PROJECT REPORT

ON

SYNTHESIS AND CHARACTERISATION OF TiO$_2$ NANOPARTICLES FOR PHOTOCATALYTIC DYE DEGRADATION

SUBMITTED BY

MARIYA THOMAS

REGISTER NO. : AM21PHY011

in partial fulfillment of

the requirements for award of the postgraduate degree in physics

DEPARTMENT OF PHYSICS AND CENTRE FOR RESEARCH

ST. TERESA'S COLLEGE (AUTONOMOUS), ERNAKULAM

2021-2023

ST. TERESA'S COLLEGE (AUTONOMOUS), ERNAKULAM

M.Sc. PHYSICS PROJECT REPORT

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This is to certify that the project **"SYNTHESIS AND CHARACTERISATION OF TiO$_2$ NANOPARTICLES FOR PHOTOCATALYTIC DYE DEGRADATION"** is the work done by **MARIYA THOMAS**

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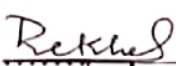**Dr. Priya Parvathi Ameena Jose**

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CERTIFICATE

This is to certify that the project report entitled "SYNTHESIS AND CHARACTERISATION OF TiO$_2$ NANOPARTICLES FOR PHOTOCATALYTIC DYE DEGRADATION" is the bonafide work done by Ms. MARIYA THOMAS (Reg. No: AM21PHY011) under the guidance of Dr. PRIYA PARVATHI AMEENA JOSE, Head of the department, Department of Physics and Centre for Research, St. Teresa's College (Autonomous), Ernakulam in partial fulfilment of the award of the Degree of Master of Science in Physics, St. Teresa's College, Ernakulam affiliated to Mahatma Gandhi University, Kottayam

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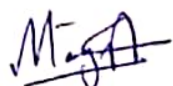|	
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Paper Title	SYNTHESIS AND CHARACTERISATION OF TiO2 NANOPARTICLES FOR PHOTOCATALYTIC DYE DEGRADATION
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I, hereby declare that the project work entitled "**SYNTHESIS AND CHARACTERISATION OF TiO$_2$ NANOPARTICLES FOR PHOTOCATALYTIC DYE DEGRADATION**" is a record of an original work done by me under the guidance of **Dr. PRIYA PARVATHI AMEENA JOSE**, Head of the department, Department of Physics and center for Research, St Teresa's College, Ernakulam in the partial fulfilment of the requirements for the award of the Degree of Master of Physics. I further declare that the data included in the project is collected fromvarious sources and are true to the best of my knowledge.

Mariya Thomas

ACKNOWLEDGEMENTS

The success and outcome of this project required a lot of guidance and assistance from many people and we are extremely grateful to have got this all along the completion of my project work. Primarily, we thank God almighty for being with us throughout the days and helping us complete the project successfully.

It is with great pleasure I express my sincere gratitude to Dr. Priya Parvathi Ameena Jose, my supervising guide, for her able guidance and encouragement throughout this work and I am deeply indebted for the personal support you had given me during moments of uncertainty.

I express my deep sense of gratitude to the Department of Physics, St. Teresa's College, Ernakulam, for extending the cooperation and facilities required from time to time.

I would like to thank everyone who has contributed to this work by their unfailing support for the success of this project.

CONTENTS

CHAPTER 3 : RESULT AND DISCUSSION

CHAPTER 4 : CONCLUSION AND FUTURE SCOPE

ABSTRACT

The need for pure water is one of the major challenges faced by the world. Water pollution majorly comes from human activities. Many industrial sectors release various effluents to the aquatic systems, which includes dyes and other heavy metal ions. These dyes have been recognized as toxic agents which are hazardous to the environment and living organisms even at very low concentrations. This may lead to a completely unbalanced ecological system in the future.

The removal of hazardous organic contaminants derived from human activities has become important for the development of sustainable water treatment strategies and processes. There are various wastewater treatments. More than 50% of water pollutants are organic dyes. The most widely used technique nowadays is photocatalytic degradation. It has been viewed as a safe, simple, efficient, nontoxic, and economical method that ensures the complete mineralization of pollutants, and by forming water and carbon dioxide, and other inorganic compounds which are less toxic and environmentally safe.

One of the most efficient photocatalysts is titanium dioxide because of its properties like high stability, low cost, toxicity, and high photocatalytic activity. In this work, we have studied the photocatalytic dye degradation of Methylene Blue and Rhodamine B dyes. A hydrothermal method was adopted for the synthesis of TiO_2. Structural analysis was done using XRD and FTIR studies while morphological analysis was carried out by taking SEM images . The optical analysis was done by UV-Visible spectroscopy and photoluminescence studies. Our project is a small step for the betterment of society, aiming at high-scale water purification.

CHAPTER 1

INTRODUCTION

1.1 NANOSCIENCE AND NANOTECHNOLOGY

The field of nanoscience has become more relevant since it deals with the study of materials in the nanoscale range. The word nanoscience' comes from two separate words nano and science. The word nano means dwarf or something very small and depicts one thousand millionth of a meter (10^{-9} m) and science means knowledge. The beginning of nanoscience can be date back to the Greeks and Democritus in the fifth century BC, when researchers debated whether matter is continuous and thus infinitely divisible in to smaller particles, or if it is made up of tiny indivisible and unbreakable particles, which researchers now refer to as atoms.

The nanoscale which we describe as being from 100nm down to the size of atoms (about 0.2 nm) is of interest to people because it is at this scale where properties of the material can differ significantly from those observed at greater scales. It is important to understand that the DNA double helix has a radius of 1 nm and a human hair is 60,000 nm thick as a comparison.

There are two basic reasons why the material characteristics vary at the nanoscale : the first one is when compared to the same mass of the material generated in a bigger form, nanoparticles have considerably large surface area , this may increase the chemical reactivity of some materials (in some cases the materials in larger form will be inert, it may become reactive when the size is reduced to nanometer scale this will affect the strength and electrical properties).The second reason is that particularly near the lower end of the nanoscale, quantum phenomena may start to dominate the behaviour of matter. This leads to changes in their optical, electrical and magnetic behaviours.

Producing New or advanced materials is a major focus of nanoscience and nanotechnology. Nanotechnology contribute to nearly every field of wisdom. In this work we aim to use these wide scale operations of nanotechnology for purification of water. It emphasis on the significance of photocatalyst in the disposal of various dye stuffs present in the underwater system by a method called photocatalysis.

1.2 **HISTORY OF NANOTECHNOLOGY**

In his well-known lecture "There's plenty of room at the bottom," renowned physicist Richard Feynman put out the notion of synthesis by direct atom manipulation, which gave rise to the concept of nanotechnology. Feynman posed the question, "Why can't we write the entire 24 volumes of the Encyclopaedia Britannica on the head of a pin?" and described a scenario in which machines could be used to build smaller machines all the way down to the molecular level. Feynman is regarded as the father of modern nanotechnology as a result of this ground-breaking idea, which illustrated the applicability of his theories. After waiting fifteen years, Norio Taniguchi, a Japanese scientist, coined the term "nanotechnology" and gave it a definition in 1974.

When the Romans used nanoparticles and structures in the fourth century AD, it was one of the most fascinating displays of nanotechnology in age. The Lycurgus cup, a piece of ancient glass art in the British Museum's collection, is one of its most outstanding exemplifications. It's the first case of dichroic glass that's extensively recognized. Dichroic glass refers to two different types of glass that can change color depending on the lighting. In 1990, experimenters used a transmission electron microscope (TEM) to probe the cup in order to better understand the dichroism events. The dichroism (two colors) that has been observed is caused by nanoparticles with a periphery of 50 – 100 nm.

In the sixteenth century, Italians also used nanoparticles to create Renaissance ceramics. They were influenced by Ottoman methods: between the thirteenth and eighteenth centuries, cementite nanowires and carbon nanotubes were utilized to create "Damascus" saber blades to give strength, resistance, and the capacity to keep a sharp edge.

Following Feynman's discovery of this new area of research that attracted the attention of several scientists, two techniques have been created that describe the various possibilities for the synthesis of nanostructures. These manufacturing techniques may be divided into two groups: top-down and bottom-up, and they vary in terms of quality, speed, and price.

1.3   <u>SIGNIFICANCE OF NANOMATERIALS</u>

Nanomaterials are quite interesting since they have a lot of potential to develop new and inventive goods in a variety of industries. Nanomaterials can be created and their properties can be unusually directed by more directly controlling the reactions and interactions between atoms at the nanoscale.

Food safety, medicine and healthcare, energy, transportation, communications, environmental protection, and manufacturing are just a few of the industries that are benefiting from nanotechnology. It is utilized in the automotive, electronics, and computing sectors as well as in home goods, textiles, and cosmetics.

1.4   <u>APPLICATIONS OF NANOTECHNOLOGY</u>

All different industrial areas are capable of employing nanotechnology and nanomaterials.

- Silicon can be replaced with carbon nanotubes which can be used for making smaller, faster and more efficient microchips and quantum nanowires. Graphene is a prime candidates for the creation of flexible touchscreens due to it's characteristic properties.

- Properties of some nanomaterials make them suitable for enhancing the early detection and treatment of cancer and some neurological diseases. These materials target cancer cells specifically without endangering healthy cells. Additionally, certain nanoparticles have been employed to improve pharmaceutical products like sunscreen.

- Heavy metal nanofiltration systems, wastewater treatment with nanobubbles, and ion-based air purification are a few of its environmentally benign applications. Additionally, nanocatalysts can increase the efficiency and lower the pollution of chemical processes.

- Nanobiosensors and nanocomposites may be utilised to detect the presence of pathogens in food by enhancing mechanical and thermal resistance and reducing oxygen transfer in packed goods.

- Nanofabrication is one of the key subfields in nanotechnology that is connected to energy. The process of creating and designing a new gadget on the nanoscale is known as nanofabrication. Hydrogen energy is a future economy in which energy is stored as hydrogen. this is more efficient energy storage method. Single-walled CNTs are used in hydrogen-powered automobiles and trucks to address the storage issue.

- Space science and research is another area where nanotechnology uses are evident. In addition to employing materials like CNT to make the exterior construction of satellite strong and light, research is being done on ways to deploy space craft with less fuel.

1.5 <u>WATER POLLUTION</u>

One of the biggest threats to our environment is pollution. Pollutants are substances that may harm the environment. Plastics, dyes, pesticides, microorganisms, organic wastes, and other contaminants are examples of these. Air pollution, water pollution, and land pollution are the three main categories of pollution, according to the environment. Any sort of pollution is bad for wildlife and human health, and it also adds to climate change, which puts the entire planet in peril. Negative effects of pollution include significant and even lethal ones.

Water is a precious natural resource that has given life to numerous civilizations and is essential for people's survival. Water therefore holds the key to preserving the ecology and quality of life on Earth. For a long time, water pollution has been a major concern around the world. It is caused by the contamination of stream, river, lake, ocean, aquifer, or other water bodies, lowering water quality and making it toxic to humans or the environment. Pathogenic microorganisms, organic waste, fertilizers and plant nutrients, toxic chemicals, sediments, heat, petroleum (oil), and radioactive substances can all pollute water bodies.

In addition to seriously harming human health, water pollution will destroy the aquatic ecology. Humans are constantly in danger from the organic water contaminants that are released from the paper, textile, and plastics industries. The most harmful organic water contaminants are phenol, dyes, and chemicals with an aromatic flavour. They may cause cancer and are poisonous. Hazardous substances in bodies of water can also harm the local flora and

fauna. When people consume these organisms, they may have minor symptoms of toxicity or more severe toxic effects.

1.6 <u>DYE POLLUTION</u>

Pollution has grown into a serious environmental issue due to man's ignorance and negligence. The release of potentially hazardous compounds into the environment is referred to as pollution. All types of pollution place the world's health, the health of wildlife, and the environment at risk while also accelerating climate change. The detrimental impacts of pollution are serious and could even be fatal. Water pollution is the release of pollutants into water bodies that taint the water and harm aquatic ecosystems. Water bodies can be contaminated by a wide range of substances, including radioactive elements, organic waste, dangerous compounds, sediments, heat, petroleum (oil), and pathogenic bacteria. These impurities are dangerous to consume and are the root of some water-borne diseases. In addition to organic and inorganic chemicals, pollutants may also appear in the form of physical, biological, radiological, or heavy metal pollutants. Industrial waste is the primary contributor to water contamination because it contains 20% of the world's annual dye consumption.

The main appeal of any fabric is its color. No matter how durable, a poorly coloured fabric can never be successful as a commercial fabric. As a result, the production and use of synthetic dyes today has turned into a massive industry. However, because these colors are hazardous, environmentalists are now quite concerned about them. The usage of synthetic colors has a negative impact on all forms of life. The presence of heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt, as well as several auxiliary chemicals, makes the textile effluent particularly dangerous. Dye contaminants are usually the first contaminants discovered in industrial effluent because of their great visibility even at low concentrations. These coloured wastewaters are a substantial contributor to eutrophication and non-aesthetic pollution.

The presence of colloidal matter, in addition to the colors and greasy scum, causes the turbidity to grow, the water to seem cloudy and smell terrible, and it hinders sunlight from penetrating, which is important for the process of photosynthesis. The oxygen transfer mechanism at the air-water interface is thus hampered, which affects marine life and the water's

ability to purify itself. If this effluent is allowed to run through the fields, it plugs the soil pores and reduces soil production. It affects the quality of drinking water in hand pumps, rendering it unsuitable for human consumption, if permitted to run in rivers and drains. Prior to ultimate disposal, it is crucial to eliminate these contaminants from the waste waters.

A variety of segments of the textile and dyeing industries depend heavily on dyes. The most often utilized dyes in such sectors are about 100000 synthetic dyes that are readily accessible on the market. The two primary sources of these colors, coal tar and petroleum intermediates, are often where they are generated. Water soluble and difficult to remove are brightly coloured dyes like reactive and acid dyes. Reactive dyes are less absorbed by the cloth during the dyeing process than other types of dyes, which suggests that the residual amount of dye is discharged directly into the wastewater. Reactive dye effluent has the capacity to last in the environment for a number of years while remaining stable.

Apart from the textile sector, the prevalence of colors in wastewater is also influenced by the leather tanning business, paper industry, food industry, hair dyes, photoelectrochemical cells, and light-harvesting arrays. The majority of dyes used in various sectors are carcinogenic and poisonous, which presents a substantial risk to both individuals and the marine ecology.

Various techniques exist for cleaning water, including chemical transformation, distillation, biological treatments, reverse osmosis, coagulation and flocculation, micro filtration, UV therapy, and ultra filtration, among others. Each of these approaches has certain drawbacks and is insufficient to completely purify water and eliminate contaminants from it. Additionally pricey, emerging nations cannot afford these solutions.

This emphasis the need for effective water filtration technology that is also affordable. According to reports, using nano materials as photo-catalysts can lead to effective and environmentally favourable outcomes.

1.7 <u>WATER PURIFICATION</u>

The source of life is water. But when contaminated, it may prove to be unhealthy, making the need for drinking water purification essential. Water that has been purified is the most crucial resource for everyone on earth. It is used for drinking, cooking, and other domestic tasks like bathing, bru shing , and washing clothes. It is crucial for maintaining the hygiene of the environment around us in addition to making our lives healthier. Water-borne diseases can be avoided if people have better access to safe drinking water, which is the primary goal of water purification.

Water contains a variety of toxic contaminants that are harmful to consumption and can lead to a variety of water-borne diseases. Pollutants can be organic and inorganic chemicals, as well as physical, biological, radiological, or heavy metal substances. Industry waste is the leading cause of water pollution because it accounts for roughly 20% of total dye consumption. The pollutants selected for this project is dye. The presence of dyes, due to their aromatic and recalcitrant nature, makes them difficult to remove using conventional methods and poses a risk to human life.

Conventional methods for removing harmful pollutants, like dyes, heavy metals, and oil, have been put in place, but they are ineffectual because of economic constraints and because the chemicals cannot be degraded without producing secondary contamination. Conventional techniques for treating waste water include flocculation, coagulation, ion exchange, biological treatment, adsorption, and nanofiltration. It has been shown that the more contemporary idea of photocatalysis is capable of totally removing and converting contaminants into more basic organic molecules

1.8 <u>PHOTOCATALYSIS</u>

The process that takes place when a light source interacts with a material's surface is known as photocatalysis. Catalysts are compounds that speed up a reaction without themselves going through any chemical changes. The influence of photons on photocatalysts accelerates the rate of reaction in photocatalysis. A conductive nanomaterial is expected to be an effective

photocatalyst substance. Direct absorption of the incident light raises it to higher energy levels, which it then transfers to a reactive substance to cause a chemical reaction. Homogeneous and heterogeneous photocatalysis are the two primary categories of photocatalysis. Both the reactant and the photocatalyst will be in the same phase in homogeneous photocatalysis, while they will be in distinct phases in heterogeneous photocatalysis.

Photo-catalysis is the acceleration of a photo-reaction in the presence of a catalyst. The substrate absorbs light during the reaction. The ease with which the catalyst creates electron-hole pairs determines the catalyst's reaction rate or activity. These electron-hole pairs react with the substrate, resulting in the formation of free radicals. Secondary reactions occur when these radicals react with the reactant to produce various useful products.

Dr. Alexander Eibnor, a German scientist, first described photo-catalysis in 1911 when bleaching dark blue pigment with zinc oxide in the presence of sunshine. Akira Fujishima and Kenichi Honda later made a successful discovery in photocatalysis in 1972 when they discovered electrochemical photolysis of water occuring between linked TiO_2 and Platinum electrode.
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Photo-catalysis is also a powerful tool in the fight against water pollution. Instead of using bulk material as a catalyst to improve photocatalytic reaction efficiency, we can use nanotechnology to improve photocatalytic reaction efficiency. When compared to bulk materials, the increased surface to volume ratio of nano materials increases catalyst efficiency.

The crystal structure of the catalyst and the energy of the incoming photons of visible or UV light control the rate of reaction in photocatalysis. Materials utilized as catalysts function as sensitizers for light-stimulated redox reactions based on their electronic structure, which is governed by filled valence and unoccupied conduction band

In this method, when the synthesized semiconductor nanoparticles/photocatalyst absorbs light of suitable energy, electrons in the valence band jumps to the conduction band. As a result photo-generated holes and electrons are formed in the valence band and conduction band respectively. Due to generation of positive hole and electron, oxidation-reduction reaction

takes place at the surface of photocatalyst , oxidation reaction positive holes react with water and produce hydroxyl radical. In reduction reaction negative electrons combines with oxygen and converted to the superoxide and ions. These superoxide and ions can be further used degrade any kind of pollutants.
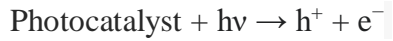
Photocatalyst + hv $\rightarrow$ h$^+$ + e$^-$

Oxidative reactions due to photocatalytic effect:

$\quad$ h$^+$ + H$_2$O $\rightarrow$ H$^+$ + $\bullet$OH

$\quad$ 2 h$^+$ + 2 H$_2$O $\rightarrow$ 2 H$^+$ + H$_2$O$_2$

$\quad$ H$_2$O$_2$ $\rightarrow$ 2 $\bullet$OH

Reductive reactions due to photocatalytic effect:

$\quad$ e$^-$ + O$_2$ $\rightarrow$ $\bullet$O$_2^-$

$\quad$ $\bullet$O$_2^-$ + H$_2$O + H$^+$ $\rightarrow$ H$_2$O$_2$ + O$_2$

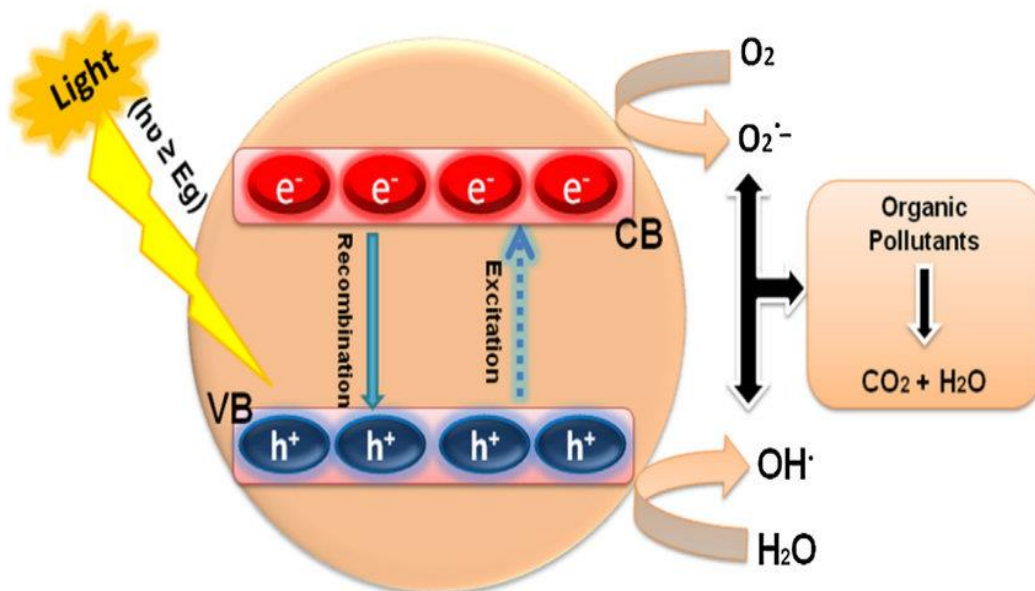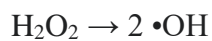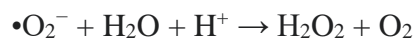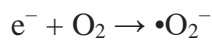$\quad$ H$_2$O$_2$ $\rightarrow$ 2 $\bullet$OH
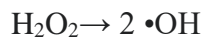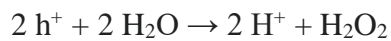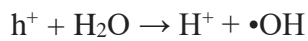
Figure (1.1) : General mechanism of photocatalysis

1.9 CURRENT WORK

A photocatalyst is referred to as any substance that demonstrates photocatalytic capabilities or the capacity to promote and expedite particular chemical reactions when stimulated by light of the appropriate wavelength. Photocatalysts are utilized in a number of applications, including the removal of contaminants from water and the air, water splitting to produce H_2, odour control, the inactivation of bacteria and cancer cells, and the management of odour. A number of photocatalysts have been utilized for different applications. They include ZnO, ZnS, CdS, SrO_2, WO_3, and $Fe-TiO_2$. Due to its low cost, excellent stability, and environmental friendliness, TiO2 is the most widely used of them all.

This work aim to use these wide scale applications of nanotechnology for water purification. For this, titanium dioxide is used as the photocatalyst which shows efficient photodegradation of numerous pollutants present in water. The degradation of two individual dyes ie, Methylene blue and Rhodamine B is analyzed, and compared the percentage of degradation of these with that of the mixture of dyes.

1.9.1 <u>METHYLENE BLUE</u>

Methylthioninium chloride, usually referred to as methylene blue, is an organic chloride salt that resembles a vividly coloured, brightly green substance. Methylene blue's chemical name is C16H18N3S. It is frequently used to treat both peadiatric and adult patients with acquired methemoglobinemia. The group of substances known as "Phenothiazine's" and more specifically "Diamino Phenothiazine's" includes methylene blue.

Methylene blue is an organic dye that is water soluble and used as both a stain and a drug. Methylene blue is a heterocyclic aromatic chemical with two side chains and a core benzene ring. The dye may interact with negatively charged molecules because it is cationic, which means it has a net positive charge. The two side-chains are crucial to how the dye works. The capacity of the dye to connect with proteins is caused by one side-chain, whilst the ability to interact with DNA is caused by the other side-chain.

Methylene Blue was created for the first time in 1876 by a German chemist by the name of Heinrich Caro. It was initially created as an aniline-based dye for the textile industry, but researchers like Robert Koch and Paul Ehrlich discovered that it could also be used as a stain for microscopy. When chloroquine and other medications hit the market, methylene blue—another therapy for malaria—was no longer utilized in Africa. In the past, cyanide poisoning and urinary tract infections were both treated with this substance. Clinical trials are also being conducted on Methylene Blue to determine whether it may be used to treat Alzheimer's sufferers. Methylene blue is a dye that is employed as a staining agent for microscopy, diagnostic procedures, and surgical procedures.
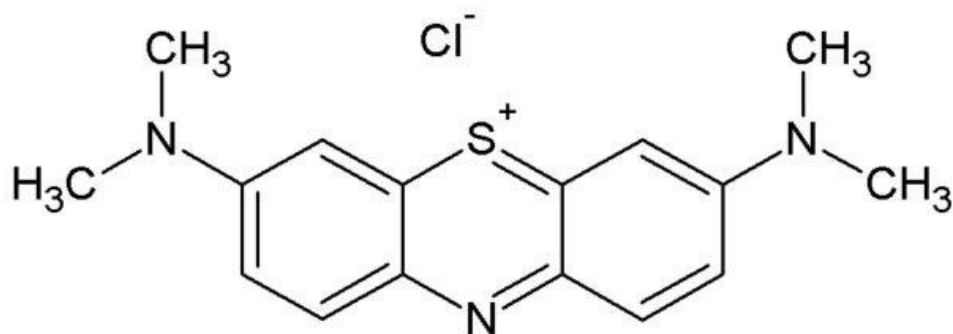
Figure (1.2) : Structure of methylene blue

1.9.2 RHODAMINE B

Rhodamine B, a synthetic color with a greenish crystalline powder-like consistency. when it is dissolved in water in high concentrations give a purple red color and in low concentrations gives a bright red color. The chemical formula of Rhodamine b is $C_{28}H_{31}N_2O_3Cl$, and it has a molecular weight of 479 g/mol.

Rhodamine B is an organic substance and fluorescent dye that is frequently used as a tracer dye in water to assess the flow and transport rates and directions. Rhodamine dyes glow, making it simple and affordable to detect them with fluorometers. It is a fluorescent dye that

may be used to stain biological specimens. It is commonly combined with auramine O to create the auramine-rhodamine stain, which is used to show acid-fast organisms like Mycobacterium. Additionally, rhodamine dyes are widely utilized in biotechnology processes including flow cytometry, fluorescence correlation spectroscopy, and fluorescence microscopy.

Herbicides are frequently combined with Rhodamine B to mark the areas where they have been applied. Additionally, it is being examined for potential application as a biomarker in oral rabies vaccinations for wildlife, including raccoons, to identify creatures that have consumed a vaccine bait. The animal's teeth and whiskers are coated with Rhodamine. Rhodamine B is a significant hydrophilic xanthene dye which is basic in nature. That is used extensively in the textile, leather, paper printing, paint, coloured glass, and plastic industries. It is also recognized for being stable. The majority of xanthene dyes are categorized as basic dyes by their method of application. A xanthene dye is one that has an amino or hydroxyl group attached to the oxygen and a xanthylium or di-benzo-g-pyran nucleus as the chromophore. They are significant because of their brilliant hues and shades between greenish yellow and purple. A lot of xanthenes are fluorescent in nature

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Rhodamine B, a dye for textiles, is harmful to human health. It frequently makes its way into the body when food is combined with it, which results in oxidative stress on cells and tissues. When used in significant quantities over a short period of time, Rhodamine B can cause acute poisoning. Nausea, headaches, shortness of breath, skin irritation, ingestion, inhalation, or direct touch, as well as significant eye damage on human consumption are some of its harmful effects
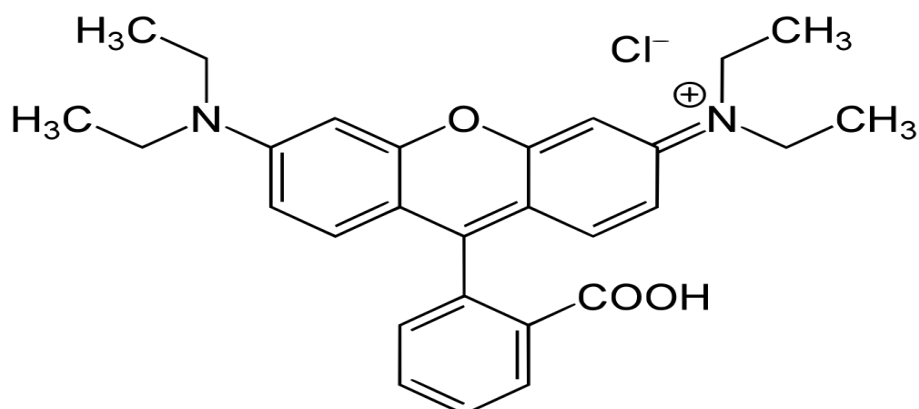

Figure (1.3) : Structure of Rhodamine B

13

1.9.3 **TITANIUM DIOXIDE**

White and opaque titanium dioxide is a naturally occurring mineral. It is also known as titania. These oxidised minerals are found naturally and may be mined to provide industry with titanium. Titanium dioxide is odourless and both absorbing. Its main use in powder form is as a regular pigment that enhances whiteness and opacity. Due to its unique properties, titanium dioxide is often used and well-known in nanoscience and nanotechnology. Titanium dioxide was one of the first materials used in nanotechnology goods.

The three crystalline forms of TiO_2 are rutile, anatase, and brookite. Brookite and anatase are metastable, while rutile is the member of the group with the highest thermodynamic stability. Rutile titanium dioxide is highly stable and has a dark red appearance. Furthermore, it is the most typical form of titanium dioxide and is found in metamorphic and igneous rocks that have undergone high-pressure, high-temperature processes. Rutile has a tetragonal unit cell with oxygen anions and titanium cations as part of its crystalline structure. Titanium cations (Ti+4) have a coordination number of 6, compared to the oxygen anion's (O^{2-}) of three.

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The following are the key features of rutile TiO_2
- Greater dispersion
- High birefringence
- Greater refractive index a visible wavelength

The fabrication of titanium dioxide pigments and metallic titanium are the two most significant uses of the rutile phase. It is also made in fine form for the manufacture of paints, papers, and plastics. rutile titanium dioxide nanoparticles can work in the cosmetics industry because they can absorb UV radiation.

Anatase nanoparticles can be either colorless or yellow. Because it contains so many impurities in its natural state, anatase titanium dioxide is dark in color. Anatase titanium dioxide has a tetragonal crystalline structure as opposed to rutile titanium dioxide. Anatase's

titanium dioxide has a metallic character. It can also be synthesized to use it in the creation of semiconductors.

A deep reddish-brown kind of titanium dioxide is called brookite.it has orthorhombic structure. It may be found in four polymorphic structures that naturally exist. Minerals with diverse structures but the same content are said to have polymorphic structures. When compared to other polymorphic structures, brookite is typically thought of as an uncommon substance. It also has a cell volume that is noticeably bigger. Iron, tantalum, and niobium are the three most frequent impurities found in this material.

The development of compounds based on titanium has been facilitated by its low toxicity and availability. Numerous methods have been created over time to enhance the characteristics of TiO_2. The nanoscale particle size reduction, morphological control, and heteroatom doping to adjust the electronic structure and structural characteristics were a few of these
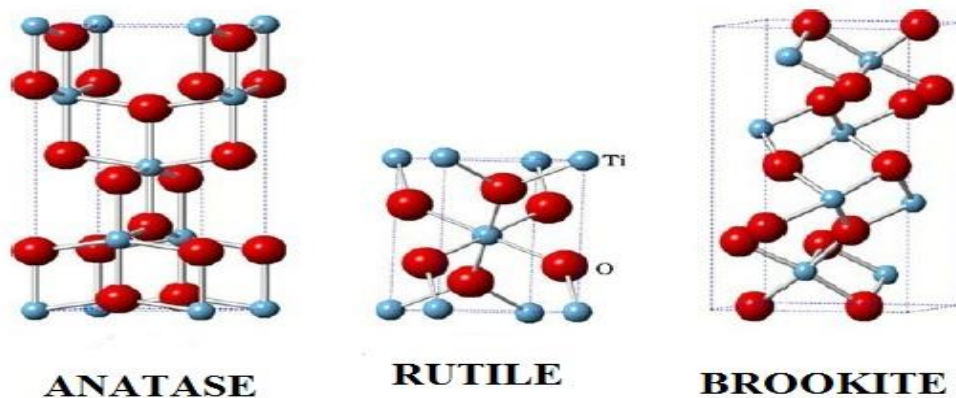
Figure (1.4): Structure of titanium dioxide

There are numerous applications for titanium dioxide:
Because of its special features titanium dioxide is well-known in nanoscience and nanotechnology. One of the earliest materials utilized in nanotechnology products was titanium dioxide.

- TiO_2 is known as titanium white, Pigment White 6 or CI 77891 when used exclusively as a pigment in paint. Because of its potent whitening abilities, it is sometimes referred

to as "the perfect white" or "the whitest white." One of the crucial basic elements for paints and coatings is TiO_2, a white pigment.

- Due to its ability to absorb ultraviolet light, titanium dioxide is used in cosmetics today, including skin care products and sunscreen lotions, with the assurance that it shields the skin from UV rays.

- Porcelain enamels have employed titanium dioxide as a bleaching and opacifying chemical to give them brightness, hardness, and acid resistance.

- Thin coatings exhibiting self cleaning and disinfectant properties under exposure to uv light is due to the photocatalytic nature of titanium dioxide.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 SYNTHESIS TECHNIQUES

There are three major methods for the synthesis of nano particles. They are biological method, chemical method and physical method. Among them the chemical method includes sol-gel method, sonochemical synthesis, hydrothermal method, co-precipitation method and Inert gas condensation method. In this work we are dealing with hydrothermal method

2.1.1 HYDROTHERMAL METHOD

Hydrothermal method is one of the popular methods for synthesizing nanoparticles. It is essentially a solution-reaction approach. Hydrothermal synthesis refers to the process of growing crystals from an aqueous solution in an autoclave at high temperatures and pressures. In hydrothermal synthesis, nanomaterials can be formed at temperatures ranging from room temperature to extremely high temperatures. . Depending on the vapour pressure of the main composition in the reaction, either low-pressure or high-pressure conditions can be used to control the morphology of the materials to be prepared.

This method is performed in a steel vessel called Autoclave in which the processing conditions are controlled by adjusting the temperature and pressure. Here the processing is done in aqueous solution. The temperature is raised above the boiling point of water, attaining the pressure of vapour saturation. The amount of solution added to the reaction chamber (autoclave) and the temperature have a significant impact on internal pressure.

The ability to control the parameters is a significant advantage of hydrothermal synthesis over other methods. Hydrothermal synthesis can produce nanomaterials that are not stable at high temperatures. It can also produce nanomaterials with high vapour pressures with minimal material loss. Hydrothermal synthesis allows for precise control of the compositions of nanomaterials to be synthesised via liquid phase or multiphase chemical reactions.

17

2.1.1.(a) HYDROTHERMAL SYNTHESIS OF TiO$_2$ NANOPARTICLES

In a 25 ml anhydrous system of absolute ethanol, 0.5 g of cetyltrimethylammonium bromide (CTAB) was added and stirred until completely dissolved. Then 12.02 mmol (3.56 mL) of titanium (IV) isopropoxide was added to the reaction mixture and stirred for 2 hours. After that, until a white precipitate formed, 10 mL of deionized H_2O was added dropwise to the solution. The suspension was stirred for 6 hours, put into an autoclave made of Teflon-coated stainless steel, heated for 8 hours at 180 degrees, and then dried under vacuum at 90 ∘C. The white precipitate was annealed in a muffle furnace at 400∘C for 2 hours.

2.1.2 PREPARATION OF DYE SOLUTION FOR PHOTO CATALYSIS

To prepare the stock solution 10 mg of the dye is dissolved in 100 ml of deionized water. From the stock solution 5 ml is taken and mixed with 45 ml of deionized water, thus we get 50 ml of 10 ppm dye.

The same procedure is done for both Methylene blue and Rhodamine B dyes.

2.2 CHARACTERIZATION TECHNIQUES

Nanoparticles are playing a more significant part in both basic science research and real-world applications. Nanoscale materials commonly differ in their electrical, chemical, mechanical, and optical properties from their corresponding bulk materials due to their high surface-to-volume ratios, which generate an exponential surge in reactivity at the molecular level. Therefore, research into such characteristics is important. The investigation of crystal structure, nanoparticle size, elemental composition, and other physical aspects has been carried out using a variety of methodologies. Both microscopic and spectroscopic methods are available for characterising nanoparticles. In spectroscopy, the relationship between electromagnetic waves and matter changes as a function of wavelength. It lists the chemical composition, crystal forms, and photoelectric characteristics. Some of these methods include infrared (IR), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Raman spectroscopy, energy-dispersive spectroscopy (EDS), ultraviolet visible spectroscopy (UV-VIS), dynamic light scattering

(DLS), and IR. On the other hand, the method used to examine and observe the surface and subsurface structure of materials is known as microscopy. Examples of microscopic methods include scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and scanning tunnelling microscopy (STM).

The following sections go into more detail about the characterisation methods used in this study.

2.2.1 <u>STRUCTURAL ANALYSIS</u>

In every study, determining the structure and size of the synthesised substance is crucial. In the section that follows, a few key methods that are frequently employed for structural analysis are explained.

2.2.1.(a) <u>X-RAY DIFFRACTION</u>

The majority of nanoparticles have crystalline structures, so basic characterization methods for these particles should be able to determine the crystallographic lattice parameters and the symmetry group that the material belongs to. Some of these parameters can be determined by x-ray diffraction from the diffraction pattern.

From the XRD pattern we compare the theta values of X-ray diffraction peaks to the standard values provided by the already known elements and obtain the best match.

2.2.1.(a.1) <u>PRINCIPLE</u>

According to Max Von Laue Crystalline materials serve as three-dimensional diffraction gratings for X-ray wavelength The X-ray diffraction method resulted from this. In this instance, the diffraction gratings will be equally organised crystal planes. It is permitted for X-rays to strike the sample. Cathode ray tubes were used to create this X-ray. Typically, 0.05 to 0.25 nm wavelength X-rays are utilised for diffraction. Diffraction patterns can be seen when the beam's wavelength is on the order of the inter-planar distance. This diffraction pattern

results from the monochromatic X-rays that are reflected from the crystalline material constructively interfering. Bragg's law, which is widely recognised, governs this.

2.2.1.(a.2) <u>BRAGG'S LAW OF X-RAY DIFFRACTION</u>
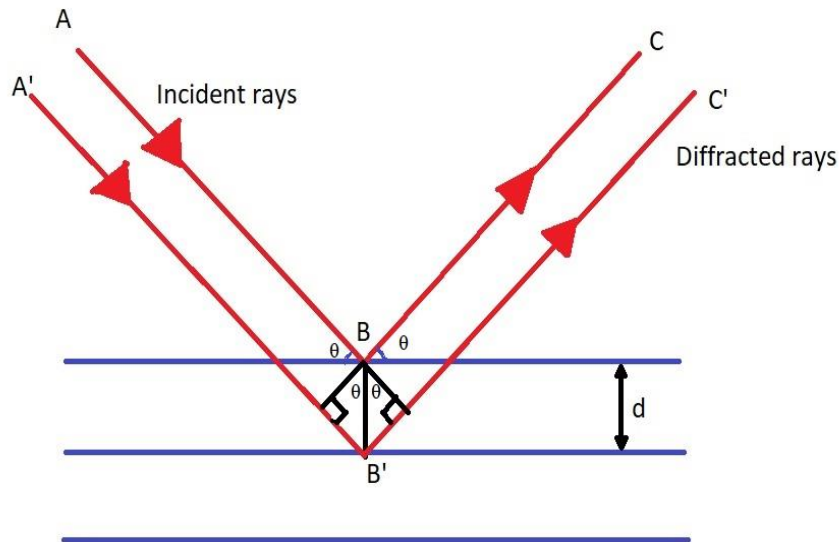

Figure (2.1) : X-ray diffraction from parallel planes in a crystal

Here different parallel planes with same (hkl) values are considered. The distance between the adjacent planes is the inter-planar distance is taken as d. AB and A'B' are the incident radiation incident on the plane at an angle theta that get reflected along BC and B'C'. The ray A'B'C' travels an extra distance of 2dsinθ which is the path difference. For constructive interference of the reflected rays to occur path difference must be integral multiple of the wavelength of the X-ray (nλ)

$$n\lambda = 2d\sin\theta \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.1)$$

The lattice parameters a, b, and c determine the inter-planar distance d in the Bragg's equation.

$$\frac{1}{d^2} = \left(\frac{h}{a}\right)^2 + = \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2 \ldots\ldots\ldots\ldots\ldots(2.2)$$

If we calculate the value of d from the detected Braggs angle, we can calculate the value of the lattice parameters, which in turn provide important information about the crystal.

The equations connecting lattice parameters (a, b, c) and the inter planar distance (d) different crystal structures are given below.

- Cubic

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$$

- *Tetragonal*

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}$$

- Hexagonal

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2}$$

- Rhombohedral

$$\frac{1}{d^2} = \frac{(h^2+k^2+l^2)+2(hk+kl+hl)(cos^2\alpha-cos\alpha)}{a^2(1sin^2\alpha-3cos^2\alpha+2cos^3\alpha)}$$

- Orthorhombic

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

- Monoclinic

$$\frac{1}{d^2} = \left(\frac{h^2}{a^2} + \frac{k^2sin^2\beta}{b^2}+\frac{l^2}{c^2} - \frac{2hlcos\beta}{ac}\right)$$

- Triclinic

$$\frac{1}{d^2} = \frac{\frac{h^2}{a^2}sin^2\alpha+\frac{k^2}{b^2}sin^2\beta+\frac{l^2}{c^2}sin^2\square+\frac{2kl}{bc}(cos\beta cos\square-cos\alpha)+\frac{2kl}{ac}(cos\square cos\alpha-cos\beta)+\frac{2kl}{ab}(cos\alpha cos\beta-cos\square)}{1-cos^2\alpha-cos^2\beta-cos^2\square+2cos\alpha cos\beta cos\square}$$

2.2.1.(a.3) **XRD PATTERN**

The X-ray pattern is a simple graph that shows the relationship between the intensity of diffracted X-rays and the angle of diffraction. To capture this pattern, the sample must be scanned through a range of angles (2θ). Because the sample is in the form of powder, it exhibits all of the beam's diffraction directions. A single peak in the diffraction pattern indicates a series of planes facing the X-ray beam at the proper angle to satisfy Bragg's condition. As a result, the peak can tag the inter-planar distance (d) and aid in the identification of the material element involved, which has a set of unique d-spacing. This is usually accomplished by comparing these values to the standard reference pattern.

It's possible that not all planes in the crystal will reflect light or satisfy Bragg's equations. For instance, only those planes in a body-centered monoatomic lattice where h+k+l = n……(2.3) produce Bragg reflection if n is an even integer. Constructive interference occurs for face-centered cubic lattices when h, k, and l are all either even or odd, which results from the influence of the structure factor. All plane reflections are possible from a simple cubic structure. Sharp peaks will make up the pattern for crystallite nanoparticles. Additionally, it is observed that the peak broadens and extends for the structures that resemble nanosheets. An example for XRD pattern is given bellow.
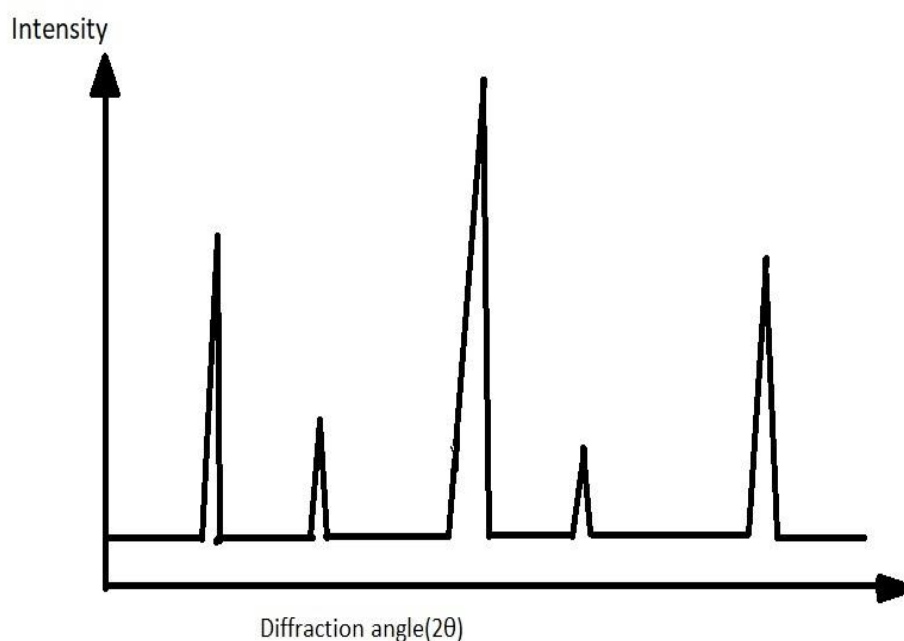

Figure (2.2) : XRD pattern

22

2.2.1.(a.4) PARTICLE SIZE DETERMINATION

In a typical XRD pattern, we can see peaks corresponding to x-ray diffraction from various (hkl) planes in the crystalline material. There are large number of crystallites in the sample. If we keep on reducing the size of the crystallites in the sample , the XRD peaks will progressively broaden. This means that the width of the XRD peaks is inversely proportional to the crystallite size. This is given by Scherrer equation.

From the width of diffraction line, the average grain size of the particles can be calculated using Debye-Scherrer formula,

$$L = \frac{K\lambda}{B\cos\theta} \quad \dots\dots\dots\dots\dots(2.4)$$

Where,

K is a constant which is nearly equal to 0.9

B is the full width at half maximum measured in radians.

λ is the wavelength of X-ray.

Θ is the diffraction angle

2.2.1.(b) FOURIER TRANSFORM INFRARED SPECTROSCOPY

Fourier transform infrared spectrometer (FTIR) is an instrument based on infrared spectroscopy. In comparison to other dispersive spectrometers, it is the most contemporary variety. Its great precision, accuracy, speed, increased sensitivity, simplicity of use, and sample non-destructiveness all contribute to this.. In comparison to other dispersive spectrometers, it is the most contemporary variety. Its great precision, accuracy, speed, increased sensitivity, simplicity of use, and sample non-destructiveness all contribute to this. A molecule's atomic vibrations, which only allow it to absorb particular infrared frequencies and energies, are the basis of infrared spectroscopy technology. Because various chemicals will have distinct infrared spectra, the molecules might be identified and categorized using FTIR.

For both organic and inorganic materials, FTIR provides quantitative and qualitative analyses. Fourier Transform Infrared Spectroscopy (FTIR) can identify the chemical bonds in

a molecule by creating an infra red absorption spectrum. The FTIR spectra will provide a sample profile that may be used to screen and scan samples for a variety of components. FTIR is a useful analytical tool for identifying functional groups and describing information about covalent bonds.

High spectral resolution data are concurrently gathered across a broad spectral range using an FTIR spectrometer. In comparison to a dispersive spectrometer, which measures intensity across a limited range of wavelengths at a time, this offers a substantial benefit. With this method, a beam of light with many frequencies is combined at once, and the amount of that beam that is absorbed by the sample is measured. A second data point is then obtained by altering the beam to comprise a new mix of frequencies. Many times, this procedure is repeated. After that, a computer uses all of these data to calculate the absorption at each wavelength by working backwards. All applications where a dispersive spectrometer was previously employed may now be performed using FTIR. Additionally, new application areas have been made possible by improvements. The spectrum of the light produced by the sample may be obtained using an FTIR spectrometer. The most frequent mechanisms that cause this type of emission are Raman scattering and luminescence. Old-master paintings' creative components are also described using FTIR.
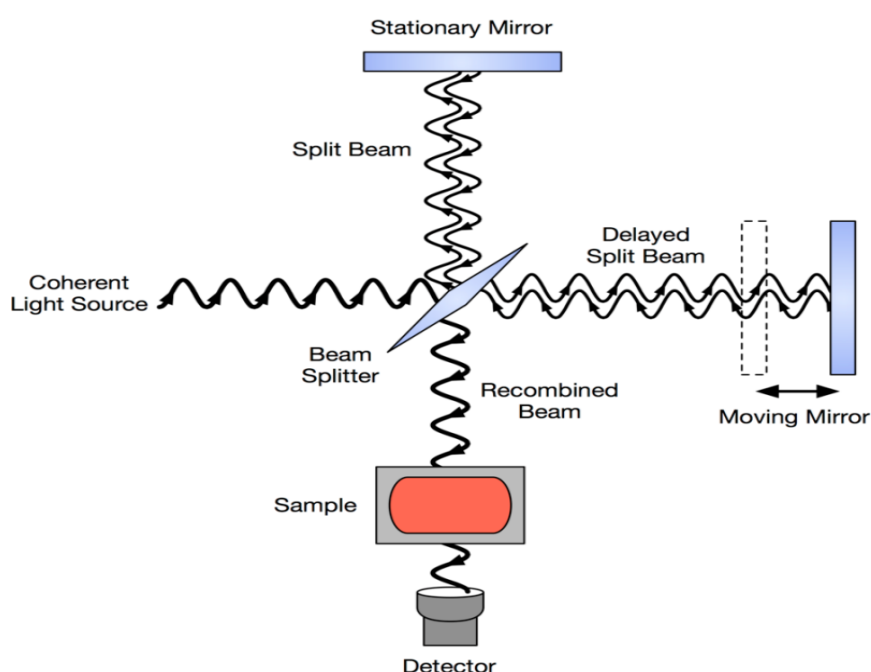

Figure (2.3) : FTIR spectrometer

2.2.2 SURFACE MORPHOLOGICAL ANALYSIS

Scanning electron microscopy is a well-known method for analysing the surface morphology. The theoretical aspects of this technique are discussed below.

2.2.2.(a) SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy is a technique used to capture a picture of a sample by moving an electron beam across the surface of specimens that have been specifically prepared. SEM offers visually stunning and virtually three dimensional views of the sample. The parts are exactly the same as those found in a transmission electron microscope.

Condenser lenses are used to concentrate the electrons from the electron gun so that they strike on a limited area of the sample surface. The beam condenses to a tiny point with a diameter of only 16 nm. The maximum focusibility of the electron beam should be few angstroms, or around the wavelength of the electron d Broglie. The resolution of the imaging beam is based on the size of the focused beam point. SEM uses secondary electrons produced by the sample atoms or electrons reflected back from the surface, to create the picture of the sample.

The sample surface is traversed by the focused beam, or scanned, and the data gathered from each location is combined to create the final image. A group of scanning coils is used for scanning, and depending on the current flowing through them, they will deflect the beam. The condenser lenses are positioned above this.

Images are built in a scanning electron microscope using secondary electrons, back scattered electrons, and characteristic x-rays. The detector will produce an equivalent light pulse by collecting electrons and x-rays. This light pulse is translated into an electrical pulse by the SEM apparatus, which is then utilized to regulate the brightness of the imaged object's spot. When operating in the back scattered electron mode (BSE), the kind of atomic species that caused the back scattering of electrons through collision will determine the kinetic energy of the back scattered electrons. As a result, the spots of different grey scale intensities in the BSE mode are directly connected to the distribution of atoms on the sample's surface.

The operation of the secondary electron mode is distinct. The strong potential field that results from the electron beam striking the sample's atoms might cause the release of electrons, which then escape as secondary electrons. These electrons will be emitted from areas near the surface or from the surface itself. The distance between the sample surface and the detector determines the intensity displayed on the screen. As a result, the brightness of the spots will vary according on the surface roughness (surface topography), and the image gives a three-dimensional impression of the surface.

Another imaging mode makes use of the characteristic x-rays. When inner electrons are released from the atoms due to the Coulomb interaction, higher orbital electrons can enter such vacancies by simultaneously producing an X-ray. These photons' energy is characteristic to atoms and is referred to as characteristic x-rays. These x-rays are also capable of creating an accurate picture of the sample. In this case, the brightness of the recorded spot is designed to be a characteristic function of the atoms present in that spot. As a result, this mode provides information on the sample's chemical composition. The final image can be digitally processed. In addition to SE and BSE electrons, there are other signals. They consist of low-energy characteristic x-rays produced by the impinging electrons, as well as cathodoluminescence. Numerous aspects of the sample, including composition, surface topography, crystallography, magnetic or electric behaviour, etc., are measured using the signals, which are collected from particular emission volumes inside the sample. The second often occurring mode for SEM is characteristic x-rays. They are employed in a process known as energy dispersive x-ray analysis (EDX or EDAX) to determine the elemental composition of the sample.

One requirement of SEM is that the specimen should be conductive so that electrons will have a path to ground that will facilitate the imaging process. Non conductive solid specimens are generally coated with a layer of conductive material by low vacuum sputter coating or high vacuum evaporation. To create this coating, materials like gold and carbon are employed. Additionally, there are conducting tubes that use silver paste to connect the sample's two surfaces. This is done to avoid the specimen accumulating static electric charge, which might deflect the impinging electrons during electron irradiation.
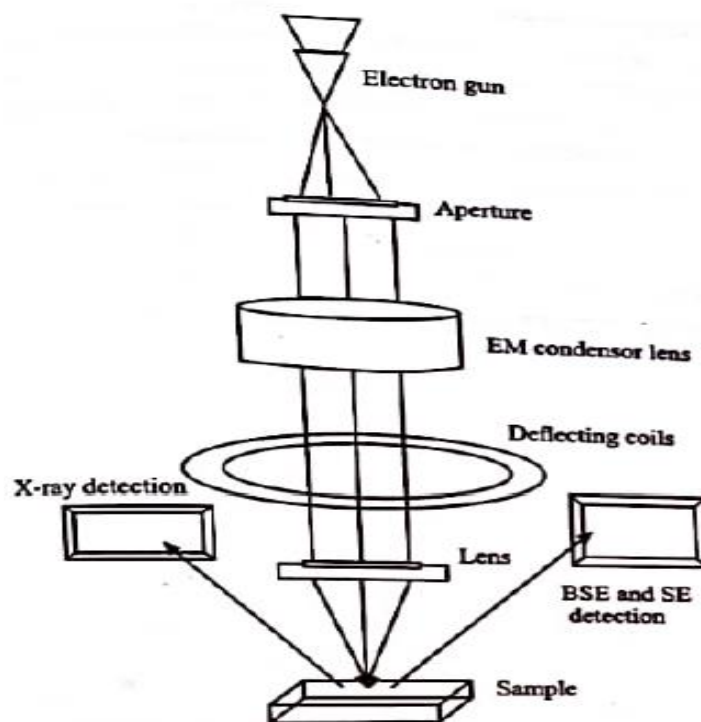
Figure (2.4): Scanning electron microscope

2.2.3 LINEAR OPTICAL ANALYSIS

The optical properties of the samples are studied using the tools such as UV-Visible spectroscopy and photoluminescence (PL).

2.2.3.(a) UV- VISIBLE SPECTROSCOPY

UV-Visible spectroscopy is widely used for the identification of chemicals and quantitative analysis. It also helps for the identification of different inorganic and organic compounds in a solution. The UV-Visible spectroscopy principle is based on the absorption of ultraviolet or visible light by chemical compounds, which results in distinct spectra. This absorption of UV or Visible radiation may lead to the transition among the electronic energy levels of the molecule. The difference in energy of ground state and excited state of electron is always equal to the amount of UV or Visible radiation absorbed by it.

UV-Visible spectroscopy is governed by the Beer-Lambert law, which states that there is a linear relation between concentration and absorbance of a solution.

$$A = \log(\frac{I_0}{I}) = \varepsilon Lc \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(2,5)$$

Where,

I$_0$ is the incident light intensity

I is the transmitted light intensity

A is the absorbance

ε is the molar absorptivity

L is the path length of the sample

C is the concentration

The Beer-Lambert law establishes a mathematical relationship between absorbance and concentration. This relation allows direct measurement of absorber concentration in a solution from absorbance for a fixed path length.
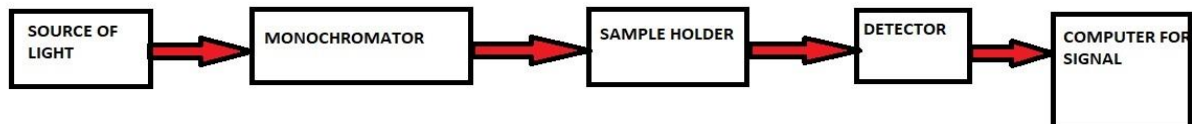

Figure (2.5): Components of UV-Visible spectrophotometer

2.2.3.(a.1) <u>DETERMINATION OF BANDGAP ENERGY</u>

Since UV-Visible spectroscopy examines electrical transitions between the valence band and the conduction band in semiconductors, it provides a practical approach for estimating the optical band gap. The band gap in the absorption spectrum indicates the point at which absorption begins to rise from the baseline, Since this reveals the very minimum of energy needed for a photon to drive an electron across the band gap and subsequently be absorbed in the semiconductor material. In real spectra there is a nonlinear rise in absorption

that represents local density of states at conduction band minimum and valence band maximum.

An ideal UV-Visible spectrum for a perfect direct band gap semiconductor shows a significant rise in absorption for photons above the band gap and nearly negligible absorption for photons below the band gap. In order to precisely predict the photophysical and photochemical characteristics of semiconductors, the band gap energy must be accurately determined.

Using optical absorption spectra, Tauc provided a method for calculating the band gap energy of amorphous semiconductors in 1966. The Tauc approach is predicated on the notion that the following equation may adequately represent the energy-dependent absorption coefficient:

$$(\alpha h\nu)^{\frac{1}{\gamma}} = B(h\nu - E_g) \dots\dots\dots\dots\dots\dots(2.6)$$

Where,

  α is absorption coefficient

  h is the Planck constant

  ν is the photon's frequency

  E_g is the band gap energy

  B is a constant.

The γ factor depends on the nature of the electron transition and is equal to 1/2 or 2 for the direct and indirect transition band gaps, respectively.
From the absorption spectrum, band gap energy is determined by plotting a graph $h\nu$ versus $(\alpha h\nu)^2$ in the region of strong absorption. The band gap has been extracted by extrapolating the straight line portion of the graph on the $h\nu$ axis at $\alpha=0$

Besides UV-Visible spectroscopy there are also other techniques for deducing he bandgap energy of the semiconductors, they include valence electron energy-loss spectroscopy (VEELS) using monochromated electrons, photoluminescence spectroscopy (PLS), photoacoustic spectroscopy (PAS) technique, and reflectance spectroscopic ellipsometry. For

optical E_g determination, the UV-Visible spectroscopy measuring method is most frequently used because UV-vis spectrometers are commonly used and easy to operate.

2.2.3.(b) <u>PHOTOLUMINESCENCE</u>

A non-destructive, contactless technique for examining a material's electrical structure is photoluminescence spectroscopy. As long as radiative recombination events dominate non-radiative recombination, it is utilized to identify the presence of impurities in semiconductors and is especially helpful for finding shallow-level impurities. With PL, impurity identification is easy to understand.

A technique known as photo-excitation involves directing light from the source onto a sample, where it is absorbed and transmits more energy to the substance. One method the sample will release this extra energy is by luminescence, which is the emission of light. The luminescence produced by the photo-excitation process is known as photoluminescence. The photo-excitation process causes the material's electrons to enter allowable excited states. Additional energy is released as these electrons reach their equilibrium states. Light emission is a part of a radiative phase but is excluded from a non radiative process. The difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state determines the energy of the produced light (photoluminescence). The intensity of the light emitted indicates the relative importance of the radiative process. It is possible to determine the type of electronic transitions that lead to photoluminescence in solids.

Extrinsic and intrinsic emission processes are the two different categories: Band to band luminescence, exciton luminescence, and cross luminescence are the three forms of intrinsic luminescence. Band-to-band luminescence happens when an electron in the conduction band recombines with a hole in the valence band. Very pure crystals exhibit this emission at larger temperatures. While it transforms into exciton luminescence at lower temperatures. If there are any impurities that have their level in the forbidden gap, they trap electrons or holes and cause them to recombine with one another, either radiatively or non-radiatively, through that level. Extrinsic luminescence is defined as luminescence brought on by artificially introduced contaminants, most frequently metallic ones. Donors and acceptors, which influence

semiconductor characteristics and function as luminescence activators, are the most significant impurities in semiconductors.

The figure shows the block diagram of basic components used in photoluminescence studies and illustrates the energy level diagram for the basic mechanism involved in PL.
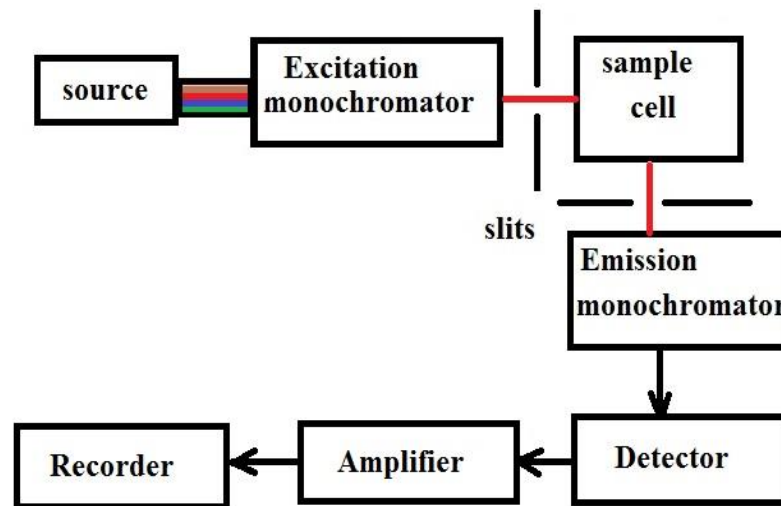

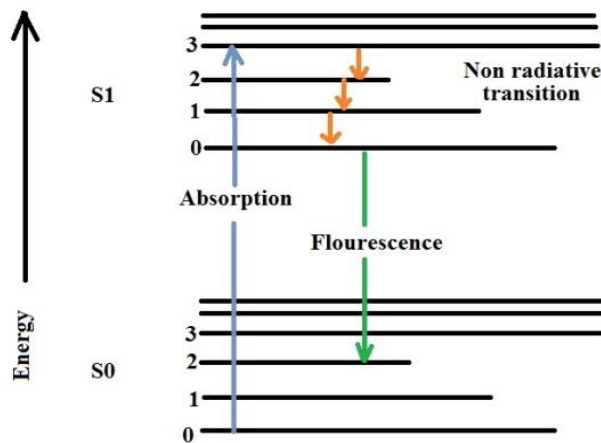**Figure (2.6)** : Schematic diagram of basic components of PL measurement setup

Figure (2.8): Energy level diagram that depicts the basic mechanism of photoluminescence

CHAPTER 3

RESULT AND DISCUSSION

Characterization techniques will enable us to investigate about different physiochemical properties of nano particles. Different characterization methods are based on different physical properties of the nanoparticles. Through these techniques we can study about the size, crystal structure, elemental composition, morphology, band gap energy and a variety of other physical properties of nanoparticles
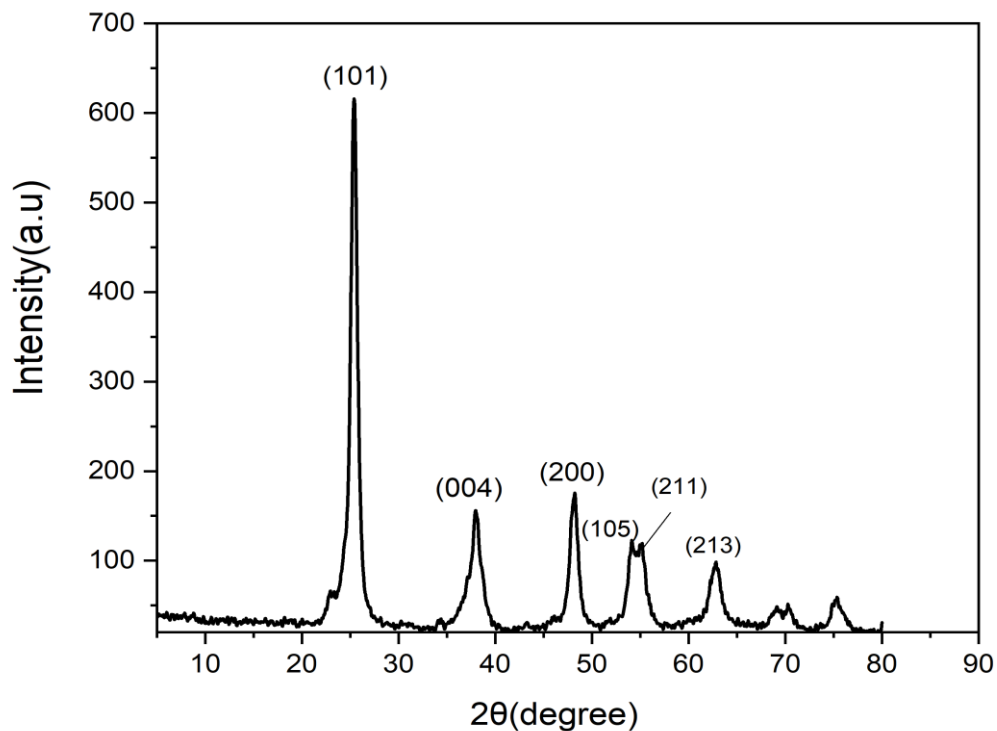
3.1 STRUCTURAL ANALYSIS

3.1.1 XRD ANALYSIS

Figure (3.1): XRD pattern of the TiO_2 nanoparticles

The figure (3.1) shows the XRD pattern of TiO_2 at 400⁰ C calcination temperature. The pattern is in excellent agreement with a reference pattern (JCPDS21-1272) of anatase phase of titanium dioxide. At 400⁰ C the XRD pattern shows a pure anatase structure with peaks at t $2\theta = 25.429^o$, 37.992^o, 48.243^o, 54.194^o, 55.049^o, 62.452^o which can be indexed to the (101), (004), (200), (105), (211), (213) crystal faces of TiO_2, respectively. The average crystal size of the TiO_2 nanoparticles treated at 400⁰ C was estimated by the Scherrer's equation. The particle sizes of the synthesized TiO_2 are tabulated below:

2θ (DEGREE)	θ (RADIAN)	FWHM (DEGREE)	FWHM (RADIAN)	PARTICLE SIZE (nm)
25.39	0.22	0.92	0.0160	8.82
37.97	0.33	1.48	0.03	5.66
48.15	0.42	1.005	0.017	8.65
54.06	0.47	0.90	0.02	9.88
55.10	0.48	1.16	0.02	7.68
62.77	0.54	1.35	0.0234	6.85
75.32	0.66	0.98	0.02	10.23
69.16	0.60	0.96	0.02	9.99
70.35	0.614	0.62	0.01	15.63

Table (3.1): Particle size determination

Average particle size = **9.27 nm**

3.1.2 FOURIER TRANSFORM INFRARED(FTIR) SPECTRUM OF SYNTHESIZED TiO₂ NANOPARTICLES

The FTIR studies are conducted for the samples using Fourier transform infrared spectrometer. In the range of 400-4000 cm^{-1} . Figure (3.2) represents the FTIR absorption spectrum of the synthesized TiO2 nanoparticles. FTIR spectrum shows an intense peak at 3401.64 cm^{-1} due to the OH stretching mode. The peak at 453.35 cm^{-1} represents the Ti-O bending mode and the peak at 1624.62 cm^{-1} represents deformative vibration of Ti-OH stretching mode.
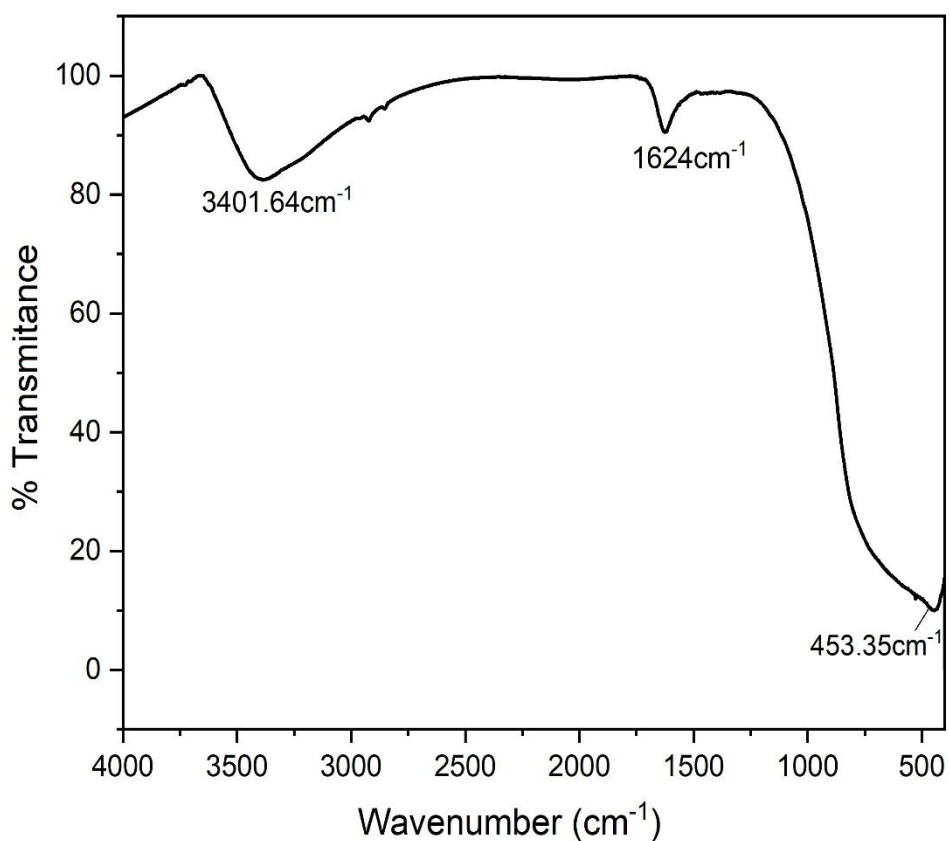
Figure (3.2) : FTIR spectrum of TiO2 nanoparticles

3.2   SURFACE MORPHOLOGICAL ANALYSIS

3.2.1 SEM IMAGE OF THE SYNTHESIZED TiO$_2$ NANOPARTICLES
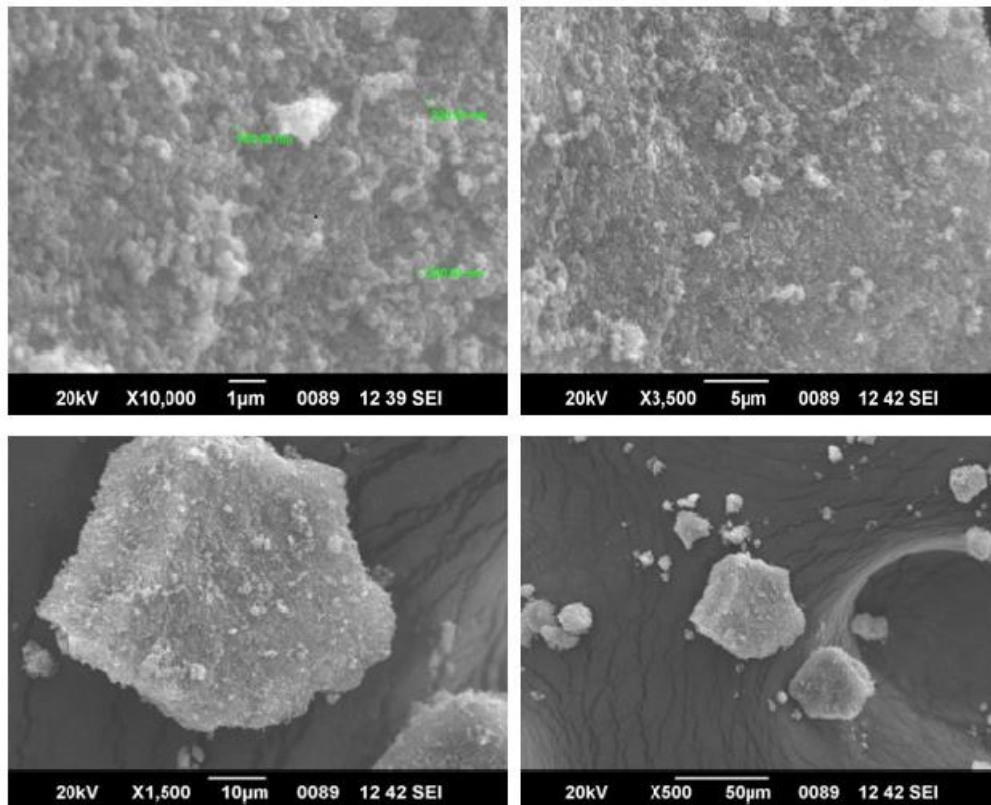

Figure (3.3) : SEM images of TiO$_2$ nanoparticles

Morphological features of the TiO$_2$ nanoparticle were investigated employing scanning tunnelling microscope. Due to its considerable depth of focus, SEM is a very helpful method for examining nanoscale materials, it gives three-dimensional pictures which reveal more details about the sample.

3.3   LINEAR OPTICAL ANALYSIS

3.3.1 UV-VISIBLE SPECTRUM OF SYNTHESIZED TiO_2 NANOPARTICLES

Optical characterization is done using UV-Visible spectrometer within the range of 200-1000 nm. The UV-Visible absorption spectrum of TiO_2 nanopowder is given in the figure (3.4). Maximum absorbance is found at UV region and absorbance peak is obtained at 303.01 nm
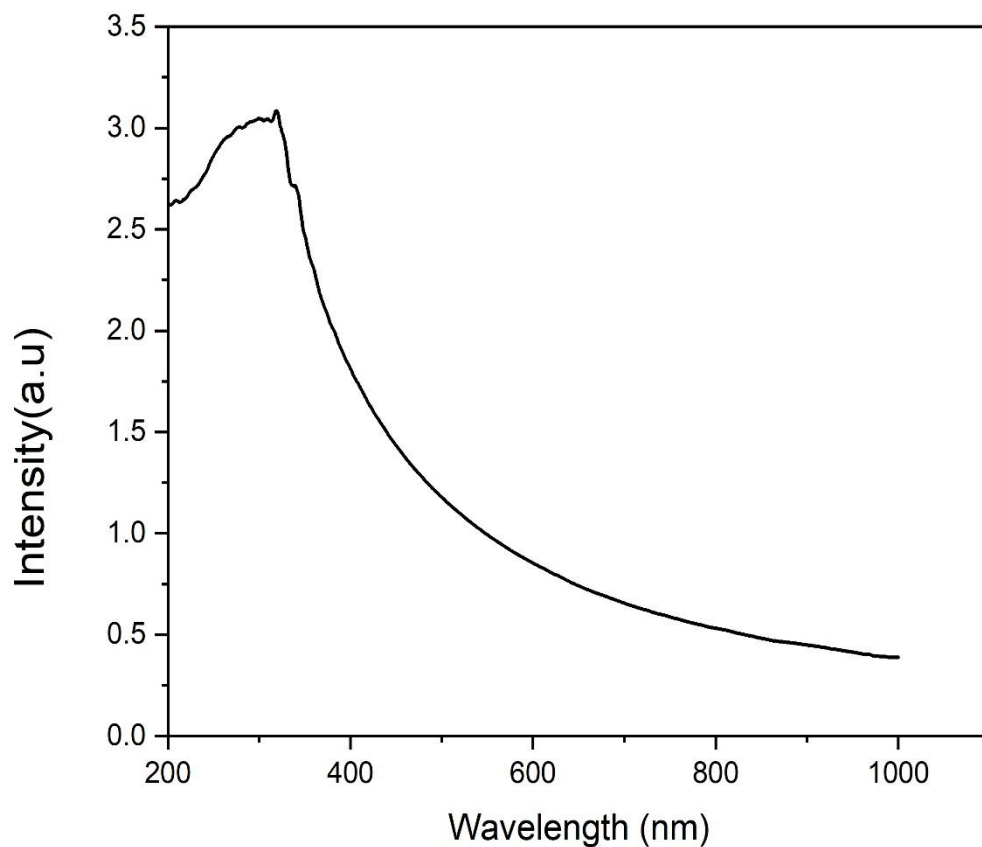

Figure (3.4) : UV-Visible spectrum of TiO2 nanopowder

3.3.2 BANDGAP ENERGY DETERMINATION OF TiO$_2$ NANOPARTICLES

From the optical absorption data, we plot a graph (Tauc plot) hv versus $(\alpha h v)^2$ to estimate the bandgap energy for the sample, where hv is the photon energy and α is the absorption coefficient. By extrapolating the linear portion of the curve to meet hv=0, we can calculate the band gap energy in eV. The figure (3.5) shows the Tauc plot of TiO$_2$.
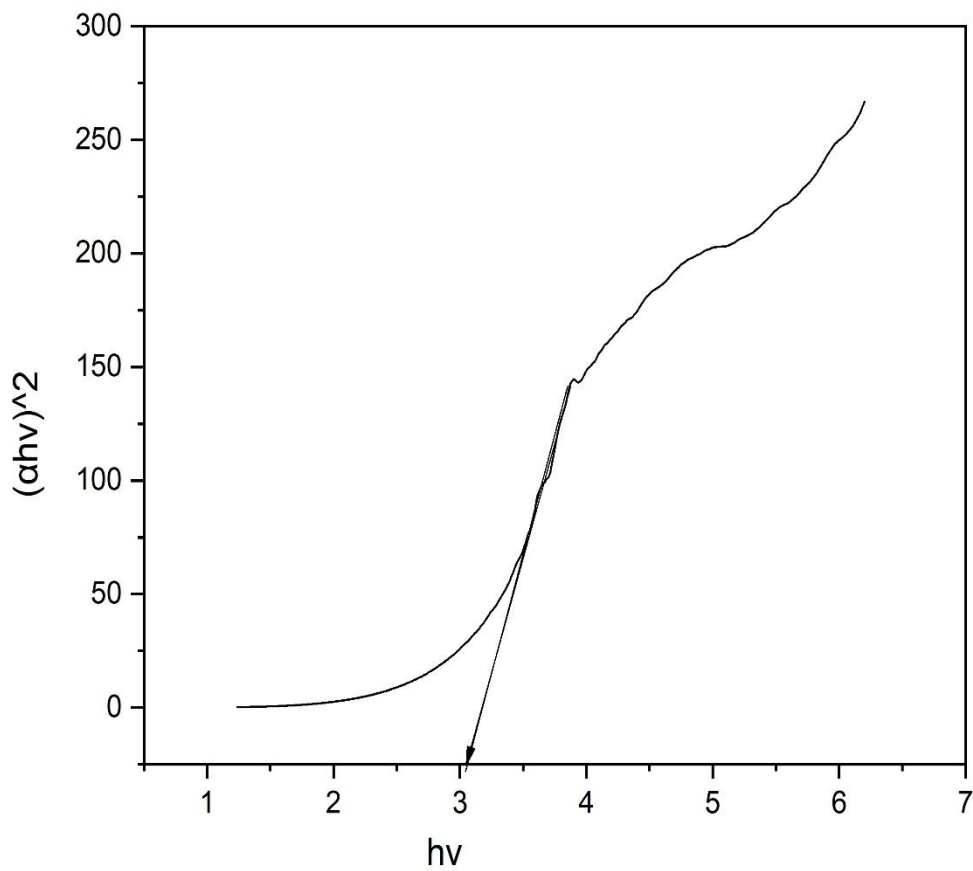

Figure (3.5) : Tauc plot

Band gap energy of TiO$_2$ nanoparticle obtained from the Tauc plot is 3.05 eV.

3.3.3 PHOTOLUMINESCENCE SPECTRUM OF SYNTHESIZED TiO_2 NANOPARTICLES

A green band at about 515 nm and a red band at 600 nm may be seen in the photoluminescence of anatase TiO_2 films. The green band closely resembles the oxygen vacancies on the surface of the (101) oriented anatase crystal, while the red band displays a significant connection with defects of the under-coordinated Ti^{3+} ions. The normal emission of the anatase nanoparticles is governed by the PL which arises from the recombination of trapped electrons with holes in the valence band, resulting in a broad spectrum with a peak in the red. Higher energy emission at 600 nm is due to the recombination of the trapped holes and mobile electrons.
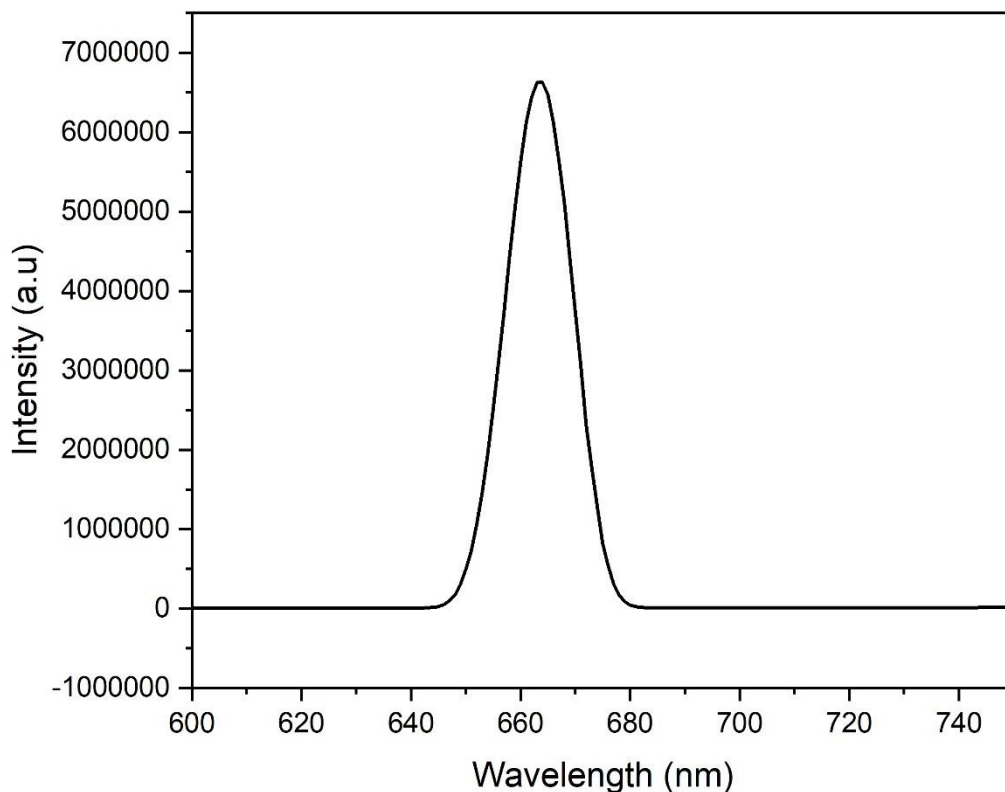

Figure (3.6) : Photoluminescence spectrum of TiO_2

3.4 PHOTO CATALYTIC STUDIES

3.4.1 DEGRADATION OF METHYLENE BLUE WITH TiO2 NANOPARTICLES

Degradation of methylene blue dye was studied by exposing 50 ml of 10 ppm of dye solution to sun light after adding 50 mg of TiO2 nano catalyst. Sample is collected at different intervals of time and UV-visible absorption spectrum is taken.

The percentage of degradation of the dye can be calculated by the equation A_t

$$\% \text{ of degradation} = \frac{A_0 - A_t}{A_0} \text{ X } 100 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(3.1)$$

Where ,

A0 – Absorbance of initial methylene blue
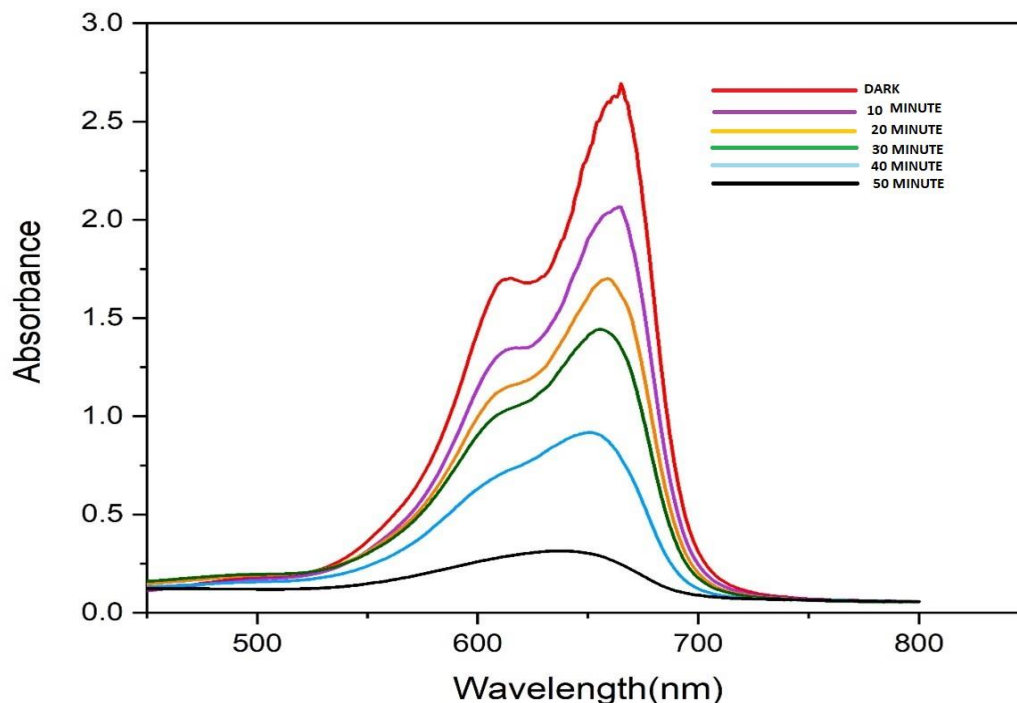
At – Absorbance after illumination at time

Figure (3.7) : Absorption spectra of Methylene Blue dye

39

The table below shows the % of degradation of MB dye as time changes

PEAK	TIME	A_t	A_0	% OF DEGRADATION
663 nm	10 min	2.0483	2.6434	22.51
	20 min	1.6885		36.12
	30 min	1.4388		45.57
	40 min	0.9159		65.35
	58 min	0.2996		88.66

Table (3.1) : Percentage of degradation of methylene blue dye
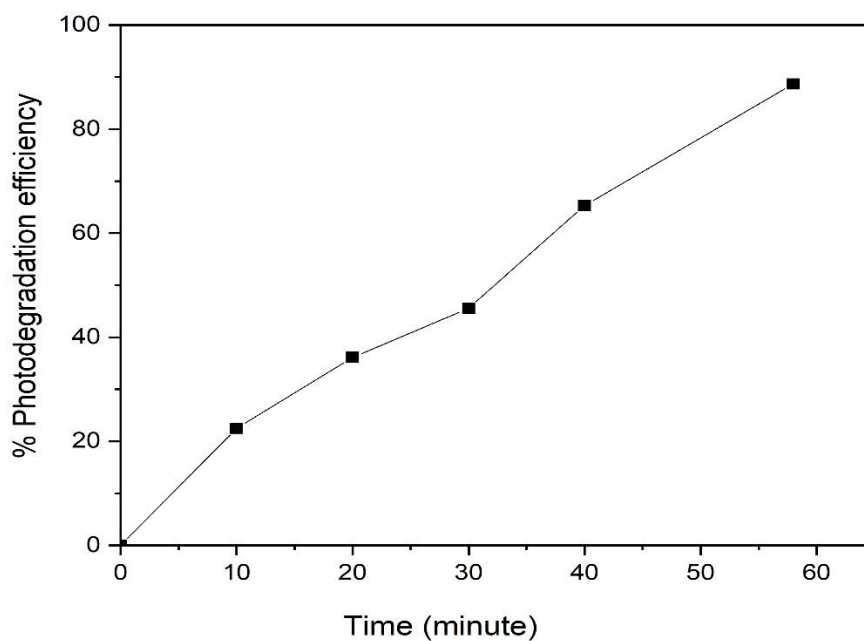

Figure (3.8) : % photocatalytic degradation curve of Methylene Blue dye

The data leads to an inference that it takes about 58 min for the degradation of 88.66 % of methylene blue dye.

3.4.2 DEGRADATION OF RHODAMINE B WITH TiO$_2$ NANOPARTICLES

Degradation of Rhodamine B dye was studied by adding 50 mg of TiO$_2$ nanopowder at different time. Rhodamine B dye shows absorbance peak at 552.91 nm and the corresponding absorbance is 1.704.

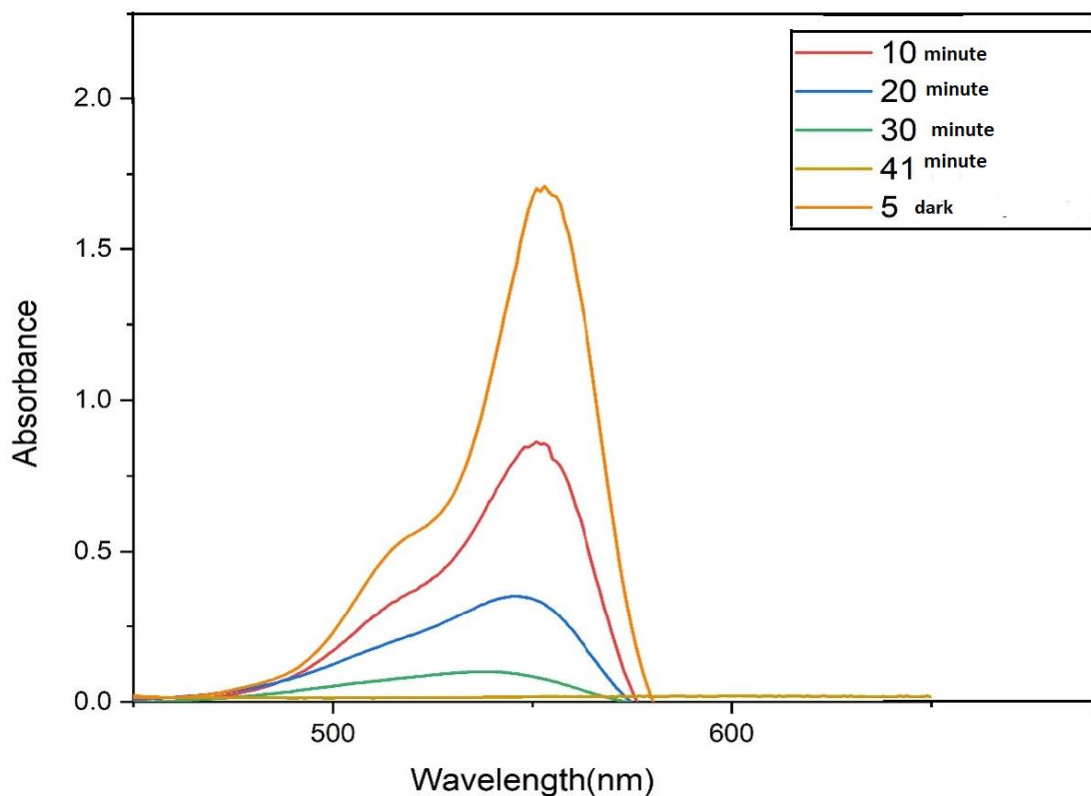**Figure (3.9) :** Absorption spectra of Rhodamine B dye

The table below shows the % of degradation of MB dye as time changes

PEAK	TIME	A$_t$	A$_0$	% OF DEGRADATION
552.9183	10 min	0.8624	1.704	49.38
	20 min	0.3497		79.47
	30 min	0.0979		94.25

Table (3.2) : Percentage of degradation of Rhodamine B dye
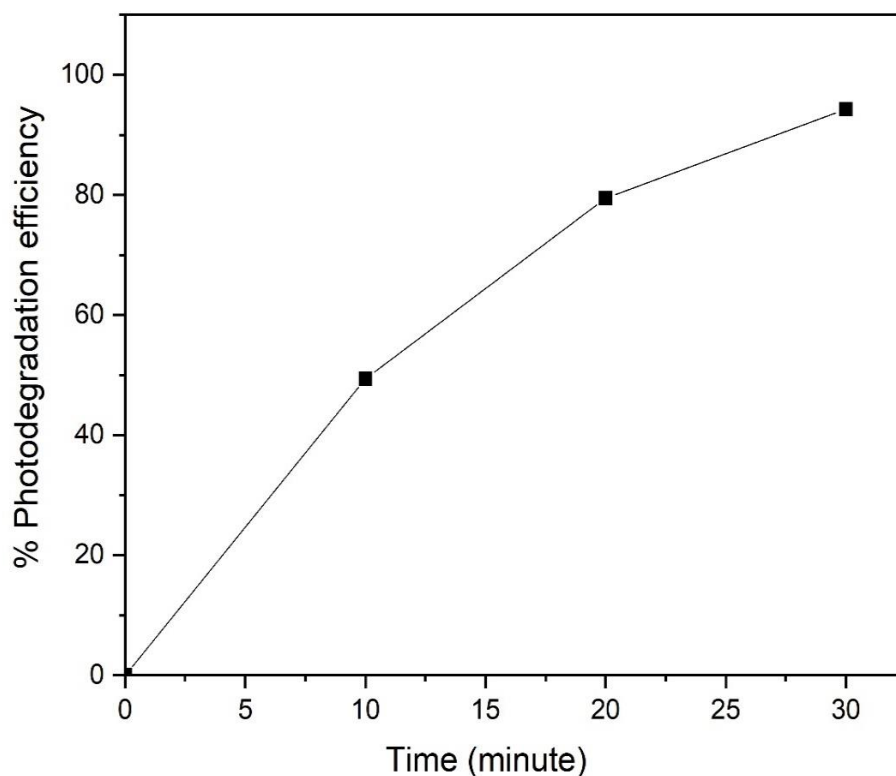
Figure (3.10) : % Photocatalytic degradation curve of Methylene Blue dye

From the data, we may conclude that TiO_2 nanoparticle prepared can cause Rhodamine B dye degradation up to 94% within 30 min.

3.4.3 DEGRADATION OF MIXED SOLUTION OF DYES WITH TiO2 NANOPARTICLES

5 ml of Methylene Blue and 5ml of Rhodamine B dye is taken from the stock solution, and mixed with 40 ml of deionized water to get 50 ml of 10 ppm of mixed dye solution. Later the photodegradation of the mixed solution of these two is also studied.
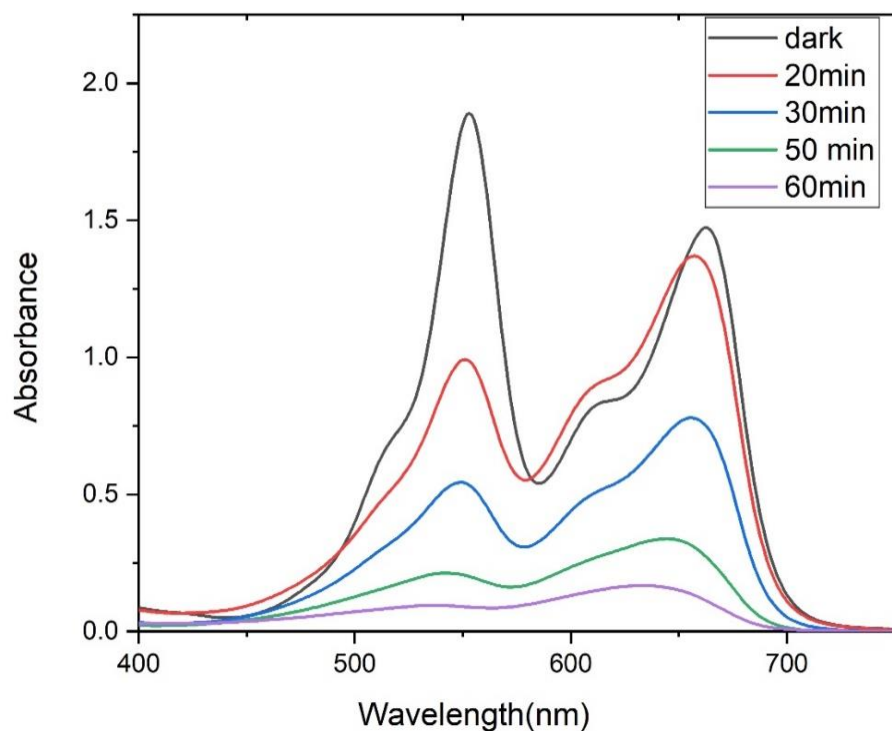
Figure (3.11) : Absorption spectra of mixed dye solution

The table below shows the % of degradation of mixed dye as time changes.

PEAK	TIME	A_t	A_0	% OF DEGRADATION
552.599 nm	20 min	0.984	1.892	47.99
	30 min	0.548		71.035
	50 min	0.213		88.74
	60 min	0.101		94.66
663.679 nm	20 min	1.351	1.4503	6.8
	30 min	0.785		45.86
	50 min	0.337		76.75
	60 min	0.169		88.34

Table (3.3) : Percentage of degradation of Rhodamine B dye

Figure (3.12) : % Photocatalytic degradation curve of Methylene Blue and Rhodamine B dye in the mixed solution.

From the data we may conclude that, TiO_2 nanaocatalyst may cause 94% degradation of Rhodamine B dye and 88% degradation of Methylene blue dye within 60 min in the mixed solution.
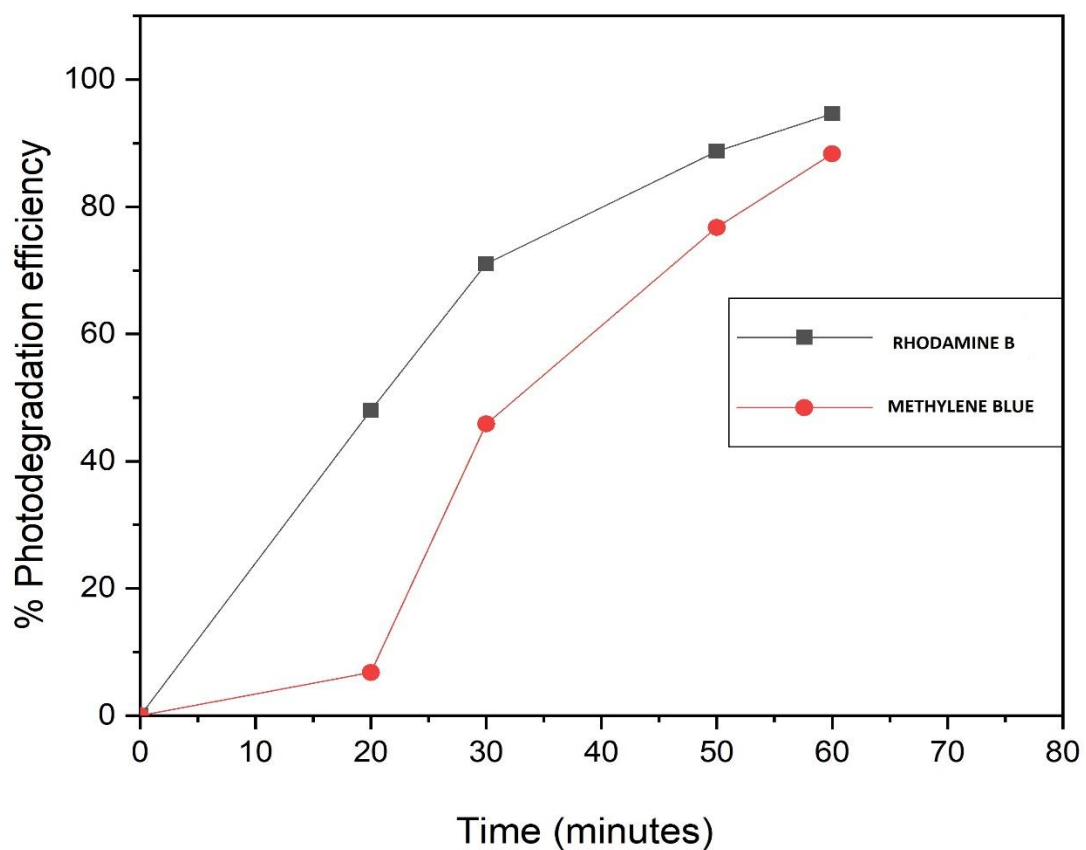
CHAPTER 4

CONCLUSION AND FUTURE SCOPE

Addressing environmental pollution has become a crucial problem around the world. The textile industry's effluents are a significant source of water contamination. In this regard, the necessity to remediate wastewater from organic pollutants is becoming more and more critical

Various industries like paint, leather, cosmetics, textiles are great source of synthetic dyes. Due to their intricate structure, they are unable to degrade easily. A good deal of synthetic dyes are very poisonous, mutagenic, and carcinogenic, which poses risks to both the environment and people. In addition to making the environment more unpleasant, dyes on the surface and subsurface of water have the potential to be a cause of water-borne illnesses, such as mucous membrane dermatitis, perforation of the nasal septum, and severe respiratory tract irritation. The two dyes we used for this project have a variety of harmful impacts. methylene blue which is , a thiazine cationic dye has adverse health effects, which include breathing difficulties, vomiting, eye burns, diarrhoea and Rhodamine B (Rh B) which is another dye that is frequently used for dying purposes.

Traditional methods only transfer this poisonous pollutants to other media. It is essential to eliminate of these toxins employing effective and ecologically acceptable approaches. photodegradation is emerging and promising method for treating waste water because it can decolorize and break down dye molecules into non toxic inorganic species like CO_2 and H_2O. Photocatalyst, a semiconductor substance activated by adsorbing photons, is used in the process to speed up the reaction without being consumed. TiO_2 is one of the most promising catalysts for the elimination of harmful organic contaminants, due to its chemical inertness, cost-effectiveness, superior durability, non-toxicity, and environmental friendliness.

The thesis has been divided into four chapters including a conclusion. The first chapter contains an introduction regarding the research and the second chapter elaborates on details of the experimental setup, materials used, and the methods adopted. The result and discussion are included in the third chapter, while the conclusion is found in the fourth chapter.

A safe and economical synthesis process, the hydrothermal approach has been used to successfully produce TiO_2 nanoparticles. X-ray diffraction (XRD) and FTIR have verified the TiO_2 nanoparticles' production. The peaks in the synthesised TiO_2's X-ray diffraction spectrum are in perfect in accordance with the reference pattern (JCPDS21-1272) for TiO_2 in the anatase phase. The synthesised TiO_2 was found to have an average particle size of 9.269 nm.The samples' morphology was described, and the SEM examination verified that the particles were spherical in shape. The sample's PL and UV-Visible spectrum have been taken for optical examination. The band gap energy of TiO_2 is determined to be 3.05 eV from the UV-visible absorption spectra. It is clear from this that TiO_2 is UV active.

The synthesized TiO_2 nanoparticle showed photocatalytic activity under solar irradiation. It showed over 88.66 % degradation of methylene blue in 58 min. Additionally the nanoparticle also caused 94.25 % degradation of Rhodamine B dye within 30 min. The dye pollution in water bodies may be due to presence of many dyes not one, hence the photodegradation of mixture of two dyes were also studied . TiO_2 nanaocatalyst caused 94% degradation of Rhodamine B dye and 88% degradation of Methylene blue dye within 60 min in the mixed solution. Thus we may conclude that the photocatalytic activity of the synthesized nanoparticle is excellent for degrading Rhodamine B and Methylene Blue dyes.

FUTURE SCOPE

For efficient photocatalytic performance the nanocatalyst should be active under visible light. Even though TiO2 is a good photocatalyst , it is active under UV region. this is because of its large band gap. If we can reduce this band gap then TiO2 can be made active under visible light. One of the effective method for this is metallic doping. By selecting suitable metal for doping we can make TiO2 nano catalyst more effective.

The photocatalytic performance can be increased in many ways . Once such way is to increase the intensity of light source. The usage of xenon lamp having high intensity is efficient to increase the percentage of degradation. By optimising the factors like effect of time, effect of temperature, nature of pollutant and nature of light source the photocatalyst property can be better commercialized

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