5% sodium hydroxide at 100 °C for 3 h. This was done to remove hemicellulose and other greasy materials. The product was washed with distilled water resulting in brown fibers. Delignification was performed using sodium hypochlorite treatment for another 3 h, again washed with distilled water and filtered. This gave a yellow product. The next step involved bleaching in nitric acid and ethanol in a concentration ratio of 1:2 for 2 h. This de-waxing process gave rise to a paler yellow product. Pure cellulose was obtained by a second series of bleaching with sodium hypochlorite and washed severally with glacial acetic acid (CH_3COOH) to produce the expected white fluffy cellulose powder. Figure 3.1 shows a graphical representation of the summarized experimental procedure.

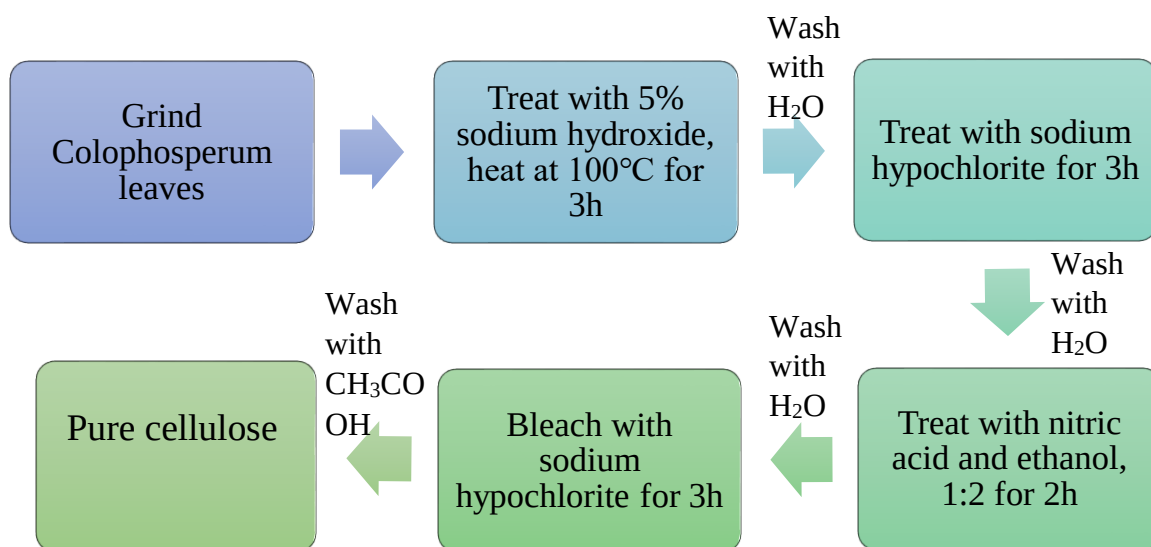


Figure 3.1: Cellulose extraction process from *Colophospermum mopane* leaves.

3.3 Preparation of Cellulose –Titanium composites

After the extraction of pure cellulose, titanium dioxide was deposited on the surface to produce a cellulose-titanium dioxide composite. As mentioned, grafting and coating are ways of composition. Solvothermal method was used to synthesize the composite. A number of composites with varying amount of TiO₂ were prepared and labeled Cell-TiO₂-x where x = 1, 1.5, 2, 3 and 4% (w/v). Using a standard cellulose weight of 0.5 g, volumes of titanium isopropoxide [0.5, 0.75, 1, 1.5 and 2 mL] were measured using a micropipette in a beaker containing 15 mL of acetone. The mixture was ultra-sonicated for 30 min in order to separate the cellulose fibers. The process of homogenization allowed complete integration between the fibers and the catalyst. The content of the beaker was emptied into the Teflon flask and transferred to the oven. At 150 °C, the reaction was left to run for 3 h and thereafter allowed to cool at room temperature. The residue was centrifuged for 5 min at 9000 rpm, washed with acetone 3 times and dried in the oven for 5 min. In synthesizing the blank catalyst, 1 mL of titanium isopropoxide and 15 mL of acetone was reacted the same way in the absence of cellulose fibers. The materials appeared to be milky white powder.

3.4 Characterization of the Cellulose and Cellulose– titanium composites

3.4.1 X-ray Diffraction crystallography (XRD) analysis

To investigate the crystal structure of cellulose fiber and cellulose- titanium composites and crystallinity index, X-ray diffraction was used. The XRD patterns data was obtained from a Bruker D8 advanced power diffractometer with a Cu tube X-ray source and a LynxEye XE energy-dispersive strip detector. The machine operated at a wavelength of 1.54056 Å covering the 2θ angles between 5 and 90 degrees at a rate of 0.500 sec/step. The current and acceleration voltage were set at 40 mA and 40 kV respectively. Crystallinity index which is the amount of crystalline cellulose with respect to amount of amorphous cellulose was calculated using Segal *et al.*, equation below [105].

$$CI = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad 8$$

Where I_{002} is the intensity of diffraction maximum of crystalline region close to 22°

While I_{am} is the intensity value for the amorphous cellulose region close to 18° [106].

The average crystallite size of cellulose and Cell-TiO₂-2 were deduced following Scherrer's equation. This catalyst sample was selected as it proved to have a better photoactivity than the other composites. Scherrer's equation:

$$d = \frac{K\lambda}{\beta \cos \theta} \quad 9$$

Where K=0.89, is the shape factor of particles, β is the peak width at half maximum (in radians), λ is the X-ray wavelength (0.15418 nm), and θ is the Bragg angle.

The d-spacing were calculated using the Bragg's Eq. (9) and the crystallite sizes were calculated from the widths of diffraction peaks using the Scherrer Eq. (10):

$$n = 2d \sin (1)$$

$$L = 0.9 H \cos (2) \quad 10$$

Above, the incident wavelength is denoted as n, spacing between planes in the atomic lattice as d. Angle between the scattering planes and incident ray is represented by Θ . The perpendicularity of the crystallite size to the plane is symbolized as L and the full width at half-maximum (FWHM), is indicated as H. The angle was set to radians [112].

3.4.2 Fourier Transform Infra-Red (FT-IR) analysis

The functional groups present in the extracted cellulose were identified using the spectroscopy technique of FT-IR. Approximately 5.00 mg of the cellulose sample and 195 mg of potassium bromide (KBr) were mixed systematically in a mortar until homogenization. The mixture was inserted into the sample chamber of a Smart Collector Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) addition of the spectrometer, which was continuously expelled with dry air. Bruker Vertex 70v FT-IR spectrophotometer furnished with a purge gas generator and DTGS KBr detector was used for analysis. The spectral resolution was set to 0.09 cm⁻¹ and the wavenumber precision to 4 cm⁻¹, 100 scans were used for each spectrum [127].

To investigate the hydrogen bond energies within the molecule, the equation shown below was used:

$$Eh = \frac{1}{k} \times \frac{V_o - V}{v_o} \quad 11$$

Where $1/k$ is a constant; 2.625×10^2 , V_o is another constant 3650cm^{-1} , V is the $-\text{OH}$ band wavelength

The hydrogen bond distance was also deduced using the equation:

$$\Delta v = 4430 \times (2.84 - R) \quad 12$$

Where $\Delta v = v_o - v$ and R is the hydrogen bond distance.

3.4.3 Scanning Electron Microscopy (SEM)

The surface morphology of the samples was studied using a JEOL JSM 7100F field emission scanning electron microscope (FESEM) coupled with an energy dispersion spectrometer (EDS) detector. The sample to be observed under the FESEM were attached on conductive adhesive tape, sputter coated with carbon and observed using a voltage of 15 kV. Focus was made on the cellulose fibers capturing images of the single cell strands, fiber bundles, titanium dioxide particles and the cellulose-titanium composites' surfaces displaying the physical properties of the tiny particles at a magnification from x400 to x5000.

3.4.4 Thermo Gravimetric Analysis (TGA)

Thermo gravimetric analysis was carried out using a Mettler Toledo TGA/DSC with built-in micro and ultra-micro balances having sub-microgram resolution over the whole measurement range. The thermal stability of both the extracted cellulose and the pretreated fibers were measured under a nitrogen atmosphere with a gas flow of 100 mL/ min and heated from 25 to 600 °C at a rate of 10 °C / min. In addition, this method can be to explore the chemical reactions that transpired during heating which resulted in the weight difference [107].

3.4.5 Ultra Violet-Visible (UV-VIS) Spectroscopy

For UV-Vis spectrophotometry, Thermo Scientific™ Evolution 201 was used to observe the photodegradation spectra of Malachite green dye in the wavelength range of 200–800

nm. Higher energy radiation in the electromagnetic range with UV (200-400 nm) and in the visible region (400 -700 nm) was used in characterizing the samples. This apparatus was used for all the samples obtained during the photo degradability. Distilled water was used to wash the cuvette after each sample run and also used to attain equilibration before every experiment.

3.5 Photocatalytic Evaluation

The selected organic pollutant was aqueous malachite green dye with molecular structure shown in Figure 3.2, color index #3c7a6e, molar mass 364.911 g/mol, and chemical formula $C_{23}H_{25}N_2$ just to mention but a few properties of the dye.

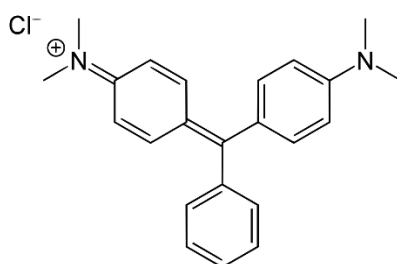


Figure 3.2: Molecular structure of malachite green dye

The photocatalytic activity of the Cell-TiO₂-x was tested by dissolving 0.1 g of the sample in 10 ppm aqueous solution of the Malachite green dye (50 mL, 10 mg/L). In a dark room, adsorption-desorption equilibrium between the photocatalyst and the dye was left to occur for 30 min with continuous stirring. After every 10 min, samples were collected in the 2 mL vials to study the adsorptivity. The samples were centrifuged for 5 min then allowed to settle. This process separated the residue from the clear solution. About 1 mL of the liquid was transferred into the cuvette for absorbance measurements. 30 min of adsorption was carried out in the dark for every reaction before exposure into the light. Photodegradation was carried out under UV light and solar irradiation for 160 min. The UV lamp used in the reaction was UVP UVG-54 operating at 0.16 A with UV output of 254 nm placed at a distance of 2 cm away from the beaker containing the solution. Sampling in this case, was done after every 20 min to monitor the photodegradation process. The samples were centrifuged at 5000 rpm for 7 min and the absorbance was measured using the UV-Vis spectrophotometer within the given range.

The absorbance of MG dye was measured using the maximum absorption peak at 616 nm of the malachite dye. Using the absorbance, final concentration/ initial concentration (C/C_0) was calculated and the degradation percentage was recorded. The percent degradation was calculated using the equation below:

$$\text{Percent degradation} = (C_0 - C/C_0) \times 100\% \quad 13$$

Where C_0 and C are initial concentration of the dye solution before and after irradiation for the selected time.

3.6 Study of photocatalyst recyclability

To test the materials stability in the photodegradation of MG dye, Cell-TiO₂-2 sample was used. Initially, 0.1 g of the sample was added to 50 mL of 10 ppm MG solution and reacted under UV irradiation for 140 min. The degradation efficiencies were tested and recorded for the first cycle. Thereafter, the material was recollected, washed and dried in preparation for the second cycle. The concentration value was maintained constant only changing the volume of the solution according to the mass measured. The same was done for the third, fourth, fifth and sixth cycle. The degradation percentages at $t = 140$ min is reported in chapter 4.

3.7 Band gap determination

The optical properties of the materials were investigated in order to identify their band gaps. About less than a gram of each sample was deposited into a beaker containing 10 mL methanol and sonicated for 5 min to disperse the powders. Then, 2 mL of homogenous mixture was sampled into the cuvette and run using the UV-Vis machine to give the absorbance vs wavelength graph.

$$\text{Band gap} = \frac{1240}{\text{wavelength}} \quad 14$$

The formula above gives the band gap after determining the wavelength at the curve.

4.0 RESULTS AND DISCUSSION

4.1 Extraction of Cellulose and Characterization of Cellulose-Titanium Composites

Extracting cellulose from the dried green leaves gave white powdery fibre materials. Most of the hemicellulose and lignin were broken down and washed off as brown slurry. The material was thereafter characterized.

Figure 4.1 presents the structural properties of cellulose and its pre-treated fibers as measured by XRD. Cellulose I² sample from the database showed a similar XRD pattern to the extracted cellulose was also displayed in Figure 4.1. The full width at half maximum was plotted in Figure 4.2 which was further used to deduce the crystallite size.

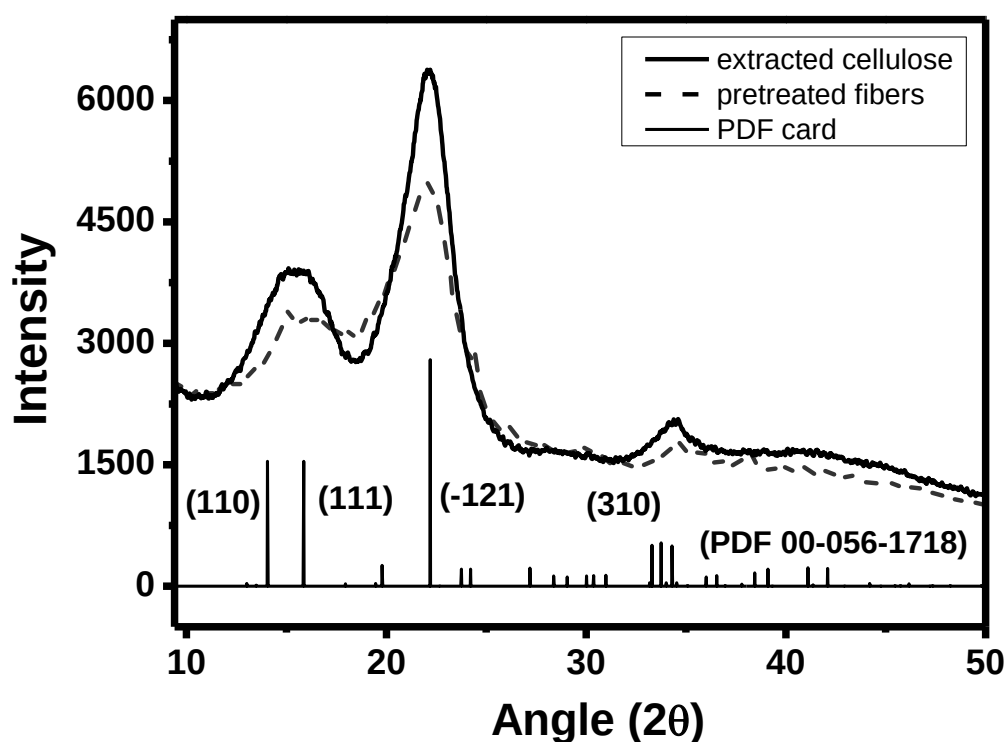


Figure 4.1: XRD patterns for extracted cellulose and pre-treated fibers compared to the JCPD card

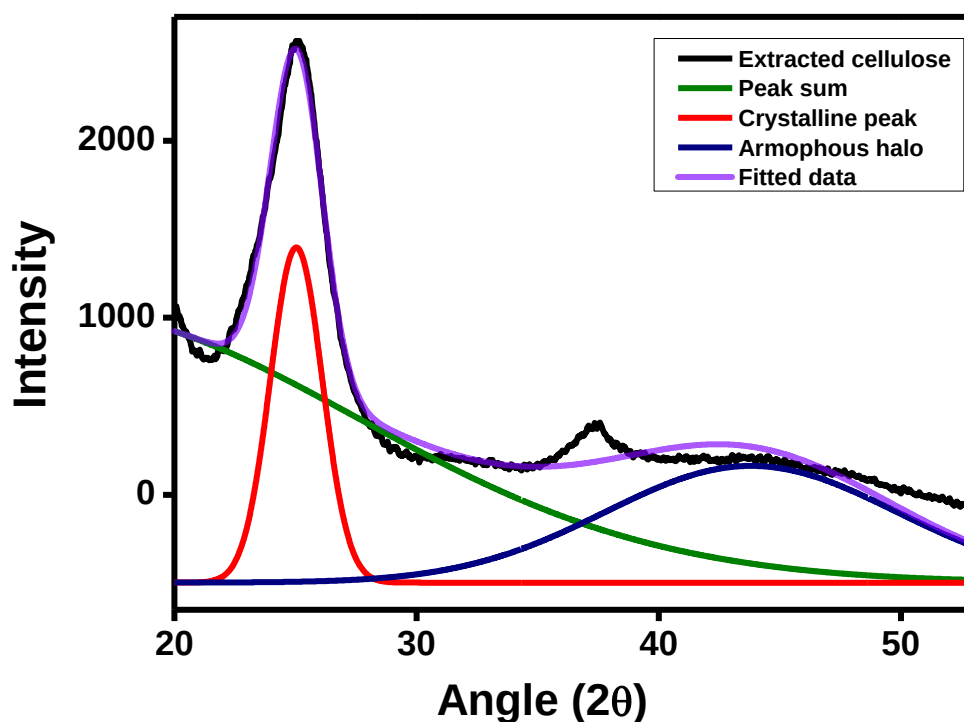


Figure 4.2: XRD pattern of extracted cellulose with calculated FWHM

The 2θ angle ranged between 15 and 50° . The rough XRD patterns observed were as a result of crystalline scattering and the diffused background of the smoothed plot. Diffraction peaks were located at 2θ values of 22.08° (crystalline area) and 18.21° (amorphous area). At around 43° , an amorphous halo is noticed. This is as a result of the scattered x-ray reflection arising from the amorphous part of the material [120].

In Figure 4.1, the cellulose peak shows a much intense and higher peak than that of the pretreated fibers. The CI, represents well orientation of the cellulose crystals along the fiber axis. The difference between the 2 peaks is due to the removal of amorphous hemicellulose and lignin. The effect of chemical treatments on cellulose during extraction also played a part, hence permitting a better packing of the cellulose chains [111]. The broadness that is viewed is contributed by the presence of non-cellulosic materials. Hydrogen bonding and Van der Waals interactions existing between hydroxyl groups of the pure cellulose molecules produces a well pronounced curve [105]. When the amorphous components are detached, the -OH groups create new hydrogen bonds which increase the crystallinity of the material [74].

The intensity values from the crystallinity phase can then be used to calculate the crystallinity index utilizing the Segal equation stated under the methods section in chapter 3 (eq. 8) . The value was recorded in Table 4.1.

XRD patterns of cellulose extracted from cotton, hemp, kenaf and velvet leaves have been reported [81] and these are summarized in Table 4.1.

Table 4.1: Summary of crystal indices from literature

Cellulose Source	Crystallinity index	Reference
Hemp	88	[89]
Kenaf	69	[113]
Velvet leaves	65	[81]
Cotton	60	[77]
Sorghum fibers	56	[82]
Mopane	56	Present study

Crystallinity index is directly proportionate to the crystallite size i.e. the lower the crystallinity indexes the smaller the crystallite size. To calculate the crystallite size of a material, the Scherrer equation (eq. 9) was used. The crystalline peaks were extracted using a curve-fitting process assuming Gaussian functions for each peak and used to calculate the full width at half maximum (FWHM). Figure 4.2 illustrates the Gaussian analysis and estimated FWHM. The R^2 value was 0.90714 indicating an accurate graph.

Using the FWHM values denoted as β , k constant being 0.9, λ as 0.15406 nm, the crystallite sizes at the three peak positions were calculated. The average D value was found to be 1.36 nm.

In addition, Figure 4.1 confirmed the documented diffraction peaks for 110, -121, and 310 crystallographic planes, which are the distinctive peaks of cellulose I lattice, were present [80]. Ragab [75] pointed out that different hydrogen bonding networks and molecular orientations are dependent on the cellulosic native source and its treatment. The XRD patterns indicates which of the polymorph the compound belongs to and from this research, the extracted cellulose XRD pattern matched mostly with JCPD card PDF 00-056-1718. This is illustrated in Figure 4.1 which shows the matching peaks and their (*hkl*) values. The database corresponded this material with 93% accuracy to cellulose I² compound having a

molecular formula of $(C_6H_{10}O_5)_n$. The unit cell has a monoclinic structure, cells with 2 chains per unit cell as shown in Figure 4.3.

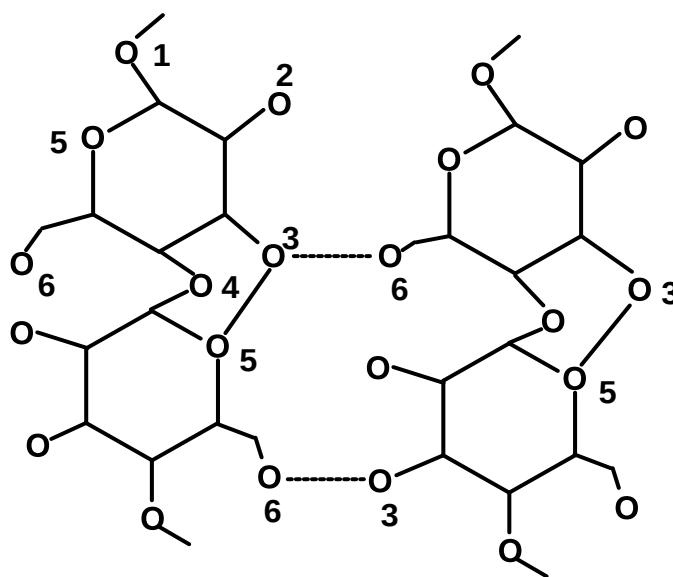


Figure 4.3: Molecular structure of Cellulose I β

Examples of non-wood fibers which are cellulosic sources include industrial crops such as hemp, sugarcane or kenaf and naturally growing crops such as grass fibers, bamboo and sorghum [75]. *Colophospermum mopane* fall under the second class, being an indigenous tree. Both these classes produce high quality pulps. The advantage of extracting from these plants is their rapid annual growth and the abundance of fibers. The extraction process can be done on an easier and smaller scale.

The use of X-ray diffraction for cellulose crystallite measurement has been reviewed [112]. It is generally agreed that the crystallinity presence contributes to mechanical, physical and chemical properties of the material. Not only is crystallinity index used in quantification but it is also applied to interpret the changes in cellulose structures after biological or physiochemical treatments. In view of this, XRD analysis always gives rise to broad diffraction peaks which are difficult to distinguish between amorphous cellulose and background scattering. The cellulose crystallite size of 1.36 nm obtained here for *Colophospermum mopane* cellulose falls within the expected range. In addition, they also reported that cellulose crystal cores are entangled with amorphous and para-crystalline layers. As can be seen XRD patterns in Figure 4.1, there is a transition between the crystalline and amorphous regions (15 to 25°) indicating the para-crystallinity of the sample.

As previously stated, cellulose happens to be a semi/ para-crystalline material. The crystallinity index of *Colophospermum mopane* cellulose is small compared to values for other fibers as shown in the table. High crystallinity means more crystalline regions in cellulose fibers, and more regular arrangement with fewer pores of the cellulose molecules compared with a fiber of low crystallinity [106]. This is the case for that of hemp, kenaf and velvet leaves. Cotton happens to have a CI value that is not far from that of mopane. It has a number of common applications especially in the textile industry [83][114].

However, mopane cellulose is less crystalline than the mentioned. Looking at the physical properties of the material, Matheus *et al.*, mentioned that the firmness or rigidity of cellulose fibrils increases and their flaccidity or flexibility decreases with a rise in crystallinity to amorphous regions [105]. As already known, hydrogen bonds affect crystallinity in such a way that they hold molecules together making the sample crystalline [114]. Cellulose from mopane leaves have weaker Van Der Waals forces and interactions compared to those reported from literature which classifies this cellulose as semi-crystalline. It is no surprise that the higher the crystallinity, the higher the crystallite size in relation to the diminishing of the amorphous regions [105]. Amorphous regions in porous materials have a tendency to regain moisture and are flexible in nature such that they are spendable [83]. This can be said about semi-crystalline materials as well.

Sorghum, on the other hand, also has a low % crystallinity. Reddy *et al.*, reported that this could be due to the fact that sorghum itself is built in such a way that it does not have to support heavy-weight grains like that of corn, hence the presence of fewer crystallized cellulose in its structure [82]. This phenomenon can also be used to explain the crystallinity of cellulose in the mopane leaves as both sorghum leaves and the mopane leaves have the same crystallinity index of 56. Sorghum fibers are conveyed to have good orientation of micro fibrils and the cellulose crystals along the fiber axis. The article went onto conclude that sorghum stem and leaf fibers have strengths similar to cotton and corn fibers, and its moisture retention makes it suitable to manufacture comfortable clothing form it [82].

Preferred orientation of the crystallites is seen from the XRD patterns. It is also referred to as the texture. The synthetic procedure, sample preparation method and crystallite nature of cellulose influences the relative diffraction peak intensities and hence affecting the CI. Park *et al.*, suggested that carefully preparing samples to minimize texture aids in the attaining

of more accurate results [77]. Non-uniform crystal strain, peak broadening impact, amorphous content and crystallite size play a role in the materials' crystallinity. Although trying to synthesize samples to give rise to narrow peaks could be a solution, the overlapping of patterns mainly contributed by the crystallite size arises. As explained, the similarity between para-crystallinity and crystal diffraction peaks makes it difficult to differentiate amongst the two and in turn derive accurate CI indices.

4.1.2 Crystallinity of cellulose-titanium dioxide composites

Titanium dioxide was grafted onto the cellulose material following the process in chapter 3. The structural property of the material was studied using X-Ray Diffraction deriving the crystallite size. The XRD patterns of the synthesized materials and matched sample are shown in Figure 4.4.

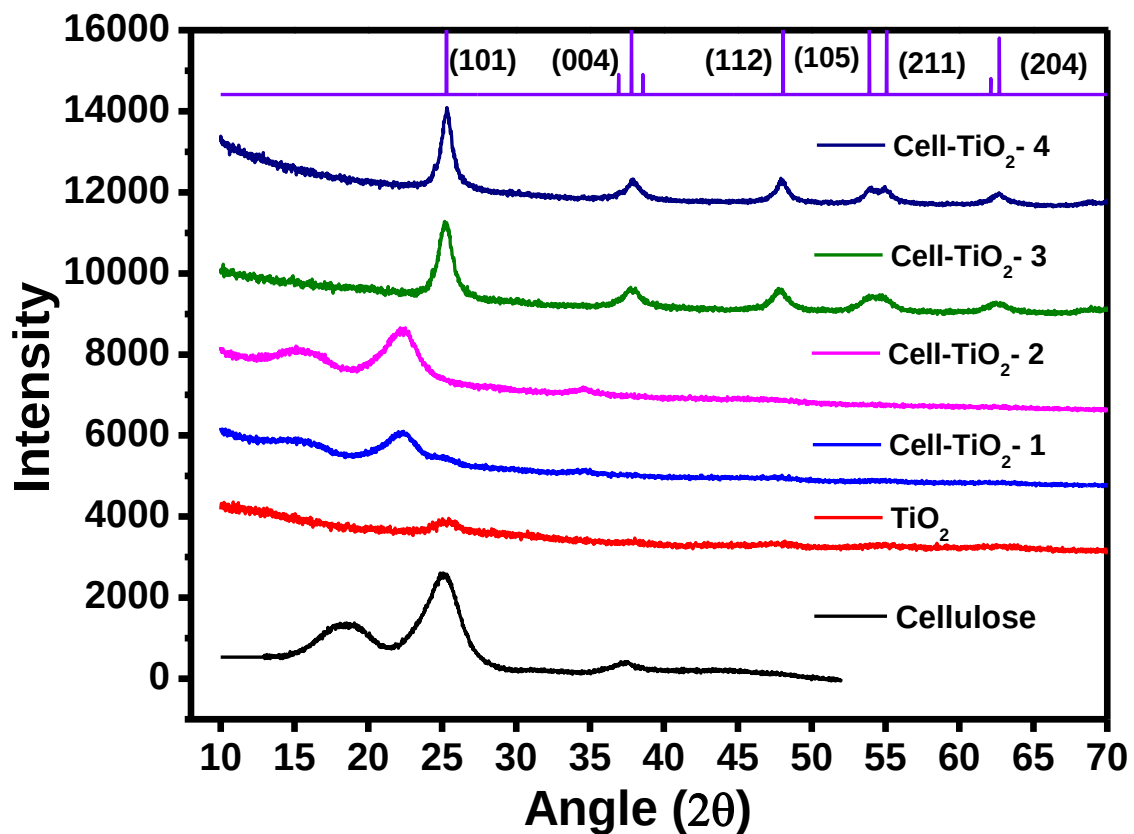


Figure 4.4: XRD patterns of cellulose fibers, pure TiO₂, and composites; Cell-TiO₂-1 to 4 samples. The JCPD card for TiO₂ is displayed

Table 4.2: Crystallite size of cellulose and titanium dioxide.

Samples	a(Å)	b(Å)	c(Å)	c/a	Unit cell volume (Å ³)	Crystallite size (nm)
Cellulose	7.7840	8.20100	10.3800	1.3335	658.36	1.36
Titanium dioxide	3.78865	3.78865	9.4976	2.5068	136.33	19.00

Wang *et al.*, published an article that displays different crystalline patterns for existing XRD patterns of different polymorphs of titania; (Brookite, Anatase and Rutile) have been reported [116]. Comparison of the patterns with pure TiO₂ to that in Figure 4.4, the diffraction peaks at $2\Theta = 26^\circ, 37^\circ, 48^\circ$ represent the (101), (004), (112) crystalline planes present on the TiO₂ pattern [116]. The JCP PDF card number 00-021-1272 match that of anatase titanium dioxide having a tetragonal lattice that was also reported by Godbert *et al.*, confirming the structure of the synthesized material [117].

Cell-TiO₂-1 gives off peaks similar to that of cellulose fibers and this is because the fibers are barely covered by the catalyst so most of the light diffraction is caused by the matrix at (-121). The pattern has broad peaks attributing to the amorphous part of the material. As the concentration of TiO₂ is increased from 1 to 2%, the (111) plane disappears with a right-shift of the (-121) peak indicating the formation of a TiO₂ layer on the surface. Cell-TiO₂-2 has sharper and pronounced peaks. Because it is a composite, the intensity is an equal mixture between that of the cellulose and titanium dioxide hence more manifest.

The (004), (112), (115), (211) and (204) peak from TiO₂ is observed but at a very low intensity so it appears as a straight line. This is affected by the large unit volume of cellulose, 658.36 Å³, compared to that of TiO₂, 136.33 Å³ (Table 4.1). The large cellulose peak at (-121) diffracts most of the light which shadows the peaks formed by the catalyst. On samples Cell-TiO₂-3 and 4, the anatase peaks are more clearly visible; both patterns appear almost identical to each other. The $2\theta = 25.4^\circ$ peak confirmed in the TiO₂ anatase structure [117] which is prominently present in Cell-TiO₂ -3 and 4 catalysts. Cellulose traits are not reflected from the last two patterns because the fibers are densely covered by the semiconductor. The crystallite size of TiO₂ was 19 nm with TiO₂ being a more crystalline

material. Chen *et al.*, reported that the crystallite size of TiO₂ particles range from 20-25 nm [118].

It is evident that the carbon surfaces under the TiO₂ could effectively influence the crystalline degree of the material [119]. Essential peaks are normally missed and the crystalline peaks are misrepresented due to preferred orientation errors [120]. This is an explanation as to why some peaks are not visible enough in the graphs.

Diffraction peak broadening has been reported [120-121], this could be as a result from instrumental errors, crystallite size, strain or stacking fault. The intensities are affected by one or more of the following: multiplicity factor, Lorentz factor, extinction, absorption, micro-absorption, anisotropic distortions (preferred orientation), crystallite size and residual stress or strain [120].

Also, amorphous materials, are crystallite cells that are not identical and shows variation which destroys the long range of order. Bragg's law is known to give the angles for coherent and incoherent scattering from a crystal lattice. The intensity of diffraction peaks and variations are related to the chemistry and atomic arrangement or crystal structure of the material [124]. As previously explained, amorphous cellulose plays its own role in crystallinity.

4.1.2 Fourier Transform Infra-red (FT-IR) Analysis

FTIR basically presents the unique characteristics of the product as obtained from different cellulose sources. The distinctive structure of extracted cellulose is the reason why cellulosic materials tend to differ in terms of strength and applicability.

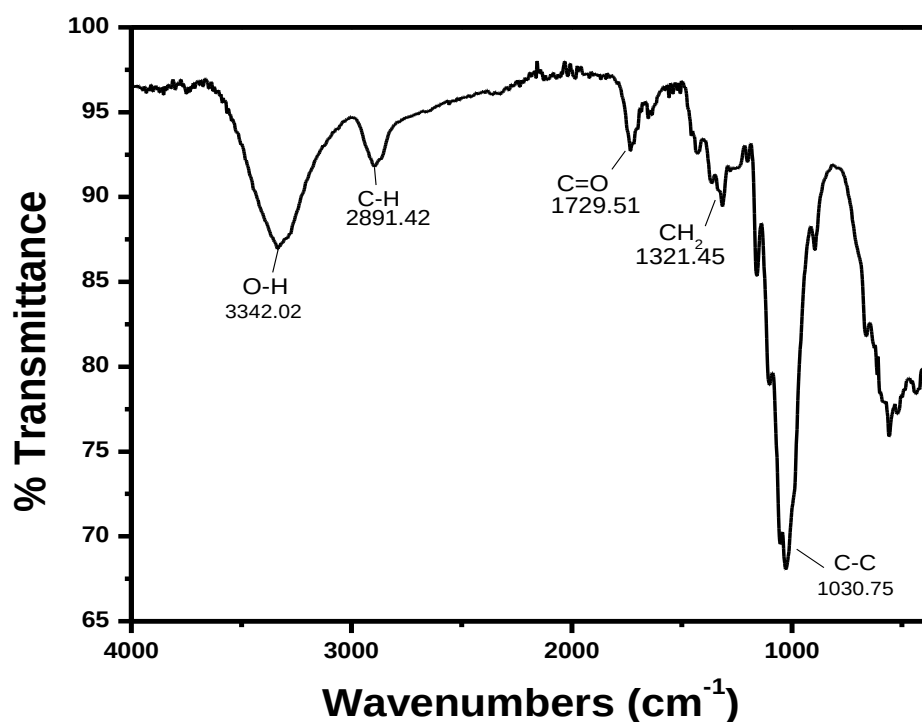


Figure 4.6: IR spectrum of extracted cellulose fibers

Figure 4.6 shows the FTIR spectrum of the extracted cellulose indicating the functional groups present as expected from the cellulose molecule. The broad peak that appears at 3342 cm^{-1} is due to the -OH stretching vibrations, the small sharp peak at 2893 cm^{-1} results from -C-H in-the-plane bending. C=O is the small sharp peak at 1731 cm^{-1} , peak at 1314 cm^{-1} caused by CH_2 rocking vibration at C_6 and lastly the long sharp peak at 1023 cm^{-1} all caused by C-C molecular vibrations and bending. These groups were also present in the extracted cellulose from MCC grade reported by Abderrahim *et al.*, [125]. The functional groups are prominent and described as the cellulose backbone [75] [85].

During the process of extraction, the hemicellulose was transformed to salt forms and the lignin was converted to carboxylic acids that were removed as water-soluble fractions leaving behind a suspended crystalline cellulose in the aqueous medium [126]. The chemical treatment used in the reaction contributed to the peaks at the unique positions. The phenolic groups in lignin are known to have a hydrogen bond peak that appears between 3568 and 3577 cm^{-1} which is not present in Figure 4.6 indicating the effectiveness of sodium hypochlorite and sodium hydroxide treatments in breaking down the lingo-cellulosic structure, giving rise to pure cellulose [90] [105] [86].

Hydrogen bonding is defined in this case as an attraction between a hydrogen atom (H) and a more electronegative atom (O-H). Inter and intramolecular bonds has a distinct effect on the physical characteristics encompassing the crystallinity. It also contributes to the mechanical properties of the cellulose and gives cellulose a strain of 20% [127].

Deqing *et al.*, explored the structural variations of hydrogen-bonding patterns in cellulose. It was highlighted that Cellulose I_β intramolecular H-bonding exists as O3-H-O5 which appears between the 3375-3340 cm⁻¹ band. They went on to describe that in cellulose I, a secondary –OH group at the carbon-3 position forms a hydrogen bond with an oxygen-5 atom at the adjacent of the ring. C3-H-O5 intramolecular bond is appraised to be well defined and standard in Cellulose I allomorph. It happens to be the strong bond in the crystalline structure on the cellulose surface mainly present in the crystalline region [128].

Figure 4.6 molecular structure of cellulose illustrates the bonding interactions. Hydrogen bond energy was calculated by the eq (11):

$$E_h = (2.625 \times 10^2) \times \frac{3650 - 3342}{3650}$$

$$E_h = 22.1494 \text{ KJ/mol}$$

In addition, hydrogen bond distance was derived using the equation (12)

$$\Delta\nu = 4430 \times (2.84 - R)$$

$$R = 2.84 - (307.98/4430)$$

$$R = 2.77 \text{ \AA}$$

Extracted cellulose from *Colophospermum mopane* has the hydrogen bonding energy to be 22 KJ/mol and the intramolecular distance calculated to be 2.77 Å. The bonding energy derived fall within the hydrogen bonding energies range of cellulose (11.798 to 22.007 KJ/mol) reported by Yong Deng [128]. The hydrogen bond energy at 3423 and 3342 cm⁻¹ are not far from that of ramie and kenaf fibers studied by Polleto *et al.*, [105]. It was mentioned that higher energy values associated with low hydrogen bond distances contribute to higher interactions between intramolecular cellulose chains playing a role in the crystallinity of the material. This is affirmed from the XRD results above.

From Figure 4.6, the wavelength plotted (attributed by the mopane cellulose) happens to be lower than that from the commercial cellulose. A report shows that the closer the chains, the stronger the hydrogen bonds [105]. Similarly, the lower the wavelength, the reduction in the force constant of the covalent bond. The length in the bonds involved during vibration absorption increases [127]. In addition, the –OH band from the extracted cellulose appears to have a sharper peak while that from the commercial cellulose is broader. The scission of the intra- and intermolecular hydrogen bonds resulted in a lower intensity hence displaying the sharper -OH band [114].

4.1.3 Scanning Electron Microscopy (SEM) Analysis

Morphology of cellulose

Below are SEM images of the extracted cellulose fibers, titanium dioxide and of cellulose composites (Figures 4.7, 4.8 and 4.9). In figure 4.7a, the aligned single cell fibers have an average diameter of less than 1 μm at a working distance of 9.4 mm with an electron acceleration voltage of 15.0 kV. Long fiber strands appeared to be bound in a fragmented network intertwined to form a bigger bundle. The external surface is shown to have a clean surface with fragmented fractions and also display characteristic convulsions. The presence of convulsions should offer better cohesiveness between the single cells and also increase the fibre strength making them more spendable. Most of the hemicellulose and the lignin were removed from the surface during extraction process [90]. The chemo-mechanical treatments applied enabled the separation of raw fibers into individual nano-sized fibers [85].

Cellulose is a material rich with hydrogen easily reacting with proton acceptors. Possessing a high surface area increases its photo activity retaining abundant active sites. Figure 4.7b show fibers in the micrometer scale. The pore size of cellulose is approximately 0.30 nm causing an advantage to the adsorptivity of the dye onto the surface. The organic molecules of the pollutant are deposited into the pores immobilizing them long enough to be decomposed by the photocatalyst. The extracted cellulose has good mechanical qualities and expected strength in reinforcing materials.

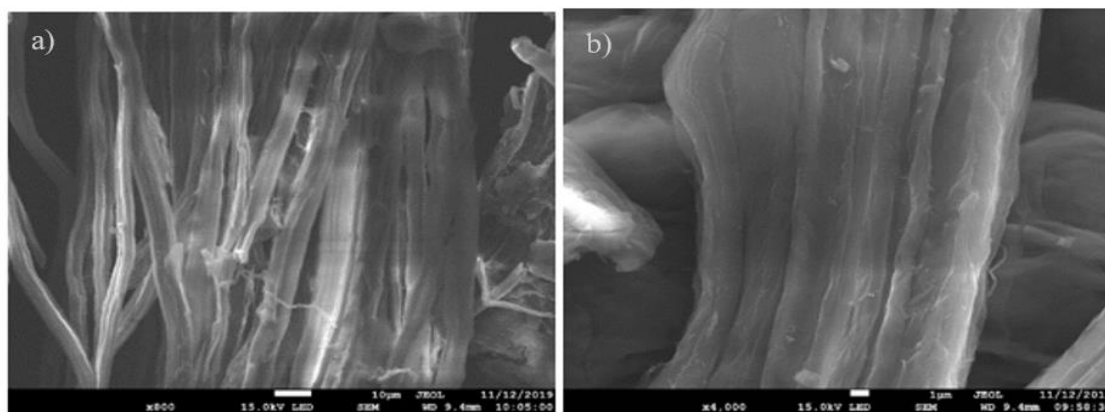
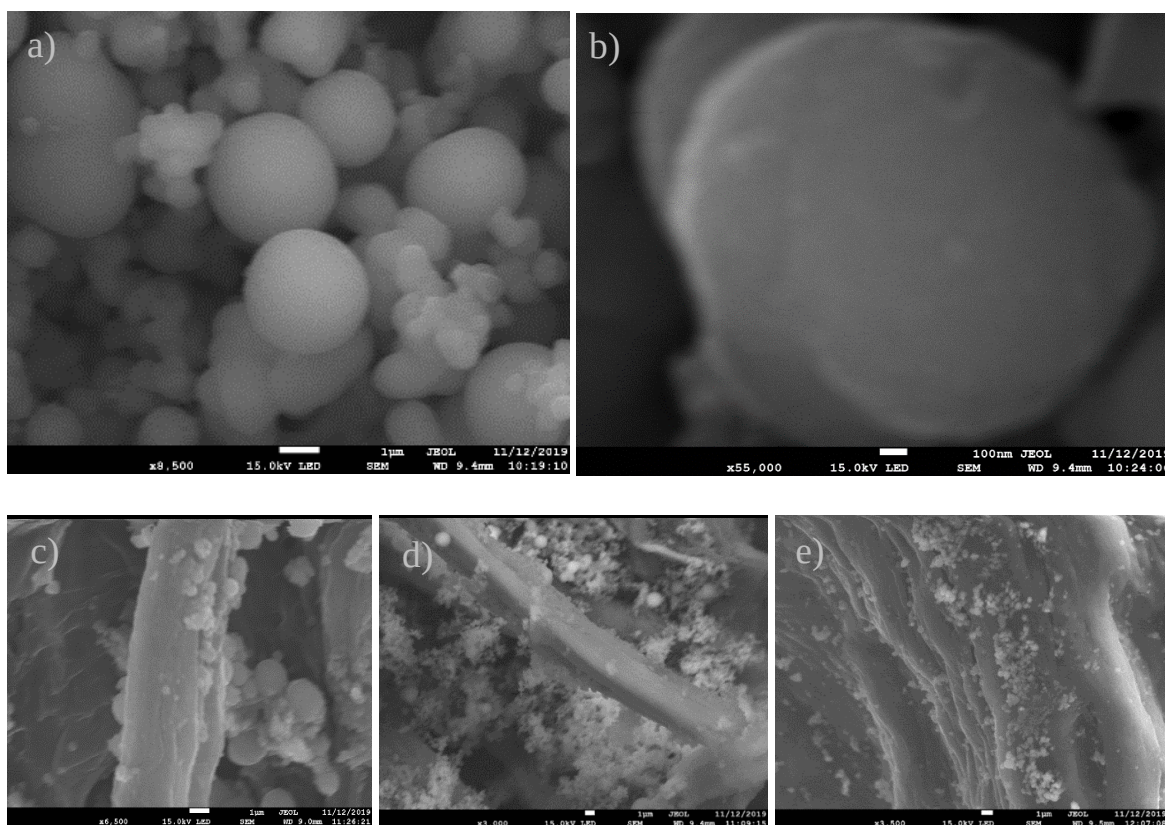


Figure 4.7: Scanning Electron Microscopic images of cellulose fibers at magnification of:
(a) x800 (b) x4000



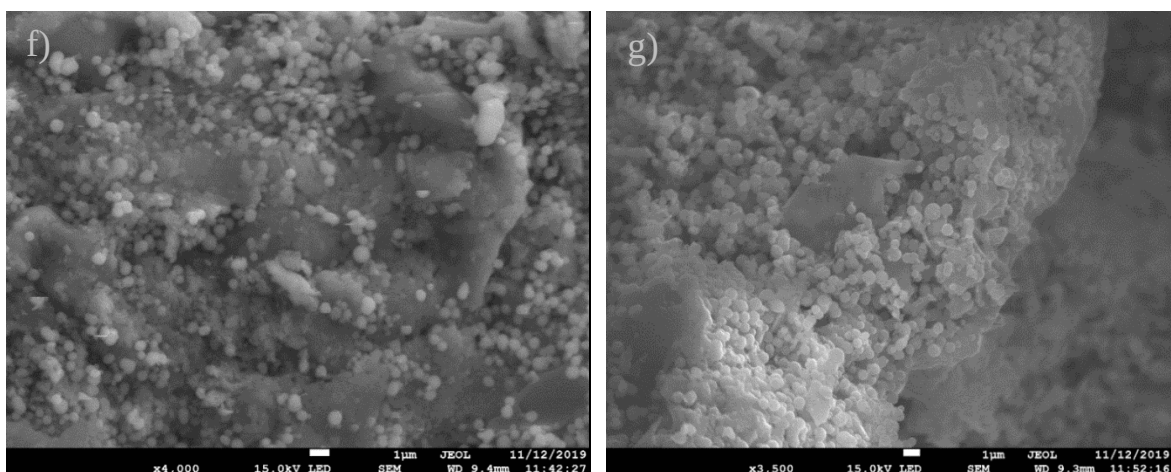


Figure 4.8: SEM image of Titanium dioxide nanoparticles at magnification of (a) x9500 and (b) x55000. SEM images of cellulose composites with TiO_2 composition at: (c) Cell- TiO_2 -1 (d) Cell- TiO_2 -1.5, (e) Cell- TiO_2 -2 (f) Cell- TiO_2 -3 and (g) Cell- TiO_2 -4

Morphology of cellulose-titanium dioxide composites

The morphologies were investigated by SEM and they are shown in Figure 4.8. Individual cellulose fibers viewed under the Scanning Electron Microscopy appear to be smooth and free from other impurities like hemicellulose and lignin (Figure 4.7). The organic molecules of the pollutant are deposited into the pores immobilizing them long enough to be decomposed by the photocatalyst. The Figure 4.8 also represent the morphological images of TiO_2 and the catalysts at micro and nanoscale.

Figure 4.8 (a and b) clearly captures titanium dioxide as spherical nanoparticles. At a nanometer scale, the surface area is highly increased and the redox reaction on the surface is catalyzed. It has been reported that TiO_2 performs better than SnO_2 [51]. However, reinforced with another material like carbon fibers speeds the reaction twice. TiO_2 as a free material, the recombination of electrons during the process is slower hence its slow rate. In addition, reusability is nearly impossible and removal of the photocatalyst are time consuming when in this form [51].

Figure 4.8 c and d (representing composites Cell- TiO_2 -1 and 1.5, the TiO_2 are scattered on the fibers and most of the cellulose fibers are barely covered by the photocatalyst. As a result, during photodegradation, the dye molecules which are adsorbed on the materials' surface are desorbed back into the solution after some time without degradation.

Figure 4.8e shows the morphological structure of Cell-TiO₂-2 catalyst. There is seen to be a balance between both matrix and reinforcing material. The best characteristics of the two components are contributed resulting in optimum results. The hydroxyl groups and porous structure of the cellulose fibers are important in the synthesis and protection of the TiO₂ nanoparticles during immobilization [48]. The hydrogen bonding between the cellulose fibers and the TiO₂ catalyst provides the conducive environment availing the active sites for reaction. Solvothermal method gave way to the consistent TiO₂ growth and nucleation on the matrix surface. Sonication before compositing allowed the complete homogeneity of the two compounds.

Figure 4.8 f and g show the Cell-TiO₂-3 and 4 catalysts. As the concentration of the semiconductor increases, the cellulose fibers tend to clog together and form a monolithic structure. This is attributed to the pressure and temperature from the solvothermal reaction in the autoclave changing its morphology. The TiO₂ are more presently seen all over the material indicating their synthesis in the cellulose matrix pores, improving the nanoparticles dispersion [48]. The clusters of aggregates were formed and anchored on the surface of the cellulose material. The cellulose fibers in the Cell-TiO₂-3 and 4 composites are saturated with titanium dioxide affecting the photoactivity of the composites preventing irradiation from accessing active sites located in the center. The excess TiO₂ nanoparticles appear to be loosely cleaved on the fibers.

According to James and Peter, crystallization is the transition phase where matter (in a solvated form) is converted from a position of high free energy to one of a lowered free energy in the crystal lattice [124]. The process of increasing the size of a pre-existing crystal is known as crystal growth. It has 4 stages which include; nucleation, coalescent coagulation, and agglomeration. From Richard's explanation, nucleation can be summarized to be the first step in the formation of a new thermodynamic phase of new structure via self-assembly [129]. Nucleation is also defined as the initial process of the formation of crystals.

Peter Vekilov observed that the faster the nucleation process, the more the number of crystals were formed simultaneously. Most of the crystals had identical shape. On the other hand, a slow reaction resulted in fewer number of crystals and various sizes of the crystals were formed [130]. In order to determine the size, polymorphism, size distribution and other crystal properties, the nucleation should be controlled. The process of nucleation and crystal

growth was fashioned in the auto clave during the solvothermal reaction causing the TiO_2 molecules to develop on the cellulose structure. Controlling the nucleation means controlling the reaction parameters. From Figure 4.8b, it appears that the crystals are almost identical indicating the fast nucleation process. These results are in agreement with those from the XRD.

4.1.4 Thermo Gravimetric Analysis (TGA)

Thermal stability of cellulose

From Figure 4.9, the dashed line symbolizes the curve of that of the pretreated fibers and the solid line is that of the extracted cellulose. The mass of the cellulose measured using the analytical balance was 5.7310 g and that of the pretreated fibers was 7.3060 g. Initially, both samples tend to degrade together within the temperature range of 50 - 233 °C. The pretreated fibers have a 2-step degradation showing a large weight loss of 52% from 223 - 362 °C. This is followed by a steady degradation leaving a char residue of 16% at the end of the heating process at 600 °C. The TGA graph of the extracted cellulose is also a similar 2-step degradation. However, there is a steeper weight loss of 73% from 213.68 - 359.26 °C which is much more than that of the pretreated fibers. The final weight of the cellulose residue was 4%.

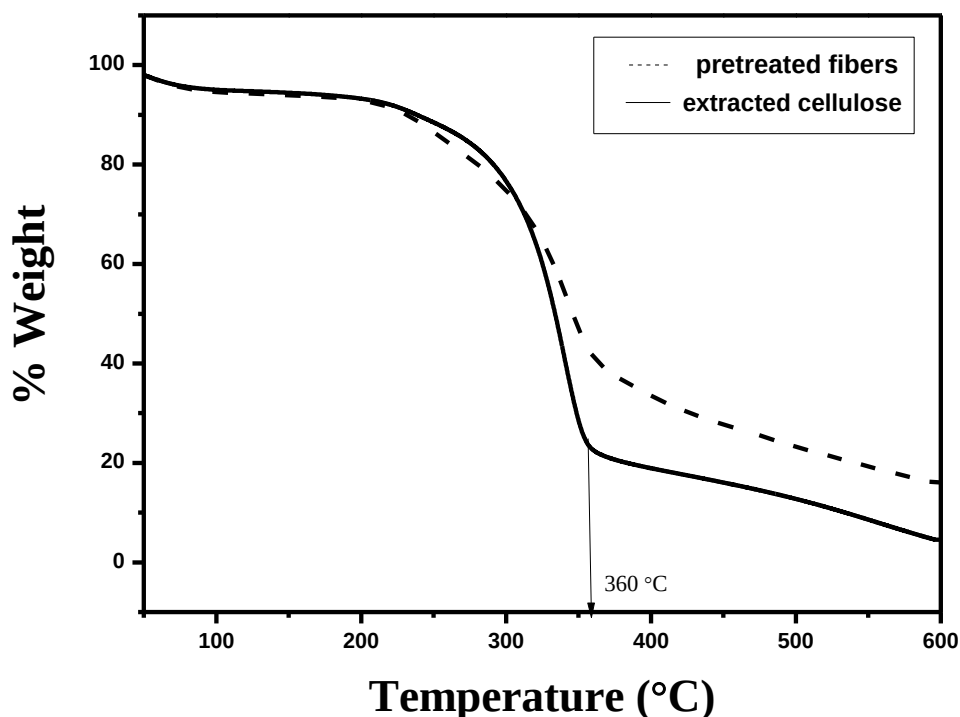


Figure 4.9: Thermogravimetric profiles of cellulose and the fibers

Thermo-gravimetry is also used to understand the possible chemical reactions that occurred. In this case, the macromolecules in cellulose were depolymerized and the primary fragments were cracked during the secondary step [107]. Both graphs show that thermal decomposition occurred with a release of gaseous products [131]. At 100 °C (initial period), the samples were melted and the steady weight loss was as a result of dehydration [132]. Starting from 200 °C, thermal pyrolysis of the cellulose skeleton chain ensued.

The absence of non-cellulosic materials like hemicellulose and lignin caused the material to be thermally stable which is another affirmation of the eradication of pure cellulose [90]. The last phase of degradation (between 389 and 600 °C), simply illustrated the release of gas and the formation of char. The weight loss within the stage was 23% for the pretreated fibers and 17% for the extracted cellulose. During this step there was a lot of burning of the impure substances in the pretreated fibers giving rise to the Figure noted. The lower weight percentage of the char from cellulose is because of the removal of ash unlike that of the pretreated fibers [90].

The relationship between crystallinity and thermal stability has been explained by Chaturbhuj *et al*, [85]. Crystalline molecules are densely packed closely together prohibiting heat transfer by diffusion through the cellulose chains. Amorphous materials, on the other hand, are less resistant to heat because of the arrangement of the cellulose chains [85]. Amorphous regions in the cellulose get degenerated during acid hydrolysis that causes an increase in the crystallinity degree. This higher crystallinity has a level of heat resistance leading to a heightened thermal stability. These results correlate with the XRD and FTIR cellulose results.

The maximum degradation temperature was 360 °C, from Figure 4.9, classifying the extracted cellulose as a stable material. Thermal stability increases its applicability in biocompatible materials or composites [80]. The thermal stability obtained from the extracted cellulose was higher than that of the pretreated fibers which indicates the sample purity [132]. Reddy *et al.*, studied the degradation of cellulose from peepal fibers [90]. Their maximum temperature was found to be 370 °C leaving a char residue of 4% which is not too far from this current research.

4.2 Photocatalytic Evaluation

The applicability of the photocatalysts were tested against MG dye studying its ability to decompose the molecules. This section reflects and highlights the adsorption, photodegradation and kinetics of Malachite green dye. From Figure 4.12a, UV-Vis spectrum of malachite green dye has a maximum absorption at wavelength of 616.531 nm. This wavelength was used to monitor the dye concentration during the experiment.

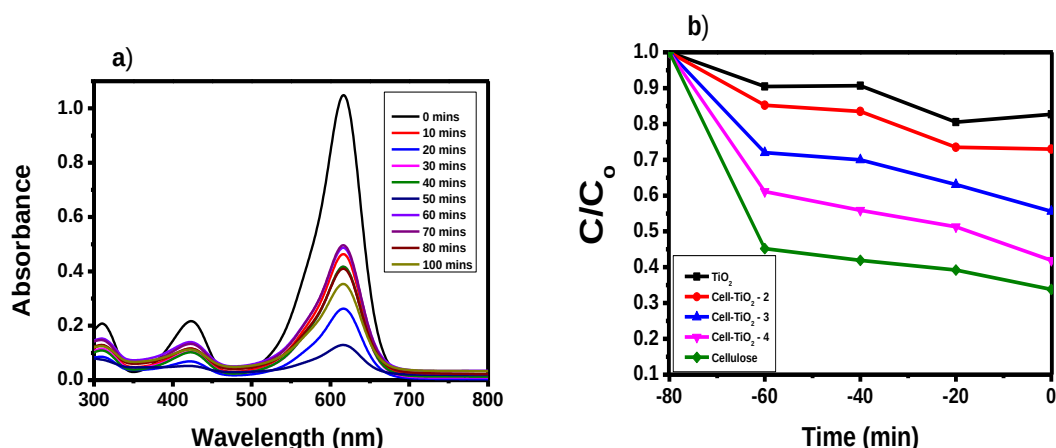


Figure 4.10: Adsorption studies of MG dye; a) UV-visible spectrum obtained from adsorption by cellulose b) plot of C/C_0 vs time extracted from blank TiO_2 , Cell- TiO_2 -2 to 4 and cellulose

The variation of the UV-VIS spectrum of MG dye with time in the presence of cellulose is shown in Figure 4.10. As the time was increased the absorbance of the dye was slowly reduced from 1.03 to 0.09 due to the dye adsorption by cellulose fibers. The reaction was observed using UV/VIS spectroscopy. At the start of the experiment, the absorbance of the dye makes 2 minor peaks at 300 and 422 nm before reaching its maximum at 616 nm before falling to level off.

Figure 4.10 a) shows the adsorption trend observed from the synthesized catalysts. With the introduction of the composites, the concentration decreased, some at a faster rate than others. The order of adsorbability is as follows: blank TiO_2 < Cell- TiO_2 -2 < Cell- TiO_2 -3 < Cell- TiO_2 -4 < cellulose fibers. Adsorption equilibrium was reached after 30 min. Fluctuation was noticed towards the end of the reaction which could be a result due to desorption of dye molecules back into the solution.

Cellulose fibers proved to be an effective adsorbent maintaining a constant decrease. Titanium dioxide on its own is the least active in adsorption during the experiment. Silva *et al.*, studied the adsorption of dyes by cellulosic materials [133]. Adsorption predominantly catches attention for its high efficiency joined with low cost. It is reported to remove chemical pollutants, decolorization of solution and depicts adsorbent recyclability. The process is reversible, permitting the regeneration of the adsorbent. Cellulose has been widely researched on its adsorption of different dyes and has proven to have reflected advantageous properties. It was reported that effective adsorption of target molecules near

the metal oxide photocatalytic surface is believed to accelerate photovoltaic electron transfer and facilitate photocatalytic activity [134].

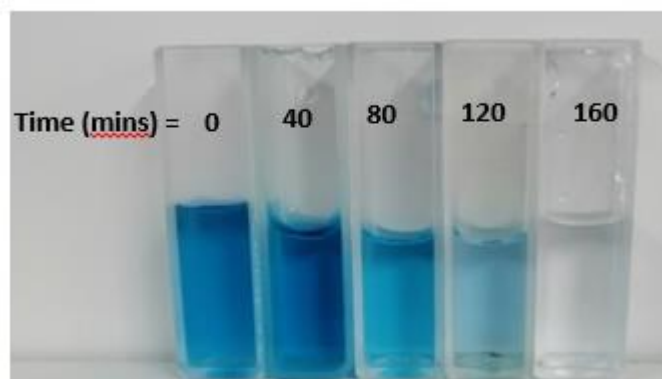


Figure 4.11: Photograph image showing decolouration of MG dye by Cell-TiO₂-2 catalyst with time (T = 0, 40, 80, 120, 160 mins) in ascending order

The picture in Figure 4.11 illustrates the decolouration of malachite green dye between 0 and 160 min. The solution changes from blue-green to colourless within that time-span. Jianwen *et al.*, [119] studied the immobilization of titanium dioxide films on activated carbon fiber (ACF) and their photocatalytic degradation properties. In their study, ACF was used in the form of cloth for easy handling. TiO₂-sol was prepared using the sol-gel method and methyl orange (MO) was the chosen dye. Adsorption was tested and it was noticed that equilibrium was reached after 15 min. The methyl orange molecules were easily adsorbed onto the surface. It was reported that the pore diameter of sorbent (ACF) and molecular size of the adsorbed substance (MO) play a role in the reaction. The smaller the molecular size, the easier it is to adsorb. When the size is larger than the diameter of the adsorbent, pollutants are not effectively caught by samples due to screening which in turn influences the photocatalytic degradation competence of the material. The reusability of the material was good with a slight decrease in degradation. Malachite green dye molecules are small enough to be adsorbed and immobilized into the cellulose-titanium composite.

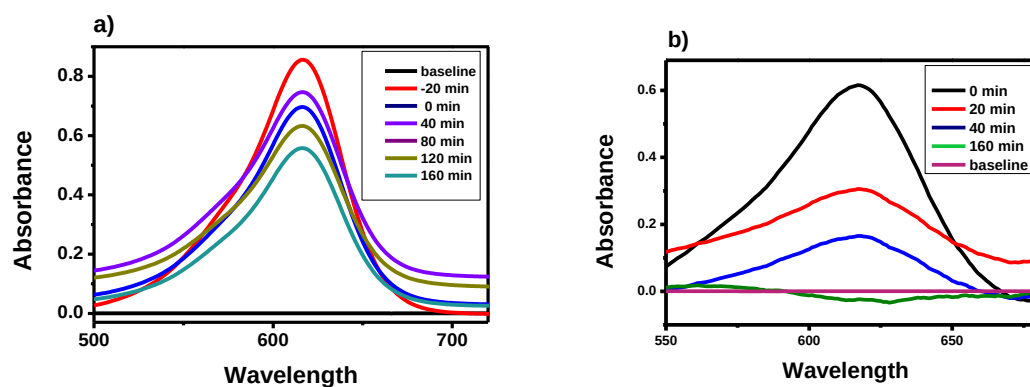


Figure 4.12: The absorbance spectra obtained from a) Cell-TiO₂-2 catalyst adsorption and b) Cell-TiO₂-2 catalyst solar degradation * -20 mins refers to the sample reading taken 20 minutes before the start of the experiment.

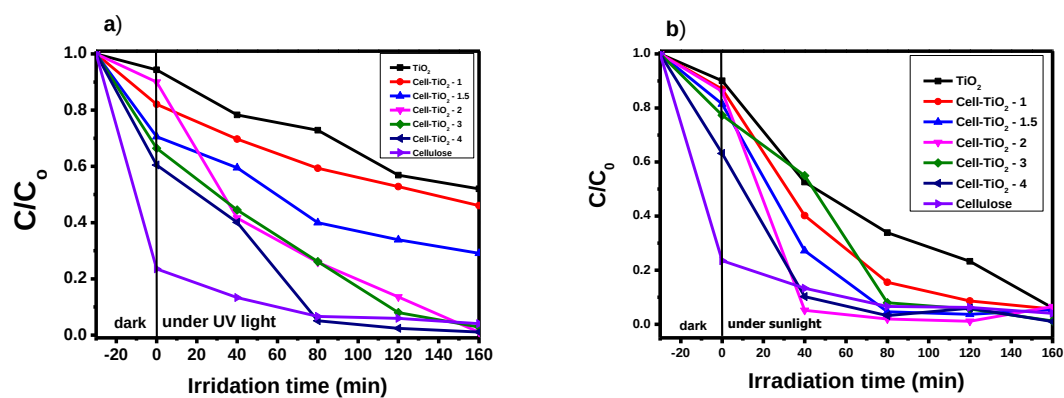


Figure 4.13: The plot of C/C_0 vs time under a) UV light irradiation. b) sunlight

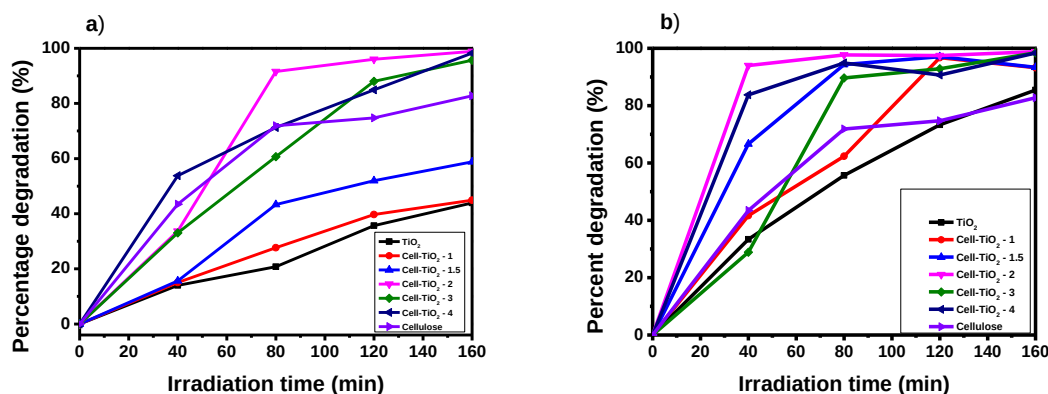


Figure 4.14: Degradation plots showing a) Ultraviolet percent b) Sun light percent irradiation

As described under the methodology section, the photocatalytic results are displayed in Figures 4.13. Figure 4.13a shows the photodegradation of malachite green dye under Ultra-Violet light and Figure 4.14a displays the results in percentages. The dye photodegradation under sunlight and the percentage results are shown in Figure 4.13b and 4.14b respectively. The percent degradation for each reaction was calculated using equation (13) stated in chapter 3.

Within the first 30 min in the dark (from Figure 4.13a), the samples adsorbed the dye at different rates resulting in varying concentrations. Using TiO₂ alone displayed a steady decrease under UV light only being able to degrade 44% of the dye. The same pattern was shown for Cell-TiO₂-1 and 1.5 catalysts. Between 0 and 40 min under UV light, Cell-TiO₂-2 had the highest photocatalytic activity with maximum degradation during that period. The dye was 99% degraded after 3 hrs. Cell-TiO₂-4 catalyst portrayed strong photoactivity during 40 to 80 min of irradiation degrading 98% of the dye. The time period of 120 to 160 min showed a steady curve indicating complete reaction. At the end of the reaction, the solution was decolorized from blue-green to colorless as seen in Figure 4.11.

Figure 4.13b is the photodegradation under solar irradiation and Figure 4.14b represents the result in percentages. A tremendous decrease in concentration was noticed under solar irradiation. Degradation was almost complete in only 80 min for Cell-TiO₂-2. Blank TiO₂ solution was more active under sunlight with a nearly linear decrease and 86% degradation after 160 min. The catalysts displayed high activity with Cell-TiO₂-2 being the most reactive. Within 40 min under the sun, the concentration rapidly reduced from 0.9 to 0.01

degrading the dye by 99 %. Cell-TiO₂-1.5, 3 and 4 composites performed notably under solar irradiation proceeding to give 93, 98 and 98% degradability respectively. Cellulose reacted consistently under both UV and Solar displaying the same pattern solely due to dye adsorption.

Figure 4.12a and b show the maximum absorbance in the dark was approximately 0.6 and a minimum of 0.5 whereas using solar degradation the absorbance reached 0.9 maximum and minimum of -0.2. This proves that photocatalysis occurred under sunlight which sped up the reaction to complete degradation within the same time frame of 160 min. The process of decolouration is much faster under sunlight than UV due to the efficiency under visible wavelength. This caused excitation of electrons by photons to occur at a quicker rate. The unattached TiO₂ reacted slower under both UV and solar irradiation indicating that dye adsorption onto cellulose fibers had an impact on the photoactivity. Compositing the cellulose with the catalyst contributes both adsorption and photocatalysis in the dye degradation.

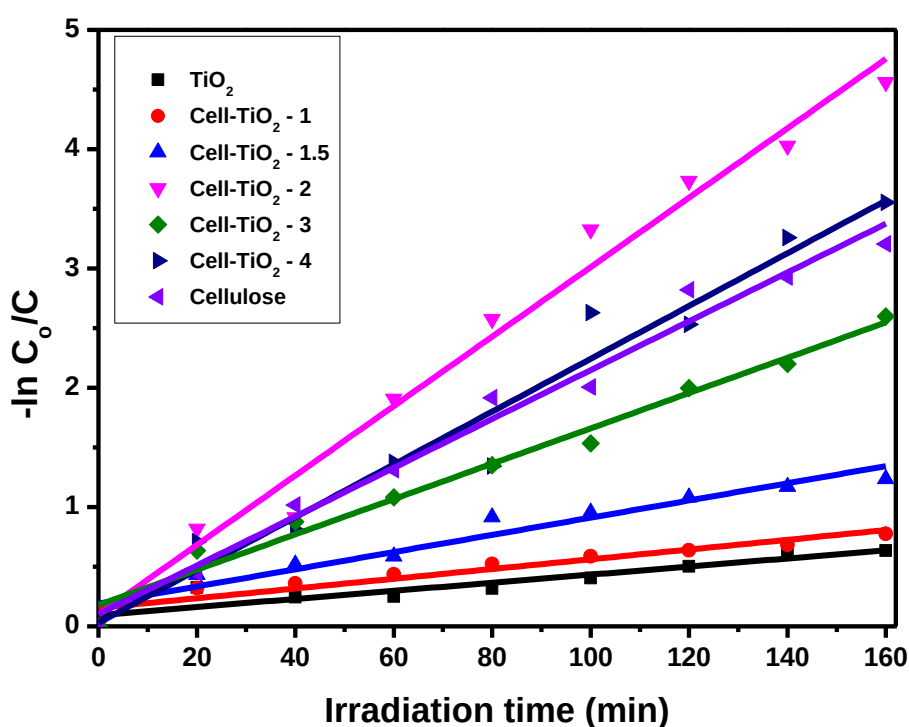


Figure 4.15: Kinetics plot of degradation under Ultraviolet light

The reaction kinetics of malachite green dye degradation was studied. A plot of $-\ln (C_0/C)$ vs time was linear and followed pseudo-first order as shown in Figure 4.16. The rate constant (k) was derived from the equation 15:

$$\ln \frac{C_0}{C} = -kt \quad 15$$

It was observed that Cell-TiO₂-2 had the fastest rate of reaction at 0.02911 min⁻¹ and the blank TiO₂ had the slowest rate of 0.00339 min⁻¹ derived from Table 4.3.

Table 4.3: Summary of UV percent degradation, solar percent degradation, rate of reaction and R² values of each of the catalysts

Catalyst	UV degradation (%)	percent Solar percent degradation (%)	Rate of Reaction, k (min ⁻¹)	R ²
TiO ₂	43.89	85.46	0.00339	0.8467
Cell- TiO ₂ -1	44.92	93.24	0.00408	0.8975
Cell-TiO ₂ -1.5	58.82	93.37	0.00721	0.9261
Cell-TiO ₂ -2	98.88	98.92	0.02911	0.9804
Cell-TiO ₂ -3	95.69	98.41	0.01481	0.9803
Cell TiO ₂ -4	98.27	98.37	0.02213	0.9564
Cellulose	82.77	82.77	0.02047	0.9803

From the XRD results and SEM images, the degradability performance of Cell-TiO₂-3 and 4 catalysts appeared as it did was due to the overload of TiO₂ which covered the cellulose fibers. Adsorption was not possible in the process which, as already seen, plays a role in catalysis. Cell-TiO₂-1 and 1.5 catalysts have scattered titanium dioxide particles on the material revealed under SEM magnification. Adsorption of MG molecules occurred during the reaction but due to the insufficient photocatalysis, the molecules desorbed back into the solution.

The effect of catalyst loading was studied increasing the titanium dioxide concentration from 1 to 4% on a standard cellulose mass. The increase in the catalyst was disproportional to the degradation increase. Negative effects on degradation was observed due to the excessive catalyst loading since speed became independent of the greater load of catalyst. Some particles were not illuminated resulting from amplified light scattering which in turn inhibited and suppressed the photocatalytic activity. The best concentration from the experiment was Cell-TiO₂-2, above this the degradation was flawed. With increasing catalyst concentration, extreme denseness of the suspension prevents the penetration of light into the reaction [135]. Furthermore, the increase of the particle-particle interaction becomes significant due to the large number of molecules, which reduces the available reactive centers and the density of electrons on the catalytic surface, resulting in deprived photoactivity [136]. The effective surface area for photocatalysis is limited [52]. This is the case for Cell-TiO₂-3 and Cell-TiO₂-4 catalysts.

Chin *et al.*, [137] have reported that amorphous co-catalysts had a greater positive effect on the performance. It could be expected that crystalline materials should have been more effective but the article reported otherwise and that crystalline co-catalysts caused the photocurrent to deteriorate. To justify the efficiency of amorphous co-catalysts, it was highlighted that the presence of large density unsaturated catalytic active sites contributed to the enhancement of efficacy. The advantage of low crystalline materials in photocatalysis was confirmed by Wanghi *et al.*, [64]. From this research the cellulose extracted appears to be leaning more toward the semi-crystallinity. This explains the high dye adsorption taking place at the many active sites in the material hence improving the photocatalytic activity.

Renata *et al.*, studied the photocatalytic activity of TiO₂, ZnO and Nb₂O₅ in the degradation of textile wastewater. They recorded the greatest absorption percentage decrease to be seen between 500 and 660 nm which corresponds to the visible-region absorbing compounds. When aromatic hydrocarbons are decomposed, the aromatic rings are disintegrated into smaller molecules i.e. aliphatic groups and simple rings. This reaction increases absorption at the indicated wavelengths. Compounds that have a high electron density and absorb at high wavelengths are prone to quick attack by photo-generated radicals and, therefore, decompose at a higher rate. It was highlighted that TiO₂-P25 had the highest kinetic (0.0079 min⁻¹) and thermodynamic efficiency compared to the rest due to its large surface area, and smaller particle size having a lower band gap energy hence increasing the absorbance [135].

Malachite green dye absorbs at a wavelength of 616 nm (Figure 4.10 a) and because this falls within the visible region, it explains why the results from solar degradation is higher than that from UV degradation. As seen from Table 4.3, the rate constants of the materials doped with TiO₂ are rapid with Cell-TiO₂-2 being the fastest at 0.02911 min⁻¹.

4.3 Effect of radicals on photocatalysis

The reaction mechanism of the photoreaction was studied. In attempt to investigate the radicals' contribution in the degradability, a set of reagents were used as scavengers. Ethylenediaminetetraacetic acid (EDTA) was used to probe for holes, tert-butanol was used to probe hydroxyls (OH[•]), p-benzoquinone was used for superoxide radical (O^{2-•}). The blank was done as a control. The experiment was conducted using Cell-TiO₂-2 as the standard catalyst. From Figure 4.16, it is noticed that the reaction done with BQ was the most stunted as compared to the rest of the graphs. The presence of BQ hindered the contribution effect of O^{2-•} radicals in the photocatalytic mechanism. Although the holes and hydroxyls were inhibited in the EDTA and TBA reactions, their photoactivity produced higher degradability results. The photocatalytic mechanism can be said to be due to superoxide radicals formed. Figure 4.17 summarizes the percent degradation of the reactions affected by the scavengers when the time is 80 mins.

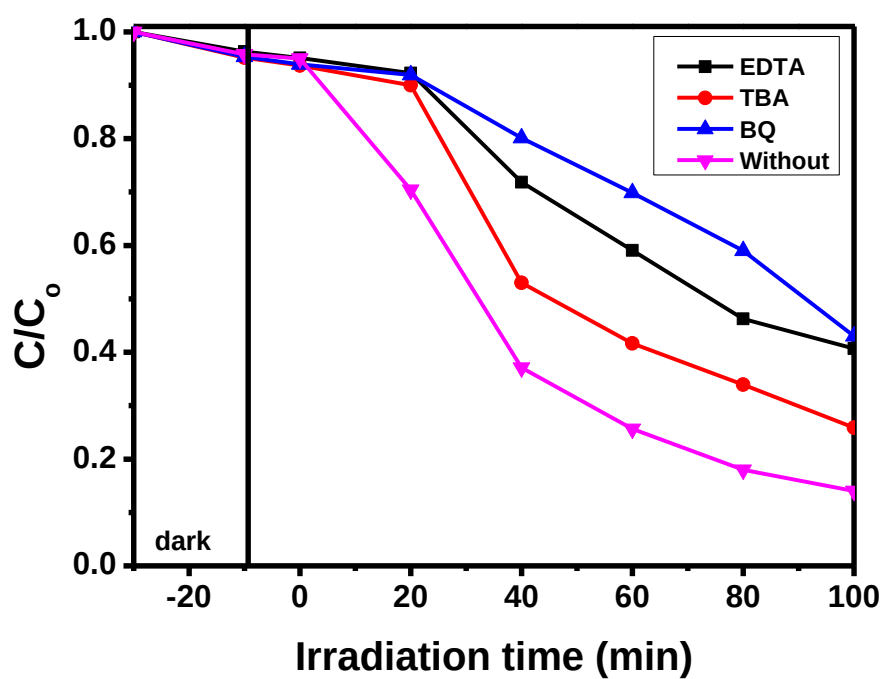


Figure 4.16: Plot of C/C_0 vs irradiation time for scavenger studies

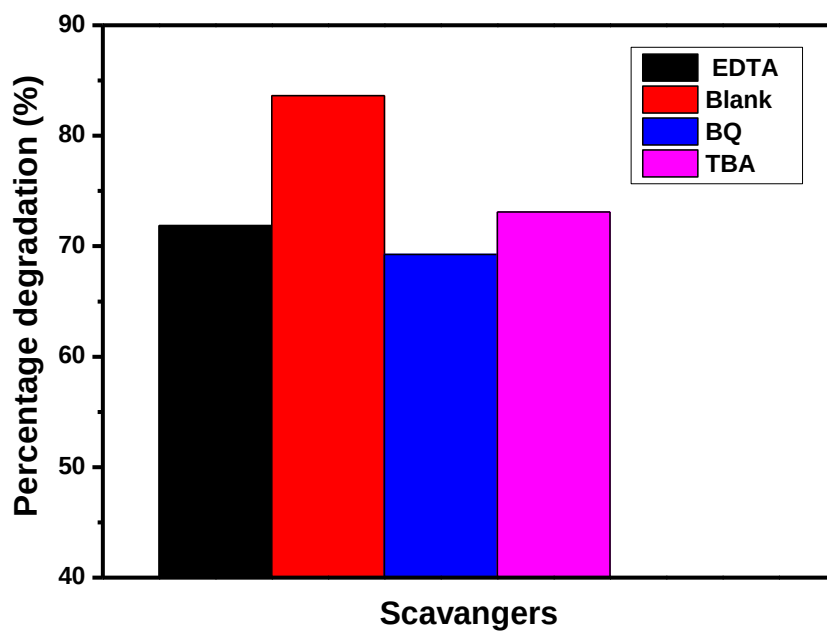


Figure 4.17: Percent malachite dye degradation under different scavengers, $t = 80$ min

Emitted electrons are effectively conveyed from the TiO₂ conduction band to cellulose fibers which subdues the electron-hole recombination on the TiO₂ surface hence producing more photoelectrons. Oxygen reacts with the trapped electrons giving rise to superoxide radicals while the holes in TiO₂ valence band reacts with water forming hydroxyl radicals (-OH). These -OH radicals are can be further converted to H₂O₂ and super oxide radicals creating more (-OH). Lastly, hydroxyl radicals degrade the MG molecules to water and carbon dioxide. The TiO₂ nanoparticles are much smaller in Cell-TiO₂ as compared to when on its own which in turn increases the surface area offering more photo-active site. Under the effect of the matrix, MG dye molecules are strongly adsorbed nearer to the TiO₂ photocatalytic surface, accelerating the transfer of excited electrons [1]. It is believed that TiO₂-based photocatalysts have an outstanding photocatalytic ability due to the presence of Ti³⁺ ions producing isolated states in forbidden gaps hence demonstrating the absorption of visible light. In addition, the ions serve as sites for trapping photo-generated electrons hence inhibiting the recombination of photo-induced electrons and holes [22].

4.4 Study of photocatalyst recyclability

Recyclability studies

The reusability of the material was studied maintaining the photocatalytic conditions with the results explained in this section. The results were obtained after t = 140 min.

The graph in Figure 4.18 shows the recyclability studies of Cell-TiO₂-2 composite degradation of MG dye under UV light for 140 min. With each reusability, the degradation performance appeared to have a slow increase from 92 to 98% until the 4th cycle. At this point, the most efficient degradability was recorded. Although there was an increase, the difference was not too significant. Cycle 5 and 6 showed similar results as cycle 4 reaching an equality. Reusable photocatalytic materials have more potential in the efficient removal of water pollutants. Its recyclability adds values in its applicability industrially leading to more opportunities. These results suggest that the photocatalytic activity of cellulose-titanium dioxide composites are very stable and this is in harmony with the work of Zeng *et al.*, [48].

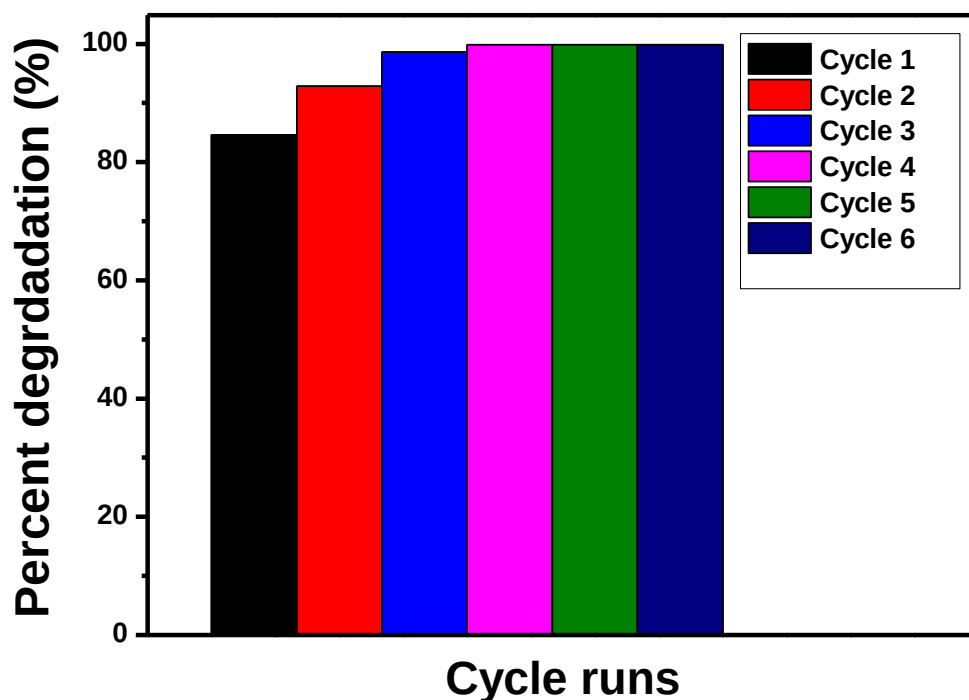


Figure 4.18: Recyclability of Cell-TiO₂-2 photocatalyst t=140 min

Another research conducted by Sorathiya *et al.*, reported similar results with the photoactivity improving with recyclability. Undergoing further analysis, they discovered that after each round of reuse, the particle size decreased. It was as a result of stirring of the material leading to “mechanical distress” on the samples’ morphology decreasing the surface area. However, regardless of the surface area decrease noticed, an increase in number of charge carriers or charge transport was enhanced hence accounting for the photocatalytic improvement [138]. Similarly, during the washing and treatment process of Cell-TiO₂-2 catalyst after each cycle, the physical structure was also affected causing the observed increase in degradation. In addition, the article highlighted that with each reuse increase, there appeared to be a redshift in TiO₂ absorption band. This change heightens the light absorption contributing to higher photoactivity as also noticed in this case.

4.5 Band Gap Determination

The relationship between the band gap and wavelength is shown in the equation:

$$\text{Band gap} = \frac{1240}{\text{wavelength}}$$

The band gap of the materials were calculated using the absorption spectrum fitting (ASF) method (Tauc plot) reported by Souri and Shomalian [139]. The method uses only absorbance values.

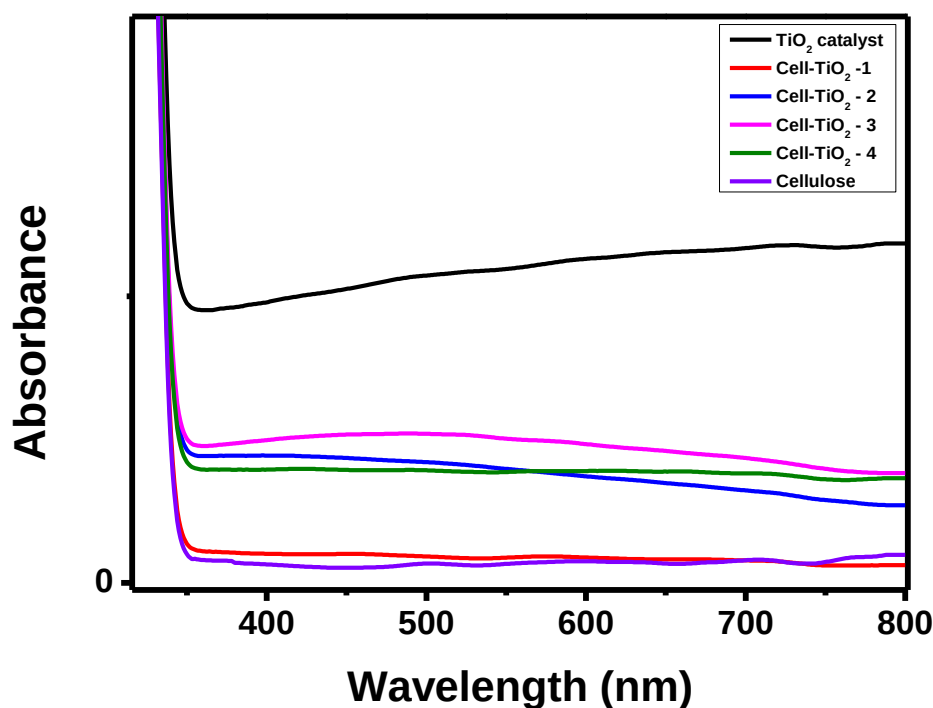


Figure 4.19: Absorbance plots of each catalysts Cell-TiO₂-1, 2, 3 and 4

A plot of Figure 4.19 for variation of $(A/\lambda)^n$ against $(1/\lambda)$ was extrapolated at $(A/\lambda)^n=0$ to determine λ

Table 4.4: Summary of wavelength and band gaps of each material.

Material	Wavelength (nm)	Band gap (eV) 1240/wavelength
Cell-TiO ₂ -1	353.10	3.51
Cell-TiO ₂ -2	357.12	3.47
Cell-TiO ₂ -3	356.36	3.48
Cell-TiO ₂ -4	355.51	3.49
Titanium dioxide	358.82	3.45

Figure 4.19 represents of the absorbance which is further used to find out the band gaps. Looking at Table 4.4, the wavelength of the photocatalysts ranged from 350 to 800 nm leaning more towards the visible electromagnetic scope. TiO_2 is known to have a distinctive UV-Vis absorbance peak dependent on concentration and particle size. The absorbance of anatase TiO_2 occurs within the wavelength range of 350–390 nm [52]. The calculated band gaps fell between 3.45 and 3.51 eV agreeing to the literature. Cell- TiO_2 -2 had the lowest band gap amongst the composites with Cell- TiO_2 -1 having the largest value. Although, if the band gap is too small, the reaction is also out of balance. Cell- TiO_2 -2 had a band gap in between titanium dioxide and Cell- TiO_2 -1. The absorbance values of titanium dioxide might be the highest but a considerable red shift towards the visible light region is observed going down the trend in Table 4.4. In TiO_2 , the band gap was low. This increases the light absorbed, but the valence band will decrease to lower energy levels. The energy band gap is strongly dependent upon the crystal structure of the material. Large crystalline sizes increase the bonding and antibonding and consequently band gap is decreased. This can be explained by the gap between valance and conduction band [71]. Apart from light intensity, particle size and reaction temperature, charge separation and transportation of photo generated charge carriers are factors affecting photocatalysis. Although TiO_2 displayed better light absorption, it failed to separate the electron-hole pairs during the reaction leading to their recombination, attributing to the low band gap it portrayed. Thus, lowering its photocatalytic performance [140]. The degradation efficiencies of MG dye by the composites under UV light and visible light were observed in Figure 4.14. The highest photoactivity was recorded in 40 min under visible light and the lowest percentage obtained in 160 min under UV. The band gap of Cell- TiO_2 photocatalyst being studied has a band gap of approximately 3.4 eV and that of TiO_2 -P25 is 3.2 eV which explains slight difference in kinetics [22].

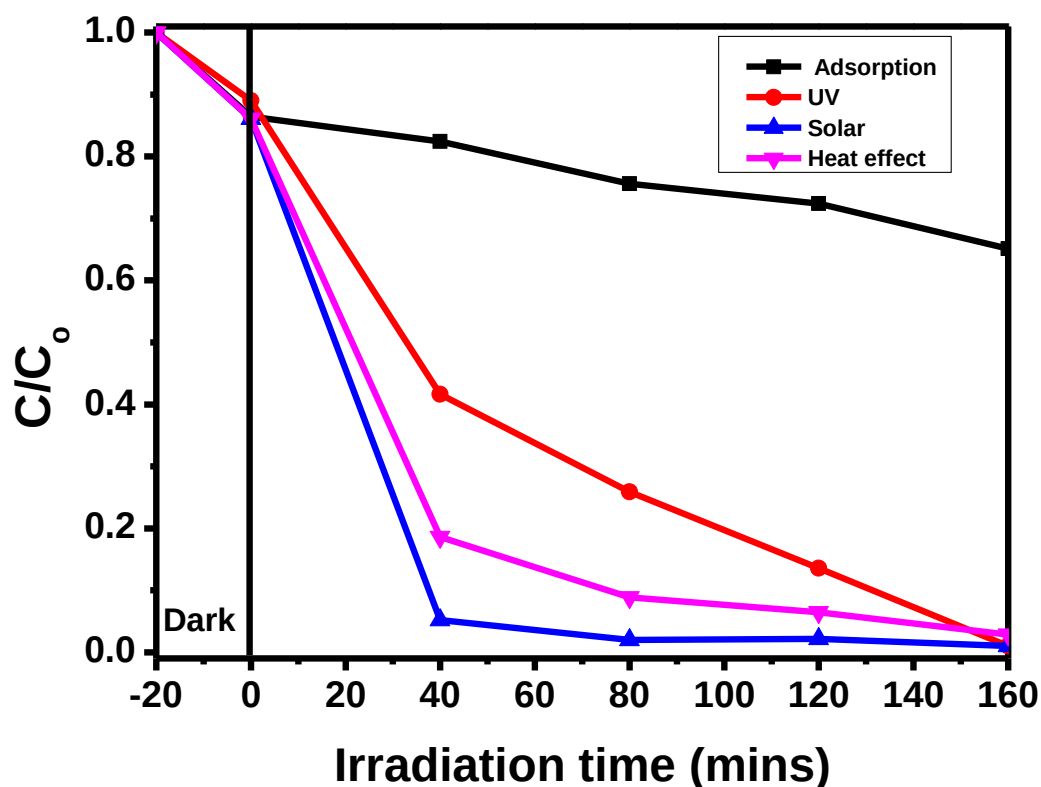


Figure 4.20: Malachite dye removal under different conditions using Cell-TiO₂-2 catalyst.

Amongst all samples tested, Cell-TiO₂-2 showed promising results and can be narrowed down to be the optimum photocatalyst. Figure 4.20 highlights the experiments conducted on the sample for easy comparison. The adsorption process does not intensely affect the absorbance of the MG dye. Although the material is highly adsorbent with the ratio of cellulose and TiO₂ as 1:1. SEM and XRD results agree to the structural characteristic being a hybrid photocatalyst/composite. When the solution was irradiated with ultra violet light, the degradation process occurred by 98.88%. It could be said that the electrons were excited to some extent by the UV light but not as much as they were under the sun, 98.92%. Two experiments were conducted under the sun. The solar reaction had three factors contributing to the photodegradation: Ultraviolet, visible and infrared radiation.

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The research succeeded in extracting cellulose from *Colophospermum mopane* leaves. The extracted product proved to be a good support material in a catalyst matrix. Complete depolymerization of hemicellulose and lignin was achieved and proven by the XRD results. The crystallite size of the material was derived to be 1.36 nm with a crystallinity index of 56. FTIR results also demonstrate the absolute removal of the impurities and the presence of -OH bonds. The hydrogen bond energy was at 22.15 kJ/mol at an intramolecular distance calculated at 2.77 Å. The hydrogen bonding reactions are augmented between the fibers and the semiconductor producing a stable cellulose-titanium dioxide composite. From the surface morphology, smooth fibers were observed that were spendable. The TGA result conclude that the cellulose is thermally stable.

Active sites present were able to react with titanium dioxide giving a photocatalytic composite. Adsorption of MG dye showed a less significant change in absorbance compared to photodegradation that transformed the blue-green solution to colorless. Malachite green dye was degraded under solar irradiation which gave a higher degradability and great absorbance gradient compared to the result done with Ultra Violet irradiation. The kinetics of the reaction obeyed the pseudo first-order law giving rise to linear graphs. The reaction constant, k_{app} was calculated with Cell-TiO₂-2 being the fastest.

The recyclability of the material was studied and was found out that the photoactivity increased up to 4 cycles before reaching stability. At the optimum catalyst loading of Cell-TiO₂-2 high photoactivity was noticed which is attributed to the dye adsorption from cellulose fibers. The hybrid photocatalyst attained a greatly enhanced light absorption and charge transfer than that of the free TiO₂ providing high specific surface area. The radicals' contribution to the mechanism was studied. It was concluded that super oxide, O²⁻ had a large effect in the photodegradation of MG dye. The band gap of the photocatalysts were measured with Cell-TiO₂-2 having an in-between value of 3.47 eV. The band gap being too large or too small inhibits the degradability effect. Contributing to the on-growing research on photocatalysis, cellulose-titanium dioxide composites prove to be useful in the treatment of waste water.

5.2 Recommendations

Investigating the effect of pH, temperature and intermediates could be done in future research. Studying the photoactivity of cellulose-titanium dioxide composite doped with a metal could be an interesting path to examine.

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Appendix A: Mechanism of photocatalysis

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