SYNTHESIS AND CHARACTERISATION OF TITANIUM DIOXIDE NANOPARTICLES AND ITS PHOTOCATALYTIC STUDY

DISSERTATION SUBMITTED TO THE UNIVERSITY OF KERALA IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF THE DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY

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CERTIFICATE

This is to certify that the dissertation bound here with is an authentic record of the project work entitled **"Synthesis and characterisation of TiO2 and its photocatalytic study"** carried out by **Fathima Shajahan, Jesna Jose, Parvathi Harikumar G and Sreelekshmi S** under my supervision in partial fulfilment of the requirement for the award of the Degree of Bachelor of Science of University of Kerala and further that no part therefore has been presented before for any other degree.

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DECLARATION

I hereby declare that the dissertation entitled **“Synthesis and Characterisation of TiO2 Nanoparticles and Its photocatalytic Study”** is the original project work carried out by me under the supervision of Dr Priya Mary Abraham, Assistant Professor ,Department of Chemistry, Bishop Moore College, Mavelikara, and it has not previously formed the basis of award of another degree,diploma, or other title.

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ABSTRACT

Presence of water on earth distinguishes it from other planets. But availability of fresh water is decreasing day by day due to man's unscientific intervention. In this modern era, nanotechnology plays a major role in water treatment. The photocatalytic activity of TiO_2 has attracted a great interest in the removal of dye molecules from water. In this work TiO_2 nanoparticles were synthesized by sonochemical method, and its properties were studied using the characterization techniques such as XRD, SEM etc. The XRD spectrum of TiO2 confirms the formation of Rutile nanoparticles. The elemental compositions in the sample were identified using EDAX. The photocatalytic activity of the synthesized TiO_2 nanoparticles were investigated by observing degradation of Methylene blue under UV light. The results show that degradation of Methylene blue occurs under visible light.

CONTENTS

CHAPTER 1

1.INTRODUCTION

A nano particle is a little particle that ranges between 1 to 100 nanometer in size. Undetectable by the human eye, nanoparticles can show altogether distinctive physical and chemical properties to their bigger material counterparts. The material properties alter as their measure approaches the atomic scale. Typically due to the surface area to volume ratio increasing, resulting in the material's surface particles dominating the material performance. Owing to their exceptionally little size, nano particles have an awfully huge surface area to volume ratio when compared to bulk material, such as powders, plate and sheet. This feature enables nano particles to possess unexpected optical, physical and chemical properties, as they are little sufficient to restrict their electrons and create quantum effects.

1.1 Nanoscience and nanotechnology.

Nanoscience is the theoretic modelling of nanoparticles. In nanoscience we study the information of nanoparticles at nanoscales, analyzes their properties and behaviour. It is a cross disciplinary, meaning scientist from a range of fields including chemistry, physics, biology medicine,computing materials . Science and engineering are studying and understanding it to revolutionize a diverse range of fields from health to manufacturing.

Nanotechnology is the science and engineering of modelling and manipulation of matter on an atomic, molecular and supramolecular state.The different types of nanotechnology are classified according to how they proceed and the medium in which they work.

Two main approaches are used to assemble themselves chemically by principles of molecular recognition.Here a simple particle through a mounting or self assembly process becomes a bigger component than the one begun with.
In the "top-down" approach or descending , nano objects are constructed from larger entities without atomic- level control. Mechanisms and the structures are scale down at the nanometer scale — from one to 100 nanometers in measure–. The impetus for nanotechnology comes from a renewed interest in colloidal science,coupled with analytical tools such as Atomic Force Microscope (AFM) and Scanning Tunnel Microscope (STM). Examples of nanotechnology in modern use are the manufacture of polymers based on molecular structure and to produce a wide variety of useful chemicals such as pharmaceuticals or commercial polymers. There are few important applications of nano technology such as aviation and space, chemical industry, optics, solar hydrogen , fuel cell, batteries, sensors, automobile designing, thermoelectric gadgets. It is currently being utilised to design specific immune responses for prophylactic and therapeutic impacts.In the future,the use of nanoparticles that having interesting immunological properties decided by their shape ,charge, porosity and hydrophobicity will empower analysts to 'customise' immune responses in unused and unexpected ways.

1.2 TiO2 and its properties

Titanium dioxide is titanium oxide with the formula TiO2. It is an odourless,white powder which is insoluble in water and alcohol but soluble in concentrated acids, used as a pigment under the names titanium white, pigment white 6 (PW6), typically extracted from ilmenite, rutile and anatase. Due to its unique physical and chemical characteristics combined with earth abundance and non toxicity as well as high thermal and chemical stability, make it one of the most employed materials in pigments

TiO2 nanoparticles are also called nano crystalline or ultrafine TiO2 ,these are particles of TiO2 with diameters less than 100 nm . It is alkaline, divalent material which is chemically stable, non toxic and bio compatible material. Nano TiO2 is a strong oxidising agent with a large surface area and, hence , high photo catalytic activities. With low production cost and high dielectric constant, it is inexpensive material.

Table. 1

Molecular formula	TiO2
Molar mass	79.866 g/ mol
Appearance	White solid
Odour	Odour less
Density	4.23 g/cm3 (rutile) 3.78 g/cm3 (anatase)
Melting point	1,843 °C (3,349 °F; 2,116 K)
Boiling point	2,972 °C (5,382 °F; 3,245 K
Solubility in water	Insoluble

TiO2 are photocatalysts, they have the capability to use energy in light to catalyse reactions with other molecules at reduced temperature. Although other photocatalytic materials are available, researchers have found that TiO2 provides best performance in sunlight.

Applications :There are many applications of TiO2 nanoparticles. The application of TiO2 nanoparticles as photocatalysts is extensively used for the removal of micropollutants in water treatment and as an alternative to the traditional disinfection

techniques. TiO2 photocatalysis is a more efficient method for the degradation of a lot of pharmaceutical micropollutants as compared to photolysis.

1.3 Role of nanotechnology in Photocatalysts

TiO2- based photocatalysts utilized for wastewater treatment contain two major factors . The first one is the separation and reuse of catalysts. The catalyst should be separated efficiently and reused for successive cycles. Various systems have been developed for wastewater treatment using TiO2 catalysts such as immobilised catalysts systems, membrane separation and gravitational separation systems.

The second major factor is the utilisation of solar irradiation for the photoactivation of catalysts. They improve the energy efficiency and consequently the economic viability of the process.

The use of TiO2 which is dispersed directly into wastewater is efficient due to the large catalyst surface area. It increases the potential of a photocatalytic reaction. Meanwhile, it has limitations such as the catalysts shifting process after the treatment. The post treatment makes capital costs rise.

Photocatalytic process has been widely investigated as a promising technology for the efficient wastewater treatment. Since it is an environmentally friendly process and has the ability to destroy pollutants without the exertion of potentially hazardous oxidants (eg :ozone, chlorine). This process can be completely decomposed into CO2 and H2O.

Process: Water pollution is a global environmental problem, photocatalysis is a technique to solve this problem. Under the UV light the TiO2 nanoparticles produce free radicals in aqueous solution which help degrade organic pollutants in water.

One way to use TiO2 is to coat TiO2 nanoparticles from precursors onto a substrate like glaze, where the catalyst can be easily recycled and adapted to different reactors. There are various coating methods based on different precursors and how the coating layer is formed. TiO2 occulted by different methods makes different properties like mass loading morphology and crystallinity that affect photocatalytic performances.

An Ideal coating has high efficiency and stability. Dip coating has better efficacy and sol gel has better stability.

1.4 Literature Review

Synthesis.

Malekshahi Byranvand et al in the review of article summarises the synthesis pathways, morphology, as well as crystallization of nanostructured TiO2. The different synthetic methods mentioned in the articles for the synthesis of TiO2nanostructures are hydrothermal method, solvothermal method, sol-gel method, direct oxidation method, chemical vapour deposition, electrodeposition, sonochemical method, and microwave method. The article concluded that the continuing progresses in the synthesis and modifications of nanostructured TiO have brought new properties and new applications with improved performance.

Photocatalytic reduction.

In the preparation and study of photocatalytic activity of TiO2nanocrystals with internal pores by Lu Ren et al, Anatase TiO2 nanocrystals with internal pores are prepared by a novel facile microwave-assisted hydrolysis of a mixture of TiOCl2 and HF aqueous solution followed by calcinations at 4000c. XRD analysis reveals that the crystal size was determined by the scherr formula is 8.8nm. TEM images show that the particle size is 6.6-38.7nm. This study concludes that the anatase TiO2nanocrystals with internal pores exhibit higher photocatalytic activity than the TiO2 solid nanocrystals.

Effect of Sn dopant on the photocatalytic activity of TiO2 nanoparticles was investigated by jing liqiang et al by means of PL, SPS, and FIPS methods. Sn-doped nanoparticles were prepared by sol-gel method and the sample cavity was evaluated by photocatalytic oxidation reactions of phenol solution. The effect of Sn dopant on the photo induced charge property and photocatalytic activity of TiO2 nanoparticles were mainly investigated by means of PL, SPS and EFISPS methods, altogether with their relationships. The results show that doping an appropriate amount of Sn can improve the photocatalytic activity of TiO2 nanoparticles by thermal treatment at appropriate calcinations temperature, which is explained from two main aspects. One is that the separation rate of photo induced charge carriers of TiO2 is enhanced after doping Sn, which is proved by the PL and SPS measurements. Another is that the ability of surface states to bind photo induced carriers to form excitons increases, which is proved by the EFISPS measurements. The two aspects are responsible for the increase in the photocatalytic activity.

Photocatalytic activity of TiO2 nanoparticles is enhanced using SnS2/RGO. TiO2/SnS2/RGO nanocomposites were prepared by liquid exfoliation and solvothermal method. Weiping zhang et al reported that TiO2/SnS2/RGO nanocomposite showed high photocatalytic activity for the degradation of Rhodamine

B under visible light irradiation. The photoactivity of TiO2 nanoparticles is enhanced by the contribution of positive synergic effect between layered SnS2 and RGO components through reducing the recombination of photogenerated electron/hole pairs, enhancing the rate of electron transfer and providing more reaction active sites for the degradation of dye molecules. The coupling formation of TiO2, SnS2, RGO at the interface of the composite photocatalyst was investigated by density functional theory. The calculation results showed that the solid-solid contact interface between TiO2 and SnS2 as well as TiO2 and RGO are connected by the chemical bonds, not the vander waals interactions. This study demonstrates that the development of noble-metal-free titania-based composites containing an inexpensive and environmentally benign SnS2/RGO hybrid co-catalyst is feasible and has the great potential in detoxification of harmful pollutants in wastewaters.

Chengzhi Luo et al introduced a new combined pulse electrodeposition with thermal oxidation method to obtain a porous micro-nano-structure NiO/ZnO heterostructural composite. The experimental results reveal that this composite had excellent photocatalytic performance, 2.5 times higher than that of pure ZnO. The reason was that the NiO/ZnO hetero-junction improved the separation rate of photogenerated electrons and holes, and therefore enhanced photocatalytic efficiency.

1.5 Motivation

Science and technology always move forward and newer, improved investigations replace the older technologies. In the twenty-first century nanotechnology is going to have a decisive role in almost all technologies. Nanotechnology has a wider range of applications. Nanosensors and nanorobots are used to monitor climate changes. Applications of nanoparticles in medicine are playing a major role in providing “good health and well being”. The environmental applications of nanoscience include waste water treatment.

Water is an essential part of human life and the availability of pure water decreases day to day. Nowadays the world is suffering from a major problem of drinking water. There are several organic and inorganic materials, microorganisms and other toxins added into water during rain, flowing water etc. To overcome this emerging problem Nanotechnology provide a potential offer to purify water with a low expense, high working efficiency in removing pollutants and reusable ability unique properties of Nanomaterials such as nano size, large surface area, highly reactive, strong solution mobility, strong mechanical property, porosity characters, hydrophilicity, dispersibility and hydrophobicity, enables it to treat wastewater. More developments occurred in nanomaterials such as nanophotocatalysts, nanomotors, and nanomembrane treatment of contaminated water.

There are many materials that are found to show good photocatalytic activity in the presence of ultraviolet-visible light. Titanium dioxide is the most widely used photocatalyst in many environmental and energy applications due to its efficient Photoactivity, high stability, low cost, and safety to the environment and humans. This photocatalytic activity is used in the water treatment process.

1.6 Objective

The main objectives of this project are to synthesize titanium dioxide nano-particles by sonochemical method. Then to study the structural and optical morphological properties using characterization techniques such as X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), UV-Vis spectroscopy and Energy dispersive X-rayAnalysis(EDAX).
As we know water pollution has become a serious issue. The photocatalytic reaction of TiO_2 has the potential for treating waste water. This work aims to study the photocatalytic activity of TiO_2 and the TiO_2 composite in different ratios.

CHAPTER 2

2. SYNTHESIS AND CHARACTERISATION

2.1 Synthesis

2.1.1 Sonochemical Method

The sonochemical method is one of the recently discovered techniques that offer a versatile way to obtain nanostructures for different applications. This represents the use of high intensity ultrasounds, which induces synthesis conditions distinct from other conventional methods such as hydrothermal synthesis, spray pyrolysis method and wet chemical method Ultrasound has been very useful in the synthesis of a wide range of nanostructured materials, including high surface area transition metals, alloys, carbides, oxides, and colloids. These specific conditions are generated during acoustic cavitation,which produce high temperature and high pressures in the centre of the bubbles formed in the solution. The bubbles are obtained when the solution is exposed to high intensity ultrasound. Using this method, different metal oxide nanoparticles have been developed. Among the metal oxides, the synthesis and applications of the transition metal oxides, and in particular TiO_2 ,ZnO and Fe_2O_3 , have attracted the interest of
the research.

2.1.2 Advantages

The sonochemical method has been used extensively to generate novel materials with unusual properties, because the method causes the formation of particles of a much smaller size and higher surface area than these reported by other methods.

Besides, it has the following advantages and also has disadvantages too.

Advantages:

⋆Improves reaction rate.
⋆Involves high energies and pressures in a short time.
⋆No additives needed.
⋆Reduced number of reaction steps.

Disadvantages:

⋆Extension of problems.

⋆Inefficient energy.
⋆Low yield.

2.2 Characterisation Techniques.

2.2.1 X-ray Powder Diffraction Method.

X- ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground homogenized and average bulk composition is determined.

The phenomenon of X-ray diffraction by crystals results from a scattering process, in which X-ray are scattered by the electrons of the atoms without changing the wavelength. A diffracted beam is produced by such scattering only when certain geometrical conditions are satisfied, which may be expressed in either of the 2 forms, the Bragg's law or the Laue equations. The resultant diffraction patterns of the crystal, comprising both the position and intensity of the diffracted beam lead immediately to provide knowledge of the size, shape and orientation of the unit cell.

2.2.1.1 Fundamental principles of X-ray powder diffraction (XRD)

Max von laue, in 1912, discovered that crystalline substances act as three dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentration, and directed toward the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg’s Law.

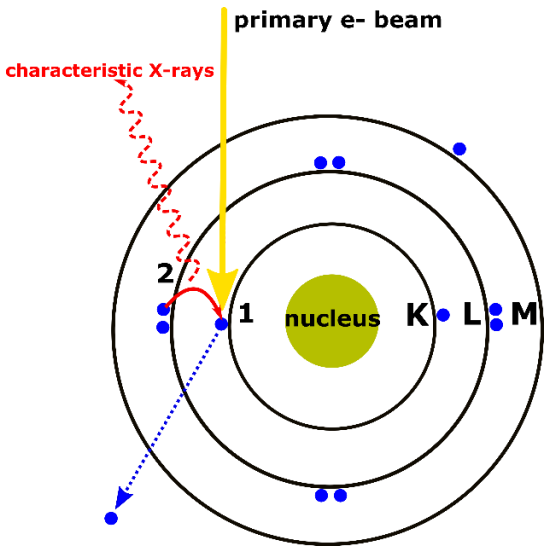
2.2.1.2 Generation of X-rays

X-rays are electromagnetic radiation of wavelength~1A◦.They occur in that part of the electromagnetic spectrum between UV-rays and gamma rays that are produced when high energy charged particles collide with matter. The X-rays that are used in almost all diffraction experiments are produced by a process that leads to monochromatic X-rays. Bombarding a metal target with a beam of electrons emitted from a heated filament normally produces X-rays for diffraction experiments. The incident electron beam will ionize electrons from the K shell of the target atom. An electron in the outer orbital immediately drops down to occupy the vacant 1s level and energy released in the transition appears as X-rays. This will give rise to intense

k_α and k_β lines. K_α transition occurs much more frequently than the k_β transition and it is more intense. Therefore k_α radiation is used in diffraction experiments.

The transition energies have fixed values and so a spectrum of characteristic X-rays results. For copper, the 2p→1s transition, called k_α, has a wavelength of 1.5418 A^0 and 3p→1s transition, k_β, 1.3922 A^0. The k_α transition occurs much more frequently than the k_β transition and it is more intense k_α radiation which results in diffraction experiments.

Crystals can act as diffraction grating to X-rays. When a crystal diffracts X-rays, it is the atoms or ions, which act as secondary point source and scatter the X-rays.



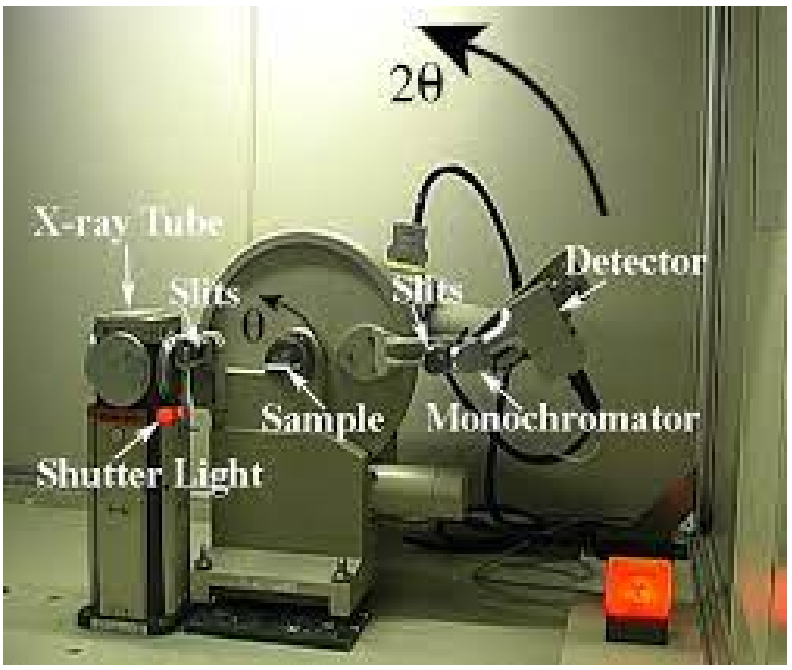
generation of x-rays

2.2.1.3. X-ray Diffractometer

X-ray Diffractometer consists of three basic elements; an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons towards a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic x-ray spectra are produced. These spectra consists of several components, the most common being Kα and Kβ. Kα consists, in part, of Kα1 and Kα2. Kα1 has a slightly shorter wavelength and twice the intensity as Kα2. The specific wavelengths are characteristics of the target material (Cu, Fe, Mo, and Cr). Filtering, by foils or crystal monochromators, is required to produce monochromatic X-rays needed for diffraction. Kα1 and Kα2 are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single crystal diffraction, with Cu Kα radiation = 1.5418$\dot{A}$.

These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded.

When the geometry of the incident X-rays impinging the sample the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor



schematic diagram of X-ray Diffractometer

The d-spacing of each peak is then obtained by solution of the Bragg equation for the appropriate value of ⍉. Once all d spacing has been determined, automated search/match routines compare the d-values of the unknown to those of known materials. Because each material has a unique set of d-spacing, matching these d-spacing provides an identification of the unknown sample. Files of d-spacing for several thousands of inorganic compounds are available from the International Centre for Diffraction Data (ICDD) as the Powder Diffraction File (PDF).

Applications

Characterization of crystalline materials
Identification of fine grained minerals such as clays and mixed layer clays that are difficult to determine optically.
Determination of unit cell dimensions
Measurement of sample purity

With specialized techniques, XRD can be used to:

Determine crystal structure using Rietveld refinement
Determine of modal amounts of minerals (quantitative analysis)
Characterize thin films samples by:

- Determining lattice mismatch between film and substrate and to inferring stress and strain
- Determining dislocation density and quality of the film by rocking curve measurements
- Measuring superlattices in multilayered epitaxial structures
- Determining the thickness, roughness and density of the film using glancing incidence X-ray reflectivity measurements

Make textural measurements such as the orientation of grains, in a polycrystalline sample

Strengths

- Powerful and rapid (<20 min) technique for identification of an unknown mineral
- In most cases, it provides an unambiguous mineral determination
- Minimal sample preparation is required
- XRD units are widely available
- Data interpretation is relatively straight forward

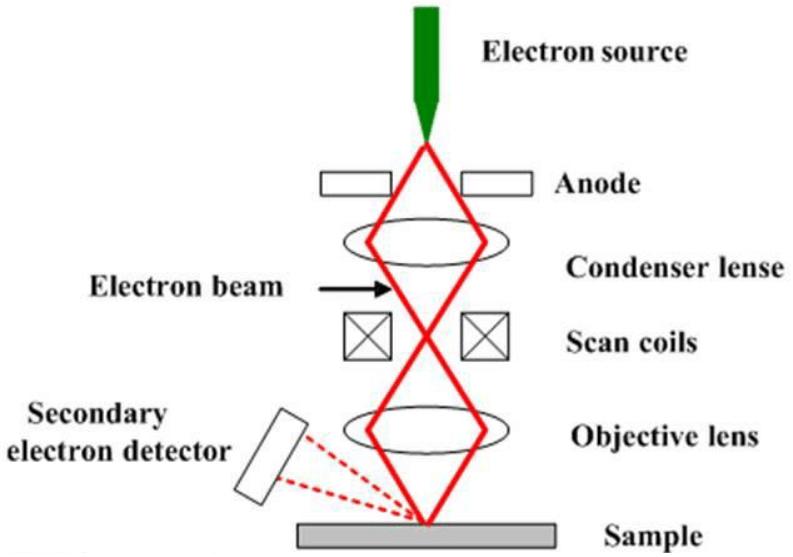
Limitations

- Homogenous and single phase material is best for identification of an unknown
- Must have access to a standard reference file of inorganic compounds (d-spacing, hkls)
- Requires tenths of a gram of material which must be ground into a powder
- For mixed materials, detection limit is ~2% of sample
- For unit cell determinations, indexing of patterns for non-isometric crystal systems is complicated
- Peak overlay may occur and worsens for high angle ‘reflections’

2.2.2 Scanning Electron Microscope (SEM)

An electron microscope is a type which uses a particle beam of electrons to illuminate a specimen and create a highly-magnified image. Electron microscopes have much greater resolving power than optical microscopes are limited to magnifications of several thousand times. Both electron and light microscopes can obtain much higher magnifications of up to 2 million times, while the best optical microscopes are limited to magnifications of several thousand times. Both electron and light microscopes have resolution limitations, imposed by the wavelength of the radiation they use. The greater resolution and magnification of the electron microscope is because the wavelength of an electron, that is, de Broglie wavelength, is much smaller than that of a phonon of visible light.

Figure shows the schematic diagram of a typical scanning electron microscope. The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms and hence makeup the sample producing signals that contains information about the sample’s surface topography, composition and other properties such as electrical conductivity



Schematic diagram of scanning electron microscope

SEM is a versatile advanced instrument which is largely employed to observe the surface phenomenon of the materials. The sample is shot in a SEM using high energy electrons and the out-coming electrons / X-rays are analyzed. These out-coming electrons / X-rays give the information about topography, morphology, composition, orientation of grains, crystallographic information, etc. of a material. The type of elements and compounds the sample consists of and their relative ratios as well as the arrangement of atoms in the single crystal particles and their degree of order can also be provided. Thus, SEM is a multipurpose instrument which is able to examine and analyze the material with high resolution.

The SEM instrument is based on the principle that the primary electrons released from the source provide energy to the atomic electrons of the specimen which can then release as the secondary electrons (SEs) and an image can be formed by collecting these secondary electrons at each points of the specimen, the basic requirement for SEM to operate under a vacuum to avoid interactions of electrons with gas molecules in order to gain high resolution. In addition, the primary electrons produced and emitted from the electron gun are accelerated by heating or applying high energy in the range 1-40 KeV. These emitted electrons are focused and confined to a monochromatic beam by magnetic field lenses and metal slits within a vacuumed column. The confined primary electrons are scanned across the sample surface by scanning coils in a raster pattern. Once the primary electron beam hits the sample surface, it will interact with the near-surface area of the sample to a certain depth I many different ways. The impinging electrons accelerated towards the specimens have substantial quantities of kinetic energy, which lose their energy inside the sample by generating several signals from the interactions of electrons with the specimen. It scattered both elastically and in- elastically in the sample.

Secondary electrons (SEs) are produced by two mechanisms and can be further differentiated as SE1 and SE2:

SE1 are those secondary electrons which are produced by the primary electron beam. Once the primary electrons enter the surface of the materials, some of the energy is transferred to the specimen electrons and gives a high-resolution signal limited by electron beam diameter.

SE2 are those secondary electrons which are produced by those electrons that first undergo several in-elastic scatterings and then come to the surface. SE2generates from surface area greater than the incoming electron's spot

2.2.2.1 Instrumentation:

SEM is an electronic and optical system which consists of the following components:

1. Electron gun
2. Vacuum
3. Column: condenser lens, scanning coil, objective lens, stigmator, sample, holder and detector

In principle, first the gun emits the electron beam which is held within a vacuum which follows a vertical travel path through electromagnetic fields and lenses. The electron beam is focused by an objective lens on the specimen surface where the focused beam is rastered across the surface of the material with the help of deflector coils, which is controlled by the scan generator. Magnification controls the size of the rastering pattern. The changes in magnification change the size of the rastered area on the sample. When the electron beam hits the material, this strike produces a huge number of signals, that is, electrons and X-rays are emitted from the specimen. These signals are detected by the detector and converted into signals where images are produced from the signals. The signal that originates from electron-sample interaction gives detailed information about the material such as external morphology, chemical composition and crystalline structure and orientation of materials making up the sample. The SEM has several advantages because it has a big profundity of field which permits to focus more specimens at one time. SEM is that it provides the researcher much more control in the degree of magnification as lens replaced by electromagnets.

2.2.3 Energy Density Dispersive X-ray Analysis

It is a technique which is widely employed in elemental or sector. The working of EDAX is based on electron beam excitation same as in SEM.

2.2.3.1 Characteristic X-ray generation.

When a sample is irradiated with a highly energetic beam of electrons, the characteristic X-ray is generated. When irradiated the electron is excited from the

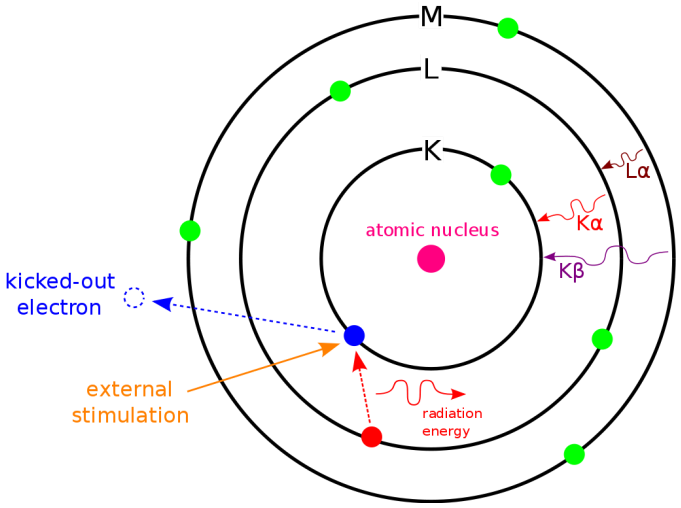
inner shell of the parent atom. The vacant place is occupied by the high energy electron from the outer shell and the energy difference between the two shells is emitted as an X-ray. The amount of energy liberated in this electron transfer depends upon from which shell it is transferring to which shell. The emitted X-ray is obtained by an energy dispersive spectrometer.

These X-rays are known as characteristic X-ray, because their energies and ⟍ are specific to the element from which it is emitted. Different types of X-rays are emitted when incident electrons strike the atomic nucleus, these are known as continuous X-rays, white X-rays or background X-rays.

2.2.3.2 Principle of EDAX

EDAX utilizes the characteristic X-ray emitted from the sample during the bombardment by the beam of electrons to understand the elements present in the specified area of the sample. The energy of the emitted X-rays is unique to each element which produced it. Therefore, the chemical composition of the sample can be identified by measuring the energy of the X-rays. The EDAX spectrum is obtained by plotting the energy of the emitted X-ray along the X-axis and the intensity along the Y-axis. From the graph, the energy corresponding to various peaks identifies the element and its intensity provides information about the percentage of element in the specified area. The device software automatically compares the energy of each characteristic X-rays and tags the corresponding peaks. EDAX provides information regarding the shells from which or to which the emission of characteristic X-rays takes place. The emission line is normally labelled

as Kα, Kβ, and Lα etc. the chemical contaminants present in the sample can also be identified using this technique.



schematic representation of EDAX

Components of EDAX

1. Electron beam source
2. X-ray detector
3. Pulse processor
4. Analyzer

Uses

Both quantitative and qualitative analysis is possible with EDAX. Qualitative analysis is to identify whatever elements present in a sample and there are 3 methods of analysis.

1. Point analysis- Spectrum is analyze from a line
2. Line analysis- Spectrum is analyze from a specified area

Quantitative analysis

As characteristic X-ray intensities are properties to the particular elements, concentration quantitative analysis can be performed. The concentration of unknown sample can be obtained by matching the intensities of characteristic X-ray of standard sample.

2.2.4 Photocatalysis

Photocatalysis is the most authentic technique for dye degradation. The photocatalytic activities of TiO_2 nanoparticles, TiO_2 composites, were investigated by observing the degradation of Methylene Blue (MB) under UV light. The absorbance of TiO_2 nanoparticles and the nanocomposites were determined using a colorimeter.

2.2.4.1 Colorimeter

A colorimeter is a light sensitive device used for measuring the transmittance and absorbance of light passing through a liquid sample. The three main components of a colorimeter are a light source, a cuvette containing the sample solution and a photocell for detecting the light passed through the solution. The output from a colorimeter may be displayed by an analog or digital metre in terms of transmittance or absorbance.

Working principle

The colorimeter is based on Beer-Lambert's law, according to which the absorption of light transmitted through the medium is directly proportional to the medium concentration. In a colorimeter, a beam of light with a specific wavelength is passed through a solution via a series of lenses, which navigate the colored light to the measuring device. This analyzes the colour compared to an existing standard. The absorption rate increases with increase in concentration. This can be identified by measuring the difference between the amount of light at its origin and that after passing the solution.

Applications

- Colorimeters are widely used to monitor the growth of a bacterial or yeast culture.
- They are used to measure and monitor the colour in various foods and beverages including vegetable products and sugar.
- Colorimeters have many practical applications such as testing water quality by screening chemicals such as chlorine, fluoride, dissolved oxygen
- They are also used to determine the concentration of plant nutrients such as ammonia, nitrate and phosphorus in soil or haemoglobin in blood.
- Colorimetry is also used in colour printing, textile manufacturing, and paint manufacturing.

Colorimeter

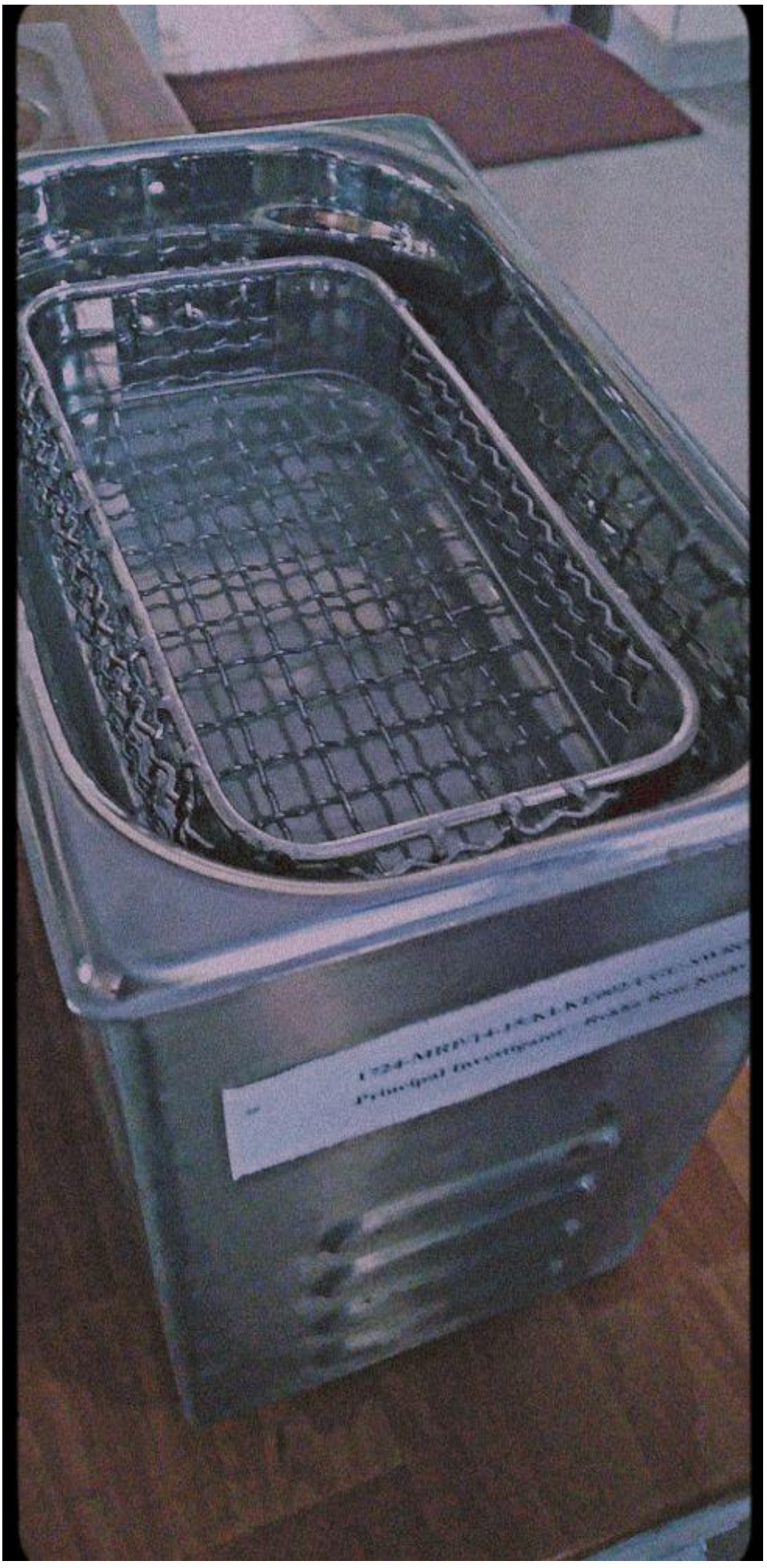
CHAPTER 3

3.EXPERIMENTAL METHODS

3.1 Synthesis of TiO2 Nanoparticles

TiO2 nanoparticles can be synthesised by sonochemical method. TiO2 pellets and NaOH solutions are taken as starting materials. The required weight of components was calculated. The stoichiometric amount of TiO2 is dissolved into 10 M NaOH solution. The product solution was vigorously stirred at room temperature for 2hr for uniform mixing and obtained a clear solution. The solution is then irradiated in an ultrasonic bath (powersonic 405, 40 KHz and 350 W) for 2 hr in ambient temperature. The resultant precipitates were then centrifuged for 10 minutes at 10000 rpm, washed and decanted with deionized water several times and dried at 600C for 24 hr.

Fig 6 : synthesised TiO2



CHAPTER 4

4. RESULT AND DISCUSSION

4.1 Structural Studies

The X-Ray diffraction patterns were obtained using a “theta-2 theta scan”

4.1.1 XRD analysis of TiO2 nanoparticles

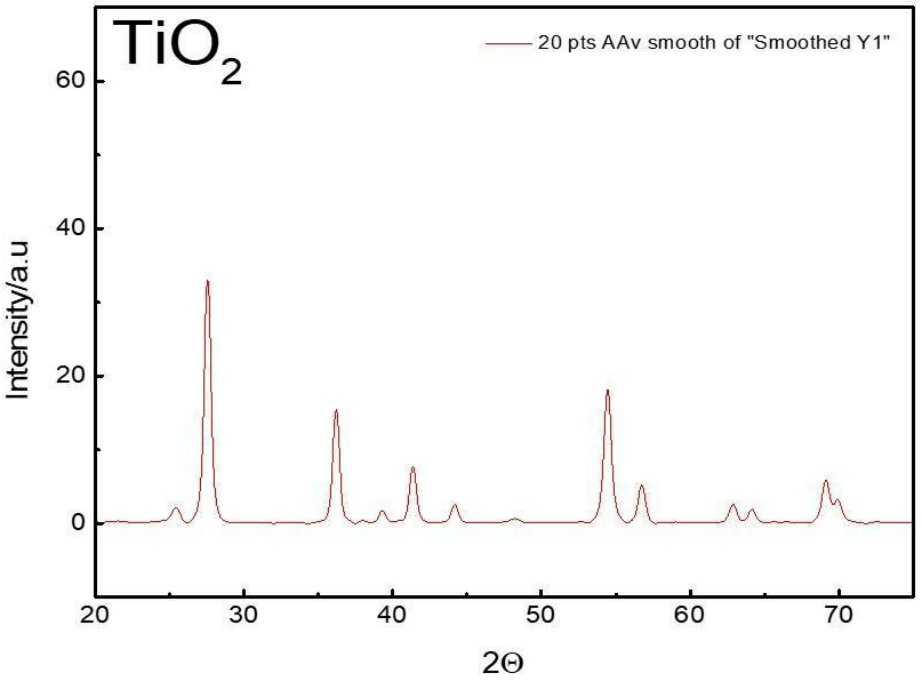
The crystal structure and phase transition of the synthesized samples were confirmed from the XRD spectra. The XRD spectrum confirms the formation of the Rutile phase of titanium dioxide nanoparticles. The diffraction pattern and relative density of the observed peaks perfectly match well to those of JCPDS Card No: 21-1276, supporting the formation of Rutile phase of titanium dioxide. The figure 4.1 shows the XRD pattern of the synthesized TiO2 nanoparticles. The prominent peaks in XRD pattern are observed at 2θ values 27.5510, 36.1990, 41.3620, 44.1730, 56.7510, 62.8970 and 69.1520 corresponds to Miller indices of (110), (200), (111), (211), (220), (002) and (301) plane respectively. The most intense peaks of titanium dioxide nanoparticles were observed at 27.5510.

The crystalline size (D) of the synthesized TiO2 nanoparticles is determined using Debye-Scherer equation;

$$D = \frac{.9\lambda}{\beta\, cos\theta}$$

Where λ is the wavelength of the X-ray used (λ=1.5406 $\dot{A}$), β is the full width at half maxima in radians and cosθ is the cosine of the angle of diffraction corresponding to maximum peak.

The calculated crystalline size of TiO2 nanoparticles was observed to be 7.25 nm.



XRD pattern of TiO2 nanoparticles

For the tetragonal structure of Rutile, the lattice parameter 'a' is calculated using the equation

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

Where a and c are lattice parameters

d- Interplanar distance

hkl - miller indices

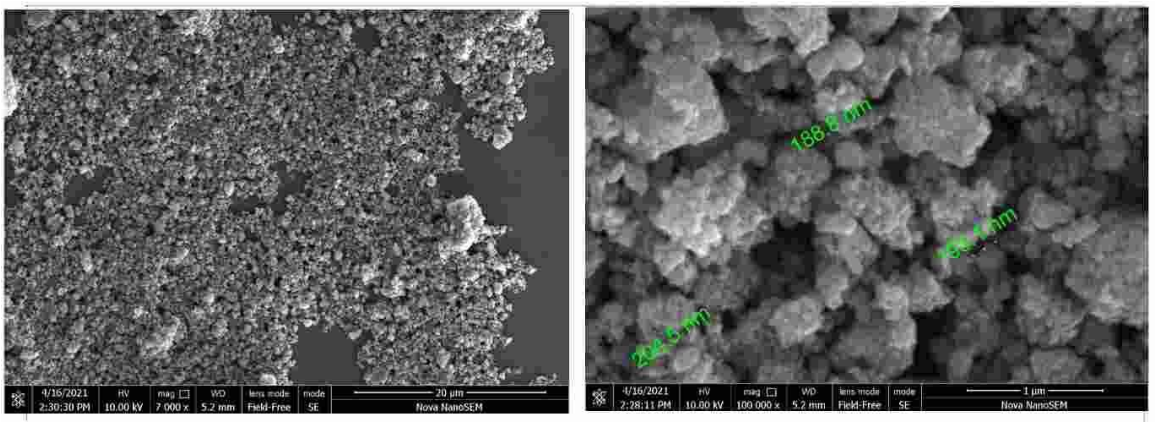
The calculated values of lattice parameters 'a' and 'c' of Titanium Dioxide nanoparticles are, 4.96 $\dot{A}$ and 2.952 $\dot{A}$ respectively.

4.2 MORPHOLOGICAL STUDIES

The morphology of the synthesized samples was examined using Scanning Electron Microscopy (SEM) operated by NOVA NANOSEM 450 (with WDS and EDS).

4.2.1 SEM Analysis of TiO2 Nanoparticles

The SEM images of TiO2 nanoparticles are presented in figure 4.6. From the SEM images the average particle size is found approximately in the range 188.8 nm – 204.5 nm.

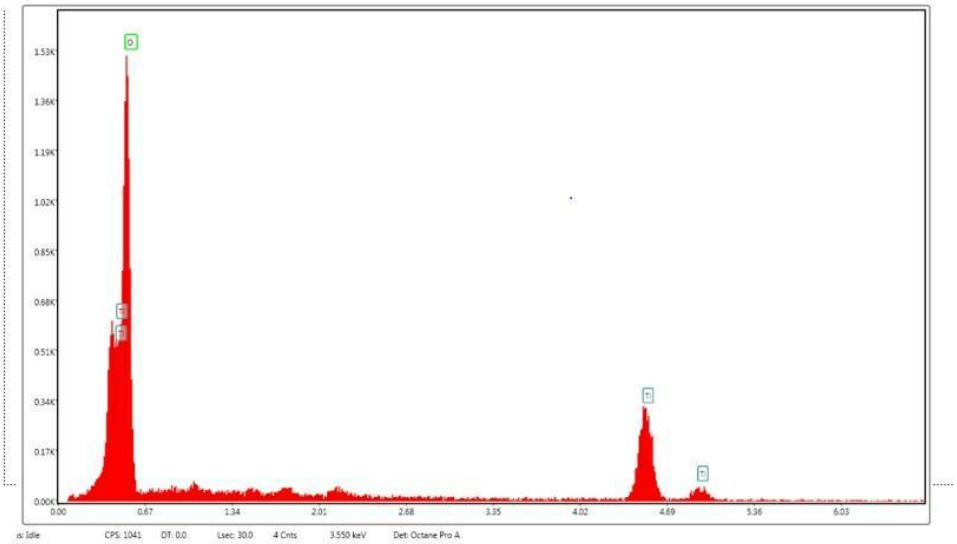


SEM images of TiO2 nanoparticles

4.3 ENERGY DISPERSIVE X-RAY ANALYSIS

4.3.1 Titanium dioxide (TiO2) Nanoparticles

The Energy Dispersive X-ray analysis (EDAX) examines the elemental composition of the particles. The EDAX spectra of TiO2 are presented and the relative elemental composition of EDAX data are represented . From the relative elemental composition table of titanium dioxide nanoparticles, it is observed that 74.49% of O, 25.51% of Ti is present in the synthesized sample



EDAX spectra of TiO2 nanoparticles

Element	Weight %	Atomic %	Error %	Net Int.	K Ratio	Z	A	F
O K	49.37	74.49	10.26	299.26	0.1675	1.1405	0.2974	1.0000
Ti K	50.63	25.51	5.87	134.05	0.4336	0.8498	1.0040	1.0036

EDAX data of TiO2 nanoparticles

4.3 PHOTOCATALYTIC STUDIES

Photocatalytic activity of TiO2 nanoparticles was investigated by observing degradation of Methylene blue (MB) under UV light. a 0.015g sample is taken into the beaker containing 5 ml Methylene blue with 5ml water. UV radiation is allowed to pass through the solution, and the optical density of the sample solution is observed by colorimeter each 5 minute during one and half hours.From the experiment it is observed that , at 0 time optical density of TiO2 is 1.39.After 10 minutes ,optical density is 1.15,at 20 minutes optical density decreases to 1.05. And after 30 minutes ,it changes to 0.63. After 40 minutes the optical density of TiO2 is 0.46. This decrease in optical density of TiO2 shows the degradation of Methylene blue under UV light.

Methylene blue + solution

Time	O.D
0 minutes	1.39
10 minutes	1.15
20 minutes	1.05
30 minutes	0.63
40 minutes	0.46

4.4 CONCLUSION

The trend of nanomaterials for water pollutant treatment is rapidly increasing in this modern era due to very horrible conditions of water. Tio2 nanoparticles as a photocatalyst have attracted a great interest in the removal of pollutants from water. Low cost, good chemical stability in aqueous medium, nontoxic nature makes it a promising material for photocatalytic water treatment applications. TiO2 nanoparticles were synthesized by sonochemical method. Its structural, morphological properties were characterized by XRD, SEM respectively. The XRD spectrum confirms the formation of Rutile nanoparticles. The elemental compositions were identified using EDAX. Photocatalytic activities of TiO2 nanoparticles were investigated by observing degradation of Methylene Blue under UV light. The decrease in optical density of the sample indicates the photoreduction property of TiO2 nanoparticles.

4.4.1 Scope for future studies

TiO2 Nanoparticles have more photocatalytic activity and this activity is used in degradation of dye molecules from water. There is a great need to synthesize some modified nanomaterials which should be effective, high efficiency, easy to handle and eco-friendly.

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