



Faculty of Sciences
Department of Chemistry and Forensic Sciences

**GREEN SYNTHESIS OF TRANSITION METAL OXIDE NANOPARTICLES USING
MORULA LEAF EXTRACT AND THEIR APPLICATION IN THE REMOVAL OF
RHODAMINE AND METHYLENE DYES FROM SYNTHETIC WATER**

by

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DEDICATION

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ABSTRACT

Transition metal oxide nanoparticles have recently been linked to favourable properties that allow them to be used in microelectronics, water purification, energy storage, sensing, and biomedicine. This has resulted in the development of a number of methods for generating transition metal oxide nanoparticles that are both less expensive and more ecologically friendly in recent years. Documented procedures include using high temperatures and pressures, as well as volatile and caustic substances including sodium hydroxide, and diethylene glycol in the manufacture of zinc oxide (ZnO). Morula leaf extract was used in the synthesis of birnessite, ZnO, and copper oxide (CuO) nanoparticles in this study. The active morula agents are extracted using boiling water followed by hydrothermal treatment with the metal oxide precursors to synthesize the metal oxide nanoparticles. There were no other hazardous substances used apart from water which is considered to be green. X-ray diffraction (XRD) analysis showed that pure and crystalline structures of CuO and ZnO were fully formed after calcination at 350 °C. birnessite structure was formed after hydrothermal treatment at 180 °C according to the XRD data. Raman spectroscopy was used to determine the molecular functional groups of the materials using the fingerprint regions on the spectra. CuO was determined by the doublet peak between 200 and 400 cm^{-1} , birnessite by the singlet peak between 600 and 700 cm^{-1} and ZnO by the characteristic peaks at 318, 429 and 566 cm^{-1} . Scanning electron microscopy (SEM) and Brunauer–Emmet–Teller (BET) analysis were used to analyze the structural morphology and the adsorptive behaviour of the materials, respectively. Platelets were discovered in CuO, while birnessite and ZnO featured flower-like and nanorod-like structures, respectively. All three materials were discovered to have larger surface areas, 26.8 m^2/g in the case of CuO, 31.6 m^2/g for birnessite and 21.29 m^2/g for ZnO. Flaws such as rough particles and cracks in the structure of the material were also discovered, which aided their respective uses substantially.

CuO and birnessite were applied in the adsorption of dyes. Two different adsorption isotherms (Freundlich and Langmuir) were used to probe the activity of these metal oxides in the adsorption of dye. The Langmuir constant (RL) values obtained are in the range of 0–1, showing that both dyes in the mixture i.e., methylene blue (MB) and rhodamine 6G (R6G), adsorb well on CuO and birnessite in an adsorption process. Furthermore, the values of n which is a constant

which depends upon the nature of adsorbent and the gas at a given temperature, exceed one, indicating that metal oxides are effective adsorbents for both dyes. CuO and birnessite have a maximum adsorptive efficiency of 78 and 99 %, respectively.

In the photodegradation of the combined dyes, ZnO was used. Its degradation efficiency was 99 %. The degrading efficiency increased as the catalyst amount, contact time, and reaction temperature were increased.

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1.0 INTRODUCTION

1.1. Background of study

One of the most critical resources worldwide is clean water, because it supports the existence of all forms of life. Therefore, the scarcity of good quality water has detrimental effects on every living creature [1,2]. Despite this fact, water pollution continues to be a significant problem in our rapidly changing world. This issue stems from the rapid explosion of industries, the global population's exponential growth, and climate change [3]. Rivers, dams, and oceans are daily getting contaminated with dyes, heavy metals, papers, and plastics [4]. These waste materials substantially and negatively impact organisms especially aquatic life, causing diseases and abnormalities [4]. Rhodamine B, Congo red, methylene blue and methyl orange are among the most commonly used dyes in industries such as textiles, cosmetics, leather, pharmaceuticals, paint, and paper. These dyes are dumped as waste into bodies of water, endangering the health of living species and the ecosystem as a whole [5–7].

Several approaches have been devised by scientists to tackle the dye pollution problem. Many physical, chemical, and biological techniques have been employed. These include adsorption [8,9], degradation [10–12], ion exchange [13,14], chemical precipitation [15], membrane filtration [16,17] and microbial technologies [18]. Because of its simplicity, effectiveness, adaptability, and insensitivity to harmful contaminants, adsorption is a preferred choice among these approaches. The adsorbent can be reused numerous times by utilizing an appropriate desorption technique, which is also due to the reversibility of the processes [9,19–21].

The most suitable adsorbent should be capable of adsorbing huge amounts of pollutants and have a broad surface area [24]. In comparison to other adsorbent materials such as polymers, zeolites, carbonate minerals, activated carbon, clay minerals and charcoal, transition metal oxides (TMOs) have been found to possess this feature. As a result, TMOs are a preferred alternative. [25–27]. Many different adsorbents have been studied scientifically, including activated carbon, carbon nanotubes, graphene, layered hydroxides, graphitic carbon nitride, and agricultural by-products

[16,28,30]. Low toxicity, broad surface area, porous architectures, thermal stability, fast recovery, O-vacancy sites, and surface flaws are some of the attributes of TMOs [27,31].

In the realm of adsorption, manganese dioxide (MnO_2)-based materials are getting a lot of traction [32]. This is because of their low cost, wide availability, and their large surface area which enables them to adsorb larger amounts of contaminants [33]. Birnessite is a two-dimensional (2D) layered form of MnO_2 composed of interstitial cations and MnO_6 octahedra with shared edges [34]. Mn site vacancies and Mn(III) substitution for Mn(IV) in the layer provide a negative charge, which the cations counterbalance. These materials are capable of cation interchange and oxidation-reduction reactions because they have oxidation levels that are easily interconverted and have exchangeable interstitial cations [35]. Due to its remarkable physico-chemical properties, birnessite has been widely used. It is usually applied in fields of water treatment, catalysis, electroactive materials, and supercapacitors [36]. According to studies, it has additionally been utilized as an adsorbent to remove dyes and heavy metal ions from wastewater. [22,23].

CuO is a basic copper compound with distinctive physical features such as electron correlation effects, superconductivity at high temperatures, and a smaller diffusion pathway which is of great advantage during adsorption [38]. CuO has favourable chemical and physical stability, is relatively inexpensive, and is simple to combine with polymers and polarized liquids (such as water). CuO nanoparticles are now used in a variety of applications as a result of this, including environmental remediations, electronics, wastewater treatment, cosmetics, polymers and agriculture [39]. In water treatment, the adsorption capacities of CuO as a dye adsorbent has been documented. Due to their high surface area to volume ratio, CuO nanoparticles exhibit chemical characteristics that are distinct from their micro and bulk counterparts [24]. Nanoscale CuO can be used to construct a variety of nanocomposites with outstanding physical and chemical properties such as catalytic and antimicrobial activity, large surface area, improved electrochemical, magnetic and optical properties, according to recent research [41].

ZnO is a semiconductor that has significantly been explored over the last decade in catalysis, including photocatalysis. It is associated with many peculiar characteristics such as the ability to form crystals of various forms and sizes, a high mobility of electrons, excellent thermal conductivity, band gap that is broad and direct [25]. ZnO has gotten a lot of attention recently as

a heterogeneous catalyst. This is because of its inexpensive, non-toxic nature[26–28]. ZnO has a lot of catalytic applications, one of which is photodegradation [10,29].

Paragraphs above are a proof that TMOs are an excellent choice of adsorbents, and this has brought up a great deal of interest amongst scientists to bring about synthesis methods that are environmentally friendly, cost-effective and easy to employ [30–33]. Numerous methods have thus far been developed, and some of them are sol-gel, sputtering and electrospinning. These methods cost a lot of money and employ chemicals that are environmentally hazardous, time-consuming, and demand advanced technical capabilities [34–37].

Recent developments in research have brought about the concept of green synthesis. This concept tries to solve the problems brought by the methods mentioned above [33]. Microorganisms, plant extracts, and biopolymers are currently being explored in green synthesis of nanosized TMOs [38]. They are employed as reducing agents and capping groups [39]. Plant extracts have gained much more popularity due to the biomass abundance of many plants and their ability to generate nanoparticles of varying size, shape, and stability [40]. Plants are even more advantageous and simple than microbes because they do not require any specific or complex methods like isolation, culture preparation, or culture maintenance [41]

Plant extracts have been widely reported to be eco-friendly and have a faster rate of reaction than traditional chemicals [39,42]. They contain a variety of active biomolecules that aid in reduction and stabilizing nanoparticles. Many different plants have been researched in this area [43,44]. These include cashew tree (*Anacardium occidentale*), *Morinda citrifolia*, *Euphorbia haterade*, Jaub root, *Euphorbia prolifera* and *Azadirachta indica* (Neem), amongst many more [45]. They are associated with the production of excellent nanosized TMOs such as ZnO applied in photocatalysis [46,47]. Mn_3O_4 has been applied as an electrode in the construction of a chemical sensor [48], MnO_2 in oxygen reduction [51], and Ag_2O in antibacterial activity [50,51]. Even with these advances in the research of plants being used in to make nanoparticles, biological production of nanoparticles is a relatively new concept that is still in its early stages of research. The field is still in its early stages, with issues such as the inability to control crystal development and stability, the shape and size of the particles as well as the aggregation of produced nanoparticles. In the synthesis of nanoparticles, these fundamental difficulties are more

common [52–54]. It is therefore imperative that the field is explored more to try to address the current limitations.

Fostering a more sustainable and improved industrial ecology is a must for maintaining a healthier environment in the future. This is proving to be difficult as people, terrestrial animals, aquatic creatures, and plants are all at risk because water sources are being polluted, primarily as a result of industrial outlets pouring a cocktail of dyes into them. Plant extracts are thus becoming increasingly popular in the environmentally friendly synthesis of metal oxide nanoparticles, which have great properties for removing dyes from textile effluents [55,56]. As a result, the focus of this study was on the application of morula leaf extract in the environmentally friendly manufacture of transition metal oxides for the removal of a mixture of colours from wastewater.

1.2. Problem statement

Several treatment techniques have been devised over the years to tackle the problem of dye pollution [57,58]. Because of its high effectiveness in dye removal, it is easy to employ, and it is highly cost-effective, adsorption is considered to be the most efficient among them [58–61]. Research has shown transition metal oxide nanomaterials to have high potential as adsorbents. This is because they have a high adsorption capacity due to their vast surface area and compact size. [62]. The synthesis of these nanomaterials has been faced with challenges like the use of toxic chemicals and high costs of production until the recent introduction of green synthesis [38], [63]. The inability to control particle shape and size, as well as the aggregation of nanoparticles created are some of the difficulties that green synthesis is still faced with [30,64]. It is because of these challenges that this research was focused on the use of morula leaf extract in the eco-friendly synthesis of transition metal oxide for the removal of a mixture of dyes from wastewater. Plant extracts are known for their environmentally benign nature and ability to produce metal oxide particles of varying composition, shapes and sizes which are great adsorbents and photocatalysts.

1.3. Objectives

1.3.1. Main objective

The primary goal of the study was to synthesize transition metal oxides; CuO, ZnO and birnessite using morula leaf extract for application in the removal of a mixture of rhodamine 6G and methylene blue dyes from an aqueous solution.

1.3.2. Specific objectives

By successfully pursuing the subsequent specific goals, the main objective was accomplished.

1. To prepare and characterize ZnO, CuO, and birnessite nanomaterials using morula leaf extract.
2. To determine and compare the activity of CuO and birnessite in the adsorption of rhodamine and methylene dyes in an aqueous solution under different conditions.
3. To determine the activity of ZnO in the photodegradation of rhodamine 6G and methylene blue dyes.

1.3.3. Research questions

The specific objectives were attained by providing answers to the following questions.

1. What are the chemical and physical characteristics of the prepared catalyst materials?
2. Are the prepared CuO and birnessite nanomaterials active towards the adsorption of methylene and rhodamine dyes, and to what extent?
3. Is the prepared ZnO active towards the photodegradation of methylene blue and rhodamine 6G dyes?

1.4. Significance of study

This study shed light on morula leaves' synthetic benefits, notably their potential in the preparation of nanoparticle metal oxides. The field of science has gained a better understanding of the necessity of promoting natural resources such as plant extracts in nanoparticle synthesis as an substitute to toxic chemicals that hurt our environment and jeopardize our lives as a result of this research. Furthermore, the findings of this study provide useful information for future

research into the use of other plants in the preparation of nanoparticles, which will lead to the manufacture of cheaper nanoparticle metal oxides with desirable properties.

2.0. LITERATURE REVIEW

The synthesis of transition metal oxide nanoparticles using morula leaf extract was the main goal of this study, as well as their use in adsorption and degradation of a mixture of rhodamine and methylene dyes. The study concentrated on morula leaf extract, which is utilized in the preparation of birnessite, CuO and ZnO. Birnessite and CuO were employed in adsorption of a mixture of rhodamine and methylene dyes whereas ZnO was applied in photodegradation of the mixture of the rhodamine and methylene dyes. As a result, the goal of this review is to draw attention to the knowledge gap in the study of synthesis and photocatalytic activity of birnessite, CuO and ZnO which was filled by the method of synthesis using morula leaf extract presented in this study.

2.1. Water pollution

Previously, water pollution was thought to be primarily a threat to the health of humans because of the spread of bacterial and viral waterborne infections. It is now recognized as a much broader concern that includes chemicals and continues to pose major health dangers to both humans and aquatic life [65]. The majority of our drinking water comes from surface water and its contamination is therefore a serious environmental issue [66]. The state of surface water has deteriorated over the years, particularly in terms of eutrophication, owing to pollution from industry, wastewater, and agricultural practices [67]. Therefore, both developing and developed countries continue to have serious public health concerns with waterborne infections. [68,92,93].

One of the industries that pollutes water sources the most and uses the most water is the textile industry. It produces chemicals which are harmful to aquatic and human life [94]. The majority of the harm that non-biodegradable organic chemicals, in particular textile dyes, inflict to water systems can be attributed to the textile industry. Textile dyes are harmful to both humans and animals and interfere with plant growth [71].

2.2. Methods of dye removal from wastewater

Every dye has a different chemical structure [72]. The chromophore in dye molecules is a cluster of atoms or electrons that gives the dyes their colour. A chromogen is a substance that contains a chromophore [73]. The most prominent categories are azo and anthraquinone [73]. Auxochrome

is a group of electrons connected to a chromophore that enhances the colour of the chromogen. The most common chromophores are methylene, azo, carbonyl, carbon-nitrogen, and carbon-carbon double bond [74]. These chromophores are the ones that induce pollution in textile wastewater, resulting in an unacceptably dark colour [75]. The auxochromes that are available are amine, hydroxyl, sulfonate, and carboxyl. Auxochromes are found in all forms of reactive dyes, including acidic, and basic dyes [72].

These chromophores and auxochromes are stable to light and physiologically inert. They resist aerobic degradation, making them one of the most difficult toxins to remove from industrial effluents [76]. Many investigations are being carried out in attempt to find the most effective dye removal procedure [77]. The biological, chemical, and physical therapies as presented in fig. 1 below, are the three types of dye removal procedures now available [78,79].

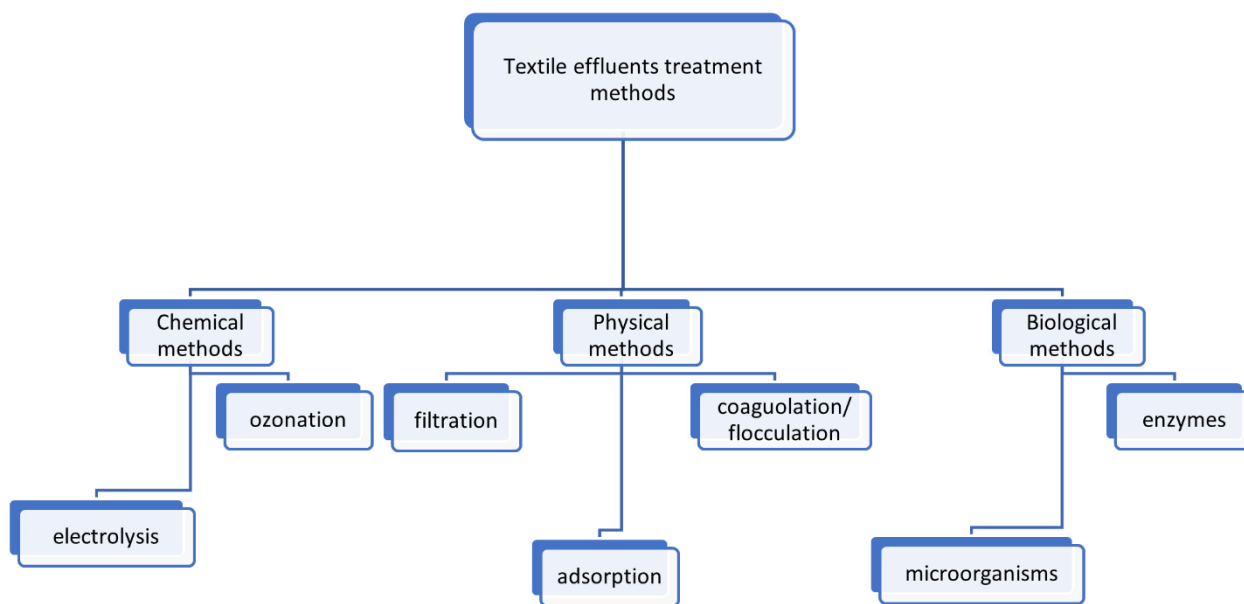


Figure 1: Different methods of dye removal [80].

2.2.1. Biological methods

One of the main areas of study in the field of environmental science is the application of microbial therapeutics to eliminate pollutants. Microbes acclimate to toxic wastes subsequently converting different dangerous compounds into less damaging forms [81]. In textile wastewater, the biological process eliminates dissolved organic materials. Temperature and oxygen levels in the system, as well as the ratio of the dye to the microbial load, are factors that influence the effectiveness of dye removal [73]. Biological processes alone may or may not be adequate, depending on local requirements. Other physical, chemical, or physicochemical actions may be required as part of the process [77].

The majority of dyes are resistant to aerobic decomposition. As a result, it is frequently recommended to combine aerobic post-treatment with anaerobic decolorization, and the process is typically costly and time-consuming. [82].

The ability of fungi to decolorize azo dyes has been examined. These dyes are not easily biodegraded by microbes, however, they can be destroyed by *P. chrysosporium* albeit with slow process kinetics. Therefore, practical application of fungal approaches for actual textile wastewater effluents is not yet feasible [80,81,83].

2.2.2. Chemical methods

Chemical oxidation techniques use oxidizing chemicals like permanganate and hydrogen peroxide to degrade or decompose dye molecules [108, 109]. In the presence of certain oxidizing chemicals, changes in the chemical makeup of substances, for instance, dyes occur making dye molecules vulnerable to destruction [110]. Advanced oxidation procedures (AOP) use oxidizing chemicals in the presence of an irradiation source or in combination with heterogeneous photocatalysts like ZnO, CuO, Mn, and Fe to completely destroy toxic dye pollutants [111,112].

The Fenton reaction method is the most used chemical method of dye removal because it is relatively inexpensive and provides good decolorization and chemical oxygen demand (COD) elimination effective for both soluble and insoluble dyes. Because of its excellent dye removal the H₂O₂/UV process is the most effective AOP technique. Furthermore, process does not result in any sludge formation and has a high COD removal retention time. [112-114].

2.2.3. Physical methods

Dye removal by physical means is often a straightforward procedure that utilizes the mass transfer mechanism [58]. Adsorption, coagulation or flocculation, reverse osmosis, filtering, and ion exchange are examples of conventional physical dye removal procedures [84,85]. Sulphur and dispersion dyes can be removed using physical procedures based on dye coagulation-flocculation, however, the process is limited when it comes to other forms of dyes such as acid dyes [86]. Furthermore, due to the limited efficacy of dye removal and the large volume of sludge produced, these treatments are rarely used. The adsorption technique has attracted a lot of interest because of its superior efficiency in eliminating a wide range of dyes [87].

2.3. Metal oxide nanomaterials in water treatment

One of the top five innovative techniques for developing water filtration systems is nanotechnology. This phenomenon is the study, development, and use of materials with a diameter of 1 to 100 nanometres [88]. According to some study, SiO₂ NPs are the most typically generated NP, followed by CuO, ZnO and CeO₂ NPs among others [89,122,123]. Despite this, due to a lack of reliable, readily available data, producing large numbers of NPs remains a significant difficulty. Improved understanding of NP manufacture would vastly increase the quality of data and simulations in the field [93].

2.3.1. Birnessite

The α -, β -, γ -, and δ - types of MnO₂ crystallographic polymorphs exist. One of these is the birnessite-type manganese oxide that has a 2D layered structure. It is made up of interstitial cations and MnO₆ octahedra that share their edges. The cations counteract the negative charge in the layers caused by Mn site vacancies and Mn(III) substitution for Mn(IV). Furthermore, this material is capable of cation interchange and oxidation-reduction reactions due to the Mn oxidation states that are easily interconverted and the interstitial cations that are interchangeable. MnO₂ has been widely employed due to these unique physicochemical features [94–96].

Birnessite appears to be important in the removal of dyes, and many other water contaminants, according to new research. Birnessite's cation exchange capacity, sorption, and redox characteristics all play a role in this activity [97–99]. Birnessite is attractive because of its inexpensive cost of raw ingredients and environmental friendliness during synthesis. Birnessite

unusual surface nature, such as its large specific surface area (SSA), low surface charge, and mesoporous structure, make it particularly valuable in water treatment [100–102].

2.3.2. CuO

Copper (II) oxide has a monoclinic structure and is a semiconducting material. It has a variety of advantageous physical and chemical properties, including low cost, antibacterial activity, superconductivity, photovoltaic abilities, and stability [103,104]. CuO nanoparticles can also be used for catalysis, batteries, and gas sensors because they have a large electrochemical capacity [105]. CuO nanoparticles have an abundant synthesis precursors. This, combined with other benefits such as a huge surface, low-toxicity and a low production cost, has led to them being explored as prospective adsorbent materials on a regular basis. [106-109].

2.3.3. ZnO

ZnO nanoparticles can be applied to many different things, including wastewater treatment, due to their bactericidal properties, great adsorption capacity, high catalytic efficiency, porous structure [110,111]. Various researchers have tested the elimination efficacy of ZnO nanoparticles and found that laboratory made ZnO nanophotocatalysts are more effective than commercial ZnO [112,113]. ZnO nanoparticles' photocatalytic activity has also been extensively studied.

ZnO is a semiconductor with a bandgap of 3.2 eV and a huge number of active sites, making it an excellent photocatalyst for producing significant amounts of OH radicals [146–148]. Its photocatalytic activities are driven by Zn interstitials and the presence of oxygen vacancies, which operate as active sites in order to prevent electron-hole recombination. The production of H_2O_2 , O_2^- , and OH radicals is increased as a result of this, all of which are required for photocatalytic activity on ZnO surfaces [148–151]. Doping causes more surface flaws, and thus transition metals doped into ZnO nanoparticles increase the photocatalytic efficiency [114–117].

2.4. Synthesis Methods

Over the years, a wide range of methods for synthesis of metal oxides have been created. In the available literature, the bottom-up and top-down approaches have been looked at as the fundamental concepts of synthesis to create nanomaterials of desired sizes, shapes, and functions [36, 37]. Different researchers have reported on a number of different methods and some of

these are shown in fig. 2 below. The downside of these methods is continuously being exposed as new technology emerges and the world is moving towards green technology [35].

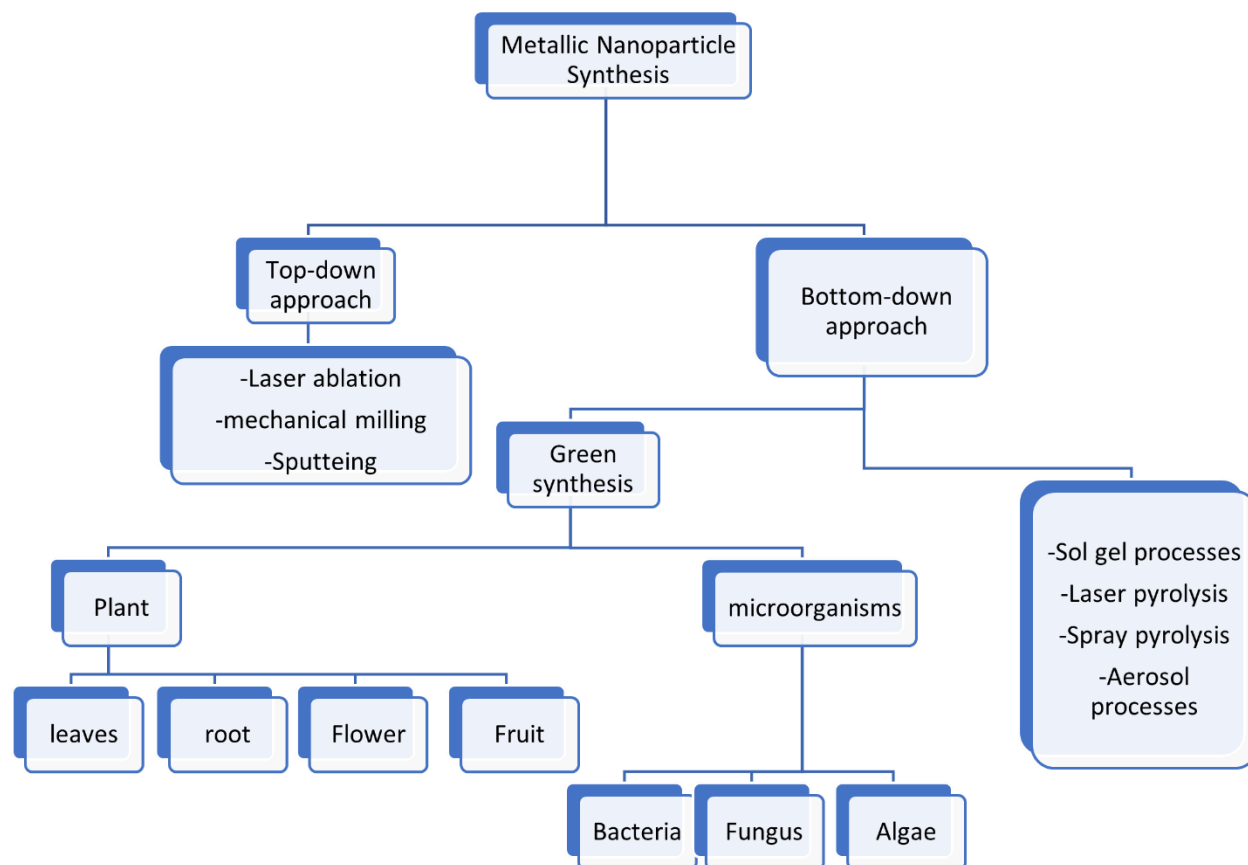


Figure 2: Different methods of nanoparticle synthesis [118].

2.4.1. Sol-gel

Sol–gel technique is commonly used to make nano-dimensional materials. A sol is a liquid-phase colloidal solution of particles. A gel on the other hand, is a submerged solid macromolecule in a liquid [157]. The most extensively used bottom-up method is sol-gel [158] because it is a simple procedure and has the ability to create many different nanoparticles. In the sol-gel process, metal oxides and chlorides are frequently utilized as precursors. Shaking, and/or sonication are used to distribute the precursor in a host liquid, resulting in a two-phase system. To recover the

nanoparticles, the required sample is subjected to thermal treatment/calcination to remove residues and water molecules [119].

Colloidal powders or films could be the reaction result of the sol–gel synthesis. One of the benefits of this technique is the ability to manipulate the end product's microstructure by altering chemical reaction parameters [120]. It entails the development of networks by mixing the sol with gelatine to create a gel network. In order to produce these colloids, metal alkoxides are typically utilized as a precursor. Tetramethoxysilane (TMOS) and tetraethoxysilanes (TEOS), which generate silica gels, are the most extensively utilized. The disadvantage of the use of these chemicals is their cost and toxicity to the environment [119,121].

2.4.2. Electrospinning

To create a synthetic web of micro- or nanofibers, the electrospinning technique is used. In this technique, a liquid solution and a collector receive high-voltage electricity that causes the solution to extrude from a nozzle and produce a jet. The jet generates fibers during the drying process, which are then deposited on the collector [162].

Among several technologies, electrospinning has shown to be the most efficient method for producing nanofibers. The method can be scaled up and nanofiber size and orientation can be controlled with precision. Electrospinning has a number of disadvantages, including limited mechanical strength of the scaffolds for load-bearing applications, toxic solvent residue, and poor cell infiltration and migration as a result of densely packed scaffold fibers [122,123].

2.4.3. Chemical vapor deposition (CVD)

On solid substrates, 2D nanoparticles and thin films are frequently fabricated using the CVD technique. When heated to extremely high temperatures in a vacuum chamber, precursors can react on a predefined substrate [124,125].

CVD is a method of fabricating materials that utilises the vapor phase. Despite the fact that it allows for the precise control of both metallic single grains and layers nucleation and development, the method is not widely used in the fabrication of biomaterials, according to literature sources. This is because the process is associated with the need for sweltering temperatures and vacuum. This leads to a high ultimate product price [126,127].

2.4.4. Pyrolysis

The most widely used commercial method for creating nanoparticles is pyrolysis [4]. This procedure entails setting the precursor ablaze. The said precursor could exist as a liquid or as a vapor and it is injected into the furnace under high pressure, and nanoparticles are removed. [169].

A laser or plasma can be used instead of a flame when a high temperature is required. High temperatures facilitate evaporation [170]. Pyrolysis provides a number of advantages, including high efficiency, low cost, ease of use, and the capacity to create a high yield in a continuous process. The use of extremely high temperatures is the main disadvantage. [128,129].

2.4.5. Laser ablation

The laser ablation technique includes irradiating a solid surface with a beam of light to remove material. When laser energy is absorbed at a low laser flux, the material heats up and finally evaporates or sublimates [130,131]. The advantages of the laser ablation process include the ability to synthesize metal nanoparticles in both aqueous and organic solvents, as well as the absence of the requirement to remove surplus chemicals [180,177].

For solution phase production of metallic element nanoparticles, laser ablation has emerged as a viable and dependable alternative to chemical reduction approaches in recent years. The laser ablation approach is used to create stable nanoparticles on a metal plate immersed in a surfactant-containing fluid [133]. Each nanoparticle is encased by a surfactant, which inhibits direct contact between them. The rapid, scalable synthesis of colloidal metal-silica nanoparticles has been described using this simple and powerful approach [134]. Using this method, various non-reactive silica-metal nanoparticles have been generated [135]. Being able to manipulate nanoparticle scale, shape, and composition, as well as the high yield, quick processing time, and scalable manufacturing, are the main advantages of this method [131,132].

There are certain disadvantages of laser ablation namely; high cost and the need for preparation of a large number of colloids on a regular basis in order to be cost effective. Furthermore, lasers consume a lot of energy (although many other synthesis approaches do as well), and large-scale synthesis of nanomaterials is not possible [136,137].

2.5. Green synthesis

As it is evidently clear that the existing methods are costly, involve the employment of harmful chemicals and require high expert skills, there is a need to come up with methods that can remedy these problems. Green synthesis is a style of synthesis that involves an environmentally friendly approach to synthesis of materials [63]. Green synthesis aims to remove toxic waste, reduce energy consumption, and employ environmentally friendly solvents [138]. Different substances and materials such as microorganisms, plants, plant extracts, sugars and biopolymers are currently being explored in green synthesis of nanosized TMOs. Green synthesis uses microbes and plants to make nanoparticles that are biologically safe, cost-effective, and environmentally benign [139]. Plants and microorganisms have evolved the ability to consume and store inorganic metal ions in their environment. Living organisms are known to produce both external and intracellular nanoparticles. The ability of a biological system to transform inorganic metal ions into nanoparticles using its own organic chemistry processes has opened up a previously unexplored arena of biochemical research. [64].

2.5.1. Microorganisms

Microorganisms are considered nano factories with a lot of potential as cost-effective and eco-friendly tools that do not use poisonous or harsh chemicals and have a low energy consumption for nanoparticle synthesis [140,141]. Because the process can be managed by modifying culture conditions such as nutrition, pH, pressure, and temperature, yeast, fungus, and bacteria have all been identified in the last several years as secretors of reducing and capping agents in the green synthesis of NPs [142–144].

2.5.2. Plants

Plant extracts are increasingly being used in the preparation of metal oxide nanoparticles (MONPs) in recent years. This is because plant extracts, particularly those from the leaves, contain important phytochemicals [38,145]. In comparison to conventional chemicals, the method is also environmentally benign and has a faster reaction rate [146]. Plant extracts are rich in active biomolecules that help to reduce and stabilize NPs. Leaf extracts in particular are commonly being employed in the fabrication of metal and metal oxide nanoparticles because they contain a wide range of chemicals, such as ketones, terpenoids, aldehydes, amides,

flavonoids, and carboxylic acids, all of which are important in the synthesis of nanoparticles. [53,146].

Recent research has found that using leaf extracts to make nanoparticles results in the generation of stable particles [43,44,147]. Plant extracts can be utilized to substitute a variety of toxic compounds in combination with any of the above-mentioned methods to produce the best-performing metal oxide nanoparticle production process.

In this area, many different plants have been studied [60,61]. Cashew tree (*Anacardium occidentale*), *Morinda citrifolia*, *Euphorbia haterade* Jaub root, *Euphorbia prolifera*, and *Azadirachta indica* (Neem) among others [62]. They have been used in the preparation of nanosized transition metal oxides, such as ZnO for photocatalysis [63,64], Mn_3O_4 for manufacturing an effective chemical sensor [65], MnO_2 for oxygen reduction [51], and Ag_2O for antibacterial activity [67,68].

Biological nanoparticles synthesis is a relatively new concept that is still in its early stages of research, despite the progress in the application of plants in nanoparticle synthesis. The control of the stability, size and shape of the nanoparticles as well as aggregation are all challenges that scientists still face with regard to this synthetic procedure [69–71]. As a result, more research into the subject is needed to alleviate the current limitations.

3.0. METHODS AND MATERIALS

3.1. Preparation of Morula leaf extract and characterisation

The Morula leaves were collected from the tree and rinsed under running water before being dried in a 60 °C oven for 6 h. After being crushed, the leaves were kept for later use in a glass bottle.

4 g of crushed leaves were boiled in 100 mL of distilled water for 5 minutes with continual stirring in order to obtain the extract. After filtering the leaves, the fresh filtrate was subsequently examined using contraAA 700 atomic absorption spectroscopy before being employed in synthesis.

3.2. Synthesis of nanomaterials

The materials were prepared using a hydrothermal process. 100 mL leaf extract was combined with 20 g of different metal precursors (zinc (ii) nitrate, cupric (ii) nitrate, and potassium permanganate). The mixture was then added to a hydrothermal reactor and moved into an oven that was preheated to 150 °C. The product was then filtered, rinsed, and dried in a 60°C oven for an overnight period.

3.3. Characterization of the nanomaterials

The crystalline structure of the materials was investigated using X-Ray diffractions (XRD) on a Bruker D8 Advance powder diffractometer. A Cu tube X-ray source ($\lambda=1.54056$ nm, 40 kV, 40 mA) was employed and the XRD was set at a scan rate of 0.500 sec/step covering 0.02 degrees of 2θ . Spectroscopic studies were performed using the LabRAM HR800 Raman spectrophotometer, which excited the samples with a 532 nm laser.

Morphological analysis of the materials was also done using the JEOL JSM-7500F Field Emission Scanning Electron Microscope (FE-SEM) Equipped with Energy Dispersive X-ray spectroscopy (EDX) which was also employed in further analysis of the materials' elemental composition. Finally, the materials surface area, pore size, and volume were determined using the Micromeritics Tristar II Brunauer-Emmett-Teller (BET) analyser.

3.4. Batch equilibrium studies (adsorption)

Investigations were done into how contact time, temperature, and other factors affected the removal of dye from wastewater by adsorption onto metal oxide nanoparticles. For the investigation, batch adsorption procedures were used. 2 ppm mixtures of methylene blue and rhodamine 6G dyes were prepared in 250 mL Erlenmeyer flasks. 20 mL of the mixture was then transferred into a beaker and 15 mg of the adsorbent dispersed into the mixture. The mixture was then constantly stirred with a magnetic stirrer until an equilibrium was attained. The supernatant liquids from the centrifuged mixtures were examined with a UV–vis spectrophotometer. Using the following formulas, the adsorption capacity and dye elimination percentage were computed:

$$Q_e = \frac{(C_o - C_e)}{W} V \quad 1$$

$$\text{dye removal \%} = \frac{C_o - C_e}{C_o} \times 100 \quad 2$$

The initial and equilibrium concentrations (mg/L) are C_0 and C_e , respectively. W is the mass of adsorbent employed (g), and V is the volume of solution (L).

3.5. Adsorption equilibrium

In adsorption, isotherm models can be used to research dye molecules affinity for the adsorbent material. In this study, the Langmuir and Freundlich models were used. The link between the initial adsorbate amount and the amount still present in the solution at equilibrium was evaluated using these models [1].

3.6. Photodegradation studies

5 mg of rhodamine 6G and methylene blue dyes were dissolved in 250 mL of distilled water to make a stock solution with a concentration of 20 mg/L. The dye solution had two lambda maximum wavelengths at 524 and 664 nm. The photocatalytic performance of ZnO was established through a batch reactor system with the mixed dye as the target contaminant. The degradation was performed under UV irradiation using GPH287T5L/S/14W UV-lamp (Wonder-Light, Hungary) with 254 nm wavelength.

15 mg of photocatalyst was typically distributed in a 40 mL 2 ppm mixed dye aqueous solution. Before being exposed to UV-lamp irradiation, the mixture was agitated in the dark for 20 mins to

allow for adsorption equilibrium to be reached. The reactor and lamp were separated by 7.5 cm. Throughout the reaction, the suspension was constantly agitated. To separate the particles from the solution for analysis, 2 mL of the aliquot was collected from the mixture at 15-minute intervals and centrifuged for 5 min at 13,000 rpm. A UV–vis spectrophotometer was used to measure the absorbance of the filtrate at 524 and 664 nm (Evolution-201, Shimadzu, Japan). Eqn. 3 was used to calculate the percentage degradation (η).

$$\eta = \frac{A_0 - A_t}{A_0} \times 100\% \quad 3$$

where A_0 and A_t are the absorbances of the mixed dye before irradiation and at different irradiation time intervals, respectively.

3.7. Radical scavenging experiment

The scavenging studies on the primary active reactive species like superoxide (O_2^-), holes (h^+), and hydroxyl ($\cdot OH$) radicals were done to research the degradation mechanism of the blended dye. During the degradation process, tert-butanol (t-BuOH), p-benazaquinone (p-BQ), and ethylenediaminetetraacetic acid disodium (EDTA-2Na) were added to reaction vessels to trap $\cdot OH$, O_2^- , and h^+ radicals, respectively. In a typical procedure, 15 mg of ZnO and 1 mM of radical scavengers were added to a 40 mL, 2 ppm mixed dye solution. Prior to being exposed to UV light for 75 minutes, the solution was mixed in the dark for 20 minutes to allow for adsorption equilibrium. Finally, the percentage degradation was calculated to measure the effect of the radical on the degradation of the combined dyes.

4.0. RESULTS AND DISCUSSION

4.1. CuO

4.1.1. Characterization of CuO

Synthesis of CuO was initially attempted without the morula leaf extract. Distilled water was the only solvent utilized in the process. Copper (ii) Nitrate was mixed with distilled water and the mixture was hydrothermally treated at 150 °C. This reaction resulted in a blue solution without any precipitate as shown in **Figure 3** (a) below. This shows that the CuO precipitation was aided by the morula leaf extract.

Figure 3 (b) depicts the XRD patterns of the CuO materials prepared using the morula leaf extract before and after calcination at temperatures of 250, 300, 325, and 350 °C. CuO was amorphous before calcination. After calcination at 250 °C, peaks began to emerge. Some of the peaks are indicative of CuO at calcination temperatures of 250 and 300 °C, but there are some contaminant peaks as well. These peaks could be associated with unreacted copper (ii) nitrate material, as well as elements from the leaf extract. Only samples calcined at 325 and 350 °C show XRD peaks, indicative of CuO with no impurities and matches Crystallography Open Database (COD) card no. 1011194. The strongest peaks were found at 34, 38, 49, 54, 59, 61, and 65° corresponding to the lattice planes (110), (111), (202), (020), (202), (202), and (022), respectively.

The particle size was determined using the Debye Scherrer equation. The average particle size of CuO was 10.8 nm after calcination at 350 °C. The sample calcined at 350 °C was subsequently taken for further study using Raman spectroscopy.

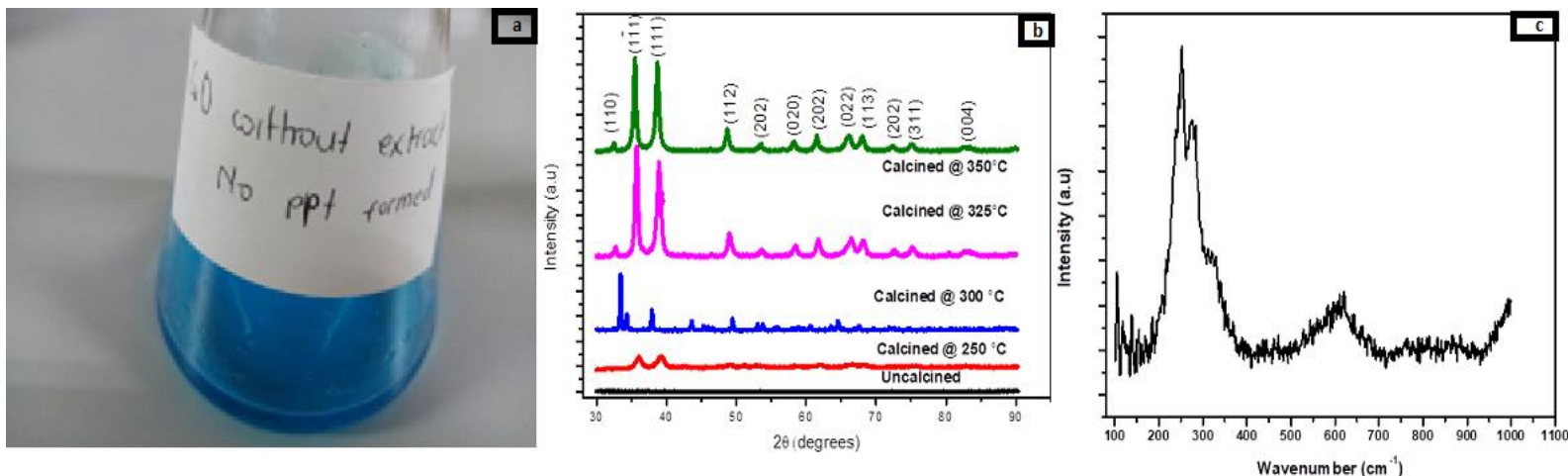


Figure 3: (a) Optical image of the solution obtained after attempted synthesis of CuO using distilled water instead of morula leaf extract, (b) XRD pattern of CuO synthesized using the morula leaf extract, after calcination at different temperatures, (c) Raman spectrum of CuO synthesized using morula leaf extract and calcined at 350 °C.

Further evidence for the formation of CuO nanoparticles after calcination at 350 °C came from the Raman spectra. Nine zone-center optical phonon nodes of CuO with symmetries $4A_u + 5B_u + A_g + 2B_g$ have been reported. Of all these, there are just three modes (A_g and $2B_g$) that are Raman active [148]. **Figure 3** (c) shows the CuO Raman spectrum, which has a singlet peak at 600 cm^{-1} and a doublet peak between 200 and 400 cm^{-1} . In the doublet peak, the 1st peak can be assigned to the A_g node and the second one of the B_g nodes. The other B_g node may be responsible for the peak at 600 cm^{-1} . There are no Cu_2O nodes detected, and the other peaks present are those of the bulk CuO crystals corresponding to A_g (296 cm^{-1}), B_g (346 cm^{-1}), and B_g (636 cm^{-1}) nodes. [88]. This illustrates that our CuO nanorods have a single-phase characteristic.

4.1.2. Morphological analysis of CuO

4.1.2.1. Scanning Electron Microscope

Scanning electron microscopy (SEM) was used to analyze the samples' morphology. **Figure 4a-c** below demonstrate images from the SEM, of CuO nanoparticles obtained by calcining at 300, 325 and 350 °C, respectively. The morphology of the material calcined at 300 °C is composed of agglomerated platelet-like structures shape, **Figure 4a**. At 325 °C, the platelet morphology transformed in thick slabs stacked into microcolumns, **Figure 4b**. At 350 °C the stacking of the slabs was destroyed due to crystal growth via sintering of slabs, **Figure 4c**.

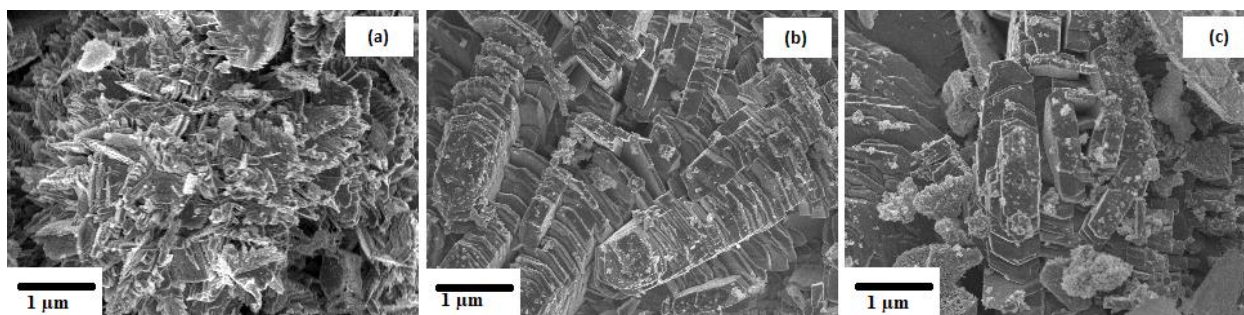


Figure 4: (a) SEM image of CuO calcined at 300 °C, (b) SEM image of CuO calcined at 325 °C, (c) SEM image of CuO calcined at 350 °C.

4.1.2.2. Brunauer-Emmett-Teller

Figure 5a is a representation of the N₂ adsorption-desorption isotherms of the synthesized materials calcined at 300, 325, 350 °C. According to IUPAC classification, all produced materials have typical type V isotherms with an H3-type hysteresis loop. The observed hysteresis loop shape is typical of samples that are mesoporous. The Barret-Joyner-Halenda (BJH) pore size distribution (PSD) profiles are presented in **Figure 5b**. PSD profiles for the materials calcined at the different temperatures show maxima around 100 Å corresponding 10 nm which falls within the 2–50 nm mesoporous range, meaning no microporosity [200,149].

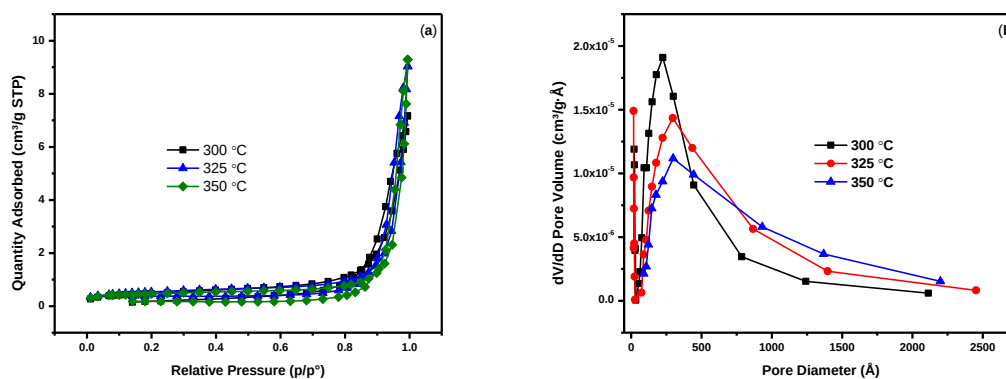


Figure 5: (a) N₂ adsorption-desorption isotherms (b) Barret-Joyner-Halenda (BJH) pore size distribution curves of CuO materials at 300, 325, and 350 °C.

Table 1 is a summary of **Figure 5** above. The table shows that when the temperature rose, the material's surface area, pore diameter, and volume all increased. The surface area of the CuO prepared at 350 °C measured by BET adsorption was 26.8225 m²/g. The particles were found to be mesoporous, with pore diameters of 14 nm and volumes of 0.000807 cm³/g. The particle size as according to BET is a significantly higher than the 10.8 nm given by the Debye Scherrer equation, but both still indicate the material to be mesoporous.

Table 1. The BET surface area, pore diameter, pore volume, and average particle size of CuO at 300, 325, and 350 °C

Temperature (°C)	BET surface area (m ² /g)	Pore diameter (Å)	Pore volume (cm ³ /g)	Average particle size (Å)
300	12.5604	101.8560	0.000707	33 135.705
325	15.6111	106.4426	0.000713	36 128.824
350	26.8225	140.1921	0.000807	39 407.957

4.1.3. Application of CuO

CuO was applied in adsorption of dye in water. **Figure 6** shows the UV/Vis spectra of the two individual dyes and the dyes combined. It also shows the spectra of the mixture dyes after 90 mins without the adsorbent. The maximum absorbances (abs) of the dyes remain the same which indicates that without the adsorbent, there is no reaction taking place between the dyes. Upon the addition of the adsorbent, a decrease in the maximum absorbances of both dyes was observed and this indicates adsorption of the dyes onto adsorbent.

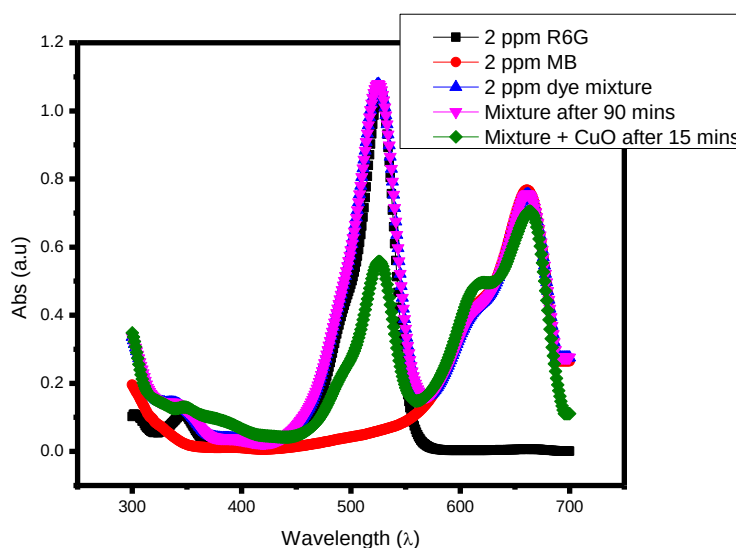


Figure 6: UV/Vis spectra of individual Rhodamine 6G and methylene blue dyes and their combined mixture.

4.1.3.1. Effects of catalyst loading

By altering the amount of CuO added (0.15, 0.2, 0.25, 0.3, 0.35, and 0.4 mg), the effect of adsorbent dosage on the effectiveness of removing an MB and R6G combination was examined while keeping a constant 2 ppm dye concentration, pH at 7.2 for 60 min. The dye adsorption efficiency rose from 21 to 39% for MB and from 49 to 66% for R6G when the CuO dosage was raised from 0.15 to 0.35 mg. The initial sharp rise in adsorption with higher adsorbent dosage is caused by the presence of additional adsorption sites. However, when the CuO dosage was increased beyond 0.35 mg, the dye removal percentage remained constant. Higher adsorbent dosages cause the "screening effect," which could be used to explain this phenomenon. At the nanoadsorbent surfaces, it is characterized by the accumulation of adsorbent particles and a narrowing of the space between adsorbent molecules, which leads to the formation of a dense screening layer. The dye molecules' binding sites were therefore hidden by the screening layer at the adsorbent's surface [55,150].

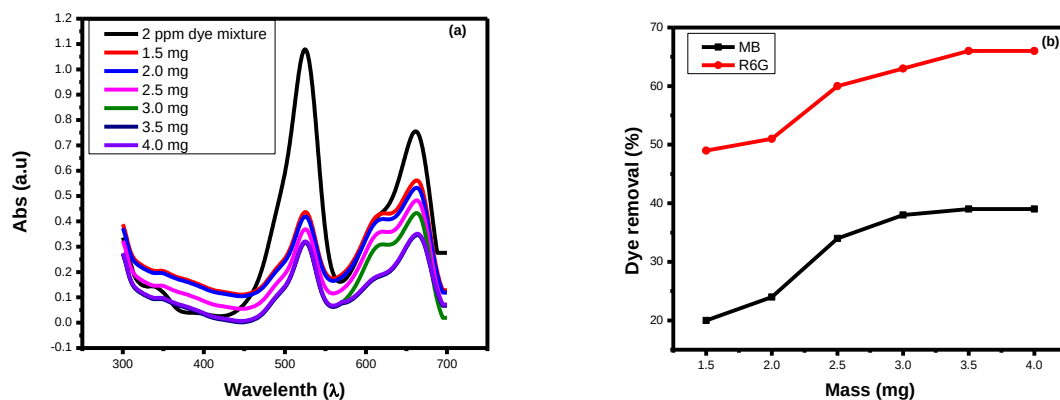


Figure 7: (a) Effects of adsorbent dosage on adsorption of dye onto CuO, (b) Plot of % dye removal versus amount of adsorbent on adsorption of MB and R6G onto CuO.

4.1.3.2. Effects of contact time

Figure 8 shows the influence of contact time on dye adsorption onto CuO at a starting concentration of 2 ppm. Data was collected at room temperature using a 0.35 mg adsorbent dose and a constant pH of 7.2. According to the graph, the adsorption of both dyes was slow in the first 15 mins. The adsorption rate increased rapidly after 30 mins before it dropped again at 45 mins. Beyond 60 mins, the adsorption rate plateaued. In the first 15 mins of the reactions, the adsorbent had not yet evenly dispersed throughout the dye solution, this caused the slow uptake of the dye molecules. Beyond 15 mins, the adsorbent was event distributed and there was a high number of active sites for dye adsorption, this resulted in increased dye uptake rate. The rate then slowed down and then became constant at 56 and 72% for MB and R6G, respectively, as the active sites of the material were getting filled up and there was no more room to accommodate more dye molecules [150].

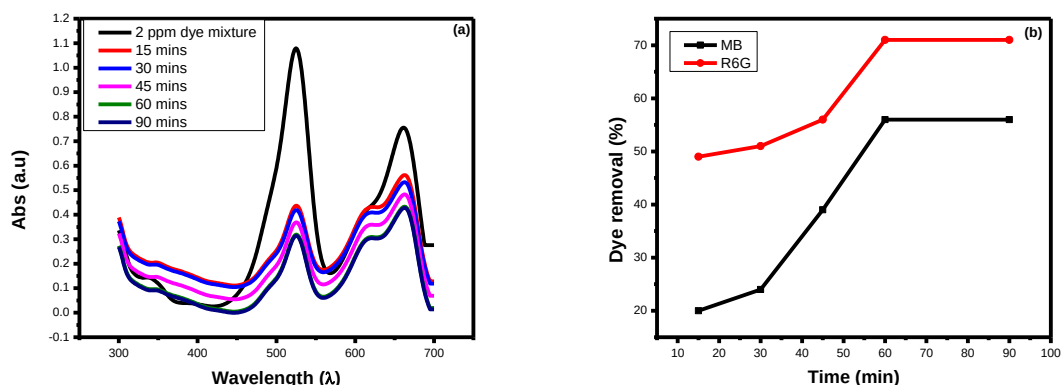


Figure 8: Effects of contact time on adsorption of dye onto CuO

4.1.3.3. Effects of temperature

Investigations into the effect of temperature on dye adsorption were made, and the results presented in **Figure 9**. The temperature ranged from ambient temperature to 90 °C. At 25 °C, CuO adsorption capability was observed to be highest reaching about 56 and 72% for MB and R6G, respectively, at room temperature. The adsorption capacity declined from 56% to 40 % for R6G and from 72% to close to 0% for MB when an increase in temperature was made from room temperature to 90 °C, demonstrating that the process was exothermic. Since molecules that have previously been adsorbed on the surface tend to desorb at high temperatures, dye adsorption tends to decrease as temperature rises. This results from the weakening of the attractive forces at high temperatures between the material and the dye molecules [89,151]. Temperature effects on dye adsorption could be used to explain the inconsistencies in the data obtained at the same time and adsorbent dosage when investigating effects of time and adsorbent dosage in figures 7 and 8 above.

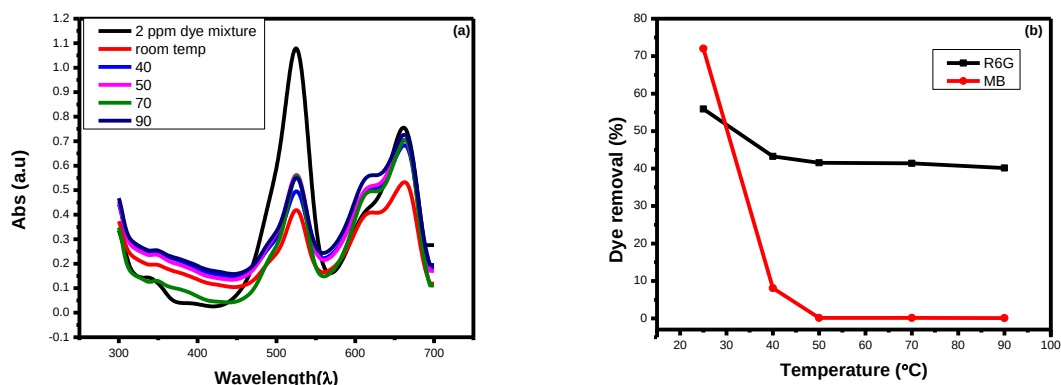


Figure 9: (a) Effects of temperature on adsorption of a dye mixture onto CuO, (b) Plot of % removal versus temperature on adsorption of MB and R6G onto CuO.

4.1.3.4. Effects of pH

Figure 10 demonstrates the effects of pH on dye adsorption onto CuO. (0.35 mg at room temperature for 1 h). The graph shows that initially there were small increments of dye uptake when pH was increased from 2 to 9. The adsorption capacity of the methylene blue and rhodamine mixture increased dramatically from pH 9 to 12, reaching 78% for MB and 86% for R6G. It is worth noting that the adsorption efficiency is influenced by the pH of the solution. The active group chemistry and surface charges of CuO changed when the pH was modified [90]. In basic aqueous media, hydroxyl (OH) groups occupy functional binding sites of the CuO material, while protons (H⁺) occupy functional binding sites of the material in acidic solutions. Between pH 2 and 7, more protons are occupying the hydroxyl vicinities of CuO surfaces. This promotes the initiation of repulsive force (between positive charged dye molecules and the CuO surface), which limits dye binding to some extent, and this results in decreased adsorption. Between 7 and 9, there is an increase in the hydroxyl ions, but it is not yet enough to increase the amount of dye uptake [4]. Beyond pH 9, the OH⁻ negative charges on CuO surfaces are widely spread which increases the electrostatic interaction potential between active binding sites and dye species. This resulted in the rapid increase in the dye uptake [152].

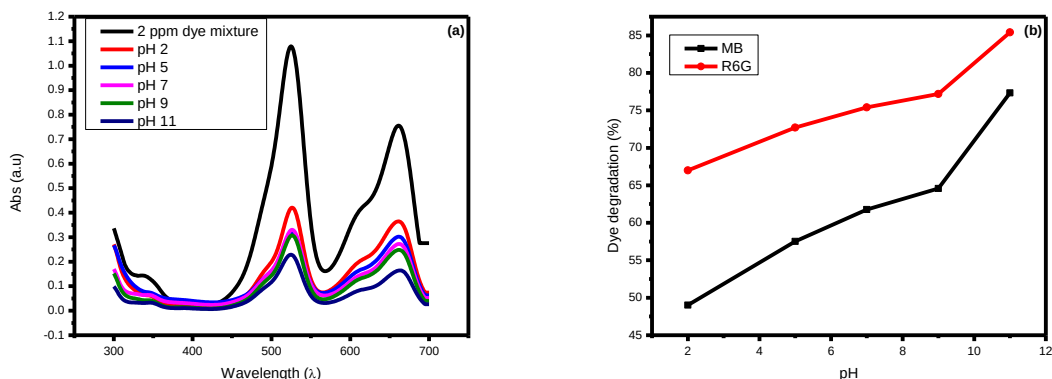


Figure 10: (a) Effects of pH on adsorption of a dye mixture onto CuO, (b) Plot of % removal versus pH on adsorption of MB and R6G onto CuO.

4.1.3.5. Effects of initial concentration of contaminant

In **Figure 11**, it is demonstrated how concentration affects dye removal using CuO. The data was gathered at room temperature with an adsorbent dosage of 0.35 mg and a constant pH of 7.2. The contact time was similarly set at 60 mins. With increasing adsorbate concentration, the amount of dye removed (%) was shown to decrease. The blocking action of dye molecules on pores and channels is thought to be the cause of the reduced dye % removal. The adsorbent sites become totally saturated when the concentration of dye increases without increasing the surface area of the adsorbent, resulting in a decrease in dye removal [22].

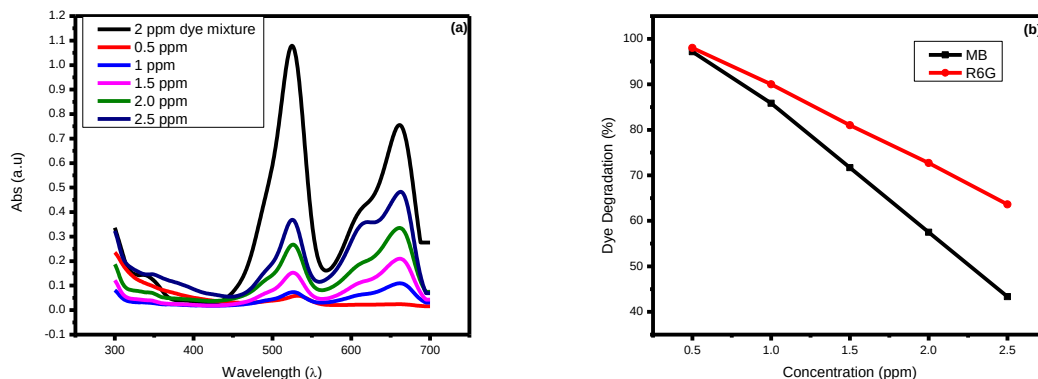


Figure 11: (a) Effects of concentration on adsorption of a dye mixture onto CuO, (b) Plot of % removal versus concentration on adsorption of MB and R6G onto CuO.

4.1.4. Adsorption isotherms of CuO

The dye adsorption onto CuO followed the Langmuir isotherm model. The high R^2 values support this conclusion. CuO has the highest R^2 of 0.99049 in Langmuir. **Figure 12 a and b** show Freundlich and Langmuir isotherms for CuO, respectively. A linear regression approach was used to get the required parameters and correlation coefficients for the two isotherm models. This is because linear regression is easier to use, and the results are simpler to interpret. **Table 2** demonstrates Langmuir parameters. According to the Langmuir isotherm model, the dyes on CuO showed highest adsorption capabilities of 56 mg/g. CuO has strong adsorption capabilities, as evidenced by the RL values observed, which are in the 0–1 range. Furthermore, $n > 1$, indicating that CuO is a great adsorbent for both dyes with a high adsorption intensity. [21,91].

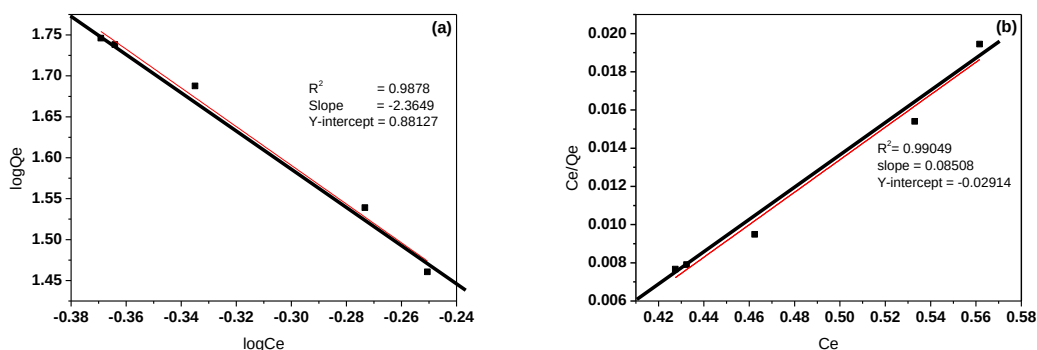


Figure 12: (a) Freundlich isotherm of CuO, (b) Langmuir isotherm of CuO

Table 2: Comparison of maximum monolayer capacities of CuO.

Langmuir parameters	Qe (mg/g)	55.72
	R _L	0.02
	R ²	0.9905

4.2. Birnessite

4.2.1. Characterisation of birnessite

Figure 13a demonstrates the critical role that morula leaf extract plays in the formation of birnessite. In its absence, KMnO_4 dissolves in water forming a purple solution and no precipitation occurs even after hydrothermal treatment. The XRD patterns of several materials obtained in an attempt to prepare birnessite using morula leaf extract is shown in **Figure 13b**. The hydrothermal reaction of KMnO_4 with morula leaf extract resulted in peaks found at 11, 25, 37 and 66°. These peaks appear broad with very little intensity. This means that the material was amorphous at this stage. This same material was then calcined as a way of trying to make it more crystalline. From the calcination, the peaks remained in the same positions but there was no observable change in their intensity. The peaks have been accurately indexed to the structure of birnessite (PDF Card No. 00-013-0106) corresponding to the lattice planes (001), (002), (100) and (110) respectively. The broadness of the peaks indicates poor crystallinity. According to the diffraction reflection and the Debye–Scherrer equation, the crystallite size on average (D_p in nm) was 62.9 nm.

Impurity-specific peaks were also discovered in the XRD pattern at 34 and 53°. In an attempt to remove these impurities, MnO_2 was used in place of KMnO_4 . This trial resulted in no observable XRD birnessite peaks. Aging KMnO_4 resulted in the formation of peaks which cannot be associated with any manganese oxide. The most intense peaks appear at 15, 20, 23, 24, 25, 26, 27, 30, 31 and 35° and they are thought to closely resemble those of KMnO_4 . This suggests that aging did not cause any chemical reaction to occur to the KMnO_4 .

In **Figure 13c**, several synthesis temperatures were utilized to increase the crystallinity of birnessite. The graph demonstrates that when the temperature rose from 150 to 180 °C, the peaks became more prominent, showing a very minor rise in crystallinity. As the temperature increased to 210 °C, no discernible difference was observed.

Figure 13d represents the Raman spectra of birnessite. One intense broad peak can be observed between 550 and 730 cm^{-1} in the spectra. A typical MnO_x Raman spectrum has two distinct marker nodes between 450 and 550 cm^{-1} and 550 and 750 cm^{-1} . The distortion nodes of Mn-O-Mn chains parallel to the basal plane (in-plane) and the stretching nodes of MnO perpendicular

to the basal plane (out-of-plane), which are usually referred to as Ag(1) and Ag(2), respectively, explain the MnO vibrations. These nodes' wavenumbers depend on both the interlayer space between MnO_6 layers and how much the octahedra in MnO_6 have been polymerized. Birnessite is one of the few manganese dioxides with Raman scattering nodes larger than 700 cm^{-1} [154], this correlates to the peak in **Figure 13d** observed between 550 and 730 cm^{-1} .

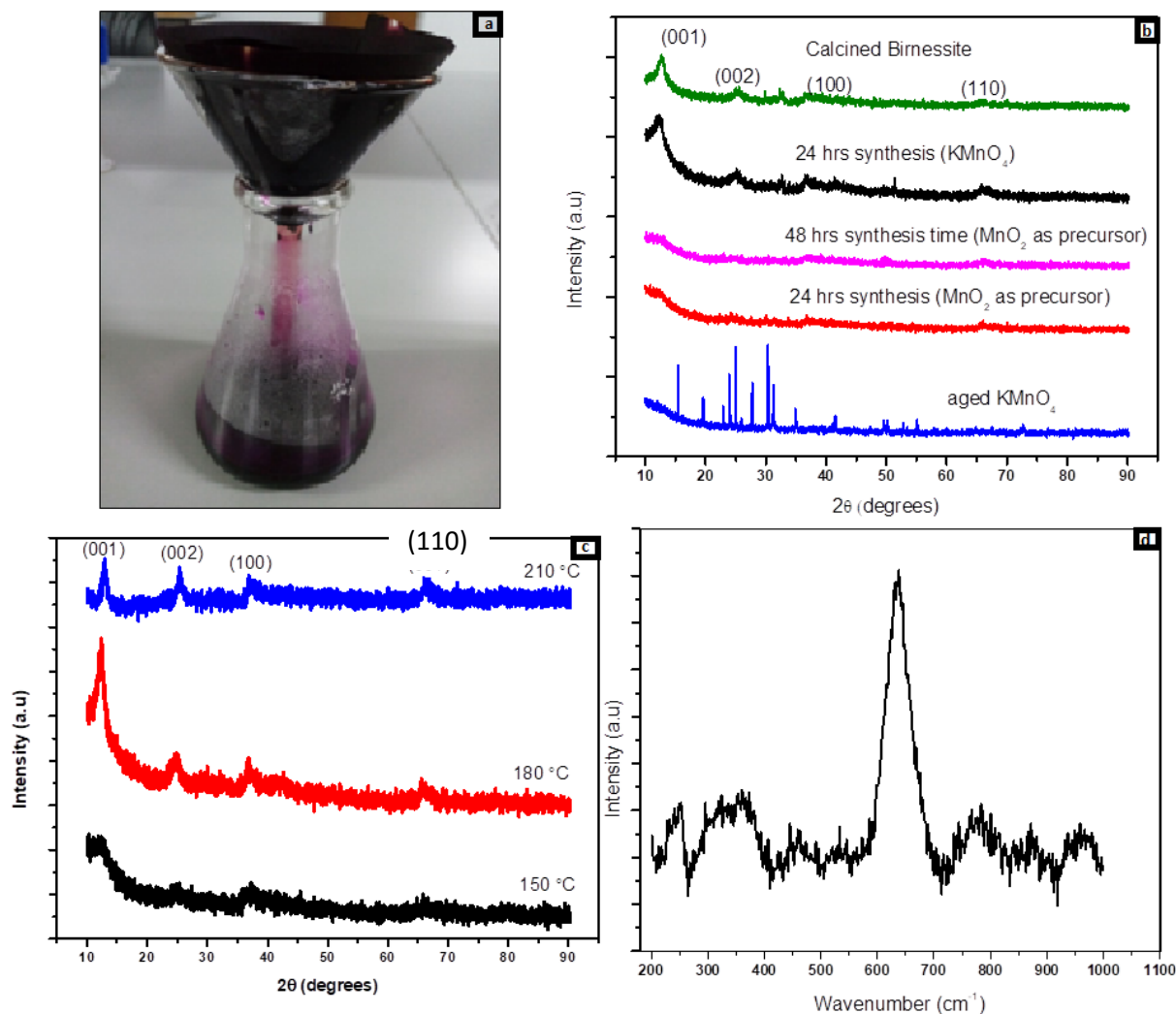


Figure 13: (a) Solution after attempted hydrothermal synthesis of birnessite without the use of morula leaf extract, (b) XRD patterns of birnessite after trying different methods of synthesis, (c) XRD patterns of birnessite after different synthesis temperatures, (d) birnessite Raman spectrum

4.2.2. Morphological analysis of birnessite

4.2.2.1. Scanning Electron Microscopy

The SEM image of birnessite nanoparticles obtained by calcining at 350 °C, and those obtained by hydrothermal synthesis at 150, 180, and 210 °C are shown in **Figure 14** a, b, c, and d. respectively. The materials in **Figure 14a** is made up of agglomerated flower shaped particles. In **Figure 14b** and c, the structures are closed packed nanospheres and **Figure 14d** is a mixture of flowers and nanospheres. Calcination and high synthesis temperatures of 210 °C seems to result in rough particles and this is evidence of an excellent adsorbent [155,156].

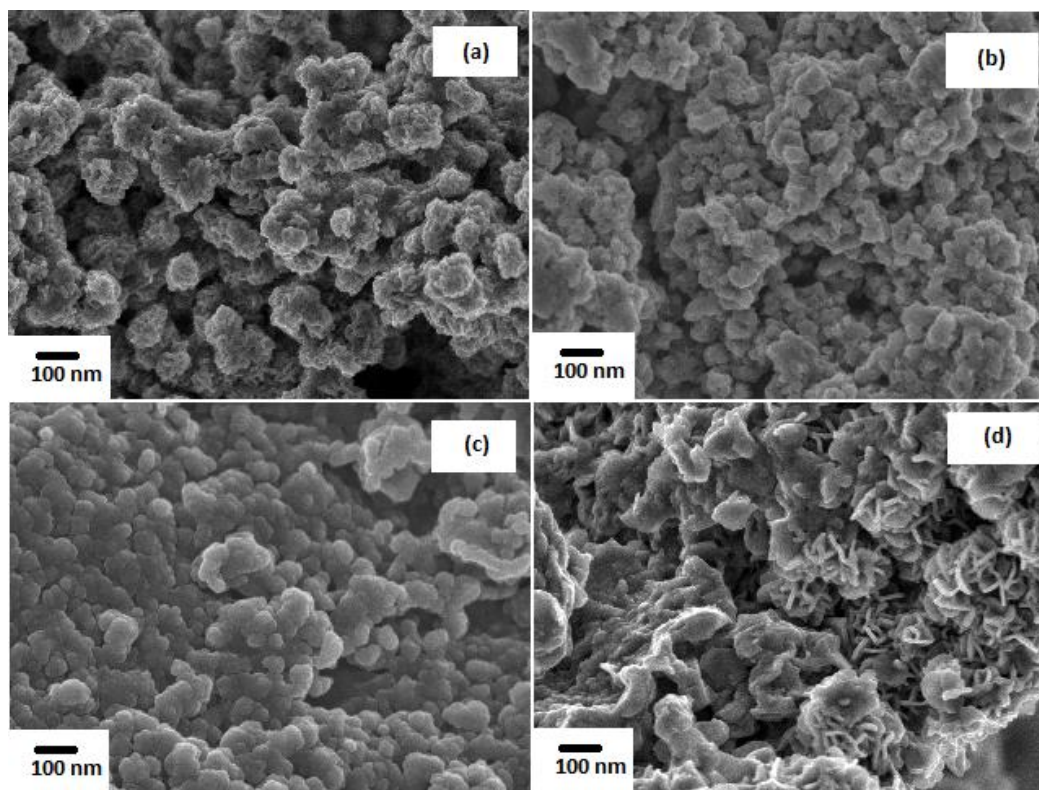


Figure 14: SEM image of birnessite calcined at 350 °C, (b) SEM image of birnessite synthesized at 150 °C, (c) SEM image of birnessite synthesized at 180 °C, (d) SEM image of birnessite synthesized at 210 °C.

4.2.2.2. Brunauer-Emmett-Teller

Figure 15a is a representation of the N₂ adsorption-desorption isotherms of the calcined birnessite materials and the birnessite materials synthesized at 150, 180, 210 °C. The shape of the hysteresis loops of all the materials allow them to be classified under the type V isotherms with an H3-type hysteresis loop as according to the IUPAC classification. The hysteresis loop shape is usually associated with samples that are mesoporous. The Barret-Joyner-Halenda (BJH) pore size distribution (PSD) profiles are presented in **Figure 15b**. PSD profiles for the materials show maxima at approximately 10 Å corresponding to the 0–5 nm mesoporous range. This means the material is mesoporous without any microporosity [200,149].

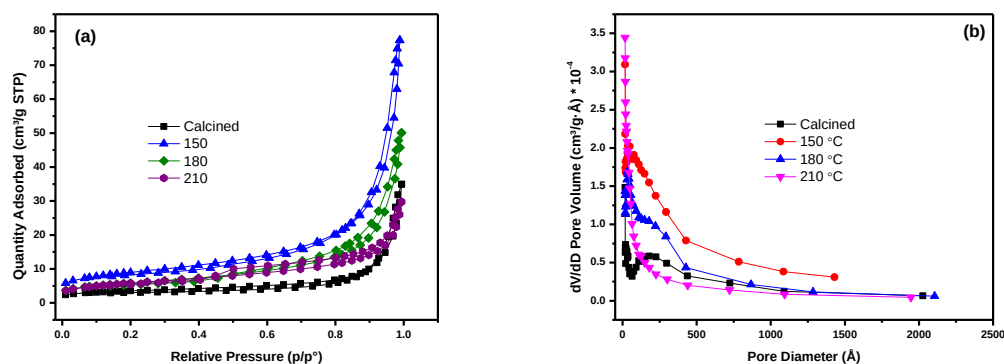


Figure 15: (a) N₂ adsorption-desorption isotherms and (b) Barret-Joyner-Halenda (BJH) pore diameter distribution curves of calcined birnessite materials and birnessite materials synthesized at 150, 180, and 210 °C.

Table 3 below is a synopsis of **Figure 15** above. The table demonstrates that the surface area, pore diameter, and volume of the material dropped as the temperature increased, and that calcination lowered the values of all the mentioned parameters. Birnessite nanoparticles is reported to have an average surface area of 16.26 m²/g [205]. According to BET studies, birnessite synthesized at 150 °C has a surface area of 31.6666 m²/g. It was also revealed that the particles were porous, with a volume of 0.013567 cm³/g and a pore diameter of 0.0082 nm. Because of the use of morula leaf extract, the nanoparticle's surface area has increased, and it has also become more porous, making it better for adsorption.

Table 3. The BET surface area, pore diameter, pore volume, and average particle size of uncalcined birnessite at 150, 180, 210 °C and calcined birnessite

Temperature (°C)	BET surface area (m ² /g)	Pore diameter (Å)	Pore volume (cm ³ /g)	Average particle size (Å)
150	31.6666	82.3153	0.013567	1894.738
180	20.6578	85.0565	0.008794	2904.469
210	20.2286	53.8064	0.008745	2966.098
Calcined	11.9120	80.3435	0.005353	5036.955

4.2.3. Application of birnessite in the adsorption of a mixture of rhodamine and methylene dyes

Birnessite was applied in adsorption of dye in water. The figures below describe how the material behaves in adsorption of dye under different conditions.

4.2.3.1. Effects of adsorbent amount

Within the range of 0.15-0.4 mg, the adsorbent loading was examined. The results are depicted in **Figure 16**. The dye adsorption increased from 20 to 70% (0.15 to 0.35 mg) for R6G and 68% for MB. According to these findings, the material's optimal adsorption occurs at 0.35 mg. Adsorption percentage remained constant beyond 0.35 mg. The “screening effect”, a phenomenon that occurs at higher adsorbent dosages, can be used to explain this scenario. Adsorbent particle accumulation and a decrease in the space between adsorbent molecules cause the establishment of a dense screening layer at the nanoadsorbent surfaces. Therefore, the dye molecule binding sites were concealed by the screening layer at the adsorbent's surface [58,150].

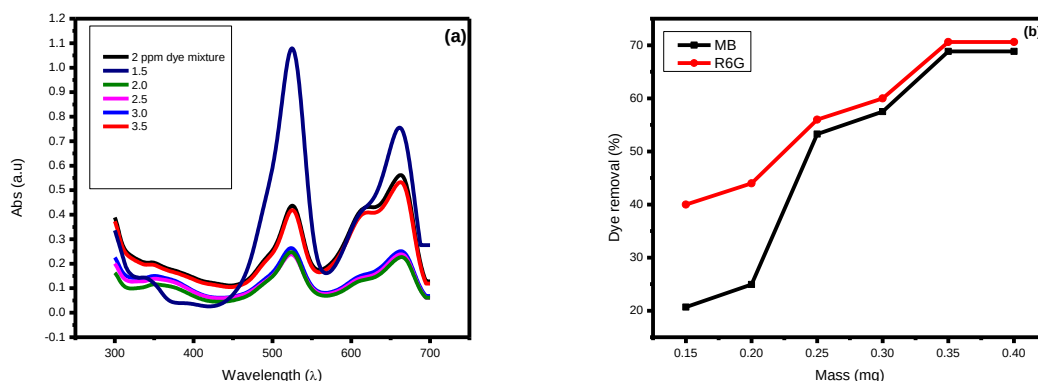


Figure 16: (a) Effects of adsorbent dosage on adsorption of a dye mixture onto birnessite, (b) Plot of % dye removal versus adsorbent dosage on adsorption of MB and R6G onto birnessite.

4.2.3.2. Effects of contact time

Using a constant starting dye concentration of 2 ppm and adsorbent dosage of 0.35 mg, **Figure 17** displays time dependent studies. The figure shows that dye removal increases rapidly in the first 15 mins for MB. From 30 to 45 mins, the dye uptake was constant for MB whereas for R6G it was constant for the first 45 mins. The uptake then rapidly went up from 45 to 60 mins after which it slowed down although it kept going up for both dyes. In the first 15 mins, there was a lot of empty active sites in the adsorbent to allow for the rapid uptake of the dye molecules. After 30 mins, the adsorption process reached a state of equilibrium in which a reasonable amount of dye molecules were adsorbed. Some active sites were still available, which means the uptake did not completely stop. These active sites became reachable after 45 mins of the reaction. This accounts for the increase in dye uptake that took place after 45 mins. The increase became slow but steady beyond 60 mins until the dye uptake flattened at 90 mins as the active sites completely got used up [57].

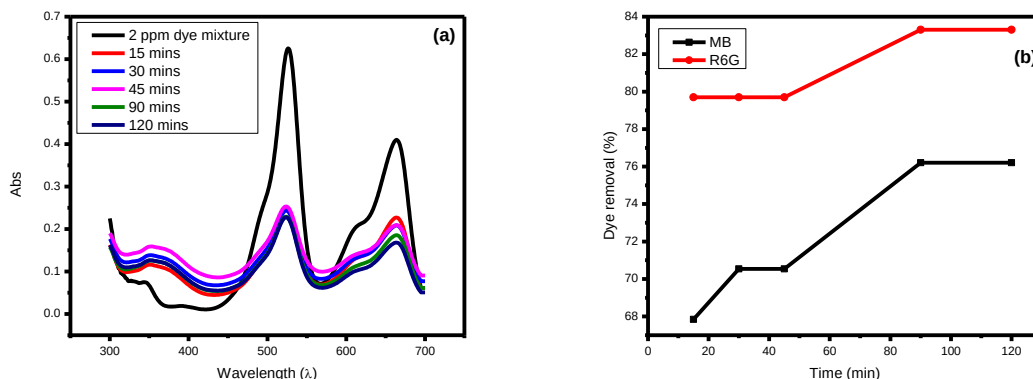


Figure 17: (a) Effects of contact time on adsorption of a dye mixture onto birnessite, (b) Plot of % dye removal versus contact time on adsorption of MB and R6G onto birnessite.

4.2.3.3. Effects of temperature

Investigations were done on how temperature affected dye adsorption on birnessite, and the results are presented in **Figure 18**. The plot demonstrates that as temperature increased, dye adsorption decreased, showing that lower temperatures (i.e., 30 °C or lower) favour the adsorption process. This shows that the birnessite adsorption process is exothermic. The attraction interactions between the molecules of dye and the outermost layer of an adsorbent substance tend to lessen at high temperatures [89,151]. This causes a decrease in adsorption and desorption of those molecules that had already adsorbed.

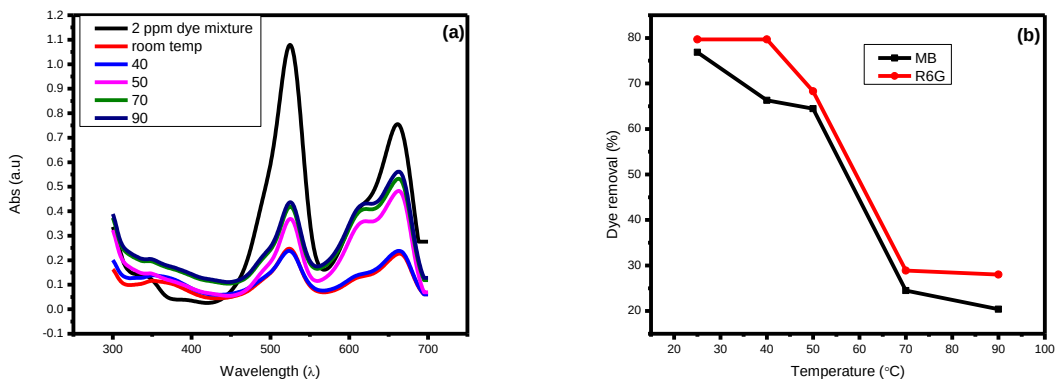


Figure 18: (a) Effects of temperature on adsorption of a dye mixture onto birnessite, (b) Plot of % dye removal versus temperature on adsorption of MB and R6G onto birnessite.

4.2.3.4. Effects of pH

At room temperature for 90 mins, the effect of pH on dye removal by adsorption onto birnessite was investigated in the pH range of 2-12. This is because the degree of ionization of the adsorbate in the solution, as well as the dissociation of functional groups on the adsorbent's active sites, are all influenced by the pH. The dye uptake increased steadily from pH 2 to 11. When the pH of the system is extremely low (pH 2) there is an abundant number of positive charges from the protons. These counteract the negative charges on the surface of the birnessite, leading to an overall positive charge. This positive charge then repels the positively charged dye molecules [57]. Increase in pH means a decrease in the positive charges. This results in more negative charges on the surface of the adsorbent resulting in an attraction of positive dye molecules hence increased adsorption of the dye molecules.

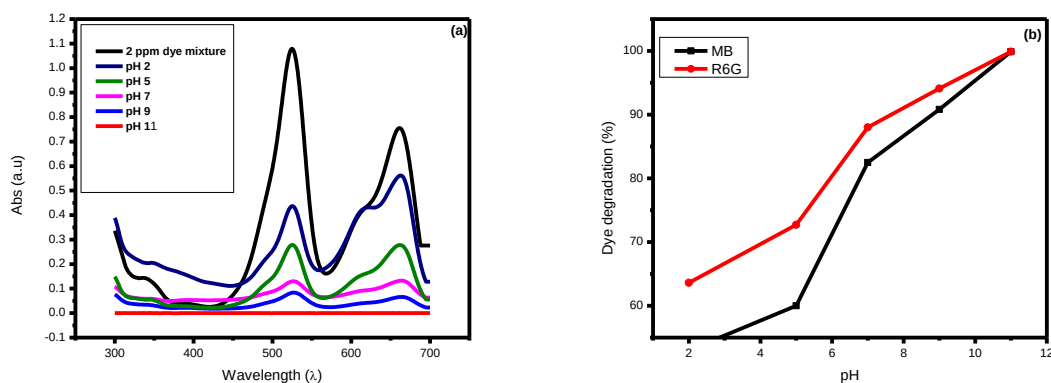


Figure 19: (a) Effects of pH on adsorption of a dye mixture onto birnessite, (b) Plot of % dye removal versus pH on adsorption of MB and R6G onto birnessite.

4.2.3.5. Effects of initial concentration of contaminant

Only a fixed amount of adsorbate species can be absorbed by a given amount of adsorbent. As a result, the adsorbate solution starting concentration is crucial. **Figure 20** shows that the amount of dye adsorbed (percentage) decreased as the original dye concentration increased. The adsorbent gets saturated when dye molecules pile on it, and no more molecules can be absorbed. As the concentration of the adsorbate rises, this leads to a decrease in uptake capacity [57].

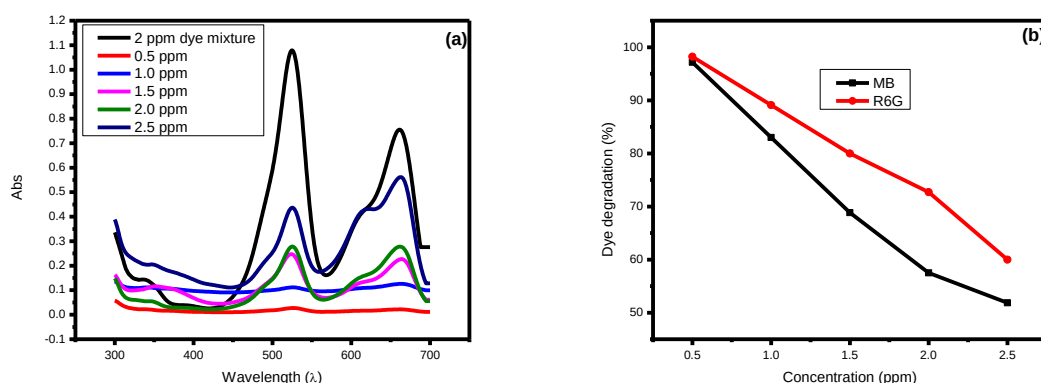


Figure 20: (a) Effects of concentration on adsorption of a dye mixture onto birnessite, (b) Plot of % dye removal versus concentration on adsorption of MB and R6G onto birnessite.

4.2.4. Adsorption isotherms of birnessite

The dye adsorption onto birnessite fitted well with the Langmuir model. This conclusion is informed by the high R^2 values. Birnessite has an R^2 of 0.9982 in Langmuir, which is the highest [23].

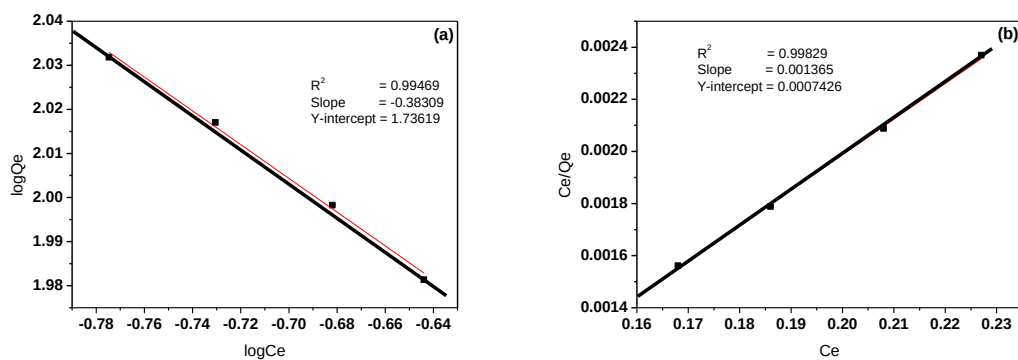


Figure 21: (a) Freundlich isotherm for birnessite, (b) Langmuir isotherm for birnessite

Table 4: Maximum monolayer capacities of birnessite

Langmuir parameters	Q_e (mg/g)	107.6
---------------------	--------------	-------

	K_L	0.000074
	R^2	0.9982

Figure 21 a and b, respectively, demonstrate the Langmuir and Freundlich isotherms for the birnessite material. A linear regression approach was used to calculate the key parameters and correlation coefficients in both isotherm models. The maximum monolayer capacities of birnessite are depicted in **Table 4** above. Langmuir correlation coefficients that are close to one. The dyes on birnessite had the highest adsorption capacities of 108 mg/g, as the Langmuir isotherm model estimates. The RL values obtained are in the 0–1 range, showing that birnessite has quite good adsorption tendencies. Furthermore, n is greater than 1, indicating that birnessite is a suitable adsorbent for both dyes with a high adsorption intensity [21,91].

4.3. ZnO

4.3.1. Characterisation of ZnO The peak at 318.762 cm⁻¹ is part of the ZnO second-order spectrum, and the optical phonons E1(L) and A1(L) are thought to be responsible for the weak broad band at about 566 cm⁻¹. [157].

Figure 22a represents a solution obtained after an attempt to synthesize ZnO without the leaf extract. The hydrothermal treatment of ZnO precursor did not result in any reaction taking place. Clear water with the ZnO stuck to the inside of the Teflon container were the outcomes of the experiment. This proves the significance of the leaf extract in the precipitation of ZnO. The peak at 318.762 cm⁻¹ is part of the ZnO second-order spectrum, and the optical phonons E1(L) and A1(L) are thought to be responsible for the weak broad band at about 566 cm⁻¹. [157].

Figure 22b shows XRD graphs of ZnO calcined at 250, 300, 325, and 350 °C as well as uncalcined. A number of impurity peaks were noticed in uncalcined ZnO. This indicates that the materials contained some Volatile Organic Compounds (VOCs) from the leaf extract prior to calcination which were then burned off as gasses during calcination. The materials were also observed to be amorphous at 250 and 300 °C, with no XRD peaks visible. Although the peaks were not very intense, XRD peaks indicative of ZnO are observable in the sample calcined at 325 °C. XRD pattern of ZnO materials calcined at 350 °C is indexed to PDF number 00-036-1451. The strongest peaks were detected at 31.79, 34.42, 36.25, 47.51, 56.60, 62.86, 67.96 and 69.00°, corresponding to the lattice planes (100), (002), (101), (102), (110), (103), (200), and (112) respectively. This means that the oxide had attained a crystalline structure at 350 °C, as shown by in the XRD peaks. The XRD peaks are broad, and this is an indication of formation of nanoscale materials. The particle size was determined using the Debye Scherrer equation, which confirmed the material's nanoscale. The material had an average crystalline size of 62.9 Å after calcination at 350 °C. The sample calcined at 350°C was subsequently taken for further investigation using Raman spectroscopy.

The Raman spectra of ZnO nanoparticles of various sizes are displayed in The **peak** at 318.762 cm^{-1} is part of the ZnO second-order spectrum, and the optical phonons E1(L) and A1(L) are thought to be responsible for the weak broad band at about 566 cm^{-1} . [157].

Figure 22c. ZnO is responsible for the three intense peaks at 318.762, 429.279, and 566.376 cm^{-1} [157]. The spectrum is dominated by the E2 optical phonon band, which may be found at 429.376 cm^{-1} . This finding is consistent with the previously published findings [158]. This may be due to the properties of the E2^{high} band, which displays a very strong anharmonicity and, as a result, a well-pronounced asymmetry. The peak at 318.762 cm^{-1} is part of the ZnO second-order spectrum, and the optical phonons E1(L) and A1(L) are thought to be responsible for the weak broad band at about 566 cm^{-1} . [157].

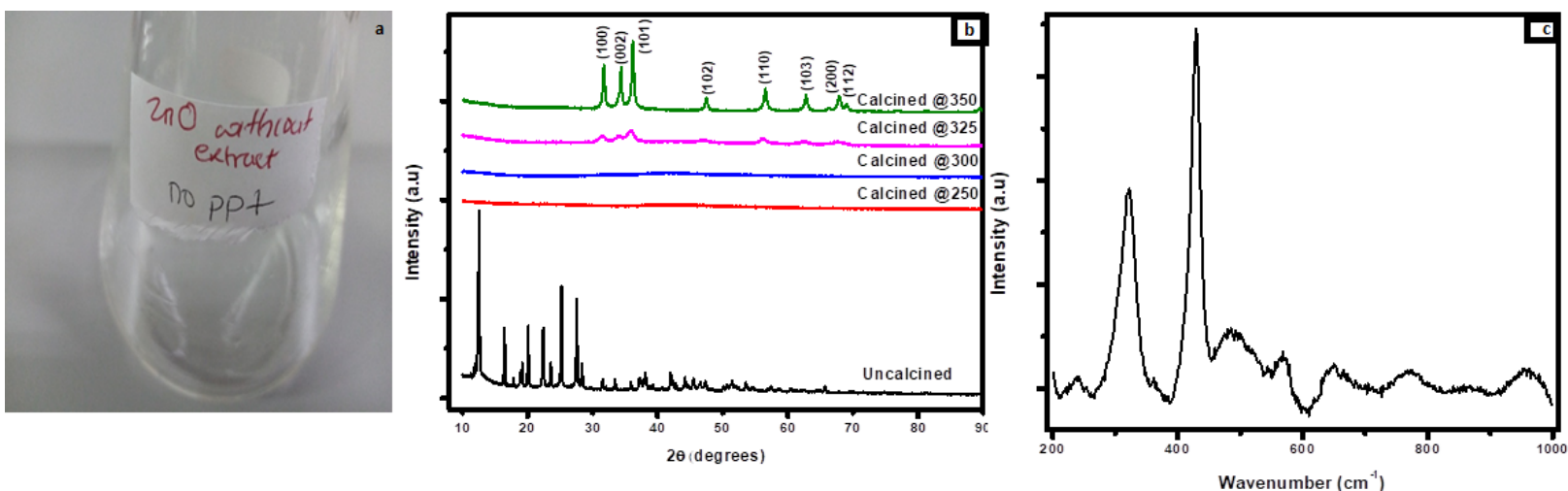


Figure 22: (a) optical image of the solution after hydrothermal treatment without the use of morula leaf extract (b) XRD patterns of ZnO after calcination at different temperatures, (c) Raman spectrum of ZnO calcined at 350 °C

4.3.2. Morphological analysis of ZnO

The morphology of the freshly generated ZnO nanoparticles was examined using SEM. The micrographs obtained from the SEM analysis with magnification of X40,000 are shown in

Figure 23. Figure 23a displayed agglomerated ZnO nanoparticles consisting of small nanorods and spheres with larger and smaller particles. The spheres and rod-like structures disappeared at 325 °C (Figure 23b). At 350 °C calcination temperature (Figure 23c), agglomerated nanorods were formed. The particles sizes ranges from 50 to 100 nm [159].

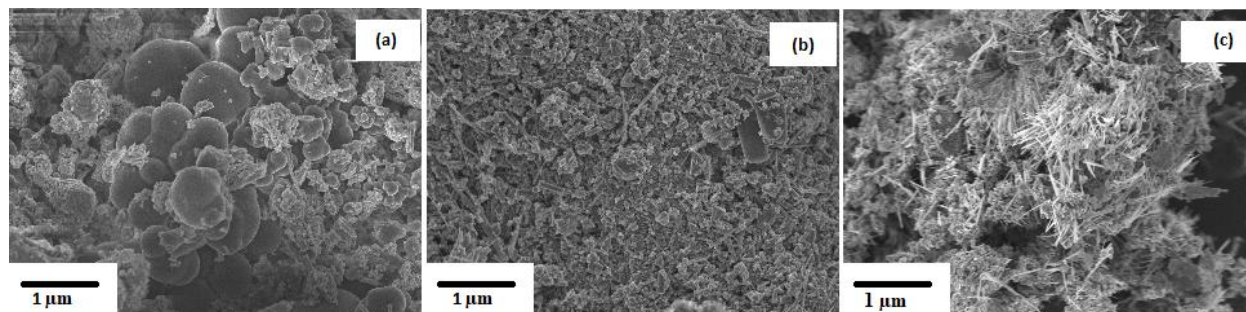


Figure 23. The SEM micrographs of ZnO nanomaterial calcined at (a) 300 °C, (b) 325 °C, (c) 350 °C, and (d) EDX spectrum and elemental percentage.

4.3.3. BET Surface area analysis

The surface area of the nanomaterials has a considerable impact on its photocatalytic performance, making it a crucial issue to consider. According to the IUPAC categorization, the isotherms derived from the analysis are type IV. The isotherms are applicable to mesoporous substances. This is because of the hysteresis loop of type H3 and a saturation plateau at p/p_0 0.6-0.95. The hysteresis loop occurs as a result of capillary condensation in the mesopores, which increases with relative pressure. Multilayer adsorption occurs at intermediate pressures, while capillary condensation occurs at higher pressures, resulting in a rapid increase in the adsorbed volume. Adsorption continues on the low exterior surface after the mesopores are completely filled. [160]. The BJH plots in Figure 24b confirms that the materials have a large pore distribution, which enables the movement of reactants and products to occur effectively. At 300, 325, and 350 °C, the pore diameter, surface area, pore volume, and average particle size of ZnO are provided in Table 1. The pore volume and surface area increased with increase in calcination temperature.

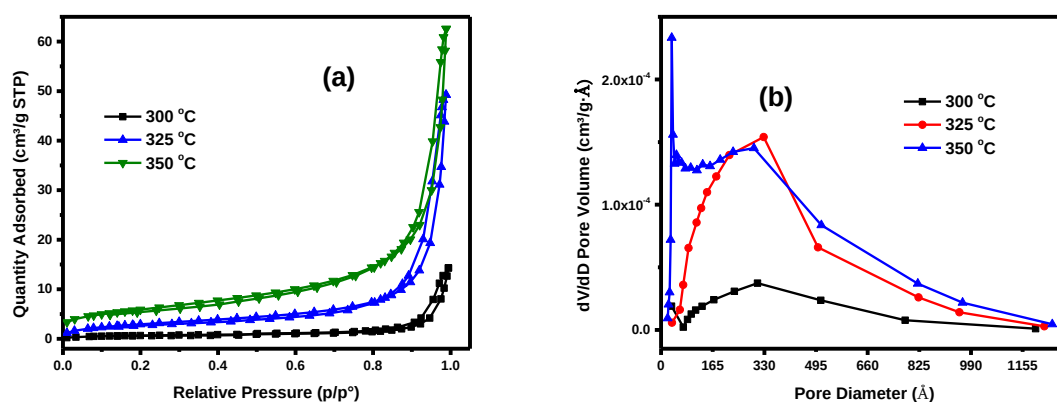


Figure 24. (a) N₂ adsorption-desorption isotherms and (b) Barret-Joyner-Halenda (BJH) pore diameter distribution curves of ZnO materials at 300, 325, and 350 °C.

Table 5. The BET surface area, pore diameter, pore volume, and average particle size of ZnO at 300, 325, and 350 °C

Temperature (°C)	BET surface area (m ² /g)	Pore diameter (Å)	Pore volume (cm ³ /g)	Average particle size (Å)
300	2.45 ± 0.03	111.99	0.000991	24449.97
325	11.03 ± 0.06	112.79	0.004360	5440.70
350	21.29 ± 0.07	86.32	0.008846	2818.35

4.3.4. Application of ZnO

As-synthesised ZnO photocatalytic performance was assessed through the removal of mixed dye (comprising mainly of R6G and MB dyes) under UV light irradiation. The suspension was illuminated for 75 mins after 20 mins of adsorption in the dark.

4.3.4.1. Effects of catalyst loading

The impact of catalyst loading on the elimination of the mixed dye combination is depicted in **Figure 25**. The catalyst loading was varied from 5 to 20 mg. Because the catalyst has a finite amount of surface area, when the catalyst loading was low (5 mg), the degrading process was controlled by the absorption of light. However, as the catalyst dosage grew from 5 to 15 mg, more active sites became available on the ZnO surfaces. Therefore, more photons and dye

molecules were absorbed thus increasing the degradation efficiency from 88.2 to 97.9% for MB and from 45 to 46.7% in the case of R6G. The degradation efficiency dropped from 97.9 to 96.8% for MB and from 46.7 to 46.3% for R6G when the amount of ZnO was raised to 20 mg. The increase in particle buildup onto the photon-absorbing surface of ZnO may be the cause of the decreased efficiency [161,162]. As a consequence of the light scattering effect brought on by an increase in the suspension's turbidity, light penetration was reduced as a result. Due to this, the effective photoactivated volume of suspension decreased, which consequently decreased the photocatalytic activity [163,164].

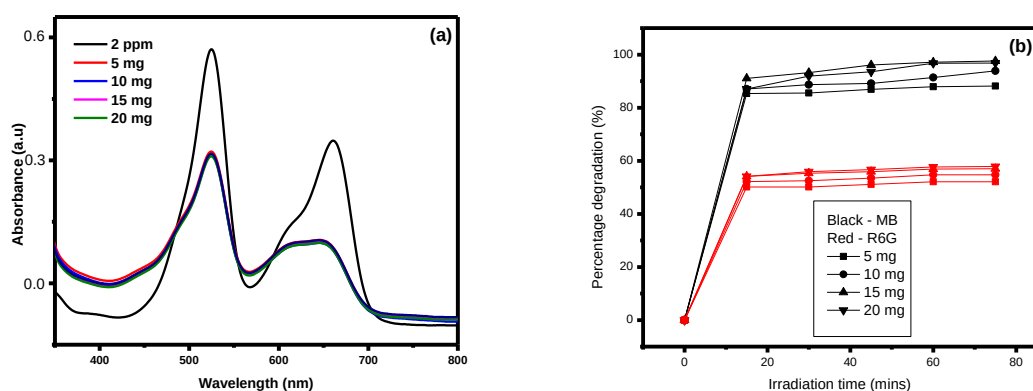


Figure 25. (a) Effects of irradiation time on the photodegradation of a dye mixture over ZnO photocatalyst, (b) Graph of % dye removal versus irradiation time on photodegradation of the MB and R6G dyes over ZnO as a photocatalyst.

4.3.4.2. Effect of pH

The value of initial pH of the mixed dye has numerous roles to play in determining the efficiency of the degradation process hence interpreting its effects is a challenging task [164]. In this study, The original pH of the combined dye was changed to 1.09, 4.01, 7.05, 9.02, and 12.65. All other experimental conditions were kept constant with catalyst loading of 15 mg, 2mg/L concentration, and 40 mL volume, the results are shown in **Figure 26**. From the results, it is evident that the amount of dye removal increased from increase in pH from 1.09 to 9.02 thereafter the rate decreased.

Due to its amphoteric nature, ZnO can dissolve in both basic/alkaline and acidic environment. From the measured Zn^{2+} ions, Evgenidou *et al.*, [165] indicated that the poor reaction rates in

acidic medium can be attributed to ZnO dissolution. In this study, the degradation efficiency was lower in a pH of 1.09 because of the dissolution of ZnO which greatly reduces the catalyst effectiveness [165]. When the pH was increased from 1 to 9, dye removal % also increased. This behavior could be due to the increase in concentration of OH^- ions, which act with photo-generated holes as strong oxidants that lead to the degradation of the dye molecules.

Increasing the initial pH beyond 9, resulted in the surface of ZnO becoming negatively charged through the absorption of OH^- ions. The absorbed OH^- ions favor the formation of $\cdot\text{OH}$ radicals. At pH lower than pH 9, the molecules of the dye cover the surface of the ZnO. When the pH value is increased, more OH^- ions are produced, and this causes more OH radicals to be formed thus increasing degradation efficiency. Increasing the pH to 12.65, on the other hand, causes an increase in electrostatic repulsion between the combined dye and the ZnO surface, lowering the degradation rate [166]. As a result, at pH 9, the maximum degradation efficiency was achieved.

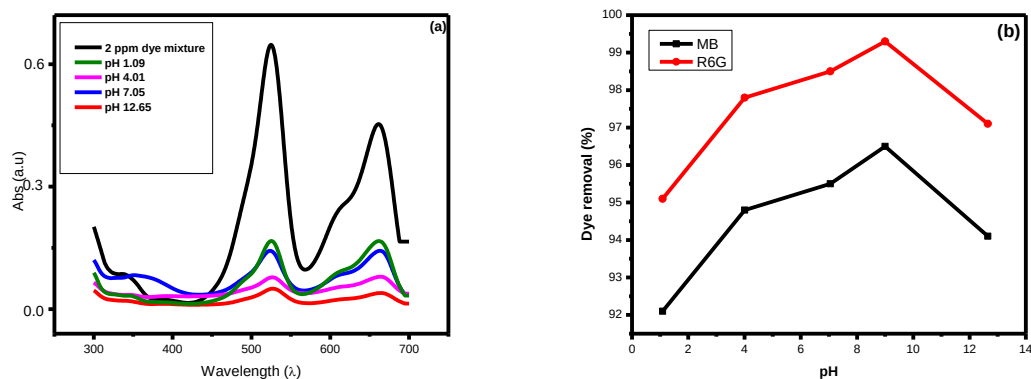


Figure 26. (a) Effects of pH on the photodegradation of a dye mixture over ZnO photocatalyst, (b) Graph of % dye removal versus pH on photodegradation of the MB and R6G dyes over ZnO as a photocatalyst.

4.3.4.3. Effects of initial concentration of contaminant

The starting concentration of the contamination influences the contaminant removal rate. The results for initial concentration investigation are given in **Figure 27**. As the initial pollutant concentration increased, the effectiveness of the catalyst degrading process decreased. From the Velmurugan and Swaminathan [167] investigation, the degradation rate constant (k) of reactive

red 120 dye over ZnO under solar light irradiation decreased from 0.173 to 0.012 min⁻¹ with increase the initial concentration from 1 x 10⁻⁴ to 4 x 10⁻⁴ M. According to Yang *et al.*, [168] it was also demonstrated that the initial concentration of the pollutant affected the removal effectiveness of MB. Their study showed a decrease in MB removal efficiency over dumbbell-shaped ZnO photocatalyst from 100 to 72% caused by the increase in the concentration of the dye from 10 to 30 mgL⁻¹.

This above phenomenon can be clarified by the observation that at high starting concentrations, the dye would absorb a large portion of the light instead of the ZnO materials. As a result, only a small number of photons reach the photocatalyst surface, decreasing the amount of OH radicals formed and hence the degrading efficiency [169-170].

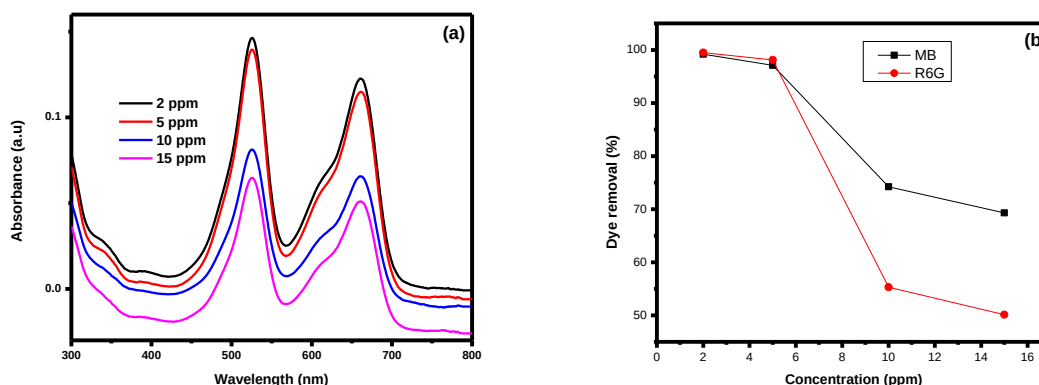


Figure 27. (a) Effects of dye concentration on the photodegradation of a dye mixture over ZnO photocatalyst, (b) Graph of % dye removal versus dye concentration on photodegradation of the MB and R6G dyes over ZnO as a photocatalyst.

4.3.4.4. Effects of temperature

The effect of temperature on the process of removal of the mixed dye was studied by changing the temperature from 293 to 313 K without changing any other variables using a hotplate with a magnetic stirrer and temperature sensor. The outcomes are displayed in **Figure 28a**. The result suggests that as temperature was raised from 293 to 313 K, degradation percentage rose. This is due to the fact that interfacial charge transfer and charge carrier mobility both increase with

temperature [165,171]. As a result, the rate of degradation is improved. The activation energy (E_a) was calculated using equations 5-7 and the Arrhenius plot of $\ln k_{app}$ against T^{-1} is displayed in **Figure 28b**. The slope from the Arrhenius plot was -1624.04 K^{-1} and it was used as the rate constant (K_{app}) to compute the E_a using equation 7 which was found to be $13370.47 \text{ Jmol}^{-1}$ (13.4 kJmol^{-1}) for the removal of the mixed dye. The lower E_a indicates that the degradation of the mixed dye over ZnO is economical since it requires less energy.

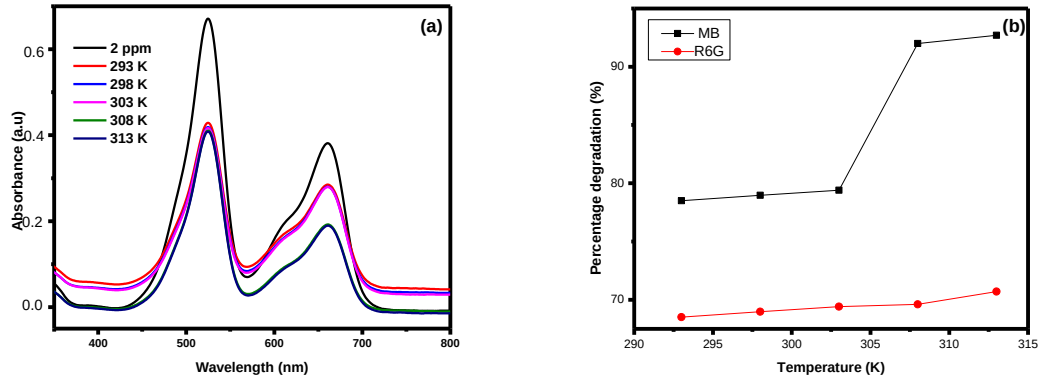
$$k_{app} = Ae^{\frac{-E_a}{RT}} \quad 4$$

$$\ln k_{app} = \frac{-E_a}{RT} + \ln A \quad 5$$

$$\ln k_{app} = \frac{-E_a}{R} \left(\frac{1}{T} \right) + \ln A \quad 6$$

$$E_a = -RS \quad 7$$

Where k_{app} , A , e , E_a , R , T , and S are rate constant, frequency factor, mathematical constant, activation energy, energy constant ($8.3145 \text{ Jmol}^{-1}\text{K}^{-1}$), absolute temperature in Kelvin, and the slope, respectively.



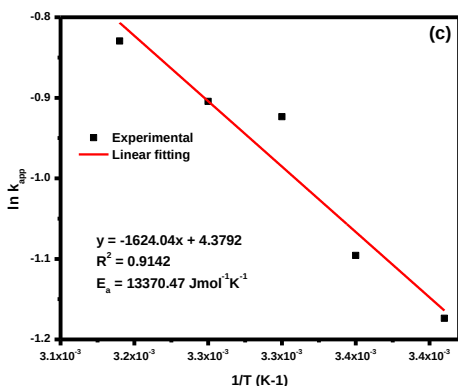


Figure 28. (a) Effects of temperature on the photodegradation of a dye mixture over ZnO as a photocatalyst, (b) Graph on the effects of temperature on the photodegradation of the MB and R6G dyes over ZnO photocatalyst and (c) Arrhenius plot of $\ln K$ versus T^{-1} for the degradation of dye mixture over ZnO.

4.3.5. Scavenging experiments

During the degradation, separation and migration of charges, photoexcitation, charge, and surface oxidation–reduction are the main reactions that occur during the process [172]. The $\cdot\text{O}_2^-$, h^+ , and $\cdot\text{OH}$ are the key active species generated when the photocatalyst is illuminated with light. Therefore, to comprehend the mechanism of degrading dyes over ZnO, it is critical to figure out which active species are involved in the degrading process. For this study, the degradation of the mixed dye over ZnO, the $\cdot\text{O}_2^-$, h^+ , and $\cdot\text{OH}$ radicals were trapped by p-BQ, EDTA-2Na, and t-BuOH, respectively.

The result of the degradation of mixed dyes over ZnO is shown in **Figure 29**. When 1 mM of p-BQ, EDTA-2Na, and t-BuOH was added to the reaction vessel, the degradation efficiency was noticeably reduced by 7.6, 19.7, and 15.1%, respectively. This trend in the reduction of degradation efficiency can be represented as EDTA-2Na > t-BuOH > p-BQ. This corresponds to the outcomes by Basnet *et al.*, [173]. Therefore, the h^+ and $\cdot\text{OH}$ are the key active radicals involved during the photodegradation of the mixed dye. When the mixture is irradiated with UV-lamp, the e^- and h^+ are formed. The h^+ produced can either directly oxidize the mixed dye or create OH radicals by reacting with H_2O . Hence, the photogenerated h^+ and $\cdot\text{OH}$ radicals

decomposed the mixed dye. The mechanisms of the reaction can be summarized according to the following equations:

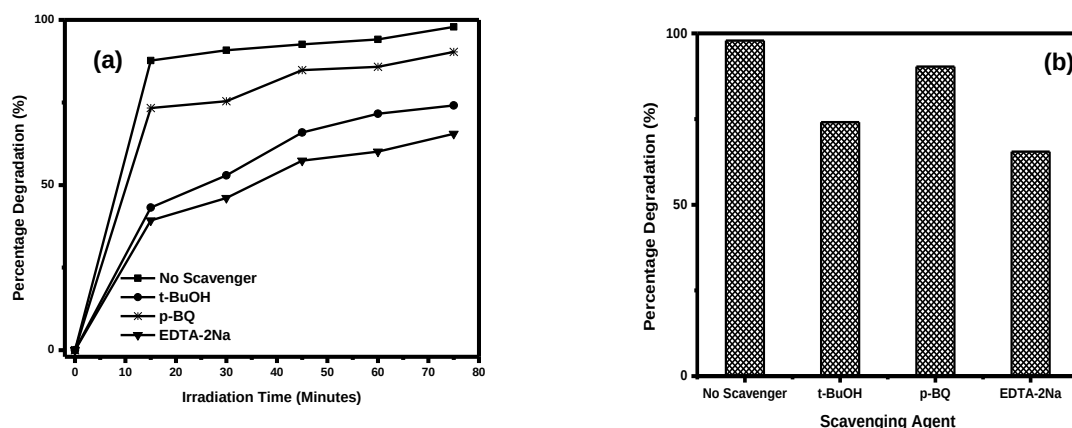
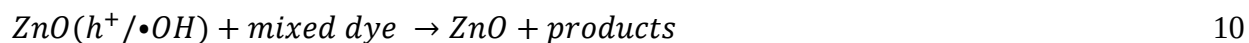
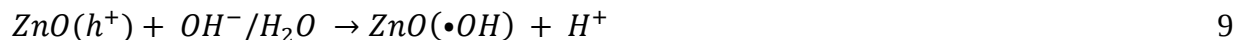


Figure 29. (a) Graph on the effects of adding p-BQ, EDTA-2Na, and t-BuOH during the degradation of dye mixture over ZnO, (b) Plot on the maximum % degradation with the different scavenging agents.

4.3.6. Reusability of Photocatalyst

A photocatalyst reusability is an important consideration for practical applications. In this study, the reusability of the as-prepared ZnO was evaluated, and the results are displayed in **Figure 30**. After every run, the as-prepared ZnO was filtered, washed, and dried in an oven overnight. The degradation efficiency reduced from 97.9 to 90.5% after 5 runs. The result shows that the as prepared is stable even after 5 runs.

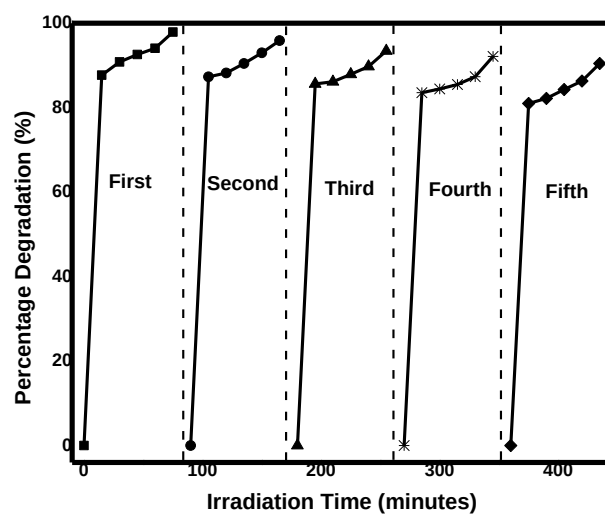


Figure 30. Repeatability of the as-prepared ZnO photocatalyst.

5.0.CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusion

CuO, ZnO and birnessite materials were successfully synthesized using morula leaf extract and this was verified to be the case using XRD and Raman spectroscopy. CuO and birnessite were utilized as an adsorbent, while ZnO was used as a photocatalyst to remove a dye combination (rhodamine and methylene blue). CuO possessed platelets like structure, birnessite was characterized by flower like structures and ZnO had nanorods.

BET, Langmuir and Freundlich isotherm models confirmed the excellent adsorptive tendencies of both CuO and birnessite. The surface areas of CuO and birnessite were 26.82 and 31.67 m² /g, respectively, which is larger than any previously reported in literature, and the isotherm models have correlations closer to one. This demonstrates that the extract was crucial in improving the surface area of the two common materials.

Adsorption of CuO is aided by increasing the adsorbent dose, pH, and contact time. Increasing the concentration of adsorbate leads to decrease in percentage removal in both CuO and birnessite due to oversaturation of active sites. High temperatures tend to weaken the attractive forces between dye molecules and the surface of the adsorbent material, so an increase in temperature is unfavorable to adsorption in the case of both nanocomposites. In the case of birnessite, increasing the catalyst dosage increases the proportion of dye removed, but only to a point. After that, the dye removal efficiency goes down. From pH 2 to 9, adsorption decreases but then increases from pH 10 upwards. Metal oxides have been shown to be effective adsorbents for both dyes, with a high adsorption intensity.

The structure of ZnO has a large pore distribution, allowing for efficient transport of reactants and products during photo degradation. This helps increase the rate of degradation. This is confirmed by the 99% degradation efficiency observed at the optimal contact time. Catalyst loading, contact time and temperature also help increase the rate of degradation as they are increased. Only until pH 9 does an increase in degradation occur, after which the rate of degradation diminishes. An increase in the concentration of the pollutant has a completely negative impact on the rate of degradation.

5.2. Recommendations

1. We recommend that more indigenous plants be explored in the synthesis of nanomaterials in order to increase the pool of information in the subject area.
2. It is important that the synthesis of different other metal oxides is explored using the morula leaf extract.
3. The reusability of the materials used in adsorption could also be explored.

6.0.REFERENCES

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Appendix A: Energy-dispersive X-ray spectroscopy

Figure 31**Figure 32****Figure 33** are EDX data on CuO, birnessite and ZnO respectively. They verify the synthesis of the three nanomaterials using the morula leaf extract. The data also confirms the existence of some metals such as Aluminium and Pottasium in all of the three materials and these are from the extract as indicated in **Table 6**.

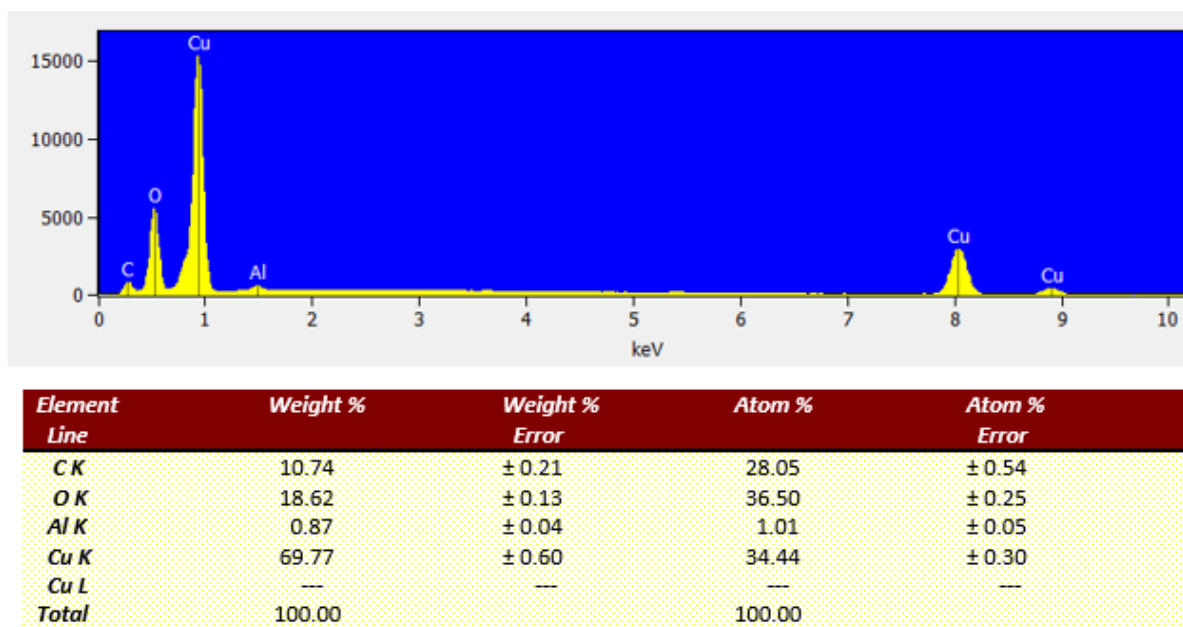
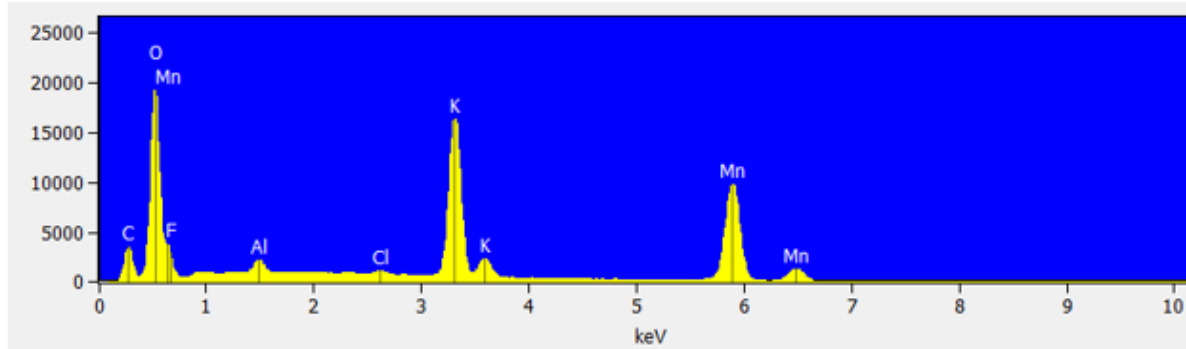
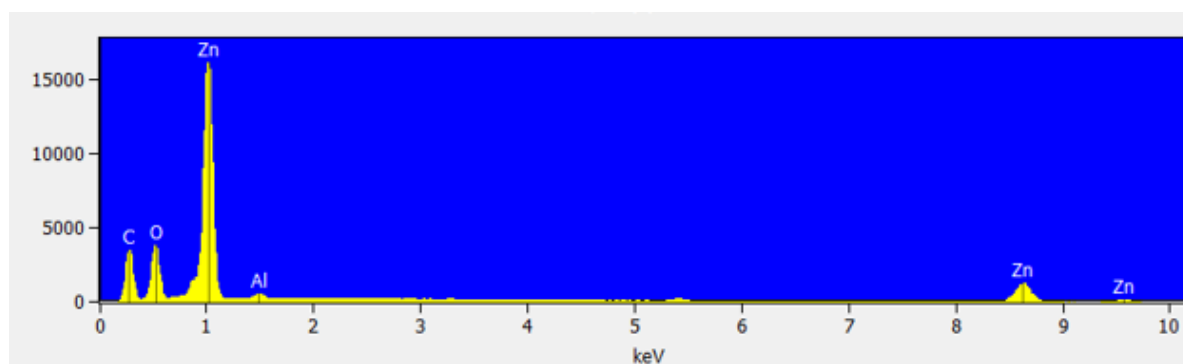


Figure 31: EDX analysis of CuO



Element Line	Weight %	Weight % Error	Atom %	Atom % Error
CK	11.24	± 0.09	22.47	± 0.19
OK	31.41	± 0.15	47.13	± 0.23
FK	2.22	± 0.17	2.80	± 0.22
AlK	0.88	± 0.01	0.78	± 0.01
ClK	0.41	± 0.03	0.27	± 0.02
ClL	—	—	—	—
KK	17.01	± 0.08	10.45	± 0.05
KL	—	—	—	—
MnK	36.84	± 0.17	16.10	± 0.07
MnL	—	—	—	—
Total	100.00		100.00	

Figure 32: EDX analysis of birnessite



Element Line	Weight %	Weight % Error	Atom %	Atom % Error
CK	38.75	± 0.26	64.61	± 0.43
OK	17.19	± 0.16	21.52	± 0.20
AlK	0.85	± 0.03	0.63	± 0.02
ZnK	43.22	± 0.63	13.24	± 0.19
ZnL	—	—	—	—
Total	100.00		100.00	

Figure 33: EDX analysis of ZnO

Table 6: constituents of the leaf extract

CONSTITUENTS	CONCENTRATION (Mg/L)
POTASSIUM	16.95
ALUMINIUM	102.6
MAGNESIUM	17.68