

**PHOTOCATALYTIC DEGRADATION OF ORGANIC DYES
WITH METAL SULFIDE NANOPARTICLES**

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
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PHILOSOPHY**

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**PHOTOCATALYTIC DEGRADATION OF ORGANIC DYES WITH METAL
SULFIDE NANOPARTICLES**

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Submitted
In partial fulfillment of the requirement of the Degree of Doctor of Philosophy in
Chemistry of Mizoram University, Aizawl.



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Certificate

I hereby certify that the thesis entitled '*Photocatalytic Degradation of Organic Dyes with Metal Sulfide Nanoparticles*' presented by Miss Lallianmawii, Mizoram University, Aizawl, Mizoram, is an authentic record of her original research endeavors undertaken under my guidance.

This thesis satisfies the University's registration and academic requirements for the Degree of Doctor of Philosophy. This work is worthy of a Ph.D. degree and has not been submitted elsewhere.

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DECLARATION
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I **LALLIANMAWII**, hereby declare that the subject matter of this thesis is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous to me or to do best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University/institute.

This is being submitted to the Mizoram University for the **Degree of Doctor of Philosophy in Chemistry**.

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ABBREVIATIONS

BET	Brunauer–Emmett–Teller
CIE	Commission Internationale de l'Éclairage
EDX	Energy Dispersive X-ray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
PL	Photoluminescence
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
UV-Vis	Ultraviolet–Visible Spectroscopy
XRD	X-ray Diffraction
ZnS	Zinc Sulfide
CoS	Cobalt Sulfide
CdS	Cadmium Sulfide
NiS	Nickel Sulfide
MgNiS	Magnesium Nickel Sulfide
Ce ³⁺	Cerium ion (trivalent)
Sm ³⁺	Samarium ion (trivalent)
Pr ³⁺	Praseodymium ion (trivalent)
Eu ³⁺	Europium ion (trivalent)
PEG	Polyethylene Glycol
PVP	Polyvinylpyrrolidone
RhB	Rhodamine B
PEG	Polyethylene Glycol
PVP	Polyvinylpyrrolidone
CR	Congo Red
MB	Methylene Blue
MO	Methyl Orange
MB	Methylene Blue
RhB	Rhodamine Blue

IC

EBT

SAED

JCPDS

Indigo Carmine

Eriochrome Black T

Selected Area Electron Diffraction

Joint Committee on Powder Diffraction
Standards

CHAPTER 1

INTRODUCTION

1.1 Nanoparticles

The intersection of physics, chemistry, biology, medicine, electronics, and information technology, modern nanotechnology is an interdisciplinary field of study that focuses on the smallest particles and their unique chemical, physical, and mechanical properties (Joudeh & Linke, 2022). The boundaries of the natural sciences are blurred and overlapped by the specific fields of nanotechnology in practice. The field of nanotechnology has evolved from a multidisciplinary study that combines ideas from engineering, chemistry, biology, medicine, and other fields to understand better and alter materials. The Greek prefix "nano" means "dwarf" or "very small" (Lines, 2008). Thus, the class of materials having at least one dimension in the nanometric range is referred to as nanomaterials. Generally, the grain size of polycrystalline materials is between one and one hundred microns (1 micron = 10^{-6} m) (Rangasamy, 2011). The National Nanotechnology Initiative (NNI) states that the diameter of a nanoparticle can range from 1 to 100 nm. Since they resemble significant naturally occurring nanoparticles, such as viruses, in terms of size, somewhat larger particles are also frequently classified as nanoparticles in the biomedical field (Kebede & Imae, 2019). Nanoparticles exhibit special properties at these sizes that may distinguish them from bulk materials and molecules. Polymers, metals, ceramics, and composites are examples of nanomaterials. Nanotechnology is the collective term for various scientific disciplines that investigate objects with one or more dimensions on the scale of a few hundred nanometers (F. Lu & Astruc, 2020). Molecular intra- and intercellular processes are the primary focus of nanobiotechnology, which is crucial for the application of nanotechnology in medical settings (Nune *et al.*, 2009). The various ways that potentially useful nanobiotechnologies for human medicine interact with medically significant nanotechnologies are one example of this. Nanosized metals show a notable improvement in yield strength and a decrease in hardness (Jeevanandam *et al.*, 2018).

It has been demonstrated that the fine-grained structures of these materials affect optical, magnetic, and electrical properties. Realizing the intriguing features of nanostructures has become feasible due to significant advancements in the technical capacity to modify and customize dimensions at the nanoscale (Batista *et al.*, 2015). Scientists believe that one of the most fascinating uses of nanoscience is in bio-nanotechnology. Recent decades have seen extensive study into the applications of nanotechnology in numerous biology-related fields, including diagnosis, medication delivery, and molecular imaging, with promising outcomes (Bayda *et al.*, 2020). One of the most exciting new technologies of the twenty-first century is nanotechnology. By seeing, measuring, adjusting, constructing, regulating, and producing matter at the nanoscale, one may transform the theory of nanoscience into practical applications (Mansoor *et al.*, 2020). Nanoscience as well as nanotechnology should be distinguished from one another. Nanoscience is the combination of physics, materials science, and biology that deals with the manipulation of materials at the atomic and molecular levels (Gnach *et al.*, 2015). Nanotechnology is the study, measurement, manipulation, assembly, control, and production of matter at the nanoscale. While several papers detailing the history of nanoscience and technology are available, none provide a comprehensive overview of the field's evolution from its beginnings to the present, including significant developments (Allhoff, 2007). It is therefore essential to outline significant developments in nanoscience and technology in order to properly understand their advancement in this sector. The application of nanotechnology has enabled the production of energy that is more environmentally friendly and cheap (Sun *et al.*, 2020), (J. Zhao & Yang, 2003). Nanotechnology and nanoscience have emerged as critical fields for industrial and medical applications, including drug delivery systems, imaging probes, and diagnostic biosensors, in a matter of decades.

Zinc oxide nanostructures, on the other hand, exhibit antibacterial activity against pathogens are transmitted through food. A wide range of nanomaterials is currently utilized in food sensors to detect the safety and quality of food for diagnostic purposes. The food industry has made significant use of nanomaterials to boost nutritional production, packaging, shelf life, and bioavailability (Yan Lee & K.Y.

Wong, 2012), (Y. Yuan *et al.*, 2019). New-generation solar cells, hydrogen fuel cells, and innovative hydrogen storage devices are being constructed using nanomaterials to provide sustainable energy to nations that still rely on conventional, non-renewable, polluting fuels (J. Xing *et al.*, 2012). Nanomaterials are employed in various fields today, including energy storage, wastewater treatment, catalytic processes, medicine, and the agricultural sector, due to their unique properties (Cordani & Somoza, 2019). Surface effects and quantum effects are two key mechanisms that lead to notable dimensional behavioral differences between nanoparticles and larger-scale materials (N. Sharma *et al.*, 2020). These elements contribute to the enhanced or unique mechanical, thermal, magnetic, optical, electrical, and catalytic properties that nanomaterials exhibit. The surface effects of nanomaterials differ from those of micro materials or bulk materials for three main reasons where there are fewer direct neighbors for the atoms at the surface of nanomaterials, there is an increase in the fraction of atoms at the surface of nanomaterials and dispersed nanomaterials have a high particle number per mass unit and a huge surface area (Geoffrion & Guisbiers, 2020), (Saba, 2014), (Buzea *et al.*, 2007).

Comparing nanoparticles to their larger-dimension equivalents, each of these distinctions has an impact on the material's chemical and physical properties (Walter *et al.*, 2006). Since a greater reaction surface results in a larger surface area and surface-to-volume ratio, larger surface areas also have a substantial impact on the structure of nanomaterials (Apelgren *et al.*, 2019), (Ayodhya & Veerabhadram, 2018a). Surface effects are mostly dependent on the dispersity of nanomaterials. The agglomeration and aggregation of nanomaterials can be caused by strong attractive interactions between particles, which have a deleterious impact on the nanoscale characteristics and surface area of the materials (Gajanan & Tijare, 2018). The degree of hydrophilicity or hydrophobicity of the nanomaterial can be optimized, the pH and ionic strength of the suspension medium can be adjusted, or the zeta potential of the nanomaterials can be increased (raising the repulsive force) (Roduner, 2006). Particular size-dependent characteristics of nanomaterials are observed in the 1-100 nm regions where quantum phenomena are present. The effect of quantum

confinement is noticeable when the material radius gets close to the asymptotic exciton Bohr radius, which is the distance between the electron and hole. Put another way, when a material gets smaller, quantum effects become more noticeable and nanomaterials become quantum. All of the charge carriers, which are electrons and holes, are contained inside the physical dimensions of those quantum structures (Gade *et al.*, 2010).

Nanomaterials are classified into four groups according to their dimensionalities. One-dimensional (1-D) nanomaterials comprise a single dimension that is not part of the nanoscale. Nanotubes, nanofibers, nanorods, nanowires, and nanohorns are a few examples (Feng *et al.*, 2016). Two-dimensional nanomaterials (2-D): This class of nanomaterials has two dimensions that are not part of the nanoscale. Nanofilms, nanosheets, and nanolayers are a few examples. Bulk, or three-dimensional, nanomaterials: These materials are not limited to the nanoscale in any dimension. Bulk powders, nanoparticle dispersions, arrays of nanowires and nanotubes, etc., are all included in this class. According to the International Organization for Standardization (ISO), nanoparticles are nano-objects with all exterior dimensions in the nanoscale, where there is little to no difference in the lengths of the longest and shortest axes of the nano-object (Challagulla *et al.*, 2017), (Ikhmayies, 2014). Terms like nanofibers or nanoplates may be preferred over the term nanoparticles if the dimensions differ greatly (usually by more than three times). They may differ in size, structure, and form. Their shapes may range from irregular to spherical, cylindrical, conical, tubular, hollow core, spiral, etc. (Roduner, 2006) The size ranges from one to one hundred nanometers. In general, the phrase "atom clusters" is preferred when the size of the particle is less than 1 nm. Nanoparticles can be amorphous or crystalline, with solids that contain one or more crystals. It may be agglomerated or loose (Suttiponparnit *et al.*, 2011), (Geoffrion & Guisbiers, 2020). Nanoparticles might consist of many layers or be homogenous. Regarding the latter scenario, the layers are often the surface layer, typically comprised of various tiny molecules, metal ions, surfactants, or polymers, the outermost layer comprises a substance that differs chemically from the innermost layer, nanoparticle's core layer, or its middle

section (Kolahalam *et al.*, 2019), (Joudeh & Linke, 2022), (Geoffrion & Guisbiers, 2020).

Classification of nanoparticles: Organic, carbon-based, and inorganic are the three general types into which nanoparticles are classified based on composition.

Organic nanoparticles: Nanoparticles composed of proteins, carbohydrates, lipids, polymers, or any other organic component fall into this class. The most well-known members of this family are protein complexes like ferritin, liposomes, nanogels, dendrimers, and micelles (Astruc, 2008), (Haroon *et al.*, 2022). These nanoparticles (NPs) are generally non-toxic, and biodegradable, and in certain instances, like with liposomes, may have a hollow center. Heat and other forms of electromagnetic radiation, as well as light, can affect organic nanoparticles (Machado *et al.*, 2015). Furthermore, they are frequently created by non-covalent an intermolecular interaction, which increase their labile character and provide an exit path for the body. The possible range of use of organic nanoparticles is determined by several factors, including composition, surface shape, stability, carrying capacity, etc. (X. Yuan *et al.*, 2019), (Mauter & Elimelech, 2008). Organic nanoparticles are a suitable choice for delivering medications due to their specific characteristics. Targeted medicine delivery to its intended sites is another common application for nanoparticles (M. Liu *et al.*, 2018), (Toshima & Yonezawa, 1998). A polymeric nanoparticle is another term used to describe organic nanoparticles. The most well-known type of polymeric or organic nanoparticle is the nanosphere (Bai *et al.*, 2017).

Carbon-based nanoparticles: Nanoparticles composed entirely of carbon atoms fall under this type. Fullerenes, carbon black nanoparticles, and carbon quantum dots are well-known instances of this class. The symmetric closed-cage structure of fullerenes is a defining characteristic of carbon compounds (Balayeva & Mamiyev, 2016). While C70 and C540 fullerenes have also been described, C60 fullerenes are made up of 60 carbon atoms grouped in the shape of a football (Bayda *et al.*, 2020). The peculiar physicochemical features at the nanoscale are combined with the unique properties of sp²-hybridized carbon bonds in carbon-based nanoparticles. Carbon-based nanoparticles have a wide range of applications, including drug delivery,

energy storage, bioimaging, photovoltaic devices, and environmental sensing applications for monitoring microbial ecology or detecting microbial pathogens (Gupta & Tripathi, 2012). These applications are made possible by their unique electrical conductivity, high strength, electron affinity, optical, thermal, and sorption properties. Their unique qualities of low toxicity and biocompatibility make them suitable for use in tissue engineering and medication delivery applications. The existence of a wide range of carbon allotropes, from well-known allotropic phases like amorphous diamond, graphite, and carbon to recently discovered allotropes like graphene quantum dots (GQD's), fullerene, graphene oxide (GO), and carbon nanotubes (CNT's), has led to discussions in recent times regarding carbon-based materials as valuable treasures (Fubini *et al.*, 2010). Graphene is endowed with a multitude of remarkable properties, each of which could contribute to its usefulness in bio-applications (Nasir *et al.*, 2022). A range of biological components can be precisely and selectively detected when the number of functional groups on the material's surface increases as a result of simple functionalization (Haroon *et al.*, 2022). The transformation of two-dimensional graphene sheets into graphene quantum dots leads to quantum confinement, which significantly enhances the photoluminescence properties of the graphene quantum dots (MG *et al.*, 2015). Graphene quantum dots outperform semiconductor quantum dots or traditional fluorochromes in terms of photo-bleaching durability and biocompatibility (Smet *et al.*, 2010). This is a result of the natural ingredients used to create graphene quantum dots. Important graphene characteristics, such as readily accessible electrons and a large surface area are also present in graphene quantum dots. Due to these characteristics, graphene quantum dots are a promising nanomaterial that can be utilized in various medical applications, including targeted drug delivery, biomolecule sensing, cancer therapy, and imaging (MG *et al.*, 2015).

Inorganic nanoparticles: Nanoparticles that are not composed of carbon or organic elements fall under this class. This class often includes semiconductors, ceramics, and metal nanoparticles (Afzal *et al.*, 2022). Metal nanoparticles can be monometallic, bimetallic, or polymetallic; they are entirely composed of metal precursors. Bimetallic nanoparticles can be generated in distinct layers (core-shell) or

from alloys. These nanoparticles have distinct optical and electrical characteristics due to their localized surface plasmon resonance features (Korbekandi & Iravani, 2012). Specific metal nanoparticles also possess unique biological, magnetic, and thermal properties. The creation of nanodevices with a wide range of physical, chemical, biological, biomedical, and pharmacological applications makes them increasingly significant materials (Haroon *et al.*, 2022). To create cutting-edge materials nowadays, the production of metal nanoparticles that are regulated by size, shape, and facet is essential. Semiconductor materials, which have characteristics of both metals and non-metals, are used to make semiconductor nanoparticles. Comparing these nanoparticles to bulk semiconductor materials, they have unusually large bandgaps and exhibit notable property changes upon bandgap tuning (Kolahalam *et al.*, 2019). Consequently, these nanoparticles are crucial components for photocatalysis, optical, and electrical devices. Inorganic solids known as ceramic nanoparticles are composed of metal oxides and metalloids, including calcium and titanium, as well as carbonates, carbides, and phosphates. They can be amorphous, polycrystalline, dense, porous, or hollow, and they are often created by heating and then cooling (Rao *et al.*, 2011). Due to their exceptional stability and high load capacity, they are primarily utilized in biomedical applications. However, they are also employed in other fields, such as photonics, optoelectronics, dye degradation, and catalysis. Chemical catalysis is a rapidly developing area that includes nanocatalysis, or the use of nanoparticles as catalysts (Buzea *et al.*, 2007), (Colmenares *et al.*, 2009).

1.2 Dyes and its toxicity

One of the biggest and most significant issues facing the modern world is environmental pollution. To meet the needs and desires of the world's expanding population, advancements in the fields of agriculture, medicine, energy sources, and all chemical industries are imperative (T. Islam *et al.*, 2023). Environmental contaminants are produced by almost every process used by humans to produce commodities and services. Microbes, plants, animals, and humans are all negatively impacted by these pollutants, which are discharged into the air, water, and soil (J. Sharma *et al.*, 2021). Humans require commodities and services to survive on our

planet; hence, efforts to produce and develop them cannot be completely abandoned. The most valuable resource for human survival, water, is confronting previously unheard-of difficulties. Water is essential to life and is utilized in many domestic and commercial processes (Ali *et al.*, 2020). Unfortunately, it is one of the most overused natural resources despite being one of the most vital. The primary causes are the growing human population, rapid industrialization, increasing living standards, and urbanization (Koe *et al.*, 2019). Due to excessive and unrestricted water exploitation, the entire world is currently experiencing a water crisis.

The swift urbanization of natural resources, coupled with the growth of industry, particularly in the textile sector, is endangering water bodies by discharging effluents containing numerous poisonous and harmful substances, primarily colour (Reza *et al.*, 2017). As a result, the water becomes hazardous to use further and loses both quality and quantity. Water contamination has been a growing concern that has garnered significant attention lately. One of the leading causes of aqueous pollution is wastewater tainted with dyes. Dye-contaminated wastewater is produced when various industries, including textile dyeing, paper manufacturing, food processing, paint production, and cosmetics, discharge their dye-contaminated effluents into the environment (Lellis *et al.*, 2019). Dyes present in wastewater significantly impact the aquatic ecosystem because the intense colour imparted by dyes to the water inhibits sunlight penetration (Hasanpour & Hatami, 2020). Water pollution has become one of the most serious global issues. However, this situation is still spreading; a large amount of wastewater is produced and poured into the water environment every year (Chiu *et al.*, 2019). Among the various types of wastewaters, dyeing wastewater warrants significant attention. Since the last century, with the continuous development of printing and dyeing industrialization process, large amounts of dyes have been released into the environment. Dyes are basic, daily chemical compounds that are widely used in many fields to colour products such as textiles, leather, paper, rubber, printing, plastics, etc. (Sarkar Phyllis *et al.*, 2022). Dyeing wastewaters are toxic and carcinogenic to both aquatic life and human beings. Adsorption technology, as a facile and effective method, has been extensively used for removing dyes from aqueous solutions for decades. Numerous researchers have attempted to

seek or design alternative materials for dye adsorption. Over 10,000 distinct dyes and pigments are thought to be utilized in industry, and 0.7 million tonnes of dyes are synthesized annually worldwide (Bhatia *et al.*, 2017). The ecology is greatly endangered by the significant concentration of dye contaminants in wastewater. For example, dye can hurt both aquatic life and humans, as it can block out sunlight and typically contains hazardous materials such as aromatics and heavy metals (e.g., lead, chromium) (Rauf & Salman Ashraf, 2012). Wastewater containing dye molecules can cause dysfunction in the kidneys, liver, brain, reproductive system, and central nervous system, as well as induce mutagenicity and carcinogenicity. Worldwide freshwater shortages are becoming increasingly acute due to the rapid growth of the global population, climate change, and industrial expansion. These factors have also had a substantial impact on water quality (Skjolding *et al.*, 2021).

The history of the textile dyeing industry dates back more than 4,000 years (Walter *et al.*, 2006). Natural sources provided dyes for all except the last 150 years. Colour significantly improves the world in which we live. Colourful items that we use daily, such as fabrics, paints, plastics, paper, and food, are particularly appealing. Around us, nature also offers a kaleidoscope of hues (Kant, 2012). Electromagnetic radiation, or light, is made up of tiny energy packets known as photons. The energy contained in the photons of different colour's of light varies. The chemical substances known as dyes give the fiber its colour. It attaches itself to the fiber's surface as well as deeply inside it (A. Mondal *et al.*, 2015). A dye must be resistant to heat, light, moisture, diluted acids, washing soaps, and other environmental factors in order to be considered reasonable. A dye that adheres permanently to the fibre's surface is referred to as a fast dye, whereas a dye that fades or washes off is called a fugitive dye (Ambrogi *et al.*, 2017). Today, the synthetic dye industry is worth billions of dollars. Pigments are chemical substances that only reflect specific visible light wavelengths. They appear colourful as a result. Pigments are what give flowers, corals, and even animal skin its colour's. The capacity of pigments to absorb specific wavelengths of light is more significant than their ability to reflect light (B. Chen & Wang, 2020). Dyes are a significant part of our daily life and have a long history. Dye industry initially relied on naturally occurring plant and insect sources before

transitioning to artificial manufacturing techniques. A number of artificial dyes, particularly azo dyes, have been proven to be hazardous and carcinogenic, leading to their global prohibition (Å *et al.*, 2007). However, azo dyes are still used and made today because of their low cost and other advantageous qualities. The removal and treatment of azo dyes from wastewater pose a unique set of challenges. Innovative remediation techniques must be investigated, as azo dyes are resistant to physical and chemical treatment methods, and traditional aerobic biological treatment is neither cost-effective nor environmentally benign.

According to one definition, dyes are compounds that, when applied to a substrate, give it colour while, at the very least, momentarily destroying the coloured material's crystal structure. They cling to suitable surfaces by solution, covalent bond formation, mechanical retention, physical adsorption, or complex formation with metals or salts. The ability of dyes to absorb light in the visible range of electromagnetic radiation (400-700 nm) determines their colour (Wu *et al.*, 2012). According to Witt theory, a coloured dye requires both an auxochrome group and a chromophore group. Auxochromes intensify the colour when added to a coloured molecule, whereas chromophores (such as nitro, azo, and quinoid groups) give dye its colour by absorbing light in the visible spectrum (Brown, 1987). Usually, dye's breakdown products rather than the pigment itself are what cause the toxicity. The most labile part of an azo dye molecule is the azo linkage, which is readily broken down by the enzyme azo-reductase, which is present in all studied animals, including humans, and a variety of microbes (Panyala *et al.*, 2008).

As a result, component aromatic amines are released, several of which have extremely high levels of carcinogenicity and acute and chronic toxicity (Bafana *et al.*, 2011). All dyes and chemicals must, therefore, be handled carefully as long-term or unintentional overexposure may pose health risks. Reactive dyes most frequently cause respiratory issues when dye particles are inhaled (Koumanova & Allen, 2005). Itching, watery eyes, sneezing, and asthmatic symptoms including coughing and wheezing are some of the symptoms of what is known as respiratory sensitization (Buzea *et al.*, 2007). The most common health issues associated with dyeing and finishing procedures may result from exposure to irritating chemicals. These

symptoms may include irritated eyes, sneezing, a blocked or itchy nose, and skin irritation. These consist of ammonia, acetic acid, formaldehyde-based resins, various shrink-resistant compounds, optical whiteners, soda ash, caustic soda, and bleach. It is also known that several dyes, including reactive, vat, and disperse dyes, are sensitive to skin (Kant, 2012). The textile industry generates significant quantities of liquid waste. Both organic and inorganic substances can be found in these textile effluents (Khataee & Kasiri, 2010). Textile effluents have been shown to contain substantial amounts of these unfixed colours. The type of fabric created also affects the amount of water is used and discharged. These effluents contain a high concentration of chemicals and colour's, some of which are carcinogenic and non-biodegradable, endangering both human health and the environment (Koe *et al.*, 2019).

Nevertheless, it has been discovered that these treatments are ineffective in eliminating all chemicals and dyes (A. K. Dutta *et al.*, 2012). The chemicals employed in the various processing stages are also present in the effluents, in addition to the high concentration of dyes used in the industry. These effluents contain certain trace metals, such as Cr, As, Cu, and Zn, which can lead to various health issues, including dermatitis, severe skin irritation, nausea, bleeding, and skin ulceration (Islam *et al.*, 2021). Additional organic and microbiological contaminants have been discovered in textile effluents. Anionic, cationic, and non-ionic dyes are the main classifications for dyes. The textile industry holds the top spot when it comes to the use of dyes in industries for colouring fibres. Materials called dyes are used to colour a variety of materials, such as paper, plastic, textiles, and other things (Joshi *et al.*, 2022). These are organic chemicals that are coloured and soluble in water, generally applied to textiles. You can use synthetic or natural dyes. Their purpose is to form a strong bond with the polymer molecules that comprise the textile fibre. To provide colour to materials that it becomes a part of, a dye is utilized (Pereira & Alves, 2012). To impart colour to goods and materials, dyes are widely utilized in a variety of sectors, such as textiles, printing, and cosmetics (Islam *et al.*, 2023). Acid dyes, basic dyes, dispersion dyes, reactive dyes, and vat dyes are a few typical types of dyes; each has unique characteristics and applications. Dyes can be

categorized into a number of groups according to their origin, chemical makeup, solubility, mode of application, and other characteristics. A frequent theory based on the chromophore principle is an electron-withdrawing group.

Typically, auxochromes are groups that release electrons and are connected to one another via a conjugated structure. That is to say, the idea of the donor-acceptor chromogen was created (Affat *et al.*, 2021). Additionally, it was noted that lengthening the conjugation, increasing the chromophore's electron-withdrawing power, and increasing the auxochromes' electron-releasing power could all result in a bathochromic shift of the colour, or an absorption band shifted to a longer wavelength (Hamnabard *et al.*, 2015). The auxochrome and chromophore concept provides a straightforward explanation for the formation of colour in dye molecules, although it is not well supported theoretically. According to this definition, the carbonyl (C=O), diazo (-N=N-), azomethine (-CH=N), and nitro (NO₂) groups are the most significant chromophores (Hihara *et al.*, 2002). Other groups, such as hydroxyl (OH) and amino (NR₂) groups, intensify the colour and cause the absorption to shift to longer wavelengths of light (Affat, 2021). The majority of chemical dye classes, including azo, carbonyl, azomethine, and nitro dyes, can utilize this principle.

Classification of dyes

Azo dyes

William Henry Perkin, then eighteen years old, made the accidental discovery of the mauveine, the first synthetic dye, in 1856. It was produced by sulfuric acid reacting with aniline (obtained from coal tar) in the presence of potassium bicarbonate, making it feasible to dye the silk purple. In 1860, the first so-called "Azo" dyes were found in Great Britain. A dye is a coloured substance, either synthetic or natural, that dissolves and disperses in a medium to interact and colour it (Benkhaya, M'rabet, *et al.*, 2020). Because of their range of colours, simplicity of synthesis, and chemical stability, these dyes are a true business and a capital of modern chemistry. Their two unique characteristics are their colour and their capacity to be fastened, via dyeing or printing processes, to solid substrates like fabrics (Chiu *et al.*, 2019). Because of their

colouring capabilities, synthetic dyes are used extensively in the paper, plastics, and textile, leather, and dye industries each year.

Due to their wide range of applications and large-scale manufacture, dyes are environmental pollutants that are both pervasive and persistent (Castro *et al.*, 2021). Azo dyes are among the most widely used dyes in various industrial applications, including the paper, textile, and cosmetics industries, all of which generate effluents high in residual colouring compounds. Azo dyes, like other dyes, have been shown to harm both aquatic life and humans, causing issues with the brain, central nervous system, cancer, and mutagenicity in humans (Chen *et al.*, 2015). This is because they may impede sunlight transmission and contain a variety of hazardous materials, including heavy metals and aromatics. Because textile industry dyes have complex chemical structures, high pH values, high chemical oxygen demands, and high temperatures that make dye breakdown extremely difficult, wastewater containing these dyes is a severe issue. They can be found in any kind of intricate matrix (Bafana *et al.*, 2011). For every colour, dyes have a different chemical structure. Three elements make up a textile dye's chemical structure: the skeleton, the chromophore groups (which give dye its colour), the auxochrome (which encourages fusion on the substrate), and the solubilizing groups (which give dye its solubility in organic solvents or water) (Abel, 2012). Auxochromes, which are crucial components of dyes, are functional groups with isolated electron pairs that colour intensify. Every textile dye has a different chemical structure. The two main components of this structure are the auxochrome, which enhances the chromophore's ability to absorb light, and the chromophore, which imparts colour (Aljamali, 2015). They are unable to introduce colour on their own, but when they coexist with chromophores in an organic compound, the chromogen's colour is enhanced (B. Said *et al.*, 2020).

Azo dyes make nearly 70% of all organic dyes produced worldwide, making them the largest group of colourants in terms of both quantity and production volume. The success of azo dyes can be attributed to their medium-to-high fastness properties with respect to light and wetness, high molar extinction coefficient, significant structural variety, and straightforward production techniques. They are used in a

variety of products, including paints, food, ink, cosmetics, medicines, and natural and synthetic material dying (Carliell *et al.*, 1998). Usually, the breakdown products of dye cause the toxicity rather than dye itself. The most labile part of an azo dye molecule is the azo linkage, which is readily broken down by the enzyme azo-reductase, which is present in all studied animals, including humans, and a variety of microbes. As a result, component aromatic amines are released, several of which have extremely high levels of carcinogenicity and acute and chronic toxicity. There are several ways in which poisonous aromatic amines produced from azo dyes are exposed to humans. Azo dyes used in clothing or food items can be metabolized by the skin or intestinal flora, which exposes a person to hazardous amines (Bafana *et al.*, 2011). Azo dyes also impede a number of biological functions, all of which are crucial to the environment. For instance, they can reduce light penetration to prevent algae photosynthesis. Microbial activities such as natural biogeochemical cycles and wastewater treatment systems may be inhibited as a result (Chung & Stevens, 1993). Additionally, by preventing seed germination, seedling survival, and shoot and root elongation, and azo dyes can have a direct impact on plant growth. Similarly, it has been discovered that benzidine completely destroys the maize root tip cells by inhibiting DNA synthesis in the nucleus and deregulates calcium homeostasis (Zaalishvili *et al.*, 2000). The majority of azo dyes' harmful effects are mediated by aromatic amines that are created as they break down. In aquatic creatures such as fish, snails, and daphnids, the ecotoxicity of aromatic amines is particularly high (Puvaneswari *et al.*, 2006). Throughout the food chain, azo dyes and aromatic amines experience bioaccumulation and biomagnification. The chemicals physico-chemical and toxic kinetic characteristics, such as their molecular size, respiratory volume, and ability to permeate gills in aquatic species, all have an impact on this. Due to their high partition coefficients, several aromatic amines and hydrophobic dyes, such as dispersion and solvent, provide a significant danger of bioaccumulation. Azo dyes have one or more azo groups in their chemical structures (-N=N-). The azo group comprises more than 70% of all dyes used worldwide, and these dyes are also the most frequently employed (60-70%) for fabric dyeing (Y. Zhu *et al.*, 2020). Numerous sectors, including textiles, pharmaceuticals, paper, non-linear optical systems, biomedicine, and medical, employ them extensively (Singh & Arora, 2011).

They have an amino or dialkylamino group, and when exposed to various solvents and pH levels, they undergo an apparent colour change. Heterocyclic moiety-based azo dyes are renowned for their superior colouring capabilities, tinctorial strength, fastness, and thermal stability. The chemical groups in these dyes that can establish covalent bonds with textile substrates are what often define them (Tasli *et al.*, 2020). They make up over half of all synthetic dyes used globally. Although they include all colours, the most common ones are yellow, orange, and red. Dye's colour is a result of the azo group when the azo bond cleaves; compounds containing aromatic structures that are hazardous to humans and other living organisms may result (Srinivasan *et al.*, 2019).

These pigments represent the majority of organic dyes produced by industrial synthesis. They are among the most extensively used synthetic dyes because they are reasonably priced and stable in a variety of pH, temperature, and light situations. An azo molecule is synthesized by the proper diazotization/coupling process or reduction/reduction reaction when a diazonium salt and a coupling component are present (Ravi *et al.*, 2020), (Pavithra *et al.*, 2019a). The nitrogen atoms are sp² hybridized and exist in a trigonal planar structure, where the bond angle is approximately 120°. The A group of monoazo dyes, the most prevalent kind, frequently has substituents that accept electrons, and the B group comprises substituents that provide electrons, especially amino and hydroxyl groups (Gregory, 1990). Carbocyclic azo dyes are those that comprise just aromatic groups, such as benzene and naphthalene. Dyes are referred to as heterocyclic azo dyes if they include one or more heterocyclic groups (Muhd Julkapli *et al.*, 2014). The chromophores and auxochromes that are connected to azo bonds determine the colour of azo dyes (Rauf *et al.*, 2011). Azo dyes are a significant class of synthetic colourants that are widely utilized in the textile, pharmaceutical, plastic, leather, paper, and printing industries (Ollgaard *et al.*, 1998). They do not occur naturally and can be synthesized relatively easily with virtually infinite substituent options. Azo dyes are almost always created by diazotizing a primary aromatic amine and then combining the resulting diazonium salt with a nucleophile that is rich in electrons (Hunger, 2002).

Anthraquinonoid dyes

After azo dyes, anthraquinonoid dyes are the second most significant class. Since they have been discovered in the mummy wrappings of mummies that date back more than 4,000 years, they are also among the oldest kinds of dyes (Saranraj, 2013). Among the many benefits of anthraquinonoid dyes are their brightness and good fastness qualities. Anthraquinones are significant natural compounds that can be found in lichens, bacteria, plants, and fungi, as opposed to azo dyes, which have no parallels in the natural world. With broad absorption bands in the long-wavelength region, most anthraquinonoid dyes have high molar extinction coefficients (Gregory, 1990). Anthraquinonoid dyes have outstanding photostability, at least when it comes to textile dyeing. Consequently, anthraquinone dyes have been applied to solar cells that are dye-sensitized. The cost of producing anthraquinone dyes is higher than that of azo dyes due to their more complex syntheses and weaker tinctorial strengths (Han *et al.*, 2001). Numerous substitutions are possible, such as joining different fused ring systems. This is by far the largest class of carbonyl dyes, comprising hundreds of substances that are used in various ways on textiles. The anthraquinone vat dyes for cotton, disperse dyes, and pigments are the most noteworthy from an industrial perspective (Christie, 2023). The synthesis of the nucleus or the electrophilic replacement of unsubstituted anthraquinone yields a few important products, which are then used to produce anthraquinone intermediates and anthraquinone dyes. Sulfonation and nitration are the two main techniques used to prepare anthraquinone derivatives modified in the α position (Bien *et al.*, 2000). Quinizarin (1,4-dihydroxyanthraquinone) and β -substituted anthraquinones are often prepared via nucleus synthesis, which begins with phthalic anhydride and a benzene derivative. The majority of anthraquinone dyes show a prominent band of absorption in the long wavelength range. They are employed for the colouring of cotton, cellulose fibres, and hydrophobic synthetic fibres. Between 2% and 50% of dyes used to colour textiles may be lost to wastewater and ultimately the environment during the colouring process (Kiernan, 2001).

Indigo dyes

One of the earliest known organic dyes is indigo dye, an organic molecule with a striking blue hue. Indigo dye, which is first made from plants, has been used for 5000 years to colour textiles. The main application of indigo dye is on denim jackets and jeans. The younger generation holds it in great regard due to its blue hue and the way it gradually fades to reveal progressively lighter tones of blue (Hunger, 2002). In addition to textile applications, the production of other indigoid chemicals finds application in medicine, semiconductors, and cosmetics. After treating the N-phenylglycine at 200° C with melted caustic soda and sodamide mixes, indoxyl is produced. Further oxidative dimerization transforms indoxyl into indigo. Indigo was derived from natural sources until the late 19th century, when the modern chemical industry emerged, making it one of the first naturally occurring compounds to be synthesized (Gregory, 1990). Dyers favored synthetically made indigo because it was of higher quality than indigo derived from plants. In the widely used method, aniline, formaldehyde, and hydrogen cyanide combine to produce phenylglycinonitrile, which is further hydrolyzed to produce N-phenylglycine. The N-phenylglycine is then treated at 200°C with molten caustic soda and sodamide mixes to produce indoxyl, which then undergoes further oxidative dimerization to yield indigo (Rebelo *et al.*, 2014), (Głowacki *et al.*, 2012).

Phthalocyanine dyes

Phthalocyanines are of tremendous interest in a variety of scientific and technological fields due to their unique qualities, which include improved spectroscopic characteristics, diversified coordination capabilities, higher stability, and architectural flexibility (Durmuş & Nyokong, 2008). In addition to providing strong colour in the visible range of 650–750 nm, the combination of aromaticity in an extended π -system comprising four fused benzenoid aromatics is crucial for the outstanding thermal and chemical stability of largely planar phthalocyanines, especially in the solid state. In coordination with most elements, particularly metals like Cu, Fe, Si, Ge, and As, phthalocyanine forms complexes (Şahin *et al.*, 2015). Pigments and dyes are made from these vividly coloured combinations of different elements. Pigments containing copper phthalocyanine have become widely used due to their good working qualities, superb colour, and durability. The fact that

phthalocyanine pigments are insoluble in lipids and water and do not show acute toxicity in animal experiments adds to their appeal (Wöhrle *et al.*, 2012), (Hunger, 2002). Typically, phthalonitrile or phthalic anhydride is used in high temperature cyclotetramerization methods to prepare phthalocyanines. This process requires the template effect provided by an appropriate metal cation. The reactions can be conducted in a range of solvents or without any solvent at all, although both methods need a high temperature (around 200 °C) and lengthy reaction times (Kantar *et al.*, 2015). Analogues of natural colours are phthalocyanines. But in contrast to these naturally occurring pigments, which are incredibly unstable, phthalocyanines are exceptionally stable and are perhaps the most stable colourants in use today. The colour of phthalocyanines is primarily limited to blue and green due to the minimal impact of substitutes. Phthalocyanines are very stable, brilliant, and strong, which makes them an affordable option (Nemykina & Lukyanets, 2010). In addition to printing inks and paints, phthalocyanines are said to have intriguing optoelectronic qualities and to have found usage in a variety of novel applications, including liquid crystals, optical and electronic devices, chemical sensors, non-linear optics, and fibrous assemblies (Gregory, 1990), (Thimiopoulos *et al.*, 2014).

Sulfur dyes

Sulfur dyes are used to colour cellulosic fibres, with a few exceptions. They are insoluble in water and must be reduced with sodium sulfide solution to a water-soluble leuco form before being applied to the substrate. The actual Sulfur dye is subsequently created by chemical or atmospheric oxidation inside the fibre pores. C.I. Sulfur Black 1, which is made by heating 2,4-dinitrophenol with sodium polysulfide, is one of the most significant dyes (Hunger, 2002). The Sulfur dyes are more difficult to identify as a chromogen than the majority of other dye types (Gregory, 1990). Sulfur dyes are only described in terms of the raw materials and manufacturing processes; they do not have clearly defined chemical structures or consistent compositions. After synthesis, excess Sulfur is, in fact, separated from the colour (Gürses *et al.*, 2016a). The essential component of a chromophore, Sulfur linkages are essentially a complicated mixture of polymeric molecules made up of a significant amount of Sulfur in the forms of polysulfur (-Sn-), disulfide (-S-S-), and

sulfide (-S-) links in heterocyclic rings. Thiazole, thiazone, and thianthrenes, are the foundations of chromatic systems. Sulfurization, which is heating Sulfur, polysulfide, or both in a combination together with aromatic amines, phenols, or aminophenols, or refluxing in solvents under pressure, is the general process used to create Sulfur dyes (Nguyen & Juang, 2013). The same method is used to create sulfurized vat dyes, but a potent reducing agent, such as sodium hydrosulfide, is needed to reduce them. Sulfur dyes are mostly used to colour textiles made of cellulosic materials or combinations of cellulosic and synthetic fibres (Nguyen & Juang, 2013). However, they are also occasionally used to dye silk, paper, and some kinds of leather. Sulfur dyes are the least colourful synthetic dyes available, but they are also very affordable, very washable, and have exceptional light fastness. Because of these qualities and their simplicity of use, Sulfur dye consumption is certain to stay high (Hunger, 2002).

Nitro and nitroso dyes

Despite their current low commercial significance, these dyes tiny molecular architectures are intriguing. The original nitro dyes were acid dyes that were used to colour natural animal fibres like silk and wool. These dyes contain one or more nitro or nitroso groups coupled via an aromatic system with a group that donates electrons. When nitrous acid reacts with naphthol and phenol, hydroxynitroso compounds are created. Although the nitroso compounds do not have dyeing capabilities in and of themselves, they can combine to generate metal complexes that can either be pigments or acid dyes if the initial chemical has hydrophilic groups (Gregory, 1990), (Christie, 2023).

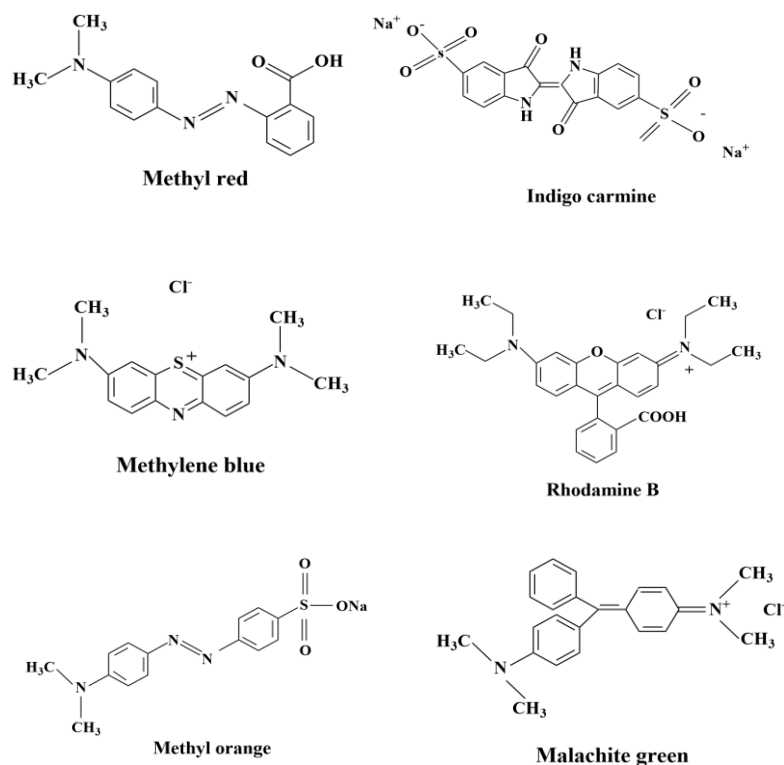


Figure 1: Structure of dyes.

1.3 Metal nano sulfides

The primary reason for the surge in interest in metal sulfide nanoparticles (NPs) is their ability to compete metal oxide nanoparticles in photo and electrochemical characteristics. Even though nanoparticles are widely employed, there is still much space for significant advancements in terms of the materials' performance. These include applications in electronics, photovoltaics, sensing, catalysis, and cosmetics, to mention a few (Xing *et al.*, 2018). Titanium oxide nanoparticles are among the most commonly utilized metal oxide nanoparticles for ease of comparison. In 2019 alone, the \$8.5 billion global nanomaterials market was largely dominated by TiO₂ nanoparticles. It is also a well-known photocatalyst that has been the subject of in-depth research and continues to be so (Etacheri *et al.*, 2015). Titanium dioxide is active in the ultraviolet (UV) region of the electromagnetic spectrum below 400 nm and has a band gap of 3.2 eV. This suggests that it only utilizes a limited portion of

the sun's spectrum, whereas metal sulfide nanoparticle photocatalysts, like CdS, have a band gap of 2.45 eV and can absorb light up to 520 nm in the visible spectrum (Wold, 1993). The energy difference between the compound's ionization potential and electron affinity is represented by the band gap, which is the energy difference between the valence and conduction bands (Hao & Lang, 2019). Sulfur's lower ionization potential and greater electron affinity than oxygens can account for the overall pattern of sulfides' narrower band gaps when compared to oxides. Because of this, sulfides are a tempting substitute for conventional metal oxide photocatalysts and can function in the visible portion of the electromagnetic spectrum. It has been demonstrated that the combined qualities of metal oxide NPs and metal sulfide nanoparticles are significantly better than the individual properties of metal oxide NPs (Mao *et al.*, 2013). Nowadays, there are numerous methods used to create metal sulfide nanoparticles. Many of the synthetic techniques are still not scalable, but they have a great deal of adjustability. Metal sulfide nanoparticles can also be made by wet chemical processes. Metal sulfide nanoparticles (NP's) can be produced synthetically and scaled through the thermal breakdown of metal oleates (Lee & Jun, 2019). Sulfide nanoparticles of lead, zinc, copper, cadmium, and manganese were created using this technique. Because it is necessary to first create metal oleate complexes from metal chloride/nitrate salts, the production of the metal oleate is a difficult process. After dissolving these complexes in a solution containing dodecanethiol and oleylamine, the compounds are heated to high temperatures (Choi *et al.*, 2009).

One popular method for synthesizing different nanostructures with different chemistries and architectures is hydrothermal synthesis (P. Kumari & Kumar, 2023). This involves placing precursor aqueous solutions in an autoclave and allowing them to react at extremely high temperatures. Thiourea was utilized as the source of sulfur in the hydrothermal synthesis that produced CuS, MoS₂, WS₂, and RuS₂ nanoparticles. Despite the fact that the size and makeup of the nanostructures may be greatly controlled, this technique is still primarily carried out in small batches (Sharma *et al.*, 2021). Due to its advantages over traditional methods, photocatalytic dye degradation is gaining a lot of attention in recent research (Turner, 1999). It is

considered a green environmental solution for a better future, primarily due to its role in oxidative decomposition and wastewater purification. Several photocatalytic systems, such as metal chalcogenides, have become effective photocatalysts for the photochemical degradation of organic dyes over the past few decades (Kubacka *et al.*, 2012). Transition metal sulfide (TMS) nano and micro-particles have drawn considerable interest due to their fascinating mechanical, chemical, optical, electrical, and catalytic properties. The variety of chemical compositions, particle morphologies, sizes, shapes, and other characteristics of metal sulfide nanoparticles makes them highly desirable (Lai *et al.*, 2012). Because of this, alterations in the chemical composition through doping, the creation of solid solutions, or the blending of several metals in a sulfide nanoparticle will grant access to an enormous variety of distinct nanoparticle types with extremely particular electrochemical and physical properties (Moon *et al.*, 2019). Within this framework, the primary reason for investigating metal sulfide nanoparticles is their ability to function as absorbers or charge (hole or electron) transport layers (C. Zhao *et al.*, 2019), (Reeja-Jayan & Manthiram, 2013). Such an approach offers several benefits, including low cost, lightweight design, high flexibility in tailoring the chemical and physical properties, improved chemical and photochemical stability of the particles used in solar cell construction, and good scalability through compatibility with flexible materials for roll-to-roll processes. As a result, much research has focused on creating solar cells with improved performance by utilizing metal sulfide nanoparticles as functional elements (Tang *et al.*, 2004), (Asahi *et al.*, 2001).

Metal and Sulfur atoms combine to form metal sulfide nanoparticles, which are tiny particles. These nanoparticles have distinct chemical, optical, and electrical characteristics. They are great options for energy storage and catalytic reactions due to their compact size and high surface area-to-volume ratio (Wu *et al.*, 2022). Pure metal sulfides, doped metal sulfides, and composite metal sulfides are the three primary categories of metal sulfides. They possess electrochemical, magnetic, and catalytic capabilities when composed entirely of a single metal (Gao *et al.*, 2019). Doped metal chalcogenides can be utilized to improve the structural, electrochemical, magnetic, photo-catalytic, and catalytic properties of metal sulfides.

Binary metals are employed in this process, where one is present in a high concentration and the other at a low concentration. It is possible to employ several metals as dopants, such as Ce, Sr, Cu, Co, etc. A substance made up of two or more different components, one of which is a metal sulfide, is referred to as a metal sulfide nanocomposite (Ao *et al.*, 2020), (Murugadoss *et al.*, 2022). There are two popular techniques for creating metallic nanoparticles: top-down and bottom-up methods. The primary distinction between these techniques lies in the type of precursor used to produce nanoparticles. Atoms or molecules are used as precursors in the bottom-up method, whereas bulk materials are used in the top-down method (Wang *et al.*, 2023).

Metal sulfide nanomaterials have emerged as an important class of advanced functional materials due to their unique structural, optical, and electronic properties. At the nanoscale, metal sulfides such as ZnS, CdS, CoS, and Ce₂S₃ exhibit distinct behaviors compared to their bulk counterparts, including quantum confinement effects, high surface-to-volume ratios, tunable band gaps, and enhanced surface reactivity (Carp *et al.*, 2004). These features make them particularly attractive for applications in catalysis, energy conversion, sensors, optoelectronics, and environmental remediation. Various synthetic strategies have been developed to produce metal sulfide nanoparticles with controlled size, morphology, and crystallinity (Alaton *et al.*, 2002). Mechanochemical processing is a notable route, where solid-state displacement reactions are induced during high-energy ball milling of metal halides with alkali or alkaline earth sulfides. This technique allows direct formation of sulfide nanoparticles such as ZnS, CdS, and Ce₂S₃ under ambient conditions, yielding particle sizes as small as 4–20 nm and even enabling structural phase transformations at the nanoscale (Ravi *et al.*, 2020). Electrochemical methods have also been employed to synthesize sulfide nanomaterials. For example, ZnS nanoparticles can be electrodeposited from zinc anodes in sulfide electrolytes, with particle size tunable by varying reaction parameters such as applied potential, electrolyte concentration, and stirring rate. Optimization studies using statistical approaches have demonstrated that electrochemical synthesis offers a low-cost, scalable pathway for producing ZnS nanostructures with tailored

morphologies(Ambrogi *et al.*, 2017).. Another effective strategy involves the use of single-source precursors such as metal dithiocarbamates. Thermal decomposition of these complexes provides an efficient route to obtain metal sulfide nanoparticles with controlled composition and purity. For instance, cobalt dithiocarbamate complexes have been utilized to generate cobalt sulfide and cobalt–iron sulfide nanomaterials, which display enhanced photocatalytic activity.

The functional versatility of metal sulfides is primarily derived from their semiconducting behavior. Their narrow to medium band gaps and strong visible-light absorption make them highly promising for photocatalysis. In particular, sulfide nanomaterials have been intensively investigated for solar-driven hydrogen production and dye degradation. For instance, CdS-based systems demonstrate remarkable photocatalytic hydrogen evolution efficiencies when combined with sacrificial agents and cocatalysts, in some cases achieving apparent quantum yields exceeding 90%(Hunger, 2002).. Similarly, cobalt sulfide and cobalt–iron sulfide nanoparticles exhibit superior photocatalytic degradation of organic dyes such as rhodamine-B and methylene green under UV irradiation, highlighting their environmental remediation potential. Beyond catalysis, ZnS nanoparticles have been widely explored for applications in optoelectronics, including photodetectors, electroluminescent devices, and solar cells, owing to their wide band gap (3.5–3.7 eV) and strong photoluminescence Chiu *et al.*, 2019. Moreover, the ability of metal sulfides to undergo polymorphic transformations at the nanoscale, as observed in CdS and Ce_2S_3 , opens additional avenues for tuning their optical and structural characteristics. The study of metal sulfide nanomaterials is therefore critical from both a fundamental and applied perspective. Their structural tunability, low-temperature synthetic accessibility, and wide-ranging applications position them as key candidates in the fields of renewable energy, photocatalysis, and nanotechnology. Current research is focused on optimizing synthesis routes to achieve greater control over particle size, morphology, and stability, while also integrating these nanomaterials into hybrid or composite systems for enhanced functionality.

Methods for synthesizing nanoparticles:

Top-down approach

In order to prepare tiny nanoparticles, bulk precursor materials must be broken down using various physical techniques, including sputtering, grinding, milling, thermal ablation, and laser ablation (Khawaga *et al.*, 2023). As a result of these procedures, nanoparticles that are smaller than the initial bulk material are formed (Aragón *et al.*, 2015). There are two categories for top-down approaches. Scotch tape method: This technique is referred to as non-destructive because it does not involve any chemical reactions. Particles resembling nanoflakes are produced by this easy method. Physical method: A variety of physical techniques are employed, including liquid-phase exfoliation, mechanical milling, ultrasonication, and electron spray pyrolysis (Nyabadza *et al.*, 2023).

Milling machines: The process of reduction transfers kinetic energy from the grinding media to the material and is a low-cost way of creating NPs from bulk. The premise of operation for this approach is reduction of particle size using high-energy ball milling. NPs are made by combining heavy balls that spin quickly with bulk powder in a container. This process produces particles of a small size (Jamkhande *et al.*, 2019). Liquid-phase exfoliation: Exfoliation techniques are effective, inexpensive, produce fewer byproducts, and are easy to use (Finegold & Cude, 1972). Exfoliation of the material produces 2D flake-like particles through mechanical processing methods, such as ultrasonication. This approach uses DMF as a solvent. Using this method, monolayer nanosheets with a thickness of <1 nm are created (Hossain *et al.*, 2023). Electrospray pyrolysis: Precursors are introduced into a hot reactor in gaseous form using this method. A nebulizer system, consisting of a vertical tubular reactor, a precipitator, and a fluid nebulizer, is used to facilitate the precursor (Suppiah *et al.*, 2023).

Bottom-up method

This method creates nanoparticles (NPs) by combining tiny particles, like atoms or molecules. Both chemical and biological methods are used in the synthesis of NPs.

Synthesis of nanoparticles using chemical techniques. When it comes to producing nanoparticles with precise and adjustable sizes at a faster rate, chemical approaches are superior. In chemical procedures, the key ingredients employed are metallic precursors, stabilizing agents, and reducing agents (Do *et al.*, 2023).

Hydrothermal technique

The hydrothermal method of producing metal sulfides requires a closed system with controlled pressure and temperature. This is an inexpensive method for creating MoS₂ nanoparticles. The Mo precursor is sodium molybdate, and the sources of Sulfur are thiourea and thioacetamide. This environmentally friendly method eliminates the need for complexing agents and pH regulation (Munyai *et al.*, 2022). FeS₂, CuS, Ag₂S, MoS, and CdS are created by this process. Heating a combination of metal salts and sulfide sources produces NPs (Hamnabard *et al.*, 2015), (M. Liu *et al.*, 2023). Metal sources that are frequently utilized include nitrates or chlorides, and sources of sulfur are organic sulfides. This method uses an autoclave to produce nanoparticles predominantly.

Microwave-assisted technique

This method involves a material-microwave interaction that transfers heat energy from the outside to the inside, causing a thermal reaction. Instead of using an external inductor, the reaction chamber generates heat within (Sambathkumar *et al.*, 2021). The use of microwave reactors replaces traditional oil bath heating with a greener, safer option. Metal acetates that undergo thermal degradation provide PbS and CdS nanoparticles (Cos *et al.*, 2016).

Solvothermal method

This process involves the synthesis of metal sulfide nanoparticles in a sealed system by chemical reactions between precursors in a solvent environment. This method requires the use of solvents in precursor processes; the two most common solvents used for this purpose are DMF and water. Temperature, solvent, time, and precursors are the main variables that affect reaction control and product size (Munyai *et al.*, 2022). MoS₂/rGO nanoparticles are synthesized using the solvothermal approach, a

straightforward method for producing nanoparticles of various forms. This economical procedure with short processing time is perfect for producing metal sulfides with small crystallite sizes (Torres-Castillo & Tavares, 2022).

Chemical precipitation method

Chemical precipitation is one of the most promising techniques for creating nanocatalysts among the various methods used to synthesize nanoparticles, as it enables the complete precipitation of metal ions. It is also a common approach for creating nanoparticles with a greater surface area. Extreme conditions are not necessary for the creation of metal sulfide nanoparticles using this straightforward synthetic approach (Rajabi *et al.*, 2013).

Chemical vapor deposition

This method creates films by depositing gaseous molecules through chemical reactions, which is a necessary step in the film-making process. In CVD systems, surface processing and substrate properties affect film growth (W. Zhu *et al.*, 2021). There are several techniques for depositions, such as thermally active chemical vapor deposition, photo-initiated chemical vapor deposition, and 90 plasma assisted chemical vapor deposition. Precursors aggregate in the CVD process to form nanosheets, which results in a high yield of nanoparticles at a low cost (Luo *et al.*, 2020). In comparison to PVD techniques, CVD requires a lower vacuum for the deposit of high-purity materials. For the creation of monolayer transition metal chalcogenides, CVD is a very useful technique (L. Hu *et al.*, 2017).

1.4 Advanced oxidation process

The main purpose of advanced oxidation processes (AOP's) is to eliminate persistent organic pollutants (POPs) from waterways and wastewaters. AOPs are significant, effective, environmentally friendly, and promising approaches (Andreozzi *et al.*, 1999). In fact, they represent effective, efficient, and environmentally safe ways to rid waterways of persistent organic pollutants (POPs). The in situ production of $\cdot\text{OH}$ radicals using a variety of chemical, photochemical, sonochemical, or electrochemical processes is the basis for a number of AOP types (Tamimi *et al.*,

2006). The Fenton method, which uses a soluble iron (II) salt and H_2O_2 as the Fenton's reagent to break down and eliminate POPs, is the most traditional and widely used chemical AOP. However, by simultaneously irradiating the treated environmental water sample with ultraviolet (UV) light (photo-Fenton method) or sunlight (solar photo-Fenton method), it is feasible to significantly increase the oxidation efficiency and utilization ease of this method (Gogate & Pandit, 2004). There have also been reports of other photochemical techniques, such as heterogeneous photocatalysis employing TiO_2 suspensions. Combining electrochemical reactions with the Fenton approach is the basis of another intriguing advancement. A variety of recently reported electrochemical advanced oxidation processes (EAOPs) exist (Konstantinou & Albanis, 2003). EAOPs have been used to produce $\cdot\text{OH}$ in situ through electrochemistry, which destroys harmful or persistent organic materials in water. Since they employ the electron, a clean reagent, EAOPs are emerging and environmentally friendly methods that significantly reduce or eliminate the need for chemical reagents (Černigoj *et al.*, 2007). $\cdot\text{OH}$ is produced in bulk solution either directly through the oxidation of water on a high O_2 evolution overvoltage anode or indirectly through the use of Fenton's reagent, which is produced electrochemically from electrode reactions (Oturán, 2000), (Brillas *et al.*, 2003). Figure 2 shows the mechanism of degradation process.

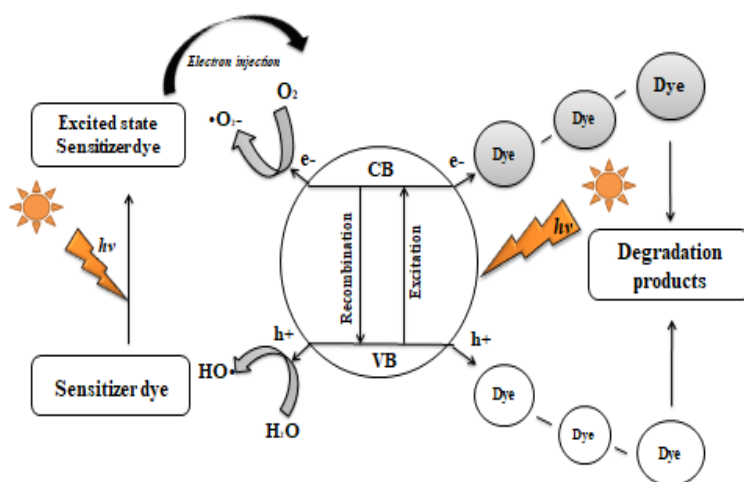


Figure 2: Mechanism of degradation of dyes.

Fenton's reagent

Fenton produced a comprehensive study on the utilization of a combination of H_2O_2 and Fe^{2+} (later known as Fenton's reagent) for the oxidation and destruction of tartaric acid near the end of the nineteenth century, marking the beginning of Fenton's chemistry. Fenton's chemistry has been the subject of multiple review papers due to its significant progress over the twentieth century and numerous applications to water and soil remediation (Oturán & Aaron, 2014). Haber and Weiss (1932, 1934) demonstrated in the 1930's that a complex radical and chain mechanism governed the catalytic breakdown of H_2O_2 by iron salts (Haber *et al.*, 1934). According to more recent mechanistic research, the creation of the hydroxyl radical triggers the Fenton process, which is consistent with the traditional Fenton reaction and can be used to break down and eliminate a variety of organic contaminants. Through the use of pulse radiolysis, several rate constants related to Fenton's chemistry have also been determined (Neyens & Baeyens, 2003). When the pH of the polluted aqueous medium is between 2.8 and 3.0, the Fenton method can be effectively used. In fact, the Fenton's reaction can spread under diverse circumstances due to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple's catalytic activity (Pignatello *et al.*, 2006). Additionally, it is crucial to emphasize that a number of variables, including temperature, pH, H_2O_2 , and catalyst concentrations, affect the practical efficiency of Fenton's reagent (Pignatello *et al.*, 2006). These variables also affect the rate at which organic materials are oxidized by generated $\cdot\text{OH}$ and the ability of Fe^{2+} to regenerate from Fe^{3+} produced during the process (Metelitsa, 1971), (Lindsey & Tarr, 2000), (Bautista *et al.*, 2008).

Perozonation

The basis of the peroxonation principle is the interaction of ozone (O_3) with H_2O_2 , which produces oxidizing radicals. H_2O_2 increases the rate at which (O_3) breaks down in water, producing more highly reactive $\cdot\text{OH}$ radicals. The peroxonation process ought to be more effective than ozonation alone. Paillard *et al.* (1988) examined the mechanism and application conditions of peroxonation, demonstrating

that a very quick reaction between ozone and H_2O_2 in its ionized state resulted in the generation of $\cdot\text{OH}$ radicals (Paillard *et al.*, 1988). The primary objectives of peroxonation water treatment are to increase the lifetime of the active coal filter by substantially reducing the concentration of micro pollutants prior to filtration.

Compared to chemical AOP's, photochemical methods provide the advantages of being straightforward, inexpensive, clean, and generally more efficient. They can also eliminate contaminants and sanitize waterways. As a result, strong oxidants like O_3 and H_2O_2 have been combined with UV radiation, sometimes through catalysis using Fe^{3+} or TiO_2 , to produce a variety of significant photochemical AOPs. Three possible reactions allow these photochemical processes to degrade and/or destroy pollutants: photodecomposition, which is based on UV irradiation, excitation, and degradation of pollutant molecules; oxidation by direct action of O_3 and H_2O_2 ; and oxidation by photocatalysis (with Fe^{3+} or TiO_2), inducing the formation of $\cdot\text{OH}$ radicals.

Photolysis of H_2O_2 ($\text{H}_2\text{O}_2/\text{UV}$)

UV radiations absorbed at wavelengths between 200 and 300 nm have the ability to photolyze hydrogen peroxide, resulting in the homolytic scission of the H_2O_2 molecule's O-O bond and the formation of $\cdot\text{OH}$ radicals, which can also aid in the H_2O_2 molecule's secondary reactions for breakdown (Kurian, 2021). There may be multiple competitive and consecutive reaction steps underse circumstances. It is vital to emphasize that the pace at which free radicals are produced is primarily determined by a number of significant factors, such as the power and emission spectrum of UV lamps as well as the physicochemical features of the medium (turbidity, pH, and UV light transmission) (Phyllis *et al.*, 2022). Since the ionization of H_2O_2 produces the HO_2^- anion which may significantly absorb UV light and form free radicals ($\text{HO}_2\cdot$ and $\cdot\text{OH}$), the reaction rate is often greater in alkaline medium at $\text{pH} > 10$. The molar absorption coefficient of H_2O_2 is relatively low in the UV area, which is a disadvantage of this AOP (Oturán & Aaron, 2014). To effectively oxidase organic contaminants, a relatively high quantity of hydrogen peroxide must be used. The $\text{H}_2\text{O}_2/\text{UV}$ AOP has been used to remove organic contaminants, such as benzene,

trichloroethylene, and tetrachloroethylene, as well as cyanides, from groundwater (Yuegang & Jürg, 1992). These groups include carbamates, aniline derivatives, organochlorinated derivatives, organophosphates, pyridine and pyrimidine derivatives, triazines, and substituted ureas (Sirés *et al.*, 2014). For the oxidation of simulated reactive dye bath effluents containing a mixture of monochlorotriazine-type dyes and various dye auxiliary chemicals at typical concentrations encountered in exhausted reactive dye bath liquors, Alaton *et al.* compared the treatment efficiency of the $\text{H}_2\text{O}_2/\text{UV}$ process to that of other AOPs (O_3/OH^- , and $\text{TiO}_2/\text{UV-A}$) (Alaton *et al.*, 2002).

Heterogeneous Photocatalysis

In the early 1970's, Fujishima and Honda (1972) demonstrated how water might be divided into hydrogen and oxygen in a photo-electrochemical solar cell utilizing titanium dioxide (TiO_2), a photo-excited semiconductor (Pelaez *et al.*, 2012). The process known as "heterogeneous photocatalysis" entails exposing a semiconducting catalyst typically TiO_2 to near-UV light. The catalyst is best in its rutile in front anatase form, which is easily photoexcited to form electron-donating and electron-accepting sites, allowing the induction of oxidation-reduction reactions. Electron-hole pairs are created when absorbed UV photons have energy greater than semiconductor's energy gap, which is the space between the valence and conducting bands. These pairs can then migrate to semiconductor surface and react with chemical species that have been adsorbed there, or they can recombine (Ayodhya & Veerabhadram, 2018a). Because titanium dioxide is nearly perfect in a number of critical areas, it has been selected primarily for the use of heterogeneous photocatalysis techniques in the treatment of water. TiO_2 is a highly stable chemically and physiologically inert material that is affordable, easy to make, and active in photocatalysis. Its energy gap is similar to that of solar photons. In addition, the photogenerated electrons are reducing sufficiently to produce superoxide from dioxygen, and the holes are potent oxidants. Under favorable circumstances, the absorbed pollutants can be directly oxidized by the photogenerated holes, or the hydroxyl groups at the TiO_2 surface can be oxidized to produce $\cdot\text{OH}$ radicals, whose redox potential is only marginally reduced (Fujishima & Zhang, 2006). As a result,

the contaminants in the polluted fluids can degrade either directly at semiconductor surface or indirectly through interactions with the $\cdot\text{OH}$ radicals; the most preferred degradation pathway is the indirect oxidation by the radicals. Additionally, adding H_2O_2 or O_3 , which can be photolyzed by UV irradiation, to the photoreactor can enhance the quantity of $\cdot\text{OH}$ radicals once again (Saqib & Muneer, 2002). The TiO_2 catalyst can be used in thin film form (fixed TiO_2 catalytic layer) or dispersed form (powder, aqueous solution) during the heterogeneous photocatalytic process. The manufacture of TiO_2 films has been greatly aided by the Fujishima group, who has applied TiO_2 coatings on a variety of support materials. The dispersed TiO_2 catalyst has a number of benefits, including ease of use, a significant specific surface area, and the ability to be aerated, which stops electron-hole pairs from recombining and raises catalyst efficiency (Carp *et al.*, 2004). The increasing development of dark catalytic sludge, which lowers UV irradiation efficiency and photoreactor performance, is a disadvantage of the dispersed form. In contrast, the catalytic layer in TiO_2 films needs to be extremely stable and active; nevertheless, there is no need to separate the catalytic particles at the end of the process (Carp *et al.*, 2004). The photoreactor, the kind and concentration of the pollutant to be treated, and the source of the radiation all influence the quantity and kind of catalyst that should be utilized. Additionally, the medium's pH value is vital to photocatalysis efficacy and needs to be adjusted first based on the kind of pollutant being treated. For instance, when weak acid pollutants are present, the photocatalysis efficiency rises with decreasing pH, resulting in a decrease in the pollutant's polarity and easier adsorption at the catalyst surface. In the past few years, heterogeneous TiO_2 photocatalysis has been used extensively, especially when dealing with organic contaminants that are resistant to oxidation by other traditional AOP's. Moreover, viruses, bacteria, and mould are among the hazardous biologic pollutants that it can totally eradicate. For the most part, this method works extremely effectively at treating a wide variety of both organic and inorganic contaminants (Halmann, 1995). Furthermore, it is important to highlight the recent advancement of a number of techniques to alter TiO_2 for the use of visible light (visible light active TiO_2 photocatalytic materials), such as linking semiconductors, dye sensitization, and nonmetal and/or metal doping (Pelaiez *et al.*, 2012).

1.5 Literature Review

Metal sulfide-based semiconductors are widely recognized as highly effective photocatalysts for the breakdown or degradation of dyes in wastewater treatment industries. These catalysts provide cost-effective, environmentally friendly, and sustainable treatment solutions that contribute to environmental preservation (Albini & Fagnoni, 2008). Environmental pollution has become a major hazard to public health and the environment in recent years. Global attempts have been made in the past to harness sunlight for water purification, environmental protection, and energy production (Ayodhya & Veerabhadram, 2018a). Photocatalysis is a key component of these efforts. "Photocatalysis" refers to a potentially novel technique that can be used to remove organic chemicals that are somewhat resistant (Xing *et al.*, 2012). This methodology is predicated on the creation of electron-hole pairs in semiconductor materials, such as metal sulfide nanostructures scattered in an aqueous media, through irradiation with light of an appropriate energy. The realization of how photochemistry differed from thermal chemistry was the pivotal moment that allowed photochemistry to stand alone as a science (Turner, 1999). In the early 1900's, a number of scientists believed that radiation was only one of several methods for accelerating a chemical process, such as heating it up or subjecting it to a chemical treatment. The word "photochemical" was appropriately used to these chemical reactions, whereas "photocatalytic" denoted reactions that were accelerated by light while following the same path as the original reactions. The 1970's saw the widespread use of the word "photocatalysis" and the emergence of a field named after it, albeit with relation to two distinct subjects. First, the oil crisis strongly encouraged the hunt for other energy sources. It was thought that by harnessing solar energy, man might create fuel like nature did, specifically hydrogen by water splitting via photocatalysis (Mamiyev & Balayeva, 2022). The second topic is the worry over the rise in chemical pollution and the suggestion that photocatalysis may purify the air and water without adding more chemicals. The two subjects were raised in disparate traditions and have stayed apart. The process of water splitting and photocatalysis to produce hydrogen on semiconductor nanoparticles was discovered in the 1970's (Koe *et al.*, 2020). Following that, research was conducted

to improve the process's efficiency for photocatalytic degradation and to comprehend the basic mechanisms underlying photocatalysis. It's interesting to note that, among all technologies, over 1900 consumer products in 2017 used nanomaterials, making nanotechnology one of the major technologies of the twenty-first century (Dreaden *et al.*, 2012). Applications for nanoparticles are numerous and include everything from commonplace items made from the food, textile, or cosmetic industries to industrial and environmental goods like paints, detergents, coatings, or catalysts. Since the rate of the photocatalytic reaction is independent of the "active site," the photocatalyst material, such as one that is activated by light, is crucial to carrying out an effective photocatalytic reaction (Byrne *et al.*, 2018). As such, care should be taken when selecting this material to ensure that it has the right electronic structure and acceptable light energy for photoactivation. The distinct photo-physical and photochemical (photocatalytic) characteristics of these nano-sized photocatalysts enable the tendency of photoactivation (Padikkaparambil *et al.*, 2013). The key factors influencing the photocatalytic degradation of hazardous chemicals (such as dyes, insecticides, and phenolic compounds) in an aqueous media are the band gap, surface area, catalyst quantity, and electron hole pair formation. The surface area has been found to be one of the most important elements in the photo-catalytic degradation of dyes. This is because a larger surface area increases the adsorption of dye molecules onto the photocatalyst surface, hence increasing the photocatalytic activity (Ayodhya & Veerabhadram, 2017).

Semiconductor nanostructures (SNSs), such as metal oxides, metal sulfides, and mixed compounds, are a common and significant class of photocatalysts that have garnered considerable attention in the last decade due to their distinctive physical and chemical characteristics. When one or more of the dimensions of semiconductor nanostructures are on the verge of or less than the exciton Bohr radius the minimum size at which a material retains its continuous band structure we speak of quantum confinement in the context of MSNS characteristics (Manivannan *et al.*, 2017). As a result, the band gap of binary MSNSs may be precisely adjusted by merely adjusting their particle sizes, all without changing the chemical composition of metal sulfide (Zinatloo-Ajabshir *et al.*, 2017). Based on this, several unique methods have been

developed in recent decades for simple artificial size control and band gap tuning of binary metal sulfides. Due to their diversity, these MSNSs can be used to target a wide range of properties and applications, including high-performance supercapacitors, energy storage devices, biological processes, photocatalysis, colorimetric, and electroanalytical techniques, as well as electrochemical devices, sensors, and transducers (Mortazavi-Derazkola *et al.*, 2017). Because of the electronic configuration of the metal atoms in chemical combination which is characterized by a filled valence band and an empty conduction band metal oxides in semiconductor nanostructures can also operate as sensitizers for light-induced redox reactions. A hole is left behind when valence band electrons are promoted to the conduction band by radiation. These electron-hole pairs have the ability to interact with other molecules independently or to recombine (Desireddy *et al.*, 2013). The holes have the potential to combine with hydroxide ions or other electron donors in the solution to form strong oxidizing agents, such as superoxide or hydroxyl radicals (Collivignarelli *et al.*, 2017). In addition to the many semiconductor materials, there are a lot of semi-conductors (complex and metal oxides). Because of its potential to solve energy and environmental issues, heterogeneous photocatalysis utilizing semiconductors has drawn a lot of attention in recent decades as a green and sustainable technology. The fundamental photochemical reactions of organic dyes, organic compounds, photodegradation of pesticides, air and water disinfection, synthesis of organic compounds, production of renewable fuels, and hydrogen generation are all included in photocatalysis (J. Xing *et al.*, 2012). Due to its combination of electronic structure, charge transport properties, excited-state lifetimes, and the ability to absorb a wide range of visible and/or UV light, MSNSs are typically employed as effective photocatalysts in semiconductor nanostructures (Sakthivel & Kisch, 2003). In today's scientific world, photocatalytic degradation of organic pollutants by MSNSs, which negatively impact human health, has been the focal point of research efforts. Because standard treatments are largely unsuccessful and not environmentally friendly, dyes generated by numerous sectors pose a significant threat to the environment due to their slow degradation. In this regard, the most intriguing way for breaking down harmful substances into non-hazardous products seems to be the application of photocatalysis, particularly photocatalysis

employing semiconductor MSNS system, as opposed to the more traditional chemical oxidation methods (Halmann, 1995). The fundamental principles of photocatalysis, which include photophysical and photochemical aspects, have been thoroughly studied and documented in several academic works. When the absorbed photon energy, equals or surpasses semiconductor photocatalyst's band gap, leaving a hole in the valence band, the photoexcited electrons are promoted from the filled valence band to the empty conduction band, starting the photocatalytic reaction. As a result, an electron and hole pair is produced together (Kant, 2012). Semiconductor photocatalysis essentially consists of the following steps: a semiconductor is exposed to light of a specific wavelength; if the energy of the incident light equals the band gap energy of semiconductor, electrons are excited from the valence band to the conduction band, leaving holes in the valence band (Hosseinpour & Hosseinpour, 2017). To produce the required degradation products, these electrons and holes can undergo further oxidation and reduction reactions with any species or other reactants that may be adsorbed on semiconductor's surface. The electronic structures of metal sulfide semiconductor nanostructures, which meet the criteria for effective photocatalysts in the heterogeneous photocatalytic degradation of dyes, can be explained by the band model. This model is characterized by a filled valence band (VB) that is separated from a vacant conduction band (CB) by a forbidden energy gap, known as the band gap (E_g) (Ferrer *et al.*, 2014). Compared to metals and insulators, semiconductor-based MSSNs materials fulfil photocatalytic criteria because semiconductor band gap energies are between 1-4 eV and higher. Semiconductor materials are particularly attractive for photocatalytic reactions in environmental applications due to their unique properties (Ayodhya *et al.*, 2016).

Because of its direct and broad band gap (3.6eV) as an II-VI compound semiconductor, zinc sulfide (ZnS) is a good choice for a transparent photocatalytic material in the visible spectrum. ZnS exists in two phases: the a-phase, which is the hexagonal wurtzite structure, and the b-phase, which is the cubic sphalerite structure (Rajabi *et al.*, 2013). Field emitters, field effect transistors (FETs), p-type conductors, photocatalysts, chemical and biosensors (including gas sensors), nonlinear optic devices, and nano-generators are just a few of the many applications

for which it has historically demonstrated remarkable versatility, new fundamental features, and diversity (Isac & Enesca, 2022). With an eye towards their potential applications, ZnS nanostructured materials have been created using a variety of physicochemical techniques, including hydrothermal, solvothermal, microwave, and coprecipitation methods. With a hexagonal shape, zinc sulfide (ZnS) creates huge specific surface area nanosheets or nanorods (Sanjeev Kumar *et al.*, 2015). Using a non-toxic ZnS semiconductor as a photocatalyst is a highly effective method for removing contaminants from the environment, particularly in the breakdown of organic dyes in water. Under photoexcitation, ZnS quickly forms electron-hole pairs and exhibits excellent physical stability in the presence of UV radiation. Various research groups have attempted to enhance the photocatalytic activity of zinc sulfide (ZnS) with different morphologies, including cubic, nanorods, nanotubes, nanobelts, and nanowires (Ayodhya & Veerabhadram, 2019). Although metal sulfides based on semiconductors are well recognized for their outstanding photocatalytic behavior, zinc sulfide (ZnS) is not a good photocatalyst due to its large energy band gap (3.66 eV), which translates to less than 340 nm, meaning that it is only active in 4% of the solar light that enters the system. Various research groups have attempted to increase the photocatalytic activity of zinc sulfide (ZnS) with various morphologies, such as cubic, nanorods, nanotubes, nanobelts, and nanowires (Ayodhya & Veerabhadram, 2019). With a straight band gap of 2.43 eV at ambient temperature, CdS is regarded as a standard II-VI semiconductor. Researchers have given this material a great deal of attention due to its prospective applications. Due to its many applications, including as a chemical sensor, photocatalyst, biotracer for tumours, and solar cells, nano-structured CdS is currently a problem (Prabhu & Abdul Khadar, 2005). Many physical and chemical techniques are used to synthesize CdS nanoparticles as films, powders, colloids, nanofibers, nanorods, and so on. Because of the unique property of size-dependent physical and chemical nature, it is of great interest to researchers. CdS has widespread applications in the construction of photo-electronic devices, in the field of medicine as bio-imaging and biosensors, and also as the best visible light active semiconductor-based photocatalyst (H. Wang *et al.*, 2016). Generally speaking, the band gap and visible area absorption of CdS nanostructures make them a great material for dye degradation. However, major disadvantages of employing

CdS in environmental cleanup are the low separation efficiency of the charge carriers, i.e., electron/hole pairs, and the corrosion problems related with it. Unceasing efforts were undertaken to augment the photocatalytic activity of CdS by dopants and semiconductor nanostructures other than CdS (Shkir *et al.*, 2020). CuS in particular are highly desirable because of their exceptional optical qualities, which have a wide range of possible uses. CuS also appears in other morphologies with varying band gap values (Hosseinpour & Hosseinpour, 2017). Due to its distinct physical and chemical characteristics and its potential applications in a variety of fields, including photocatalysis, low-temperature superconductors, optical filters and superionic materials, nano-switches, lithium-ion batteries, sensors, and thermoelectric cooling material, the covellite CuS is one of the most extensively studied copper sulfides (Blachnik & Müller, 2001). The visible light source is the primary focus of research on covellite CuS photocatalysis because of its narrow band gap and good optical absorption characteristics in the visible-NIR range (Sakamoto *et al.*, 2003). The dimensions, surface area, and shape of CuS semiconductor nanostructures influence their photo-catalytic activity. Strong affinity for visible light absorption is possessed by CuS. CuS NCs and other copper chalcogenide composites have garnered a lot of interest due to their distinctive physicochemical characteristics and wide range of possible uses (Šetkus *et al.*, 2001). Bismuth chalcogenides have garnered a lot of attention lately because of their strong photocatalytic activity in dye degradation process. Bi₂S₃ is one among these bismuth chalcogenides that has drawn a lot of interest in photocatalysis due to its distinct optical characteristics and band gap (1.3 eV) (Sambathkumar *et al.*, 2021).

Recently, the photocatalytic activity of NiS based on Bi₂S₃ has garnered much attention from researchers. The vast array of potential applications for CoS semiconductor nanostructures, including optical and electronic devices, biological imaging, photocatalysts, light-emitting devices, gas sensors, and photovoltaic devices, has garnered considerable attention. With regard to lithium-ion batteries, cobalt sulfides (CoS, CoS₂, Co₃S₄, Co₉S₈, etc.) in particular have garnered a lot of interest due to their superior optical, photocatalytic, electrical, and magnetic properties (Hosseinpour *et al.*, 2018). Due to its special properties, which include a

tiny direct and indirect band gap, a high absorption coefficient in sunlight, abundance and non-toxicity in nature, and inexpensive cost, CoS, a notable binary compound semi-conductor, has drawn a lot of attention (Gu *et al.*, 2013). CoS is a suitable photocatalyst because of its appropriate band gap and strong adsorption characteristics. CoS semiconductors, which offer an interface with an aqueous medium and induce an enhanced oxidation process, have shown to be a promising green technology for environmental purification when used in the photocatalytic treatment of organic dyes or chemicals in wastewater (Sohrabnezhad *et al.*, 2009). It was not until several decades after the field of heterogeneous photocatalysis first emerged that transition-metal sulfides, such as CdS or ZnS, had sufficient documentation as photocatalysts. Specifically, CdS can absorb visible light up to 520 nm and has a bandgap of 2.4 eV (Lang *et al.*, 2015). This attribute further elevates it to the status of one of the most exemplary visible light-active semiconductor photocatalysts. The production of solar fuels and the use of metal sulfide photocatalysts to degrade environmental contaminants have received the majority of focus. However, in the suspended systems of semiconductor photocatalysis, these attempts typically need the transfer of several electrons for a successful turnover of a single molecule, which is highly demanding (H. Xu *et al.*, 2020). For metal sulfide photocatalytic interfacial methods to wait for advancements in resolving impending energy and environmental concerns, molecular understanding is required. It was discovered early on that photocatalytic selective transformations of organic molecules are important on metal sulfide semiconductors. The goal of photocatalytic treatments for many organic dyes was their decolonization rather than their complete breakdown into CO₂ and H₂O. In this rebirth, metal oxides like as TiO₂ are at the forefront, controlling the changes in small organic molecules that contain heteroatoms through surface complexation (Beranek, 2011). The development of new techniques for the synthesis of materials, the search for novel mechanisms, or the integration of metal sulfides with metal oxides, metal nanoparticles, or other emerging materials has reignited interest in metal sulfide photocatalysis for visible-light-induced selective organic transformations (L. Cheng *et al.*, 2018).

More significantly, in addition to providing a greener substitute for selective organic transformations, the distribution of products is moderately narrow, making analysis easier, and the interfacial reaction pathways of small organic molecules on metal sulfides are reasonably observable. Due to these qualities, the changes in small organic molecules can be considered an effective indirect means of characterizing the freshly synthesized materials (Hao & Lang, 2019). All metal oxides are limited to using photocatalysis in the presence of UV light, which makes up around 4% of the electromagnetic spectrum (Etacheri *et al.*, 2015). The goal of photocatalysis over the years has been to reduce photocatalyst bandgaps so that visible light can be utilized in place of UV radiation. But the process of narrowing the bandgap is expensive. Moreover, another issue that must be resolved during photocatalysis is the recombination of electron-hole pairs. With lower bandgaps than metal oxides, metal sulfides are able to directly absorb and use readily available visible light, giving them an advantage (S. Zhu & Wang, 2017). Metal sulfides react effectively to sunlight because their conduction bands are positioned higher than those of metal oxides. They are appropriate for reducing water as well. Sulfides are poorer agents for splitting water because of their reduced ability to oxidase due to their superior absorption capacity compared to oxides. Therefore, in order to create a hydrogen photocatalyst during water reduction, a sacrificial reagent is required. Because sodium sulfite (Na_2SO_3) functions as a sacrificial reagent, any sulfide will function better in the presence of this aqueous solution of sodium sulfide (Na_2S) (Tahir *et al.*, 2020). As nanostructured photocatalysts, metal sulfides are both economical and environmentally benign. Additionally, they can separate water into hydrogen and oxygen. Metal oxides and metal sulfides are the most often utilized semiconducting materials as photocatalysts (Djurišić *et al.*, 2014). Due to the localized nature of 2p oxygen and the fact that its holes are essentially hefty and large, metal oxides exhibit a broad bandgap (Nazri & Sapawe, 2020). The open exposure of active sites, combined with potent catalytic and photocatalytic properties, short energy bandgaps, and advantageous band locations, makes metal sulfides highly intriguing. Their modest effective mass allows them to exhibit size-based quantum phenomena. Metal sulfides have shallow valence bands, as opposed to metal oxides (Saeed *et al.*, 2022). Sulfides are effective photocatalysts because of their dazzling behavior towards light

(photons), availability in a wide range of crystalline forms and structures, and chemical compositions. These characteristics demonstrate the sulfides' ability to use a broad range of the solar spectrum. These days, a wide range of metal sulfides and associated nanostructures are employed in energy conversion applications, surface morphology, conductivity, and storage. In order to synthesize metal sulfides efficiently, it is important to first define their shape, structure, morphology, size, and defect states (Balavijayalakshmi & Sonia, 2021). Solar energy can be a feasible source of energy for heterogeneous photocatalysis, an advanced oxidation process, provided that the catalysts are carefully chosen. High absorption capacity solar light and conductivity for photogenerated charge carriers are the criteria for selecting catalysts (Yan *et al.*, 2013). Thus, the enhancing the efficient use of solar energy through the design and development of semiconductor materials with a wide solar selective spectrum response, improved activity, and stability are important goals in fascinating research areas: solar energy conversion and environmental treatment, including hazardous waste cleanup, water and air purification, and disinfection (Srinivas *et al.*, 2015). Metal sulfides are a significant class of semiconductor-based photocatalysts, for which the bandgap can be slightly adjusted without changing the chemical composition by merely adjusting the particle sizes. The design and development of highly active, stable, and inexpensive photocatalytic materials with improved solar energy conversion efficiency is a major area of interest for current research. Visible light absorption can be increased by doping or surface modification; however, photo-induced electron and hole recombination in a single semiconductor remains an unresolved issue. The creation of heterojunction structures is the most widely used method for enhancing the photocatalytic performance of semiconductors. This approach has at least two benefits: it increases the photo-response range of semiconductor materials and boosts the efficiency of the separated photogenerated electrons from holes (Chandrasekaran *et al.*, 2019). The majority of dyes, including non-ionic, cationic, and anionic (acid, reactive, and direct) dyes, are synthetic. They are categorized as azo, anthraquinone, indigoid, nitroso, and nitro dyes based on their chemical structure. Due to their chemical stability and resistance to deterioration, dyes are widely used in various sectors, including textiles, leather, paper, rubber, printing, and plastics (Aljamali, 2015). As a result, they may remain in

water for extended periods. The release of an abundance of dyes into water poses a serious threat to the ecosystem, as they can block sunlight and contain hazardous materials such as aromatic compounds and heavy metals like chromium and lead (Pavithra *et al.*, 2019b).

1.6 Objectives and Scope of the study

Scope of the study

The scope of the study is to synthesize nanoparticles and measure and characterize the photocatalytic activity of metal sulfide nanoparticles, such as Cadmium Sulfide (CdS), Zinc Sulfide (ZnS), and Copper Sulfide (CuS), for the breakdown of organic dyes and pollutants. Synthetic and Natural dyes that make life colourful can harm our ecosystem. Removing these dyes is an environmental issue. Different organic dyes will be used for testing the photocatalytic activity. Organic dyes are the primary pollutants in wastewater produced by the textile industry due to the release of synthetic dyes into an aqueous environment. Textile dyes are synthetic substances that add colour to fabrics, which are non-biodegradable and pollute the environment. The use of visible light will be one of the goals. Various applications of nanoparticles involve removing pollutants from water bodies. The scope of the studies will also involve illustrating the possible mechanisms involved in metal sulfide nanoparticle synthesis, and the catalytic capability of the synthesized nanoparticles in the reduction/degradation of different organic dyes will be determined.

Objectives

The main objectives of the present studies will be as follows:

1. Synthesis of the photocatalyst using co-precipitation, hydrothermal, and reflux methods.
2. Characterization of the photocatalyst through techniques such as Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), UV–Visible Spectroscopy (UV–Vis),

Photoluminescence (PL), and Fourier Transform Infrared Spectroscopy (FTIR).

3. Evaluation of photocatalytic activity for the degradation of various organic pollutants, with particular emphasis on efficiency, stability, and feasibility.

CHAPTER 2

INSTRUMENTATION

2.1 Introduction

The optical characteristics of nanoparticles, such as absorbance, fluorescence, and scattering, can be studied by researchers using tools including UV-Vis spectrophotometers, fluorescence spectrometers, and Raman spectrometers. Due to the unique characteristics and size-dependent behaviors of nanoparticles, instrumentation plays a crucial role in their characterization. Evaluating the characteristics and possible uses of nanoparticles requires an understanding of their chemical composition. Quantum confinement effects and surface Plasmon resonance are responsible for the distinctive optical characteristics of nanoparticles. The capacity of instrumentation to offer comprehensive details about the size, shape, chemical composition, surface characteristics, and optical, mechanical, thermal, magnetic, electrical, and dynamic behaviors of nanoparticles makes it crucial for their characterization. Understanding the relationships between a nanoparticle's structure and properties is crucial for optimizing its performance in various applications across disciplines, including materials research, medicine, electronics, and environmental science.

2.2 X-ray diffraction (XRD)

Researchers can ascertain a nanoparticle's crystal structure using XRD. The arrangement of atoms within the crystal structure can be determined by examining the diffraction patterns that result from X-rays interacting with nanoparticle crystal lattice. Knowing this knowledge is essential to comprehending the characteristics and actions of nanoparticles. The crystal size and micro-strain of nanoparticles can be determined from the breadth and shape of the diffraction peaks in an XRD pattern. Researchers can determine the average crystallite size of nanoparticles and evaluate the degree of strain within the crystal lattice by using methods like the Scherrer equation. X-rays are a form of electromagnetic radiation with a wavelength of

around 1 Å, which is much shorter than light yet of the exact same nature. The crystalline material functions as three-dimensional diffraction gratings at X-ray wavelengths comparable to the distances between the planes in a crystal lattice, as Max Von Laue found in 1912 (Bunaciu *et al.*, 2015). A potent method for identifying and measuring the structural characteristics of individual crystalline phases in materials is X-ray powder diffraction (XRD). The thickness of thin films, multilayers, and atomic arrangements in amorphous materials, such as polymers, as well as at interfaces, is also measured using XRD. Quantitative and precise information on the atomic arrangements at interfaces can be obtained from XRD intensity. Its structure, average particle size, unit cell diameter, and sample purity can all be ascertained using it. The basis of X-ray powder diffraction is the constructive interference of crystalline materials with monochromatic X-rays. When fast-moving electrons are focused on a metal target, some of their kinetic energy is transformed into X-rays, which is how these X-rays are produced. White radiation is the term used to describe the continuous range of wavelengths that the target emits of X-rays. In a continuous spectrum, the electron accelerates towards the target in direct proportion to the supplied voltage, which determines the minimum wavelength. In addition to the white radiation, the target *also* produces a distinctive high-intensity radiation with a particular wavelength if the applied voltage is high enough. Both kinds of radiation are included in the radiation that a target emits (He, 2003). Due to its great intensity, $K\alpha$ radiation is frequently employed in diffraction research. For a typical copper metal target, the wavelength of this radiation is 1.54056 Å. The electron of the atom that makes up the crystal interacts with an X-ray beam directed towards it. Bragg's law governs the diffraction effect generated by the crystal's three-dimensional grating. X-rays are able to non-destructively enter solids and reveal details about their internal structure (H. Khan *et al.*, 2020). When an X-ray beam is incident upon a crystal, it functions as a natural diffraction grating in all directions. The Bragg's law, which states that $n\lambda = 2d\sin\theta$, describes how the X-rays are diffracted. Here, n represents the order of reflection, λ stands for wavelength, d for the distance between the crystal lattice planes that cause a given diffracted beam, and θ for the angle the incident beam makes with the lattice planes (Thamaphat *et al.*, 2008). In a typical X-ray powder diffraction pattern, the width of the Bragg's

reflection can reveal the average grain size. Because of the reduction in the coherently diffracting domain size; this can be taken to be equal to the average crystal size, the peak breadth increases as the grain size decreases. Scherrer's relation $D = k\lambda/(\beta\cos\theta)$ is used to estimate the average crystallite size.

Where β is the full width at half maximum (FWMH) of the most intense diffraction plane, λ is the target wavelength = 1.54Å, D is the crystal size, and θ is the Bragg's angle. The correction factor $k = 0.9$ accounts for particle shape. A finely powdered sample, ideally with crystals randomly distributed in every possible orientation, is exposed to a monochromatic X-ray beam. The different lattice planes are present in this powder sample in all possible orientations. Diffraction occurs for these crystals and planes because for any set of planes, at least some crystals must be oriented concerning the incident beam at the Bragg angle, θ . The diffracted beams could also be found using a movable detector, such as a Geiger counter, scintillation counter, or image plate, connected to a chart recorder or computer (diffractometer), or by encircling the sample with a strip of photographic film (Debye-Scherrer and Guinier focusing methods) (Ermrich & Opper, 2011). An efficient analytical method for determining the phase of a crystalline material, X-ray powder diffraction can also measure the material's crystalline nature and yield details about unit cell dimensions and lattice plane spacing. Amorphous materials can also be found in samples of nanoparticles using XRD. Unlike crystalline materials, amorphous materials show wide scattering characteristics rather than distinct diffraction peaks. Researchers can determine the amount of amorphous material in a sample by examining the XRD pattern. A flexible method for characterizing nanoparticles, X-ray diffraction can reveal important details about the crystalline structure, size, phase composition, and structural behavior of the particles under various conditions (Bunaciu *et al.*, 2015). For scientists and engineers working in disciplines including materials science, nanotechnology, catalysis, and pharmaceuticals, its broad range of applications makes it a vital tool.

2.3 Scanning electron microscopy (SEM) and EDAX

One of the most valuable tools for examining and analyzing microstructure morphology and chemical composition characterizations is the scanning electron microscope (SEM). To comprehend the foundations of electron microscopy, one must be familiar with the fundamental ideas of light optics. SEM is a potent method for closely observing a material's surface structure. In contrast to optical microscopes, which enlarge objects using visible light, SEM produce images by focusing an electron beam. Surface topography, crystalline structure, and chemical composition can all be determined via SEM (W. Zhou *et al.*, 2007). It is possible to attach different specialty stages (such as hot, cold, or made to allow for in situ mechanical testing) to analyses behavior under different circumstances. Because cathodoluminescence, or the emission of light, is stronger at temperatures close to absolute zero than it is at normal temperature, for instance, images created by the light released by a cold specimen are far less noisy. SEM has a wide depth of field, which allows it to focus on the majority of the specimen's surface concurrently, regardless of surface roughness. Since there is very little depth of field for optical microscopes operating at high magnification, the smoothness of the surface has a significant impact on image quality (Joy & Joy, 1996). Almost any kind of material can yield enlarged images and in situ chemical information through the use of scanning electron microscopy (SEM) and x-ray microanalysis. The two devices typically operate in an arid, high-vacuum environment to generate the high-energy electron beam required for analysis and imaging. With a few noteworthy exceptions, the majority of specimens intended for SEM analysis are weak conductors made up of beam-sensitive light components with varying water contents.

SEM is fitted with lenses to compress the spot and focus the electron beam on the specimen, as the spot size created by the gun is too large to produce a sharp image. The majority of SEMs have spots with a size of less than 10 nm, and the signals needed to create an image are produced by electrons gathered from the final lens interacting with the specimen and penetrating to a depth of approximately 1 μm . The specimen's picture is created point by point through the movement of the scan coils, which direct the electron beam to specific areas in the form of straight lines,

ultimately creating a rectangular raster on the specimen's surface. The method is contingent upon the necessary magnification (Echlin, 2009). The scan coils cause the beam to deflect across a smaller region if the operator desires a greater magnified image. It is important to note that the working distance, the distance between the specimen's surface and the last lens, affects magnification. Without detectors, every signal produced by the electron beam's interaction with the sample's surface could produce an incomprehensible image on its own. When creating SEM images, both backscattered electrons (BSE) and secondary electrons (SE) are employed. Both SE and BSE will be collected when a positive voltage is applied to the collector screen (Abdullah & Mohammed, 2019). On the other hand, if a negative voltage is given to the collector screen, only BSE will be collected. After the signals are shown on the viewing screen, the operator can adjust the brightness and intensity to get a reasonably clear image. The information supplied is influenced by the electron voltage mode (emitted from the cannon). If modest accelerating voltages are employed, less than 5 kV, the scanned image will have significant surface information. On the other hand, the high acceleration voltages (15-30 kV) that permeate the surface will cause the reflected signal from the surface to contain information about the samples inside (Mehta, 2012). SEM image, which is somewhat three-dimensional, depends on how the sample's topography is visualized in terms of shape, size, and surface texture. Moreover, the quantity of BSE and SE determines this. After that, the specimen is the focus of this beam. The electron beam scans the sample's surface. Different signals are released when the beam interacts with the sample. Secondary electrons (SE) and backscattered electrons (BSE) are the main signals used in SEM imaging. SE's are low-energy electrons that the incident electron beam causes to escape from the specimen's surface. Electrons that scatter back from within the sample are known as BSEs. These signals reveal the surface topography and composition of the sample. Detectors gather the signals that the sample emits and transform them into a picture (Echlin, 2009). Through the manipulation of variables, including beam intensity, focus, and detector setup, SEMs may generate superior depth of field and high-resolution images. SEM enables detailed imaging of surface features with resolutions as low as a few nanometers,

offering a superior depth of field that allows for the precise imaging of three-dimensional structures.

EDAX

Energy-Dispersive X-ray Analysis, which provides details on a sample's elemental makeup, is essential to Scanning Electron Microscopy (SEM). EDAX is a tool used mostly for elemental analysis of samples under SEM examination. Typical X-rays can be released from the sample when the electron beam interacts with the atoms therein. Every element release X-rays at particular energy levels that are exclusive to that element. Through the identification and analysis of these distinctive X-rays, EDAX can determine the elements included in the sample as well as their relative concentrations. The sample surface's elemental maps can be produced via EDAX (Rao *et al.*, 2011). EDAX can produce spatial maps illustrating the distribution of various elements on the sample surface by concurrently analyzing the X-rays released and scanning the electron beam across the sample. This feature is quite helpful for researching the variability and composition of materials. EDAX offers numerical data regarding the sample's elemental composition. EDAX can precisely determine the concentrations of different elements in the sample by calibrating the equipment using recognized standards. For many scientific and industrial applications where precise information on elemental composition is required, this quantitative analysis is indispensable. The various phases or chemicals present in the sample can be identified with the use of EDAX. Using databases of known elemental compositions, EDAX can help identify specific minerals, phases, or compounds present in the sample by comparing the measured X-ray spectrum with those in the database. The elemental information provided by EDAX enhances the overall characterization of the materials under investigation in SEM. Researchers can obtain a thorough understanding of the composition, structure, and characteristics of materials at the micro- and nanoscale by fusing elemental analysis with high-resolution imaging capabilities (W. Zhou *et al.*, 2007).

2.4 Transmission electron microscopy (TEM)

The powerful imaging method known as transmission electron microscopy (TEM) is used to view the structure of materials at the nanoscale. In contrast to traditional light microscopes, which illuminate specimens with visible light, transmission electron microscopy (TEM) uses an electron beam to view objects. This enables the achievement of significantly better resolution and magnification, allowing scientists to study the minute details of a material's structure with greater precision. The specimen's atoms interact with the electrons as they move through it, resulting in scattering and absorption (Wang, 2003). After that, the scattered electron pattern is gathered and utilized to create an image. The interaction of an electron beam with a thin object to create an image is the basis for the operation of transmission electron microscopy (TEM).

TEMs use high-voltage electron cannons are used by TEMs to produce an electron beam. Usually, a field emission source or tungsten filament powers these electron cannons. The electromagnetic fields inside the microscope column are used to accelerate the produced electrons to very high speeds. The electrons are accelerated with voltages as high as several hundred kilovolts (Sigle, 2005). The condenser lens system is the set of electromagnetic lenses through which the accelerated electron beam passes. The electron beam is focused and shaped by this apparatus before it interacts with the specimen. To allow electrons to pass through, samples for TEM investigation must be incredibly thin, typically less than 100 nanometers. This calls for specific sample preparation procedures, such as freeze-fracture techniques for biological specimens or ultramicrotomy for solid materials. The accelerated electron beam passes through the thin specimen. The electrons in the specimen scatter and absorb as a result of their interactions with the atoms. The specimen material's atomic number, thickness, and density all affect the amount of it that is scattered and absorbed. The objective lens system gathers and focuses the scattered electrons after they have passed through the specimen (Sigle, 2005). The dispersed electrons are magnified and focused onto a detector by this system's array of electromagnetic lenses. When concentrated electrons hit a fluorescent screen or a digital detector, they produce electrical signals or visible light. A picture of the specimen is

subsequently created by processing these signals. As an alternative, contemporary TEMs might image directly using digital cameras.

The resulting image provides comprehensive details about the specimen's internal structure, including flaws, shape, and crystal arrangement. To directly visualize nanomaterials and obtain quantitative measurements of their size distribution and shape, transmission electron microscopy (TEM) is a crucial characterization technique. Because electrons have a tiny de Broglie wavelength, TEM can image at a much higher resolution than light microscopes. Since a single column of atoms is hundreds of times smaller than the smallest resolvable object with a light microscope, this allows instrument users to inspect exquisite detail. Transmitted electrons are used to create TEM pictures, which have a resolution better than 10 Å and a magnification detail up to 1,000,000x (Woods & Stirling, 2007). A common analytical technique in many scientific domains, including the physical, biological, and especially the material sciences, is TEM. A transmission electron microscope (TEM) can be used to conduct crystallographic experiments using selected area electron diffraction (SAED). SAED can be used as a diffraction technique to look at crystal flaws and determine crystal structures. It is comparable to X-ray powder diffraction, but it differs in that it can examine areas as small as several hundred nanometers, whereas X-ray diffraction typically examines larger areas. In X-ray diffraction, samples are usually areas where a magnetic lens with a variable focusing power is formed, with the shape of the lens originating from the distribution of magnetic flux. Electrons may also be deflected through a constant angle by electrostatic forces. A shift in the beam path can arise when two deflections in opposite directions with a tiny intermediate gap form. With quick electrical switching, the optical configuration of TEM can be quickly altered or completely disabled; nevertheless, the speed of this process is restricted by factors such as the lens's magnetic hysteresis(Sigle, 2005).

2.5 Fourier Transform Infrared Spectroscopy (FTIR)

The most common method for determining the infrared (IR) absorption and emission spectra of most materials in recent years has been Fourier transform infrared (FTIR)

spectroscopy, which offers significant advantages in resolution, speed, detection limitations, and signal-to-noise ratio. The primary advantage of the FTIR technique over other spectroscopic methods is that nearly all compounds exhibit characteristic absorption or emission in the infrared spectrum, enabling both quantitative and qualitative analysis of the molecules (Bacsik *et al.*, 2004). For several decades, there has been a search for extremely sensitive detection techniques for atmospheric trace gas samples, whether in remote sensing settings or laboratory environments. The rapid advancement of FTIR spectroscopy techniques has accelerated the field of atmospheric trace gas analysis. By identifying changes in functional groups, the Fourier transform infrared (FTIR) spectroscopy method can detect modifications in the overall composition of biomolecules. FTIR is used to quantify how molecules rotate and vibrate in response to infrared radiation at a specific wavelength (Al-Holy *et al.*, 2006). Through the identification of structural variations in molecule binding, information regarding the existence of their interactions can be gleaned. Transmission Attenuated Total Reflectance (TATR), micro-spectroscopy, and FTIR are the most widely used FTIR-based techniques for characterization. By identifying changes in functional groups, the Fourier transform infrared (FTIR) method of spectroscopy is able to identify modifications in the overall composition of biomolecules. FTIR is used to quantify how molecules rotate and vibrate in response to infrared radiation at a specific wavelength. Through the identification of structural variations in molecule binding, information regarding the existence of their interactions can be gleaned (Bacsik *et al.*, 2004). The most often used FTIR-based techniques for characterization are micro-spectroscopy FTIR, attenuated total reflectance (ATR–FTIR), and transmittance FTIR. For both organic and inorganic materials, FTIR provides quantitative and qualitative examination. An infrared absorption spectrum is produced using Fourier Transform Infrared Spectroscopy (FTIR), which is used to determine the chemical bonds of a molecule. The profile of the sample, created by the spectra, is a unique molecular fingerprint that can be used to screen and scan samples for various constituents. To identify functional groups and describe covalent bonding data, FTIR is a useful analytical tool (Shao *et al.*, 2010). The main benefit of infrared (IR) spectroscopy compared to other methods is

that, except for homonuclear diatomic molecules (N₂, O₂, H₂, etc.), all chemicals exhibit IR absorption and can therefore be subjected to analysis.

Infrared (IR) measurement is a non-destructive, non-contact method that enables both in-situ and remote detection. From a practical standpoint, IR spectroscopy is arguably the most adaptable analytical method available, as it can record the spectrum of nearly any sample seconds, without requiring complex preparations (Berthomieu & Hienerwadel, 2009). Vibrations in molecules are investigated via infrared spectroscopy. The fundamental vibrations of functional groups are correlated with characteristic infrared absorption bands that can be attributed to them. Strong infrared absorptions are noted for groups that have polar bonds or a permanent dipole. As a result, the polypeptide backbone's carbonyl groups play a significant role in the infrared absorption spectra of proteins. Two basic forms of vibrations are detected in the mid-infrared region vibrations along chemical bonds, known as stretching vibrations (ν), which include changes in bond length; and vibrations involving changes in bond angles, particularly bending vibrations (Mallakpour & Hussain, 2021), (Bacsik *et al.*, 2004). According to the fundamental principle of FTIR spectroscopy, molecules absorb infrared light at specific frequencies that correspond to the vibrational modes of their chemical bonds. A portion of the infrared light is absorbed when it interacts with a sample, with the remaining light being either transmitted or reflected. Functional groups contained in a molecule can be identified by FTIR thanks to the distinct vibrational frequencies of each type of chemical bond, such as C-H, O-H, and C=O.

2.6 Photoluminescence spectroscopy (PL)

According to Western literature, the first artificial phosphor was created in 1603. Then, in an attempt to manufacture gold, Vincenzo Cascariolo, an Italian shoemaker and alchemist, utilized barite (BaSO₄), a naturally occurring mineral that found near Bologna (Smet *et al.*, 2010). It is evident that he did not obtain gold from heating the ground stone under decreasing conditions, but rather a material that continued to glow (Virk, 2015). Lumen, which means light in Latin, is the root of the phrase luminescence. The German scientist and science historian Eilhard Wiedemann

introduced the term “luminescent” in 1888 to refer to all light-related phenomena other than incandescence that are not exclusively dependent on temperature increases. A species that is not in thermal equilibrium with its surroundings and is electrically or vibrationally excited will spontaneously emit radiation, a phenomenon known as luminescence (Lakowicz, 2006). The various forms of luminescence are categorized based on the method by which they are excited. Specifically, photoluminescence is the light emission that results from the direct photoexcitation of emitting species. The most well-known types of photoluminescence include fluorescence, phosphorescence, and delayed fluorescence. Other forms of luminescence include chemiluminescence, bioluminescence, electroluminescence, cathodoluminescence, radioluminescence, sonoluminescence, thermoluminescence, and triboluminescence, which vary depending on the method of excitation. When a luminous material absorbs energy, it is referred to as excitation. This process moves electrons from their ground state to higher energy levels, or excited states. Thermal energy, electrical current, or photons of light can all be examples of this energy. An excited state is produced when electrons reach higher energy levels due to the absorbed energy. The energy needed to excite a material varies according to its unique characteristics, including its bandgap and electrical structure. When a material's excited electrons return to their ground state, or lower energy levels, they emit light as a result of their release. Depending on the luminous material and its characteristics, the emitted light may differ from the absorbed light in terms of wavelength, frequency, or energy. Fluorescence, phosphorescence, and bioluminescence are examples of various luminescence emission processes. The difference between fluorescence and phosphorescence was based on the length of emission following the end of excitation for a considerable amount of time after G. (Braslavsky, 2007).

Fluorescence was thought to be an emission of light that vanishes simultaneously with the end of excitation, whereas phosphorescence's emission of light continues after the excitation has ended. In numerous scientific and technological domains, including physics, chemistry, materials science, biology, and medicine, photoluminescence, the emission of light resulting from excited electronic states and

the subsequent absorption of light, is significant. Fluorescence has been utilized to develop numerous important applications, particularly those based on it (Berberan-Santos, 2001). Examples of these applications include tracers in hydrogeology, forensic science, fluorescent and phosphorescent paints, phosphorescent labels and safety signs, detection and analysis, visualization (e.g., fluorescence microscopy), diagnosis, fluorescent tubes and lamps, optical brighteners, plasma screens, and more (Valeur & Berberan-Santos, 2011). The emission of light from a substance other than a black body (thermal emission) is known as luminescence. This type of emission includes excitations from higher energy photons (UV, X-ray, and gamma rays), chemical agents (free radicals, cationic luminescence, and chemiluminescence), particle radiation (alpha particles, for example), electrons (cathodoluminescence, beta-excited luminescence), ions (ion-luminescence), sound (sonoluminescence), and mechanical action (triboluminescence). Although luminescence typically results from the sum of two electronic absorptions (two-photon transitions) or thermal plus electronic absorptions, in which case the emitted photon energies are greater than the single highest energy excitation photon (anti-Stokes luminescence), luminescence can also result from other processes (Waychunas, 2014). Fluorescence, also known as photoluminescence, or PL, is the emission of a visible photon following the absorption of a photon with a higher energy; the Stokes shift is the difference between the two. Usually, but this word is occasionally used for IR or UV emission. Fluorescence can have a wide range of lifetimes, depending on the electronic transitions involved in absorption and emission.

Although the phrases "phosphorescence" and "afterglow" relate to luminescence emission that occurs after the excitation source is destroyed, there is conflicting usage of the term "phosphorescence" in the literature. The term "phosphorescence" was initially used to describe the extended fluorescence lifetimes associated with spin-forbidden singlet-triplet electronic transitions in organic materials (Gfroerer, 2000). Low-dimensional materials, such as quantum wells, have produced significant fundamental discoveries and crucial optoelectronic applications, having a significant impact on the science of semiconductor physics. Quantum dots are the pinnacle of semiconductor-based quantum-confined systems. They are the zero-dimensional

analogue of quantum wells. It is projected that these structures, also known as "artificial atoms," will exhibit a spectrum of ultra-narrow transitions that is tunable with the size of the quantum dot, as well as discrete, atomic-like energy levels (Empedocles *et al.*, 1999). Luminescence is a general term used to describe events involving the absorption of energy and the subsequent emission of light. Phosphors are luminous substances that, when stimulated by radiation, release light. They are typically thin films or microcrystalline powders intended to produce visible colour emission. Thousands of phosphors have been developed over decades of research and development, and some of them are widely used in numerous fields (Shinde *et al.*, 2012). An apparatus known as a spectrofluorometer, comprising an illuminating spectrometer and an analyzing spectrometer, produced these spectra. By employing this fixed illumination colour to scan with the analyzing spectrometer, a spectrum of the fluorescent emission is obtained. After setting the analyzer to the strongest emission colour, the fluctuation in emission intensity at this fixed wavelength is measured using the illuminating spectrometer to obtain an excitation spectrum. The objective of normalizing these spectra to a relative intensity scale is to facilitate the design of filters (Parreu *et al.*, 2006). The colour spectrum can be quantitatively characterized by the light's wavelength. The nanometer (nm) is the most often used wavelength unit to describe fluorescence spectra. The visible spectrum's colours can be divided into roughly equivalent wavelength ranges (Bamfield, 2002), (Blasse & Grabmaier, 1994).

2.7 Brunauer Emmett Teller (BET)

A frequently used method for determining a material's specific surface area is the Brunauer-Emmett-Teller (BET) hypothesis. This is especially true for porous solids, such as powders, adsorbents, and catalysts. In 1938, Edward Teller, Paul Hugh Emmett, and Stephen Brunauer created it. The multilayer adsorption of gas molecules onto a solid surface is the foundation of the BET theory (Irwansyah *et al.*, 2022). It is assumed that gas molecules adhere to a solid surface in monolayers and that successive layers adhere to one another uniformly. Materials that are solid or porous can have their surface area measured using the Brunauer-Emmett-Teller (BET) hypothesis. It provides crucial details on their physical makeup because a

material's surface area determines how it will behave in its surroundings. For precisely calculating the surface area of porous materials, the Brunauer-Emmett-Teller (BET) method is frequently employed. This paper provides a thorough tutorial on applying the BET method to ascertain the specific surface area of inorganic materials (Ragadhita & Nandiyanto, 2021). One important factor that affects the performance of inorganic materials in various applications is their specific surface area.

Brunauer Emmett Teller (BET) method is a fundamental approach for determining the specific surface area of porous materials, including powders and solids. Particularly when dealing with materials that have porous properties, surface area is crucial. This particular analysis has been employed in numerous studies concerning the adsorption process. It bears the names of the three scientists who on its development: Edward Teller, Paul Hugh Emmett, and Stephen Brunauer. The 1938 work "Adsorption of Gases in Multimolecular Layers" was the first to present the technique (Matshitse, 2010). A material's specific surface area is a crucial characteristic that influences its behaviour in various settings, including chemical reactions, gas adsorption, and catalysis. The BET method is widely used to calculate the surface area of materials with high precision and repeatability in scientific research, industrial processes, and quality control (Thomas, 2023). The adsorption of gas molecules onto the surface of the substance is the basis of the BET method's principle. Attractive forces cause a gas to adhere to the surface of a solid when it comes into contact with it, creating an adsorbed layer of molecules. A multilayer adsorption phenomenon occurs when the gas pressure increases, resulting in the formation of additional layers. The BET technique assumes that gas molecules adsorb in a monolayer fashion, forming a homogeneous layer on the surface.

Additionally, it makes the assumption that once the molecules are adsorbed on the surface, they won't interact with one another. The solid material is first exposed to a gas at a predetermined temperature (Aranovich & Donohue, 1995). The amount of gas adsorbed at each pressure is measured as the gas pressure is gradually increased. BET isotherm, a graph that shows the amount of adsorbed gas (usually nitrogen) against the relative pressure, is then plotted using these data. The linear zone at

intermediate pressures is used for study, and the BET isotherm exhibits distinctive geometries. The specific surface area of the material can be ascertained by using the BET method to compute the monolayer capacity of the gas adsorbed on its surface. The linear part of the BET isotherm can be extrapolated to zero relative pressure in order to get the monolayer capacity (Shimizu & Matubayasi, 2022). A large variety of porous materials need to be characterized, and gas adsorption is crucial for this. Nitrogen has continued to be the most often used gas among the numerous other gases and vapors that are readily available and have the potential to be used as adsorptive. A portion of a gas or vapor phase that comes into touch with a solid is absorbed and stays outside, adhered to the surface. There is a weak Van der Waals attraction between the adsorbate and the solid surface during physisorption, also known as physical adsorption (Shimizu & Matubayasi, 2022). Characterizing porous materials is helpful because it makes it possible to calculate the volume, distribution of pore sizes, and specific surface area of the material. By measuring the amount of gas adsorbed at a constant temperature (usually liquid N₂, 77K) over a wide range of relative pressures, an adsorption isotherm can be derived.

On the other hand, desorption isotherms are obtained by monitoring the gas that is removed when the pressure drops. Pores of type I are usually microporous, with the exposed surface almost entirely contained within the microspores, which, after they are filled with adsorbate, leave little to no exterior surface available for additional adsorption (Sinha *et al.*, 2019). When the first adsorbed monolayer is almost completely completed, an inflection point occurs. Adsorption proceeds as long as the adsorbate's interaction with an adsorbed layer is larger than its interaction with the adsorbent surface. Type III ads are distinguished by heats of adsorption that are lower than the adsorbate heat of liquification. Type IV occurs on adsorbents that are porous and have pores between 1.5 and 100 nm in size. The slope increases in absorption of adsorbate at greater pressures as pores fill; the inflection point usually happens close to the first monolayer's completion (Osterrieth *et al.*, 2022). Similar to type III, type V is exhibited in situations where there are tiny adsorbate-adsorbent interaction potentials and is linked to pores in the 1.5-100 nm range. Adsorption on a uniform surface, each adsorbed molecule in a layer being a potential adsorption site

for the subsequent layer, no steric limitation on the multilayer's thickness, no interactions between molecules in the same layer, and a higher energy of adsorption on the first layer than the others are the underlying presumptions of the BET model (Sing, 2001).

2.8 Ultraviolet–visible spectroscopy (UV)

Light absorbance or transmittance can be quickly established using UV-visible spectroscopy, an analytical method. Most spectrophotometers have a working wavelength range of 200-1100 nm, although the visible component can extend up to 800 nm, and the UV range spans from 100 to 380 nm. UV-vis spectroscopy has a practical range of 200-800 nm; wavelengths below 200 nm are referred to as vacuum UV, and wavelengths over 800 nm are classified as infrared. Matter's hue is determined by its capacity to both absorb and emit light, and the human eye can distinguish between up to 10 million different colour's (Barbosa-García *et al.*, 2007). Light is transmitted through media, reflected off of transparent and opaque surfaces, and refracted by crystals. Certain wavelengths are absorbed by covalently unsaturated compounds whose electronic transition energy differences are equal to the energy of UV-visible light. These substances are called chromophores, and they are responsible for giving things their colour. Auxochromes are covalently saturated groups that influence the absorption of chromophore groups but do not absorb UV-visible electromagnetic energy. Auxochromes are electron-donating substances that can change the colour of chromophores without changing their colour (Gürses *et al.*, 2016b). When UV-vis radiation strikes chromophores, electrons in the ground state transition to an excited state, a process referred to as electron excitation. Due to their transparency and lack of absorption in the UV-vis region, alcohols and water make suitable media for UV-visible spectroscopy.

Dimethylformamide (DMF) and acetone are suitable solvents for substances that are insoluble in alcohol and water; however, they are only suitable above these cut-off wavelengths since they absorb light below 320 and 275 nm, respectively. A chromophore's absorbance bands are distinctive (Asahi *et al.*, 2001). The wavelength and intensity of absorption can be affected by modifying their environment, which

can be achieved by adding a different substance or by changing the physical environment, such as increasing the temperature. Red-shifting a band to longer wavelengths is a bathochromic shift; blue-shifting a band to shorter wavelengths is a hypochromic shift. The cornerstone of UV-VIS spectroscopy is the absorption of light, whereby the quantity of light absorbed is directly proportional to the quantity of analyte contained in a sample solution. Light absorption increases linearly with an increase in analyte concentration light transmission decreases exponentially. Different vibrational energy levels comprise an electronic energy level, whereas different rotational energy levels comprise a single vibrational energy level. If the energy delivered by the photon matches the energy difference in these levels, then interacting with a molecule with a photon may cause a shift in electronic energy levels. To obtain the spectrum, the amount of radiation absorbed by the analyte is measured and plotted against the wavelength of the EMR. As a result, a typical UV-VIS spectrum is a plot of frequency or wavelength against absorption intensity. An organic molecule's ability to absorb electrical energy levels (UV-VIS radiations) is linked to the excitation of valence electrons from their ground state into their excited state.

A method for examining how molecules absorb ultraviolet (UV) and visible light is called UV-visible spectroscopy. The analytical assessment of various solvents and materials is referred to as spectroscopy. For the past 37 years, UV-visible spectrometers have been widely utilized. Spectroscopy is often favoured, particularly by small-scale enterprises, because it requires less equipment and has fewer maintenance issues. The analytical technique measures the absorption of monochromatic light by colourless substances in the 200-400 nm near ultraviolet region of the spectrum. The basis of ultraviolet (UV) spectroscopy, a physical method of optical spectroscopy that employs light in the visible, UV, and near-infrared ranges, is the Beer-Lambert law, which states that a solution's absorbance is directly proportional to its path length and the concentration of absorbing species. As a result, it can be used to find the absorber concentration in a solution for a specific path length. UV-VIS spectroscopy has become the most essential analytical tool in modern laboratories over the last 37 years, and it is necessary to know how quickly

the absorbance varies with concentration (Rocha *et al.*, 2018). When radiation induces an electronic transition inside the structure of a molecule or ion, absorption occurs in the visible or ultraviolet spectrum. As a result, when a sample absorbs light in the visible or ultraviolet spectrum, its molecules' electrical states change as well. Electrons will be promoted from their ground-state orbitals to higher-energy orbitals, known as excited states or antibonding orbitals, by the energy provided by light. Furthermore, the transition σ^* orbital may involve two different kinds of antibonding orbitals, an orbital of π^* , and n^* antibonding orbital does not exist since n electrons do not form bonds. Thus, the absorption of visible and ultraviolet light might result in the following electronic transitions. Due to their high energy requirements, the σ to σ^* and n to σ^* transitions occur in the far ultraviolet region or are weakly observed in the 180-240 nm range. Saturated groups do not show significant absorption in the normal UV spectrum as a result. Currently, it will be observed that the molecular structure determines both the intensity of absorption and the wavelength of maximum absorption. If the molecular structure is altered, transitions to the π^* anti-bonding orbital, which happen in the ultraviolet region for a certain molecule, could potentially occur in the visible region. A large number of inorganic substances in solution exhibit visible area absorption as well. These include salts of elements whose ions are complexed by hydration and have incomplete inner electron shells, primarily transition metals. These absorptions result from a process known as charge transfer, in which the energy from visible light causes electrons to move across the system. Spectrophotometry is typically used, particularly by small-scale enterprises, due to its low equipment cost and low maintenance requirements. The analytical technique measures the amount of monochromatic light absorbed by colourless substances in the near-ultraviolet region of the spectrum (between 200 and 400 nm). The basic idea behind how a UV spectrophotometer works is that light with a specific wavelength range passes through a solvent-filled cell and is detected by a photoelectric cell, which converts the radiant energy into electrical energy that a galvanometer can measure. To determine the absorbance spectrum of a substance in solution or as a solid, ultraviolet-visible spectroscopy is utilized (Verma & Mishra, 2018). Spectroscopic observations actually record the absorption of electromagnetic radiation, or light

energy, which drives electrons in a compound or material from their ground state to their first singlet excited state. The fundamental idea underlying absorbance spectroscopy is the Beer-Lambert Law. According to this fundamental concept, the path length of the sample and the concentration of the absorbing species directly correlate with the absorbance of a solution. An absorbance versus wavelength map is called an absorption spectrum. It offers details on the range of light wavelengths and absorption intensities that a molecule can handle. Strong absorption occurs at wavelengths indicated by peaks in the spectrum. Which transitions in a molecule's absorption spectrum are permitted or prohibited are determined by selection rules. Electronic transitions between chemical orbitals are usually engaged in UV-visible spectroscopy. The symmetry of the molecule and the electrons' spin state are two examples of variables that affect the rules. A molecule's chromophores are functional groups or sections that give it colour. They have π -electrons, which are capable of undergoing electronic changes. Auxochromes are groups that change the electron density or lengthen the conjugation of a chromophore to change its colour (Gürses *et al.*, 2016a). Electronic transitions in UV-visible spectroscopy refer to the excitation of electrons from their ground state to an excited state. When UV-visible light equals the energy needed to elevate an electron to a higher energy level, it is usually absorbed (Verma & Mishra, 2018).

CHAPTER 3

Effect of Eu^{3+} on the luminescence and photocatalytic properties of ZnS nanoparticles

3.1 Introduction

The global textile sector employs about 35 million people, generates about \$1 trillion in revenue annually, and accounts for 7% of all exports worldwide. Numerous negative environmental effects can be attributed to the textile industry (Desore & Narula, 2018). Among the things that cause air pollution are the releases of dust and particle matter, as well as Sulphur and nitrogen oxides and volatile organic compounds. Because dyes have the potential to impair human health and ecosystems, their toxicity in the environment is a serious problem (Muthu & Khadir, 2022). Dyes can enter the environment through a variety of channels, including industrial discharge, inappropriate disposal, and unintentional spills. They are utilized in many different industries, including textile, leather, paper, and cosmetics. The main sources of solid waste are leftover yarns and textile fabric scraps as well as empty containers. However, the textile sludge, which frequently contains large concentrations of organic matter, micronutrients, heavy metal cations, and pathogenic microbes, indicates issues with excess quantities and undesired composition (Hassan & Carr, 2018). Organic compounds that are soluble are used as colors; these include reactive, basic, and acidic chemicals. They are very soluble in water, which makes it challenging to eliminate those using standard techniques. Because of chromophoric groups in its molecular structures, one of its characteristics is the ability to provide color to a certain substrate (Setiadi Tjandra *et al.*, 2005). Auxotrophic groups, on the other hand, and have the ability to attach to polar groups in textile fibres, which is how they impart color to the material. In addition to harming the water bodies aesthetics, textile dyes' color inhibits light from penetrating the water, slowing down photosynthesis and depleting the water's supply of dissolved oxygen, which impacts the entire aquatic biota (Lellis *et al.*, 2019).

One of the first semiconductors to be discovered is zinc sulfide, a high band gap II–VI group compound that is primarily found in two structural polymorphs: hexagonal wurtzite and cubic sphalerite (Tran *et al.*, 1997). At ambient temperature, these two structural polymorphs exhibit wide band gaps of 3.77 eV and 3.72 eV, respectively. Due to its fluorescence, it can be used in a variety of ways. Because of its wide band gap, it can be used as a host material for a wide range of dopants. For example, in optical coatings, solid-state solar window layers, electrooptic modulators, photoconductors, field effect transistors, optical sensors, photo catalysts, electroluminescent materials, phosphors, and other light-emitting materials, it has been thoroughly studied for a wide range of applications (Ong & Chang, 2001). In fact, when doped with divalent manganese ions, ZnS has found particular utility in lasers, flat panel displays, and thin film electroluminescent devices. Zinc Sulfide (ZnS) is a crucial phosphor material that can be found in both doped and undoped forms. In general, the wurtzite form is superior to the sphalerite form (Bredol & Merikhi, 1998). An electron-hole pair must exist at the surface in order for organic contaminants, such as dyes, to be broken down by photocatalysis. To improve ZnS NPs' photocatalytic activity, a variety of synthesis techniques have been used to produce NPs with varying sizes and forms (Sooklal *et al.*, 1996). There are still a few significant drawbacks to its use as a photocatalyst, despite these efforts. Due to its very large 3.6 eV band gap, zinc sulfide (ZnS) can only function in the presence of ultra-violet (UV) light irradiation, which makes up a very minor portion of solar energy (Singh Lotey *et al.*, 2013).

3.2 Experimental details

3.2.1 Sample preparation

Europium (III) nitrate hexahydrate, $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Alfa Aesar purity 99.9%, Zinc acetate dihydrate, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Alfa Aesar, purity 98.0%, and Sodium Sulfide, Na_2S , purity 98.0% Alfa Aesar was used to synthesized Eu^{3+} -doped ZnS. Eu^{3+} -doped ZnS (2, 4, 6 at.%) was synthesized using the reflux method. Zinc acetate dihydrate and europium (III) nitrate hexahydrate were dissolved in 50ml of distilled water and stirred for 1 hour at room temperature. After stirring at room temperature, sodium sulfide was added drop by drop, and the solution was re-fluxed at 1500 C for

3 hours. The obtained precipitate was ultrasonically treated for 30 minutes. Finally, the solution was to centrifuge at 7000 rpm. After drying, the samples were used for characterization.

3.2.2 Sample characterization

Rigaku Cu K α Smart Lab was used to obtain XRD data. Image from TEM was taken by FEI Tecnai (G2 F20 X-TWIN). Supra 55 FESEM model with a high resolution was used to capture the FESEM image. Shimadzu IR affinity-1S FT-IR data were collected. Photoluminescence studies were done using a Hitachi F-7000 fluorescence spectrometer. Thermo scientific evolution of 220 was used to study UV visible spectrophotometer.

3.3 Results and discussions

3.3.1 X-ray diffraction (XRD)

Figure 3.1 displays the XRD patterns of Eu^{3+} -doped ZnS nanoparticles. The planes (111), (220), and (311) of the face-centred cubic (FCC) structure of ZnS were observed as three prominent peaks corresponding to (JCPDS No. 05-0566). The Debye-Scherrer equation is used to determine the particle size (Annalakshmi *et al.*, 2020): $D = K\lambda / \beta \cos\theta$, where the catalyst's crystal size is denoted by D , λ is the X-ray wavelength, the maximum diffraction angle is θ , and K is a constant (0.9). No similar diffraction peaks were observed for samples that contained Eu, indicating that the Eu ions are properly integrated into the ZnS lattice. The full-width half maximum (FWHM) of the diffraction peaks broadens as the doping concentration increases due to the quantum size effect. Dopants frequently serve as nucleation sites during the synthesis of nanoparticles, lowering the energy needed for the formation of the first particle and promoting the growth of a higher number of smaller ones (Murugadoss *et al.*, 2022). The drag force of the dopant atoms against the increase in crystallite size is the primary cause of this effect. The particle size was found to be 9-13 nm. Table 3.1 shows the crystal size, cell volume and lattice parameters from XRD.

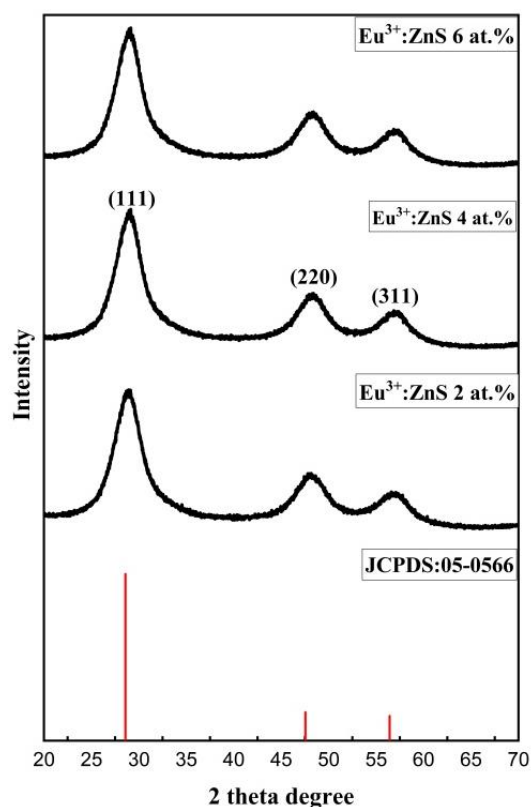


Figure 3.1: X-ray diffraction of Eu^{3+} doped ZnS 2, 4, 6 at.%.

Table 3.1: Calculation of crystal size, cell volume and lattice parameters from XRD.

Sample	Lattice parameters ($\text{\AA}$)	Cell volume ($\text{\AA}^3$)	Crystal size (nm)
Eu^{3+} 2 at. %	5.344	157.76	9.45
Eu^{3+} 4 at. %	5.835	157.79	11.21
Eu^{3+} 6 at. %	5.423	157.81	13.54

3.3.2 Morphological analysis of SEM

Many optoelectronic applications heavily depend on microstructure and surface shape. Figure 3.2 (a) shows the morphology of the as-prepared Eu^{3+} doped ZnS nanoparticles as determined by SEM. Small, uniformly sized grains with a uniform shape can be found in SEM image of Eu -doped ZnS. Due to the Eu^{3+} doped ZnS's

reduced size and increased surface energy, the sample is more aggregated. From Figure 3.2(b), the EDX spectra confirm the presence of Eu, Zn, and S. The average particle size, calculated from Eu³⁺-doped ZnS (4 at.%), was found to be 22 nm, as shown in Figure 3.2(c).

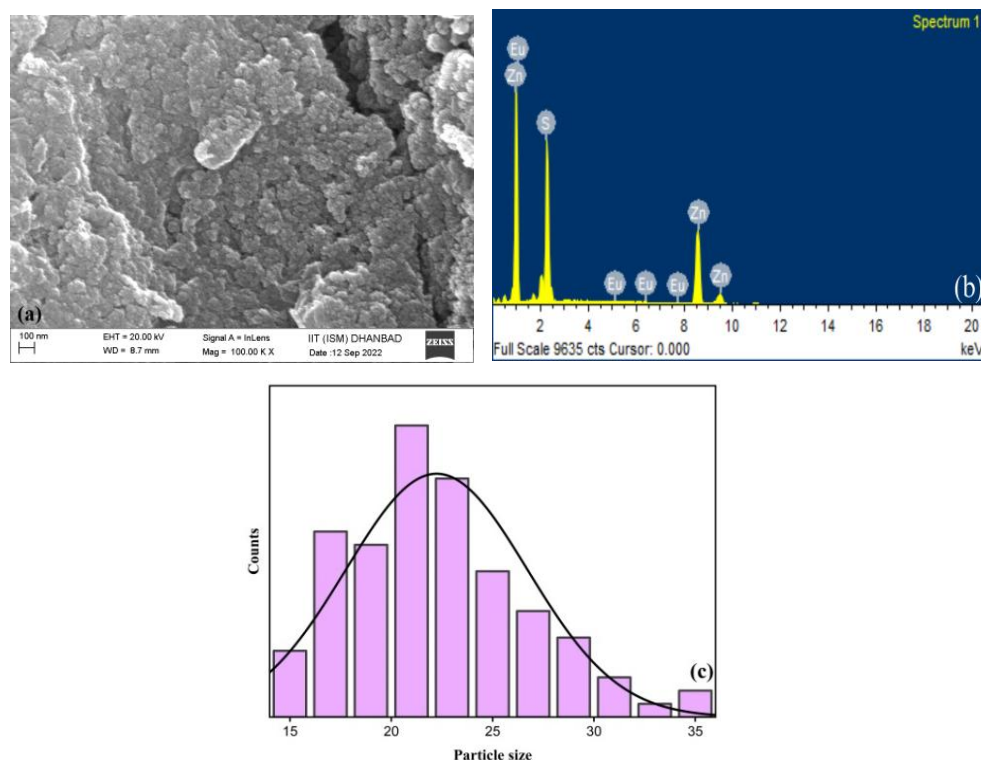


Figure. 3.2: (a) SEM image of Eu³⁺ doped ZnS 4 at.% (b) EDX spectra of Eu³⁺ doped ZnS (c) Average size particle size of Eu³⁺ doped ZnS 4 at.%.

3.3.3 Transmission Electron Microscopy (TEM)

Figure 3.3. (a) shows a TEM image of Eu³⁺ doped ZnS 4 at.%. The particle size was found to be 13 nm. It agrees exactly with the results of the XRD's Scherrer Equation-based calculation of crystallite size. The catalyst's photocatalytic activity is greatly influenced by the size of its particle. A thin layer of ZnS was laid over the surface of the Eu³⁺ doped ZnS nanocrystals. It depicts the formation of a thin ZnS shell layer on top of the nanocrystals (J. Cao *et al.*, 2009). A reduced particle size produces a wide surface area which is ideal for high photocatalytic activity. The SAED pattern

enables the exact indexing of various rings (311, 220, and 111) in the same positions given in Figure 3.3. (b).

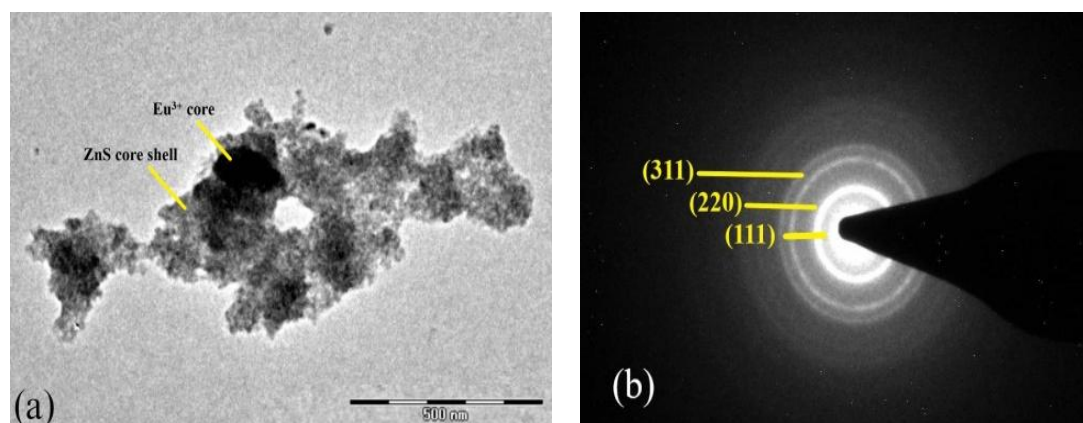


Figure. 3.3: (a) TEM image of Eu³⁺ doped ZnS 4 at.% (b) SAED spectra of Eu³⁺ doped ZnS.

3.3.4 Fourier Transform Infrared (FTIR)

Figure 3.4 illustrates a large absorption band at 3460 cm⁻¹, which is associated with the stretching vibration of N-H. The distinctive stretching vibration of C-H is what causes the peak to appear at 2342 cm⁻¹. The N-H and C-H bending peaks are visible at 1612 cm⁻¹ and 1406 cm⁻¹, respectively. In addition, the peak at 592 cm⁻¹ belongs to the stretching vibration of Zn-S, a phenomenon also reported in the literature (Rivera *et al.*, 2016).

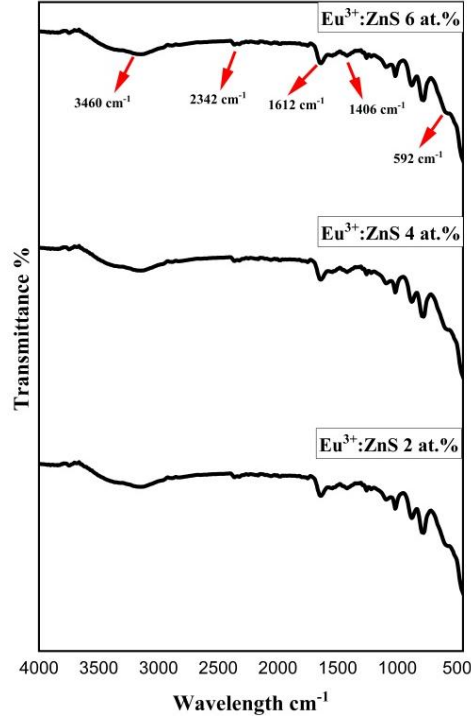


Figure 3.4: FTIR spectra of Eu^{3+} at 2 at%, 4 at%.

3.3.5 Photoluminescence (PL) Spectroscopy

At room temperature, the excitation and emission properties of solid state photoluminescence were studied. When excited at 350 nm the major emission peaks observed are given in Figure 3.5 (a). Different transition of 528 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), 543 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$), 565 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_3$), 572 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_4$), 603 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_5$), and 636 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_6$) were obtained. The strongest was the induced electric dipole transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$, which is especially susceptible to the chemical bond in close proximity to an ion of europium (III) and emits red when exposed to UV light (Monteiro *et al.*, 2015), (Hussain *et al.*, 2019). Whereas the electric dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) is relatively strong, the magnetic dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) is less susceptible to the coordinated environment. When emitted at 510 nm, the excitation peaks of europium are observed at 362 nm ($^7\text{F}_0 \rightarrow ^5\text{D}_4$), 377, 380, 382 nm ($^7\text{F}_0 \rightarrow ^5\text{L}_{7,8,9}$), 395 nm ($^7\text{F}_0 \rightarrow ^5\text{L}_6$), 415 nm ($^7\text{F}_0 \rightarrow ^5\text{D}_3$), 463 nm ($^7\text{F}_0 \rightarrow ^5\text{D}_2$), given in Figure 3.5 (b).

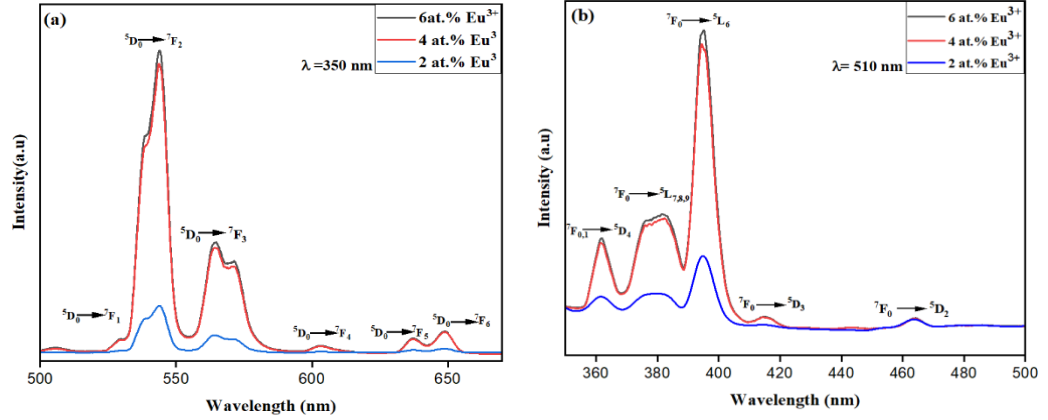


Figure 3.5: (a) Photoluminescence emission spectra of Eu^{3+} doped ZnS (b) Photoluminescence excitation spectra of Eu^{3+} doped ZnS.

3.3.6 CIE analysis

The chromaticity diagram from the Commission Internationale de L'Eclairage (CIE) shows that the coordinates are highly helpful in defining the perceived colour of a phosphor's emission Figure 3.6. The emission spectra-derived colour coordinates and their accompanying correlated colour temperatures are provided in Table 3.2. McCamy's equation 3.1 was used to determine the correlated colour temperatures (CCT) (Naorem *et al.*, 2022a) for Eu^{3+} -doped ZnS.

$$\text{CCT} = -437n^3 + 3601n^2 - 6861n + 5514.31 \text{ and } n = \frac{(x-x_e)}{(y-y_e)} \quad (3.1)$$

The determined colour coordinates are represented by x and y in this case. Figure 3.6 depicts the CIE chromaticity diagram for the obtained Eu^{3+} -doped ZnS doped with various concentrations.

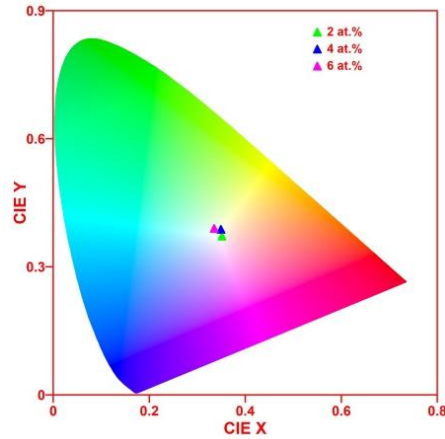


Figure 3.6: CIE chromaticity diagrams of the Eu³⁺ doped ZnS (2, 4, 6 at.%).

Table 3.2: CCT colour coordinates of Eu³⁺ doped ZnS (2, 4, 6 at.%).

Sample	Calculated colour coordinates		CCT
	x	y	
2 at.% Eu ³⁺	0.351	0.372	4854
4 at.% Eu ³⁺	0.349	0.388	4965
6 at.% Eu ³⁺	0.335	0.390	5417

3.3.7 Lifetime study

Eu³⁺ doped ZnS nanoparticles have been assessed based on their luminescence decay curves. The excitation and emission wavelengths were fixed at 350 nm and 510 nm, respectively, for each concentration to measure the decay curves. Figure 3.7. displays the calculated decay curves. Using of the bi-exponential equation 3.2, all observed decay curves are successfully fitted (Premjit Singh *et al.*, 2019).

$$I = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2) \quad (3.2)$$

In this case, I_1 and I_2 stand for the intensities at two distinct time points, whereas τ_1

and τ_2 stand for the respective decay times. The following equation can be used to calculate the average decay time. Average lifetimes of 1.41, 1.69, and 1.79 ms were determined for Eu^{3+} doped ZnS concentrations of 2 at.%, 4 at.%, and 6 at.%, respectively. Their goodness of fitting (R^2) for the aforementioned concentrations is 0.958, 0.968, and 0.983, respectively.

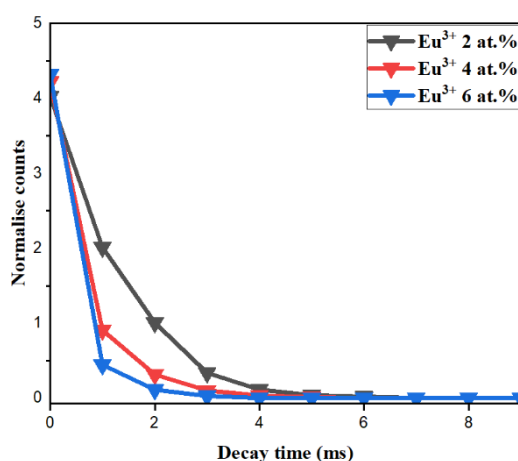


Figure 3.7: Bi-exponential fitting of the photoluminescence decay curve of Eu^{3+} doped ZnS.

3.3.8 UV-visible spectroscopy

Effect of initial dye concentration

At various concentrations ranging from 5 to 30 ppm, the effect of the initial dye concentration on the photodegradation of methyl red was investigated. The degradation at varied initial dye concentrations is shown in Figure 3.8. When the initial dye concentration was increased, it was observed that the per cent degradation gradually decreased. This could be a result of the reaction mixture's colour darkening as dye's initial concentration increases. This limits the ability of light to reach the catalyst's surface. Since dye molecules largely absorb light photons and are unable to reach the catalyst surface, their concentration will decrease as dye concentration increases (Sahoo, 2005). As a result, dye's ability to degrade becomes less effective as dye concentration rises. We found that 15 ppm was the optimum dye concentration.

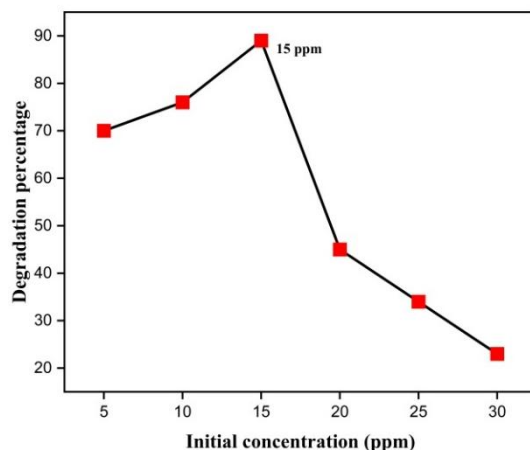


Figure 3.8: Effect of amount of catalyst (mg/L) for the degradation of methyl red.

3.3.9 Effect of pH

Figure 3.9 displays the rate of methyl red degradation as a function of time and pH. This anionic dye degraded more quickly under photochemical conditions at pH 3, as shown in the Figure. The electrostatic interactions between a semiconductor surface, substrate, and charged radicals during a photocatalytic oxidation are highly dependent on the pH of the solution. The surface of the catalyst has a higher positive charge in an acidic environment, which facilitates the adsorption of dye molecules. Acidic media also reduce the amount of e/h^+ recombination (Thota *et al.*, 2014). The catalyst surface becomes negatively charged as the pH rises, and dye molecules may repel one another, resulting in low molecular adsorption and a reduction in degradation efficiency. Hence, raising pH maximizes photocatalytic performance.

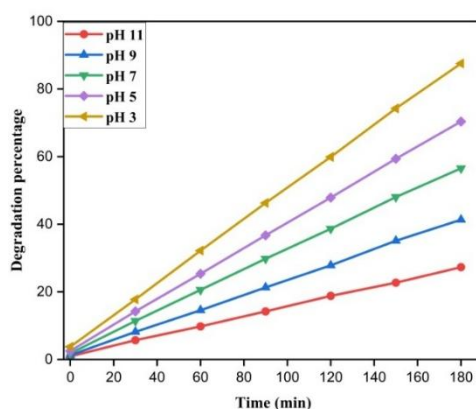


Figure 3.9: Effect of pH for the degradation of methyl red.

Methyl red was degraded following the optical parameters such as the effect of catalytic dosage, initial concentration and amount of catalyst. Using 15ppm of initial concentration, 6 mg/L of catalytic dosage and pH 3, methyl red was degraded within 180 minutes. The percentage degradation of dye was calculated from the following equation 3.3:

$$\text{Percentage of Degradation} = A_0 - A_t / A_0 \times 100 \quad (3.3)$$

A_0 is the initial dye absorption before degradation and the absorbance of dye is A_t . The degradation percentage of methyl red was found to be 90% shown in Figure 3.10.

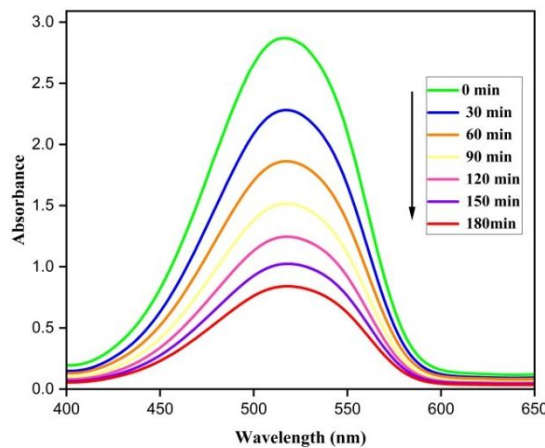


Figure 3.10: Degradation of methyl red within 180 minutes.

3.3.10 Kinetic studies

Kinetic studies can be used to clarify the process and efficacy of the photodegradation given in Figure 3.11. A linear fitting of $\ln C_0/C_t$ vs t was used to apply the first-order kinetic model given in equation 3.4 (Naorem *et al.*, 2022b):

$$\ln C_0/C_t = kt \quad (3.4)$$

where (k) is the response rate constant and (t) is the time. As a result, it is evident

that under UV light illumination, catalysts doped with 6 at.% have better photodegradation efficiencies than those doped with 2 at.% or 4 at.%. Table 3.3 shows the kinetic values for the degradation of methyl red.

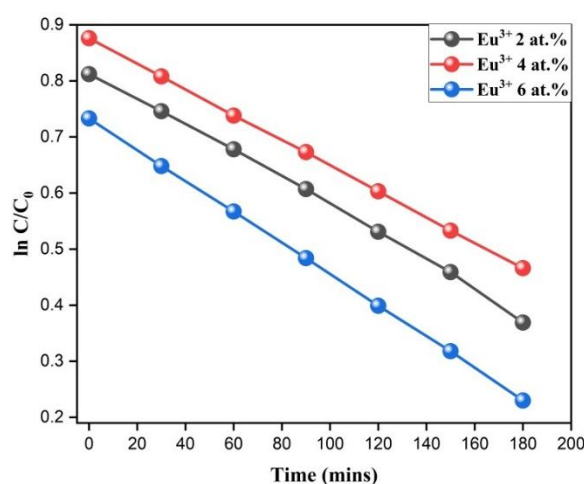


Figure 3.11: Kinetic study of Eu^{3+} doped ZnS 2, 4, 6 at.%.

Table 3.3: Kinetic study of Eu^{3+} doped ZnS.

Sample	Rate constant k (min^{-1})	R^2	Degradation percentage (%)
Eu^{3+} 2 at.%	4.04×10^{-3}	0.958	62%
Eu^{3+} 4 at.%	3.12×10^{-2}	0.968	87%
Eu^{3+} 6 at.%	3.89×10^{-2}	0.983	90%

3.3.11 Stability analysis

After the first cycle was completed, the catalyst was carefully removed by centrifugation, washed with an ethanol/water mixture, and dried at 120°C to conduct the stability study. Within 180-minute dye solution degradation process, the regenerated catalyst was used to assess its stability and reusability. The same amount

of catalyst and dye was used for each cycle. The degradation of methyl red was 82% after the fourth cycle, as shown in Figure 3.12.

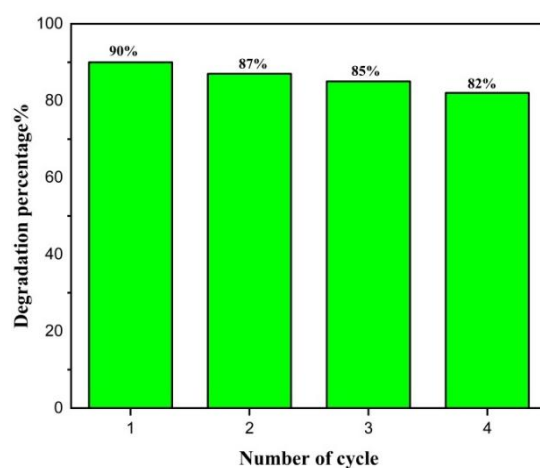


Figure 3.12 Stability analyses within 4 cycles.

3.4 Conclusion

We can conclude that Eu^{3+} -doped ZnS nanoparticles of 2 at.%, 4 at.% and 6 at.% were successfully synthesized using a reflux method. The XRD studies show that particles are nanosize. Different transitions of 528 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), 543 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$), 565 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_3$), 572 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_4$), 603 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_5$), and 636 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_6$) were obtained from the photoluminescence studies. According to the CIE diagram, all of the prepared samples produced a nearly white colour that may be employed in optical devices. Methyl red can be degraded successfully by employing 6 mg/L of the catalyst, an initial concentration of 15ppm and at pH 3. The degradation percentage was found to be 90% and it also follows first-order kinetics. The synthesized Eu^{3+} doped ZnS nanoparticles can be used for removing toxic chemicals present in the environment.

CHAPTER 4

Photoluminescence and photocatalytic degradation of Methylene Blue and methyl red using Pr³⁺ doped CdS nanoparticles

4.1 Introduction

The textile industry generates a significant amount of harmful, non-biodegradable coloured dye effluents. These dyes release hazardous and possibly cancer-causing chemicals into the aqueous phase, resulting in serious environmental pollution issues (Hoffmann *et al.*, 1995). There are numerous chemical and physical methods for removing colour from textile effluents, including air stripping, flocculation, adsorption, precipitation, reverse osmosis, and ultrafiltration. Heterogeneous photocatalysis has been identified as a financially viable substitute for traditional physical, chemical, and biological methods of wastewater treatment (Dai *et al.*, 2007). One of the most promising methods for treating wastewater is photocatalytic degradation, which has several advantages over conventional methods: it can oxidize contaminants in the ppb range quickly, prevent the creation of polycyclic products, and more (Y. Liu *et al.*, 2005). The primary process of photodegradation involves the production of hydroxyl radicals, which are generated when holes react with water or surface hydroxyl groups and subsequently attach to organic materials. Metal chalcogenides have garnered considerable interest lately due to their demonstrated and potential applications in optical, superconducting, and electrical devices. Applications for cadmium sulfide as a semiconductor include photoelectronic devices, solar cells, and photocatalyst degradation (Kansal *et al.*, 2007). The use of TiO₂ for the photocatalytic treatment of wastes containing dyes has also been extensively documented in the literature.

On the other hand, the usage of other semiconductors, including doped cadmium sulfide, has been limited to the nanoscale (Sahoo, 2005). Greater photon absorption on the photocatalyst surface is possible due to the increased surface area-to-volume ratio of nanoscale semiconductor particles compared to their bulk counterparts (Hoffmann *et al.*, 1995).

Furthermore, when the size of semiconductor particle decreases, the electron-hole pair's recombination within the particle is significantly decreased. Higher redox potentials in the system resulted from a significant increase in bandgap energy when semiconductor particle size was reduced to the nanoscale. As a result, it is anticipated that the photocatalytic activity of the nanoscale semiconductor will be higher than that of its bulk (Robinson *et al.*, 2001). Cadmium sulfide (CdS) is regarded as one of the most promising materials because of its nonlinear optical features and excellent band gap of 2.42 eV for photocatalytic destruction of hazardous compounds (Prabhu & Abdul Khadar, 2005). Because of these characteristics, it is a more intriguing photocatalyst in the visible spectrum; nevertheless, because photogenerated electrons and holes recombine quickly, its photocatalytic effectiveness decreases (Lin *et al.*, 2002). A number of techniques, including chemical precipitation, reverse micelle, sol-gel template, solvothermal, and ultrasonic irradiation in an aqueous solution, have been reported for the manufacture of CdS nanostructures with controlled shape. Nowadays, colours are removed from water using advanced oxidation techniques (AOPs), which do not create any harmful byproducts. The idea behind AOPs is centered on the creation of extremely reactive intermediates, such as hydroxyl radicals (OH), which quickly oxidize a wide range of pollutants (Gouvêa *et al.*, 2000).

The potential use of rare earth (RE) doped wide bandgap II–VI materials as multicolour cathode (CL), electro (EL), and photoluminescence (PL) displays has prompted extensive research into these materials. Semiconductor nanoparticles benefit significantly from the presence of lanthanide ions, which is crucial for fluorescence labelling (Banerjee *et al.*, 2000). By employing distinct ions, they provide the possibility of multi-colour imaging utilizing a single wavelength of stimulation. Due to their relatively long lifetimes, lanthanide ions are crucial for photo-bleaching in fluorescent compounds that require significant reduction, as well as for time-resolved techniques (Georgiou *et al.*, 2002). Trivalent samarium ions' strong fluorescence efficiency in the visible and infrared has piqued interest in spectroscopic investigations. One of the most popular techniques for modifying the electrical and optical characteristics of semiconductors is doping, which involves

adding distinct energy levels for the excited electrons in the band gap (Hanifehpour *et al.*, 2017). Three different crystal forms exist for CdS: high-pressure rock-salt phase, zinc blende, and wurtzite. The bulk and CdS nanoparticles (NP) exhibit distinct changes in their physical, chemical, and structural characteristics. Owing to their numerous uses in a variety of spheres of life, CdS NP have been produced in large quantities. The same substance can crystallize in a variety of configurations during size reduction, depending on the reaction conditions (Iqbal *et al.*, 2019).

4.2 Experimental details

4.2.1 Sample preparation

Without additional purification, all compounds were used as received. Praseodymium (III) chloride hydrate, $\text{PrCl}_3 \cdot 7\text{H}_2\text{O}$ Alfa Aesar, Sodium sulfide hydrate, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, HIMEDIA, Cadmium nitrate tetrahydrate, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ Merck & Co. (MERCK) was used. Ethylene glycol was employed as a capping agent to prevent the aggregation of the particles, and distilled water was utilized as a solvent. The reflux technique was used to prevent the solvent of a reaction mixture from evaporating. Samples with 0, 5, 7, 9, and 11 at.% doping were synthesized using Pr^{3+} doped CdS nanocrystals where praseodymium (III) chloride hydrate the doping agent. Aqueous solutions of cadmium nitrate tetrahydrate and praseodymium (III) chloride hydrate were stirred for 30 min. The aforementioned solution was stirred for two hours at room temperature with the addition of an aqueous sodium sulfide hydrate solution drop by drop. Finally, the entire mixture was refluxed at 130°C for 1 h to get a saturated solution of Pr^{3+} doped CdS nanoparticles. For 25 min, the precipitate was ultrasonically processed to prevent the formation of the most aggregated nanoparticles possible. Then, the whole solution was subjected to centrifugation (8000 rpm) to settle down nanoparticles. The sample was used for characterization after drying.

4.2.2 Sample characterization

Rigaku Smart Lab was used to produce the X-ray diffractograms. Using a Field emission scanning electron microscopy (FE-SEM) model above 55, high-resolution imaging appropriate for evaluating different materials for surface was examined.

Field electron and Ion Company, (FEI) TECNAI transmission electron microscope G2 F20 X-TWIN was used to capture transmission electron microscopy (TEM) images. Using the IRAffinity-1S Shimadzu, Fourier transform infrared (FTIR) data were collected. The photoluminescence properties were investigated using a fluorescence spectrometer F-7000 with a (150 W) Xenon lamp. To investigate the photocatalytic capabilities, a wavelength range of 190 to 1100 nm evolution 220 Ultraviolet-visible spectrophotometer was utilized.

4.3 Results and discussions

4.3.1. X-ray diffraction (XRD)

X-ray diffraction of Pr^{3+} doped CdS 0, 5, 7, 9, and 11 at.% are displayed in Figure 4.1. According to XRD analyses, the samples are crystalline and of a nano-size. The hexagonal CdS is represented by the diffraction peaks (100), (002), (101), (102), (110), (103), (004), and (202) Joint Committee on Powder Diffraction Standards (JCPDS) card: No. 41-1049. Applying the Scherrer equation, nanoparticle crystallite sizes are determined using the formula given in equation 4.1. (Mansoor *et al.*, 2020):

$$D = K\lambda/\beta\cos\theta \quad (4.1)$$

where D represents the crystallite size (nm), 0.9 represents the Scherrer constant, λ represents X-ray wavelength, β represents the line broadening at full width at half maximum (FWMH), and θ represents the Bragg's angle. The XRD patterns show that the crystallinity of nanoparticles increased with increasing Pr^{3+} concentrations. The particle size with different doping concentrations of 0, 5, 7, 9, and 11 at.% are found to be 12.25, 13.44, 16.50, 20.38, and 22.24 nm, respectively. Table 4.1 lists the obtained lattice parameters, cell volume, and average crystallite size.

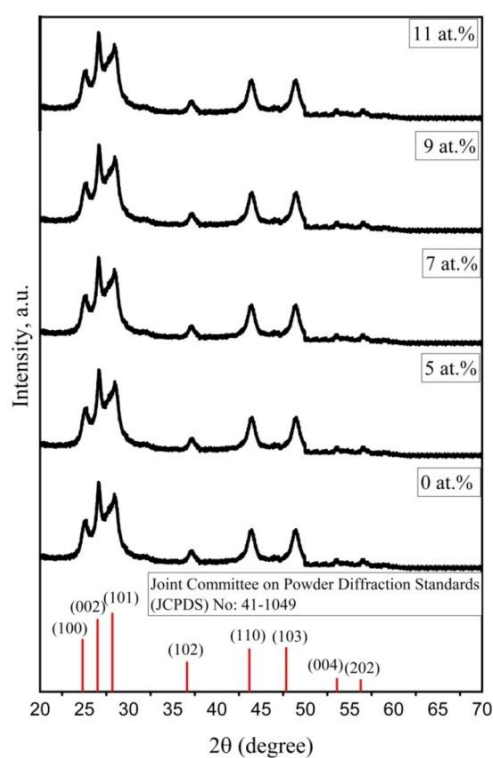


Figure 4.1: X-ray diffraction pattern of $\text{Pr}^{3+}:\text{CdS}$ (0 at.%, 5 at.%, 7 at.%, 9 at.%, 11 at.%).

Table 4.1: Calculated lattice parameters, cell volume, and average crystallite size.

Pr ³⁺ doping percentages (at.%)	Lattice parameter (Å)			Lattice volume (Å) ³	Average crystal size (nm)
	a (Å)	b (Å)	c (Å)		
0	4.132	4.138	6.534	99.67	12.25
5	4.111	4.122	6.449	99.56	13.44
7	4.092	4.091	6.389	99.66	16.50
9	4.086	4.088	6.559	99.45	20.38
11	4.077	4.069	6.654	99.43	22.24

4.3.2. Scanning electron microscopy (SEM) and transmission electron microscopy analyses (TEM)

The morphology of the samples is examined using a field-emission scanning electron microscope image. Figure 4.2 (a) displays SEM image of the synthesized Pr^{3+} doped CdS (11 at.%). When the doping concentration is elevated, agglomeration occurs more frequently, which is caused by uncontrolled particle growth from Ostwald ripening. The particles were irregular, non-uniform spherical nano grains, revealing that the compounds comprise small particles to form clusters. In the process of producing CdS nanoparticles, primarily two reaction processes are involved: the maturation of Ostwald and the agglomeration of particles. The crystallization process follows the primary path of Ostwald ripening during in-situ precursor heating, and a drop in surface energy highlights this path as large particles are created by combining smaller particles. However, the development of nanoparticles is influenced by a variety of factors, such as the precursor's temperature and the species reactivity, resulting in the identification of two-time courses for the growth of CdS nanoparticles (Arunadevi *et al.*, 2015). Transmission electron microscopy (TEM) micrograph of 11 at.% shows well-formed nanocrystalline structure of Pr^{3+} : CdS with nearly rod-shaped structure. It shows the particle within a diameter of 12.78 nm, which agrees with the data obtained from the XRD examination shown in Figure 4.2(b). Selected area electron diffraction (SAED) patterns are shown in Figure 4.2 (c).

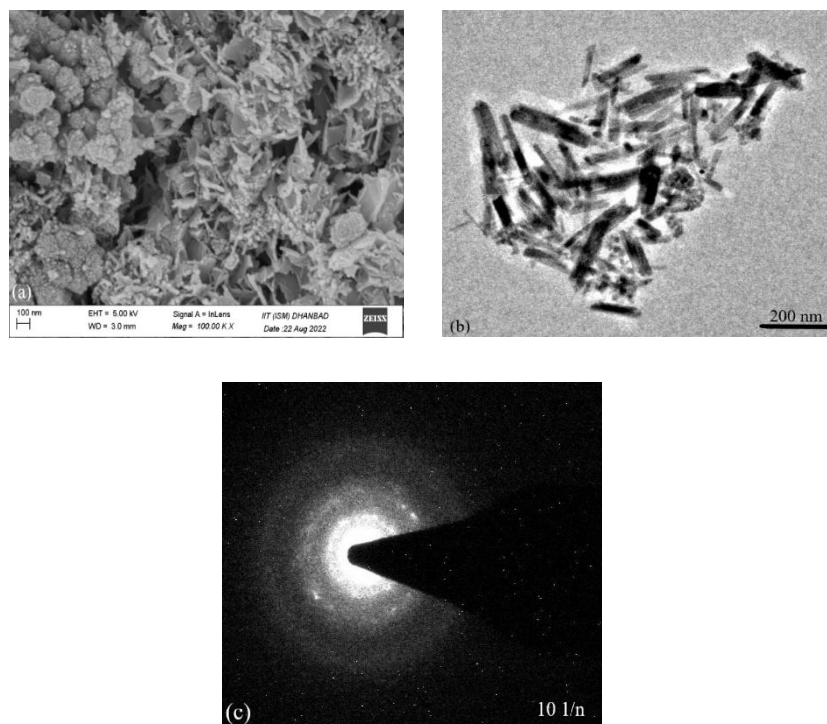


Figure 4.2: (a) SEM image of Pr^{3+} doped CdS (b) TEM image of Pr^{3+} doped CdS (c) SAED pattern of Pr^{3+} doped CdS 11 at.%.

4.3.3. Fourier transformed infrared study (FTIR)

The functional groups on the surface were confirmed from the FTIR study given in Figure 4.3. It was verified using FTIR which displayed functional groups of O–H, C–H, C=O, N–H, and C–N (W. Li *et al.*, 2017). The current broad peak at 3301 cm^{-1} , attributed to O–H, indicates water's affinity for cadmium sulfide. A 2950 cm^{-1} absorption band was also connected to C–H stretching vibrations, 1650 cm^{-1} belongs to the carboxyl group's C=O stretching modes, 1366 cm^{-1} denotes the N–H bending vibration, 1064 cm^{-1} attributed to the C–N stretching vibration (H. Li *et al.*, 2018), (Xie *et al.*, 2019). Peak at 614 cm^{-1} confirmed the existence of cadmium sulfide stretching modes (Junaid *et al.*, 2019).

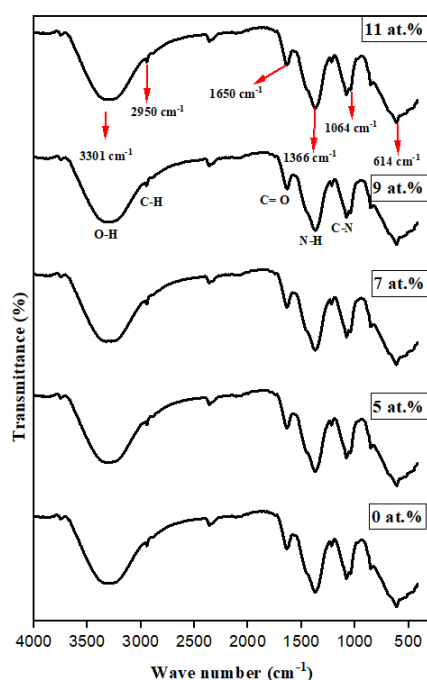


Figure 4.3: FTIR studies of $\text{Pr}^{3+}:\text{CdS}$ showing (0 at.%, 5 at.%, 7 at.%, 9 at.%, 11 at.%).

4.3.4 Photoluminescence studies

With Pr^{3+} doping in CdS, each peak's intensity, sharpness, and position were all enhanced and shifted, respectively. The increase in peak intensity indicates a decrease in the full width at half maximum (FWHM) of the peak, suggesting that the doping has higher crystallinity than pure CdS (Shkir *et al.*, 2020). We select an emission and excitation wavelength of 510 nm and 423 nm to record spectra. When excited at 423 nm the photoluminescence spectra contain emission band at 535 nm which is related to the energy gap emission caused by the radiative recombination of excitations $^3\text{P}_1 \rightarrow ^3\text{H}_5$, $^3\text{P}_0 \rightarrow ^3\text{H}_5$, transition, along with low intensity broad emission band at 638 nm attributed to the transition of $^3\text{P}_0 \rightarrow ^3\text{H}_6$ which overlap within the $4f^2$ configuration (Li *et al.*, 2017), 645 nm attributed to the transition $^3\text{P}_0 \rightarrow ^3\text{F}_2$ displayed in Figure 4.4 (a). When the emission wavelength is at 510 nm, the resultant excited peak is at 300 nm and 440 nm, given in Figure 4.4 (b), peak intensities rise when doping ion concentrations rise due to the energy transfer from the doping ion's

energy levels (Saravanan *et al.*, 2014), (Němec *et al.*, 2003). Agrawal *et al.* stated in a similar manner that increasing the concentration of La on-Cadmium sulfide-Se films leads to the emission spectrum shifting toward longer wavelengths, which is brought about by the transfer of energy from the La ion energy levels. Furthermore, a tiny shift in the band edge emission's wavelength in the direction of a higher one can be detected (Agrawal & Khare, 2015).

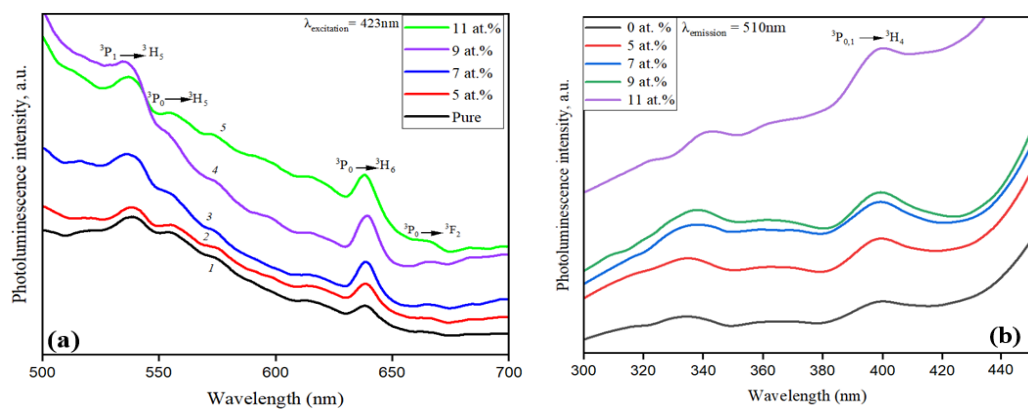


Figure 4.4: (a) Photoluminescence emission spectra of 1 – 0 at.%, 2 – 5 at.%, 3 – 7 at.%, 4 – 9 at.%, 5 – 11 at.% of Pr³⁺ : CdS, $\lambda_{\text{excitation}} = 423 \text{ nm}$; (b) photoluminescence excitation spectra of 1 – 0 at.%, 2 – 5 at.%, 3 – 7 at.%, 4 – 9 at.%, 5 – 11 at.%, $\lambda_{\text{emission}} = 510 \text{ nm}$, of Pr³⁺ : CdS.

4.3.5 Commission Internationale de l'eclairage chromaticity (CIE)

Analysis by the Commission Internationale de l'yclairage (CIE) is a crucial component in disclosing the emission light for actual use. When addressing light sources that are predominantly white, colour temperature is a relevant statistic. A specific location on the black body curve is described by the absolute, one-dimensional metric known as colour temperature. Moving further down the curve, the colour temperature value rises (down and left, towards the blue region). The majority of light sources, including natural sunlight, do not, however, truly produce light that is precisely on the black body curve. It is possible to determine the calculated colour temperature (CCT) using McCamy's approximation. The CCT is calculated using the formula given in equation 4.2 (Naorem *et al.*, 2022b):

$$\left. \begin{aligned} \text{CCT} &= -437n^3 + 3601n^2 + 5514.31 \\ n &= (x - x_e)/(y - y_e) \end{aligned} \right\} \quad (4.2)$$

where e is the difference between two colours designated as two points in the Lab colour space, the CIE chromaticity diagrams of the produced samples follow excitations at 423 nm with various amounts of doping. All of the produced samples computed colour coordinates from emission spectra are provided, along with the related colour temperature. The CIE diagram shows that all of the synthesized $\text{Pr}^{3+}:\text{CdS}$ displayed virtually white light colour when the doping concentration level was increased to 11 at.% when stimulated at 423 nm given in Figure 4.5. This shows that the white emission decreased in the cold white area and may have potential applications for lightning outdoors. From the observations, it is clear that employing various excitation wavelengths could result in a tunable colour. Table 4.2 shows CIE chromaticity coordinates and CCT of the room-temperature-produced $\text{Pr}^{3+}:\text{CdS}$ upon 423 nm excitation with different doping concentration levels.

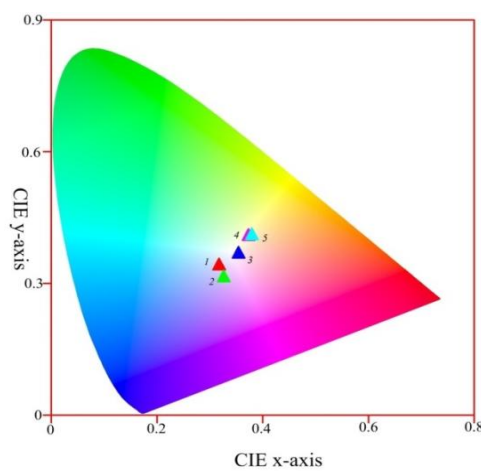


Figure 4.5: Commission Internationale de l'Elclairage (CIE) diagram of 1 – 0 at.%, 2 – 5 at.%, 3 – 7 at.%, 4 – 9 at.%, 5 – 11 at.% of $\text{Pr}^{3+}:\text{CdS}$.

Table 4.2: CIE chromaticity coordinates and CCT of the room-temperature-produced $\text{Pr}^{3+}:\text{CdS}$ upon 423nm excitation with different doping concentration levels.

Sample (at.%)	CIE coordinates		CCT
	x	y	
0	0.317	0.344	6200
5	0.326	0.369	5746
7	0.354	0.371	4752
9	0.373	0.411	4385
11	0.379	0.413	4248

4.3.6 Lifetime study

The bi-exponential function can be used to fit the samples using the formula $I = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2)$, where τ_1 and τ_2 are the appropriate decay durations (τ can be calculated using the formula $\tau = I_1 \tau_1^2 + I_2 \tau_2^2 / I_1 \tau_1 + I_2 \tau_2$ where I_1 and I_2 are the intensities at two distinct intervals of times, t . The bi-exponential fitting decay curve of $\text{Pr}^{3+} : \text{CdS}$ at different doping concentration levels is obtained (Premjit Singh *et al.*, 2019).

The lifetimes with different doping concentration levels of 0, 5, 7, 9, 11 at.% are found to be 1.40, 0.85, 0.71, 0.67, 0.44 ms, respectively, and their fitting for (R^2) for different concentrations is 0.914, 0.993, 0.908, 0.985, 0.976, respectively. The quenching effect leads to a decrease in lifetime values while the doping concentration rises, as shown in Figure 4.6.

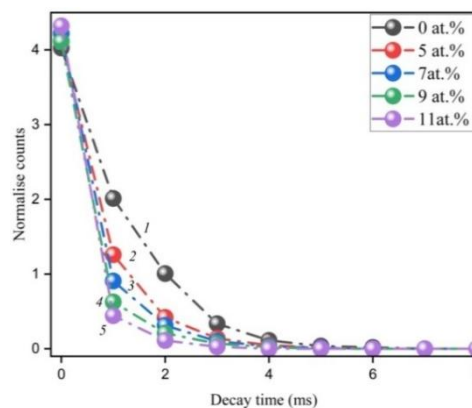


Figure 4.6: Decay lifetime of 1 – 0 at.%, 2 – 5 at.%, 3 – 7 at.%, 4 – 9 at.%, 5 – 11 at.% of Pr^{3+} : CdS.

4.3.7 UV-studies optical study

To determine the stable catalytic dosage for degradation, several mg/L catalyst dosages were investigated. To determine whether a synthetic catalyst was capable of performing a suitable degradation, the degradation was also studied in the presence and absence of a catalyst. The majority of synthetic dyes have both acute and long-term negative impacts on aquatic life and humans. Complex organic molecules can be broken down into less hazardous substances, such as carbon dioxide and water, through a process called photocatalytic degradation when they are exposed to light. This method is frequently used in wastewater treatment and environmental remediation to lessen the effects of contaminants. Photocatalysis depends heavily on the electron-hole pairs created by photon absorption. Both the holes in the valence band and the electrons in the conduction band can interact with other species in chemical processes. It is possible for organic pollutants to degrade or for reactive species to be produced due to the redox chemistry initiated by electron-hole pairs. These reactive species can neutralize hazardous compounds. While the holes in the valence band are insufficient to oxidize water or hydroxide ions to hydroxyl radicals, the free electrons in the conduction band of cadmium sulfide have a sufficient reduction potential to convert oxygen molecules to superoxide radicals. Superoxide radicals are the result of the reaction of free electrons with the oxygen molecule. Hydrogen peroxide can also result in the system's production of the hydroxyl radical. These hydroxyl radicals would react with dye, causing it to decompose into smaller particles. The energy levels involved must be compatible for an efficient transfer of electrons to take place from the excited state of dye to the conduction band of the photocatalyst. This normally indicates that the energy of dye's excited state should be at least as high as the energy needed to transfer an electron from dye to the photocatalyst's conduction band. The mechanism of degradation for Methylene Blue and methyl red is given in Figure 4.7. After giving appropriate energy (i.e, UV/visible light), the electron and the hole will separate and, and this separated

electron or hole will react with dye molecules and can degrade it efficiently, if electron and hole can separate successfully then, it is easy to achieve the maximum photocatalytic activity (Kundu *et al.*, 2017). Below is a potential degradation mechanism for methyl red and Methylene Blue equation 4.3:

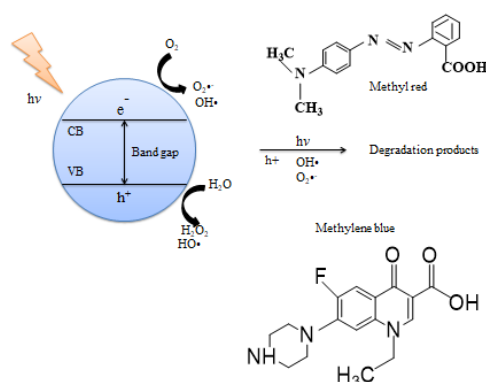
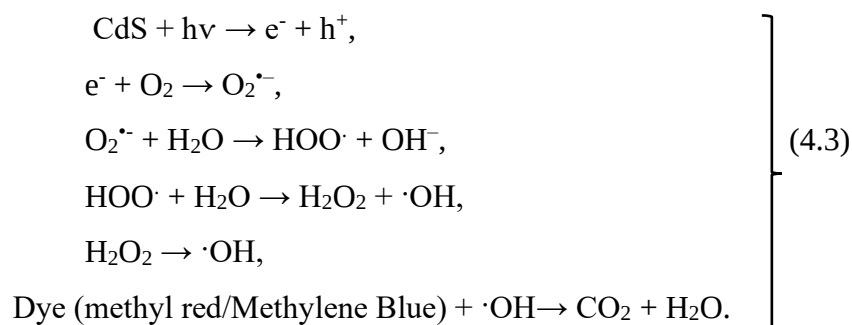


Figure 4.7: Degradation mechanism of Methylene Blue and Methyl Red.

4.3.8 Effect of catalytic dosage

It is crucial to determine the optimum loading for the effective removal of dye or organic chemicals in order to prevent the usage of excess catalysts. Catalysts are essential to these reactions, and the number of them can have a significant impact on the reaction's effectiveness and efficiency. To achieve the highest possible photocatalytic activity, the amount of catalyst utilized is crucial. When the catalyst is insufficient, light energy may not be used as effectively as it could be, and when the catalyst is excessive, electron-hole pairs may recombine more frequently. Therefore, determining the ideal catalyst loading is crucial for maximizing the photocatalytic

reaction's efficiency. We experimented with a range of levels of catalyst from 1–7 mg/L to evaluate the impact of the amount. Throughout the whole experiment, methyl red and Methylene Blue concentrations were maintained at 30 ppm. The findings demonstrate that the percentage of methyl red degradation was lowest in the case of 1 mg/L catalyst and increased sharply up to 5 mg/L, the same thing was observed for Methylene Blue, the optimum dosage was found at 5 mg/L. Figure 4.8 (a) and (b) illustrate the effect of the amount of catalyst dosage of methyl red and Methylene Blue. This has been explained in light of the fact that as the catalyst load increases, the turbidity of the solution also increases hence causing scattering of light, which consequently decreases in the volume of photoactivated molecules and UV light penetration. 5 mg/L of methyl red and Methylene Blue was shown to be the ideal dosage.

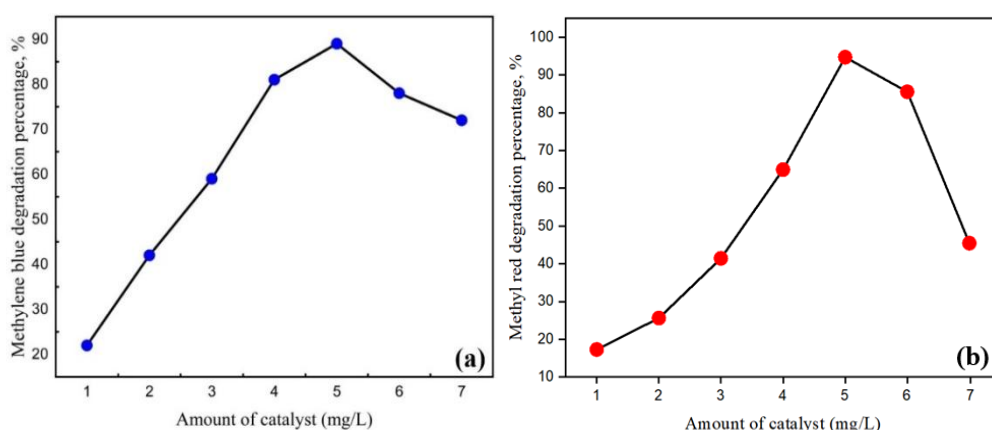


Figure 4.8: (a) Effect of catalyst amount on the degradation of Methylene Blue (b) effect of catalyst amount on the degradation of methyl red.

4.3.9 Effect of pH

Interpreting the impact of pH on the degradation process's effectiveness is a particularly challenging task. This is because different reaction routes, including oxidation by the hydroxyl radical and oxidation by the positive hole in the conduction band, can influence the degradation of dye. The pH and the substrate influence each individual's contribution. The catalyst amount used was 5mg/L. The effect of the pH solution on the degradation of methyl red and Methylene Blue at 1,

3, 5, 7, 9, and 11 pH values is shown. The degradation performance of Methylene Blue exhibits optimum degradation at a pH of 9. For methyl red, the degradation percentages at pH 1 and pH 3 are the lowest, and degradation is optimal at pH 11, as shown in Figure 4.9 (a) and (b). Increased electrostatic interaction with cationic dyes enhances dye adsorption capacity and, consequently, photocatalytic degradation when pH rises because the catalyst surface is less positively charged. The opposite is true for anionic dyes, where a rising pH decreases adsorption capability and increases photocatalytic degradation due to increased repulsive contact. Overall, the findings demonstrate that a wide range of dyes in the solution can be photocatalytically decomposed.

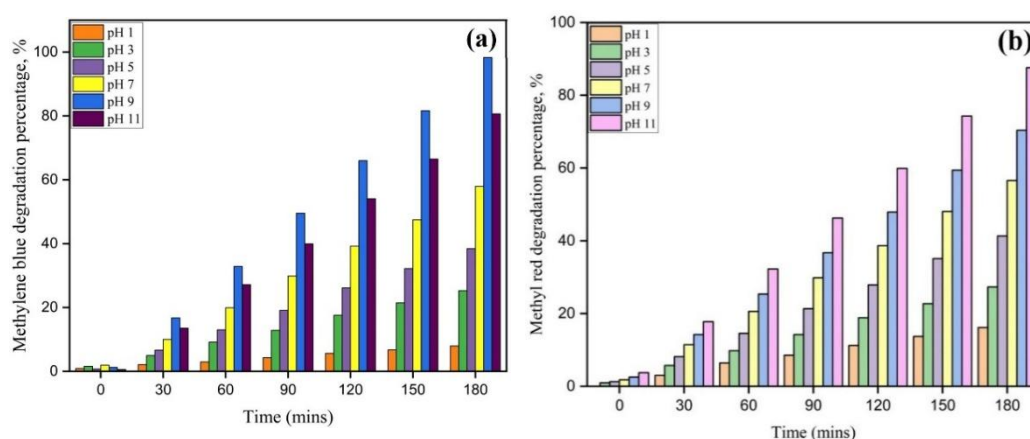


Figure 4.9: (a) Effect of different pH on degradation of Methylene Blue (b) effect of different pH on degradation of methyl red.

4.3.10 Effect of degradation with or without catalyst

A 50 W Light-emitting diode (LED) degradation experiment was done to test the process efficacy both with and without the addition of a catalyst. Dye concentration was maintained at 30 ppm, and the photocatalyst was used at a dosage of 5 mg/L. We can assume that the degradation percentage for carrying out the photocatalytic degradability was higher and more stable in the presence of the catalyst as shown in Figure 4.10 (a) and (b). Assuming all the necessary factors for stable degradation are present, the maximum pH values for photocatalysis were found to be pH 9 for Methylene Blue and pH 11 for methyl red. 5 mg/L catalytic dosages were shown to

be the most effective, and 30 ppm was used for dye concentration given in. Methyl red and Methylene Blue were degraded within 90 minutes, employing LED's of 50W power. The optimum value for the removal of dyes was calculated using (percentage removal of dye = $C_0 - C_t / C_0 \times 100$), where C_0 is the initial concentration, and C_t is the final concentration. The degradation percentage was found to be 94% for methyl red and 89% for Methylene Blue, respectively shown in Figures 10 (c) and (d). Table 4.3 shows the rate constants for the degradation of Methylene Blue and methyl red.

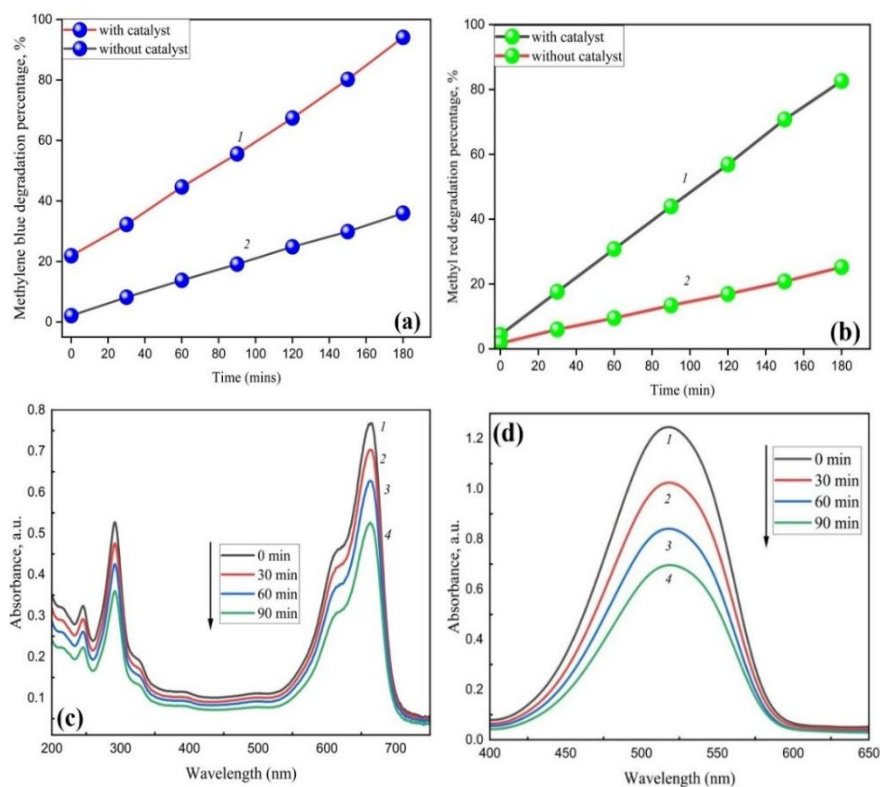


Figure 4.10: (a) and (b) Degradation with or without catalyst (c) and (d) Degradation of Methylene Blue and methyl red within 90 minutes.

Table 4.3: The estimated rate constants for the degradation and other optical parameters obtained.

Dye	λ_{max} (nm)	Catalytic dosage (mg/L)	pH	Degradation (%)	Photocatalytic degradation rate constant (min^{-1})
Methylene Blue	662	5 mg/L	9	89	0.2879
Methyl red	518	5 mg/L	11	94	0.3125

4.3.11 Effect of enhancers

Figure 4.11 (a) and (b) show the effects of most widely used enhancers, peroxy disulfate ($\text{K}_2\text{S}_2\text{O}_8$), hydrogen peroxide (H_2O_2), and potassium periodate (KIO_4) for Methylene Blue and methyl red. Dye concentration of 5 mg/L and an enhancer concentration of 20 mg/L were used. Dye degradation increased slightly when the aforementioned enhancers were added. Reactive species ($\cdot\text{OH}$, $\text{H}\cdot$, $\cdot\text{O}$, $\cdot\text{OOH}$, and H_2O_2), are produced in large part by ultrasonic irradiation (Kumari & Kumar, 2023). Due to cavitation in aqueous solutions, hydroxyl radicals may recombine to produce H_2O_2 . When ultrasonic irradiation is present, the generation of higher-intensity ultrasound facilitates H_2O_2 formation (Annalakshmi *et al.*, 2020). In addition, the presence of hydrogen peroxide (H_2O_2) speeds up the generation of $\cdot\text{OH}$ radicals by reducing the conduction band (L. Cheng *et al.*, 2018). Peroxydisulfate may potentially improve the degradation percentage by generating sulphate radicals that, when combined with water, yield $\cdot\text{OH}$. Advanced oxidation processes (AOPs) for the treatment of water and wastewater commonly utilize the extremely reactive and potent oxidants sulphate radicals ($\text{SO}_4^{\cdot-}$) and hydroxyl radicals ($\cdot\text{OH}$). Periodate ions can be thought of as examples of the development of more reactive secondary radicals. When the generated electrons are trapped in the conduction band, potassium periodate is more advantageous for degradation (Phyllis *et al.*, 2022), (A. Khataee *et al.*, 2015).

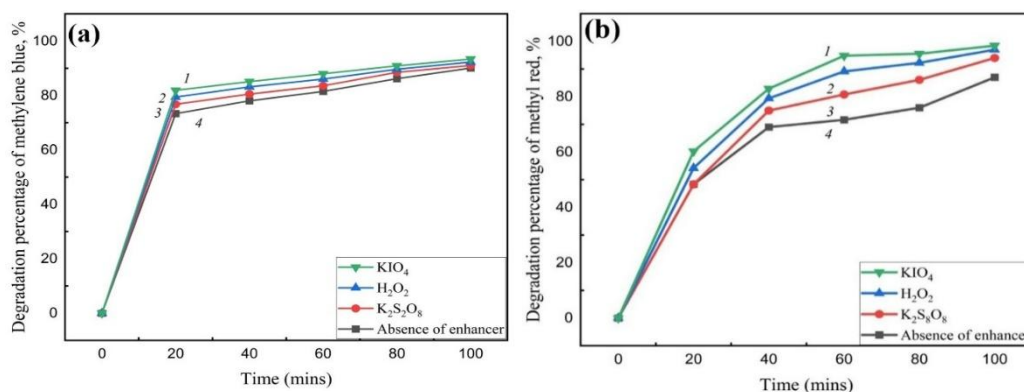
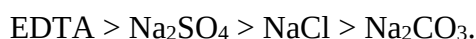


Figure 4.11: (a) Effect of enhancers on degradation of Methylene Blue: 1 – KIO₄, 2 – H₂O₂, 3 – K₂S₈O₈, 4 – absence of enhancer; (b) effect of enhancers on degradation of methyl red: 1 – KIO₄, 2 – H₂O₂, 3 – K₂S₈O₈, 4 – absence of enhancer.

4.3.12 Effect of scavengers

Sodium sulphate (Na₂SO₄), ethylenediamine tetraacetic acid (EDTA), sodium chloride (NaCl), and sodium carbonate (Na₂CO₃), the most often researched radical scavengers, were used for this study at a concentration of 20 mg/L each given in Figure 4.12 (a) and (b) the fact that all scavengers slowed dye degradation demonstrated that the principal mechanism underlying the process was a free radical attack. Therefore, the rate of Methylene Blue and methyl red degradation was greatest when ·OH scavenging agents were not present. In the following order, scavengers reduced dye degradation:



The Scavengers' inhibitory effect on degradation was caused by the scavenging of the ·OH during the process. The presence of a scavenger could deactivate the active species, preventing them from reacting during dye degradation and resulting in a drop in degradation performance (Khataee *et al.*, 2015), (Khataee *et al.*, 2017).

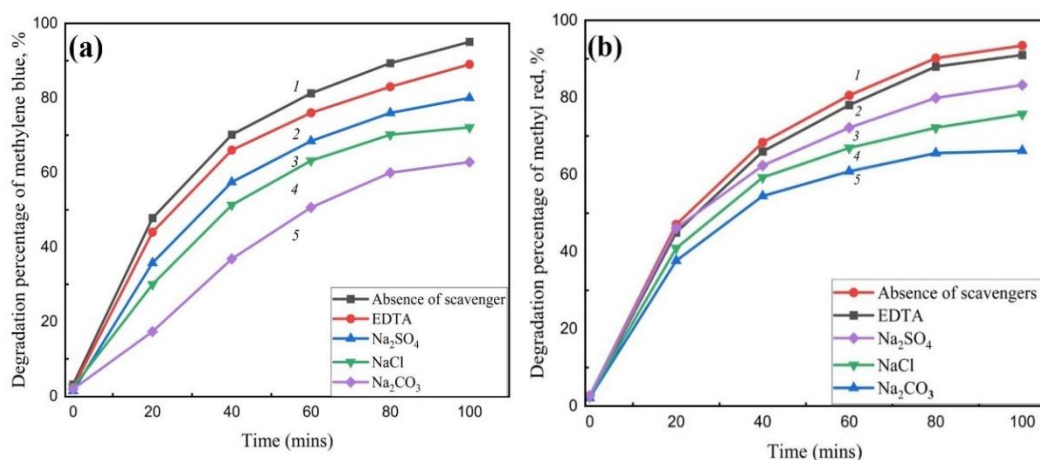


Figure 4.12: (a) Effect of scavengers on degradation of Methylene Blue: 1 – absence of scavenger, 2 – EDTA, 3 – Na₂SO₄, 4 – NaCl, 5 – Na₂SO₃; (b) effect of scavengers on degradation of methyl red: 1 – absence of scavenger, 2 – EDTA, 3 – Na₂SO₄, 4 – NaCl, 5 – Na₂SO₃.

4.3.13 Kinetic studies

The deterioration agreed with the notion of pseudo-first-order (PFO) kinetics, which was given in Figure 4.13 (a) and (b) for Methylene Blue and methyl red. The slope of the straight-line plot of $\ln(C/C_0)$ over time (t) served as the basis for the apparent response rate constants (k_{app}). The values of the k_{app} and correlation coefficients (R^2) were 0.996 and 0.998, respectively. The strong R^2 value suggests that, under ideal circumstances, the degradation followed the PFO kinetics model. The optimal conditions (catalyst dosage = 5 mg/L, reaction duration = 100 min) for the linear relationship between $1/k_{app}$ and C_0 are shown. Since the $R^2 > 0.900$, the degradation process followed the Langmuir–Hinshelwood (L–H) mechanism; the current study may be fitted using this model given in Figure 4.13 (c) and (d) for Methylene Blue and methyl red. The calculated value for the surface reaction rate constant (k_1) is 0.2753 mg/L·min and 0.3122 mg/L·min. The equilibrium constant for Langmuir–Hinshelwood adsorption was 0.1294 mg/L and 0.1441 mg/L. At the optimum experimental circumstances, the data fit the PFO kinetics model more closely than the L–H kinetics model. Due to the fact that photocatalysis is a branch of heterogeneous catalysis, the initial works on the subject frequently employed

Langmuir–Hinshelwood rate forms. This analytical function has typically dominated the latter field given in equation 4.4: (Ollis, 2005), (Ahmadi *et al.*, 2020):

$$\text{Rate} = \frac{K_{cat} K_{ads} C}{1 + K_{ads} C} \quad (4.4)$$

where K_{ads} is historically the adsorption equilibrium constant of the Langmuir isotherm and K_{cat} is a basic expression of catalytic activity and C stands for the concentration of adsorbates or reactants on a catalyst's surface:

$$K_{ads} = k_1/k_{-1}$$

where the adsorption and desorption constants for the reactants are k_1 and k_{-1} , respectively, an active species such as $\cdot\text{OH}$ radicals or semiconductor hole concentration, h^+ , and a rate constant, k' , are combined to form k_{cat} in photocatalysis. The quantities of these active species, and consequently the catalytic rate constant, k_{cat} , are anticipated to depend on the amount of light present, as they are thought to be the outcome of photoactivation. The rate constants k_1 and k_{-1} in the conventional L–H method, which does not imply adsorption/desorption equilibrium, do not depend on intensity.

The experimental finding that K_{cat} and K_{ads} both depended on intensity suggested the failure of the equilibrated adsorption assumption. By using a pseudo-steady-state assumption (PSS), which is frequently applied in other kinetic analyses involving highly unstable intermediates like free radicals, this issue has been resolved. Through this approach, any value for K_{cat} in relation to k_1 was possible. Specifically, the PSS analysis produced an apparent adsorption constant, K_{ads} , which was dependent on K_{cat} and so varied with intensity given in equation 4.5:

$$K_{ads} = \frac{k_1}{k_{-1} + K_{cat}}. \quad (4.5)$$

We could be expecting that all such conversions require PSS rather than L–H studies since all photocatalyzed aqueous phase oxidations conducted in the presence of water and molecular oxygen yield the same active species, $\cdot\text{OH}$ and h^+ (Ahmadi *et al.*, 2020).

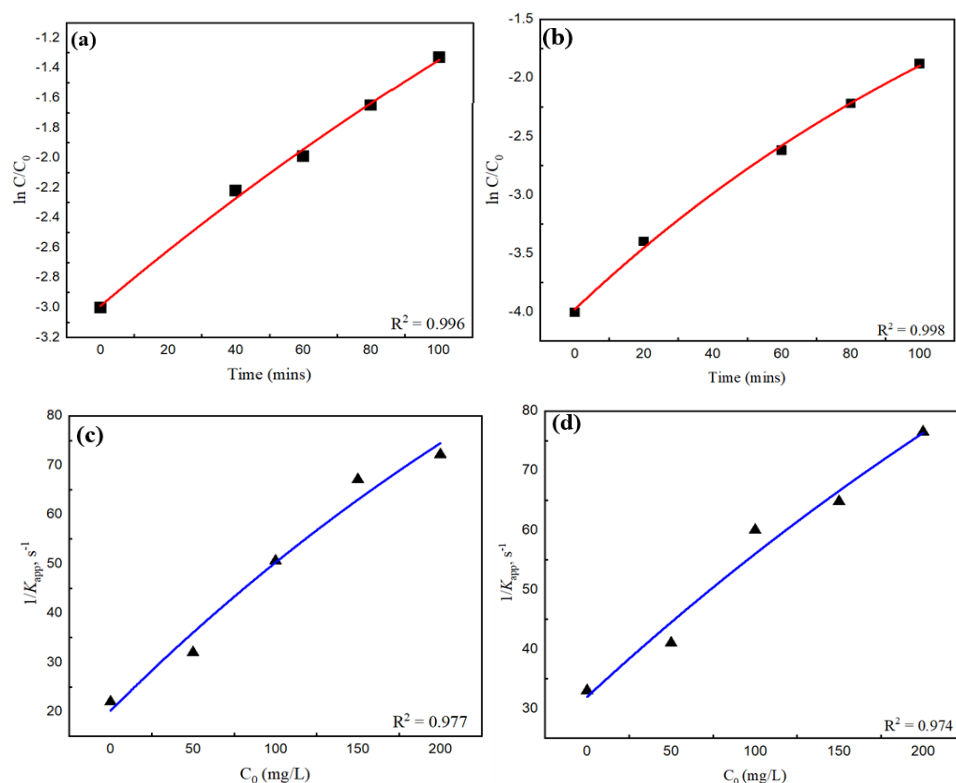


Figure 4.13: (a) Pseudo first order kinetics of Methylene Blue; (b) pseudo first order kinetics of methyl red; (c) Langmuir isotherms of Methylene Blue; (d) Langmuir isotherms of methyl red.

4.3.14 Analysis of stability

For a catalyst to be used in practice, long-term stability is a crucial consideration. Utilizing the substance for four cycles allowed researchers to assess the stability of Pr^{3+} :CdS. In the first cycle, Methylene Blue was destroyed at a rate of 95%; in the second and third cycle, the rates were 93% and 89%, respectively, and in the fourth cycle, 86% given in Figure 4.14 (a). Methyl red had degradation rates of 97% in the first usage following irradiation, 95% and 89% in the second and third cycles, and 85% in the fourth cycle, as shown in Figure 4.14 (b). After the fourth cycle, a minimal drop in degradation efficiency was seen. The mass loss brought on by reusing the sample was one of the potential causes of the drop in efficiency. In addition, the drop was likely caused by some methyl red and Methylene Blue that

was adsorbed onto the Pr^{3+} : CdS, which had not been destroyed, thereby increasing dye concentration in the subsequent recycled test.

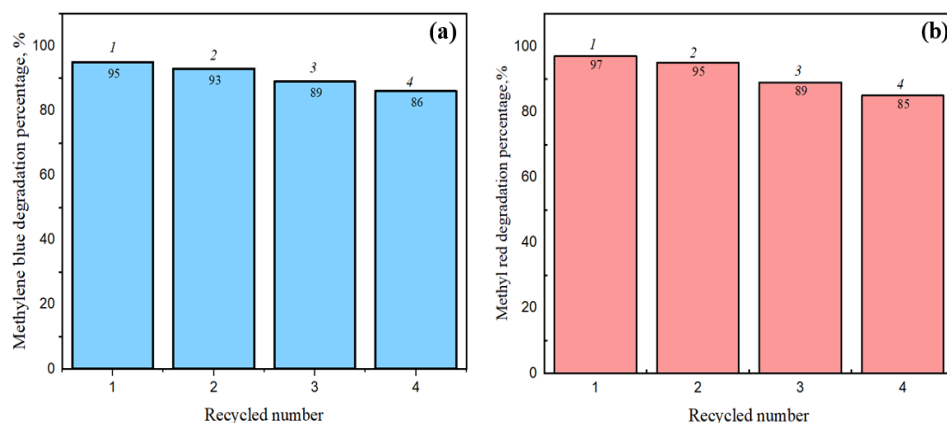


Figure 4.14: (a) Reusability of Methylene Blue: 1 – 95%, 2 – 93%, 3 – 89%, 4 – 86%; (b) reusability of methyl red: 1 – 97%, 2 – 95%, 3 – 89%, 4 – 85%.

4.4 Conclusion

The influences of Pr^{3+} doping on the structural, optical, and photocatalytic characteristics of CdS have been investigated using XRD, SEM, TEM, FTIR, photoluminescence, and UV-Visible spectroscopy. Pr^{3+} : CdS was in a hexagonal and crystalline phase from the XRD data. The Commission Internationale d'Eclairage also indicates that doped metal sulfide nanoparticles are considered to have potential applications in various domains, including optical devices. The results show that the ideal catalytic dose for the degradation of Methylene Blue and methyl red was found to be 5 mg/L at pH 9 and pH 11, respectively. The degradation percentages were 89% and 94%, respectively. Both the pseudo-first-order (PFO) and Langmuir–Hinshelwood (L-H) kinetics models were followed by the degradation of Methylene Blue and methyl red. Pr^{3+} doping in CdS enhances photocatalytic activity and is found to be effective for the breakdown of carcinogenic dyes in the environment, making it a promising candidate for real-world applications.

CHAPTER 5

Luminescence and Photocatalytic Degradation of Indigo Carmine in the Presence of Sm³⁺ doped ZnS nanoparticles

5.1 Introduction

Hazardous dye levels in wastewater, resulting from industrial activity, have been recognized as a major global environmental concern (Asadullah *et al.*, 2013). Many pigments and dyes have aromatic rings in their structures, which render them harmful to aquatic ecosystems and human health as well as non-biodegradable, carcinogenic, and mutagenic. The removal of harmful colours from industrial effluents prior to their release into water bodies has garnered considerable attention lately. Even at extremely low concentrations, dye contamination is evident, and both aquatic life and humans greatly benefit from the removal of these dyes from wastewaters (Thongrom *et al.*, 2014). Removal of remaining colours in wastewaters has been achieved using a variety of physical and chemical treatment approaches, including ion exchange, adsorption, photocatalytic degradation, and electrochemical processes (Yin *et al.*, 2016). Adsorption is one of these procedures that have been effectively used to remove dyes from hazardous wastes because of its convenience of use, high efficiency, and cheap maintenance costs. In addition to adsorption, another significant destructive technique for completely mineralizing the majority of organic contaminants is photocatalytic degradation (Yagub *et al.*, 2014), (Allahveran & Mehrizad, 2017). Advanced Oxidation Processes (AOPs) are substitute methods for eliminating colours and numerous other organic materials from wastewater and effluents. These procedures often use UV/H₂O₂, UV/O₃, or UV/Fenton's reagent to break down pollutants oxidatively (Priyadarshini *et al.*, 2022). One recently developed AOP that is easily applicable to the breakdown of dye contaminants is semiconductor photocatalysis.

Semiconductors, including TiO₂, ZnO, Fe₂O₃, CdS, and ZnS, possess an electronic structure that allows to combine and form a filled valence band and an empty conduction band, which can operate as sensitizers for light-induced redox reactions

(Kurian, 2021). When exposed to radiation, electrons in the valence band move into the conduction band, creating a hole in the process. These pairs of electrons and holes have the ability to interact independently of one another or to recombine. The holes have the ability to react with both hydroxide ions and electron donors in the solution to form strong oxidizing species such as super oxide radicals and hydroxyl (oxidation potential 2.8 V) (Hoffmann *et al.*, 1995). A variety of techniques, including doping metal ions into metal sulfides and combining metal sulfides with metal oxides and carbonaceous materials to form composites, have been proposed to stop electron-hole recombination (Chakrabarti & Dutta, 2004). The metal sulfide and carbonaceous material composites have garnered significant interest owing to their substantial surface area and facile charge separation (Bhatkhande *et al.*, 2002). Photocatalysis, an advanced oxidation process (AOP) is currently being utilized to remove colours from water without producing any hazardous by-products. Photocatalysis is a theory developed by Fujishima and Honda that focuses on producing extremely reactive intermediates such as hydroxyl radicals ($\cdot\text{OH}$), which oxidize a variety of contaminants quickly (J. Xing *et al.*, 2012). The light sources have a significant impact on the photocatalyst's catalytic activity; ultraviolet (UV) radiations has also been employed (X. F. Cao *et al.*, 2011). A substance that helps a light-induced reaction accelerate and intensify without being consumed is called a photocatalyst (X. Y. Wang *et al.*, 2009). Through the use of a photocatalyst, solar energy can be converted into chemical energy that can be used for pollution control and environmentally friendly processes such as water filtration, environmental remediation, self-cleaning surfaces, hydrogen synthesis through water cleavage, and the conversion of CO_2 into hydrocarbon fuels. With its hexagonal wurtzite and cubic zinc blende crystal structures, zinc sulfide (ZnS) is a crucial semiconductor material in the II-VI group with a direct and large band gap energy of 3.63–3.92 eV (Biswas & Kar, 2008). The ZnS crystal exhibits distinct features, including a large ionization transition and a phase stability under typical atmospheric circumstances (H. Zhang & Banfield, 2004). ZnS semiconductor NPs have been the subject of intensive research over the past 20 years in a variety of electronic domains due to their exceptional optical, electrical, luminescent, and photochemical capabilities. ZnS nanoparticles exhibit a wide range of potential uses in several fields, including optoelectronics,

photocatalysis, solar cells, UV light-emitting diodes, field emitters, injection lasers, spintronics, infrared windows, sensors, flat-panel displays, thin-film electroluminescent devices, and antibacterial activity (Moore *et al.*, 2004). Zinc sulfide nanoparticles (ZnS NPs) have exceptional photocatalytic degradation capabilities, particularly with regard to inorganic pollutants including Methyl Orange dye (MOD), Rhodamine Blue dye (RBD), and Methylene Blue dye (MBD), etc. (Devi *et al.*, 2014). When treated under UV visible light, metal-doped ZnS generates high electron-hole pairs rapidly through photoexcitation and highly negative reduction potentials of excited electrons. This increases the property of dye degradation because ZnS's surface area and particle size have an impact (X. Wang *et al.*, 2011).

5.2 Experimental details

5.2.1 Sample preparation

Sodium sulfide (98.0% purity), $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, Alfa-Aesar, Zinc acetate dihydrate (98.0-101.0% purity) Alfa Aesar, $\text{Zn}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$, and Samarium(III) nitrate hexahydrate, (99.9% purity), $\text{Sm}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, Alfa-Aesar were used in the reflux method to synthesize nanoparticles of Sm^{3+} doped ZnS. Sm^{3+} -doped zinc sulfide nanoparticles with varying concentrations (1, 3, 5, 7, and 9 at. %) were synthesized using the reflux process. Samarium and ZnS were mixed and stirred at room temperature for 45 minutes. Drop by drop, sodium sulfide was added to the aforementioned solution. The entire solution was then refluxed at 160°C for three hours. The resultant residue was washed with acetone, centrifuged at 7000 rpm and dried at 100°C for 5 hours. Various doping concentrations of Sm^{3+} -doped zinc sulfide nanoparticles were synthesized using the same process. Samarium is incorporated into the ZnS lattice as a dopant by carefully adding samarium nitrate to the zinc precursor solution. The doping concentration is determined by the amount of samarium introduced, and it can be adjusted to modify the characteristics of nanoparticles. The reaction is usually conducted at elevated temperatures under controlled conditions using a mixture of zinc and sulfur precursor solutions. As a result, ZnS nanoparticles start to form. During the nucleation process, the doped samarium ions are integrated into the ZnS lattice, creating Sm^{3+} -doped ZnS

nanoparticles. Nanoparticles continue to expand as the reaction progresses. Stabilizing agents or surfactants may be applied to control the size, shape, and aggregation of nanoparticles. The reaction mixture is removed from the Sm^{3+} -doped ZnS nanoparticles, typically by centrifugation or filtration, and nanoparticles are cleaned and purified to remove any unreacted precursors or byproducts.

5.2.2 Sample characterization

Different characterization techniques were used to characterize the prepared samples. Using Rigaku Smart Lab, the crystal structure and phase composition were discovered using XRD. SEM image was obtained using a Carl Zeiss Supra 55 FESEM. Using the FEI TECNAI G2 F20 S-TWIN, TEM images were captured. Shimadzu's IRAffinity-1S was used to collect FTIR data. A fluorescence spectrometer F-7000 with a (150 W) Xenon lamp was used to evaluate the photoluminescence characteristics. Novatouch LX Quantachrome was used to collect BET data. A wavelength range of 190 to 1100 nm evolution 220 UV visible spectrophotometer was used to evaluate the photocatalytic properties.

Photocatalytic degradation procedure and analysis

The photocatalytic activity was investigated by observing the photodegradation of Indigo Carmine. Different dye concentrations (ranging from 10 to 40 ppm) with catalytic doses (5-30 mg/L) and pH levels (1, 3, 5, 7, and 11) were studied. Each reaction was stirred with a magnetic stirrer for 60 minutes to ensure a uniform catalyst suspension throughout the reaction for the degradation tests, and then exposed to UV light from a Philips PL-S 92/WP BLB. Samples were taken regularly, filtered using Millipore membrane filters, and centrifuged to remove any undissolved materials, allowing for the calculation of the percentage of dye degradation. A small amount was extracted using a syringe and filtered through a 0.45 μm pore size Millipore syringe filter. The composite nanoparticles were repeatedly cleaned with distilled water after each experiment in order to allow for reuse. A UV-visible spectrophotometer was used to measure the UV absorbance in the 200-700 nm region at 30-minute intervals, and dye concentration was calculated accordingly. This allowed for the determination of the photodegradation efficiency of the

composite nanoparticles. By evaluating the photodegradation efficiency, the durability and usability of the photocatalytic catalysts were determined from equation 5.1.

$$\text{Efficiency (\% of photodegradation)} = \frac{C_i - C_t}{C_i} \times 100 \quad (5.1)$$

where C_i denotes the starting concentration and C_t denotes the concentration at time 't'. After each cycle of degradation, the photocatalytic catalyst's durability and usability were evaluated. The catalyst was filtered out and repeatedly rinsed with distilled water before dyes were photodegraded under the same circumstances.

5.3 Results and discussion

5.3.1 X-ray diffraction (XRD)

Figure 5.1. (a) Confirms the XRD cubic zinc ZnS structure (JCPDS No. 05-0566) with the lattice parameters and volume given in Table 5.1. When the amounts of Sm^{3+} doping increased, nanoparticle crystallinity also increased. The diffraction peaks of Sm^{3+} -doped ZnS exhibit a slight shift towards higher 2θ values. The synthesized materials exhibited distinct diffraction peaks, demonstrating the sample's crystallinity. Using Scherrer's formula, the average particle size was calculated using the formula $D = (K\lambda)/\beta\cos\theta$, where 'K' is a constant (0.9) and the wavelength of X-rays employed ' λ ' (1.5406 Å) (Poornaprakash *et al.*, 2016). According to the Scherrer equation, Sm^{3+} -doped ZnS nanocrystals have a particle size of 3-12 nm. Furthermore, the experimental results show that the broadening for small crystallites is distinct from the strain-induced broadening. Therefore, the full-width half maximum (FWHM) of the XRD pattern provided in the equation 5.2 may be calculated using the linear sum of the FWHMs of size, strain, and instrument (Mercy *et al.*, 2014):

$$\beta_{\text{tot}} = \beta_{\text{size}} + \beta_{\text{strain}} + \beta_{\text{instrument}} \quad (5.2)$$

The instrument broadening β_{hkl} was adjusted by each diffraction peak, and a Lorentzian profile was fitted. Strain broadening is the term used to describe the contribution of lattice strain to peak broadening, which is often caused by local deformation of the lattice. If the strain is taken to be constant throughout all crystallographic orientations and the crystal is isotropic, the strain broadening can be

depicted as follows (Mercy *et al.*, 2013):

$$\mathcal{E} = \beta_{hkl}/4\tan\theta \quad (5.3)$$

Substituting values of β_{size} and β_{strain} in the above equation:

$$\beta_{hkl} = K\lambda/D\cos\theta + 4\mathcal{E} \quad (5.4)$$

The above equation can be rearranged by:

$$\beta_{hkl} \cos\theta = K\lambda/D\cos\theta + 4\mathcal{E}\sin\theta \quad (5.5)$$

The parameter of the micro-strain is

$$\mathcal{E} = \Delta D_{hkl}/D_{hkl}. \quad (5.6)$$

A graph is drawn between $4\sin\theta$ and $\beta_{hkl} \cos\theta$, as shown in Figure 5.1. (b) For the samples corresponding to 1, 3, 5, 7, and 9 at. %. The micro-strain calculated from the graph is -0.0331, -0.0241, -0.0235, -0.0154, and -0.0164, respectively. The R^2 values for different concentrations were also found to be 0.982, 0.973, 0.955, 0.942, and 0.933. Williamson-Hall plots of samples show a negative slope, which denotes the particle's compressive strain. Figure 5.1. (c) Displays the synthesized Sm^{3+} -doped ZnS FTIR spectra at 1, 3, 5, 7, and 9 at.%. This demonstrates the capability of infrared spectroscopy to recognize the sample's functional groups. IR spectroscopies, which depends on the absorption of infrared light, are used to determine the vibrational energy of molecules (Osuntokun *et al.*, 2016). A massive peak of 3204 cm^{-1} , which was most likely caused by the adsorptive moisture on the surfaces of the materials, was attributed to the stretching of the -OH. This peak may indicate adsorptive moisture on the material's surface since it indicates the existence of hydroxyl (alcohol) functional groups in the substance. The significant peaks detected around 1630 cm^{-1} can also be attributed to the carboxyl ($\text{C}=\text{O}$) stretching vibration because the functional group is present in the adsorbed residues (Yaemphutchong *et al.*, 2020). This suggests that the adsorbed residues contain carboxylic acid or ester groups. The peak observed at 1076 cm^{-1} is caused by oxygen (O_2). It can be a reference peak or show that the substance contains oxygen-containing functional groups. The usual ZnS primary bonding peak (Zn-S stretching or lattice vibrations) is seen at 449 cm^{-1} . The primary bonding in ZnS is linked to the peak at this wavenumber. It is frequently related to lattice vibrations or Zn-S stretching and can be used to determine whether ZnS is present in the material.

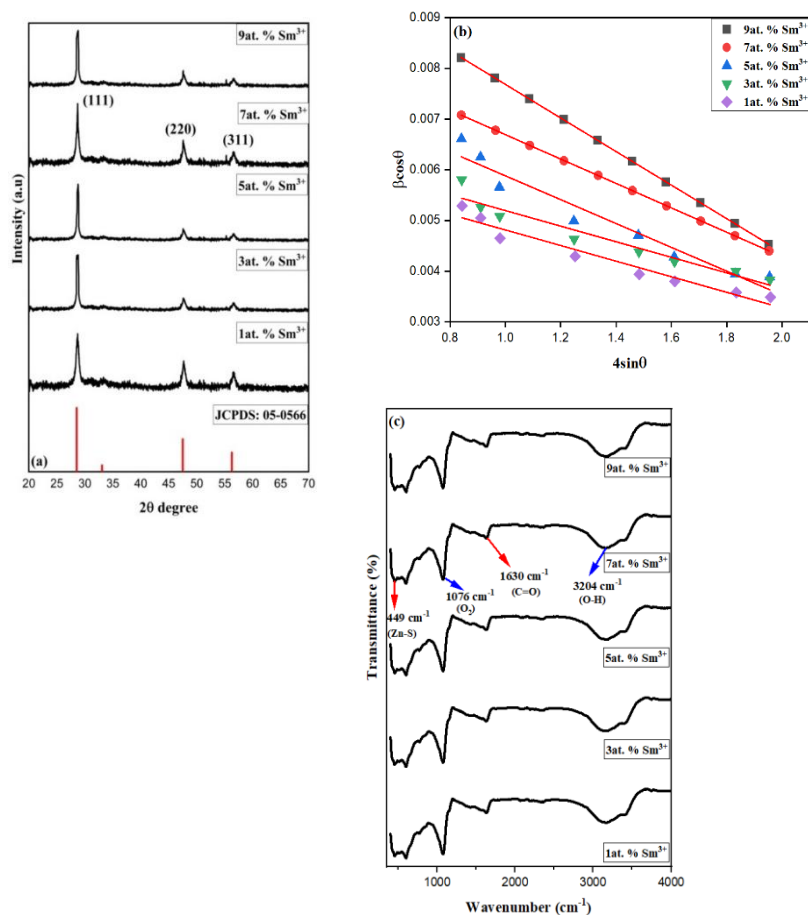


Figure 5.1: (a). XRD pattern of Sm^{3+} -doped ZnS with different concentrations (1, 3, 5, 7, 9at. %). (b). Plot of $4\sin\theta$ vs $\beta\cos\theta$ of Sm^{3+} -doped ZnS with different concentrations (1, 3, 5, 7, 9 at. %). (c). FTIR spectra of Sm^{3+} -doped ZnS 1, 3, 5, 7, 9at. %.

Table 5.1: Comparison of standard values for Sm^{3+} -doped ZnS their lattice parameters and volume.

Standard parameters	Standard values	1at. % Sm^{3+}	3at. % Sm^{3+}	5at. % Sm^{3+}	7at. % Sm^{3+}	9at. % Sm^{3+}
Lattice parameter Å	5.406	5.322	5.442	5.301	5.228	5.202

Lattice volume (Å ³)	157.99	157.78	157.65	157.92	157.45	157.40

5.3.2 Scanning Electron Microscope (SEM) and Transmission Electron Microscopy (TEM)

SEM images and relative EDX spectra of 9at. % Sm³⁺-doped ZnS samples are shown in Figure 5.2 (a) and (b). According to their morphology and microstructure, the samples are composed of various agglomerated particles that are largely irregular, non-uniform, and spherical. The term "agglomeration" describes the clustering or gathering of different particles. Since the samples are made up of various aggregated particles, it is clear that the zinc sulfide-doped samarium particles tend to collect rather than distribute evenly. The particles are described as having an erratic shape. This shows that the particles shapes need to be more homogeneous and clearly defined. They may have uneven edges or rough surfaces as a result of many things, such as the synthesis process or the growth environment. The particles have a spherical form in addition to being classified as irregular. The synthesis technique, temperature, pressure, and other processing variables can all impact the observable morphology and microstructure of zinc sulfide doped with samarium. Atomic and weight percentages from the EDX are displayed in Table 5.2. The samples had an average diameter of 5.15 nm, as shown in Figure 5.2 (c). Figure 5.2 (d) Displays a TEM image of Sm³⁺-doped ZnS 9at. %. The estimated particle size from the TEM image was spherical as well as rod-shaped was found to be 5 nm. The nanometer (nm) range of this size measurement suggests that the sample's particles are quite small. The particles were both spherical and rod-shaped. Various synthesis processes or the presence of various crystallographic phases may have resulted in the coexistence of distinct particle morphologies. Especially in fields like catalysis, optics, and materials science, the size and form of nanoparticles can significantly affect both their characteristics and uses. Their size and form, as well as their crystalline structure and dopant dispersion, can all be affected by the precise synthesis process and conditions used to create these nanoparticles. Figure 5.2 (e) displays the SAED patterns of Sm³⁺-doped ZnS nanoparticles as well as the

locations of the three diffraction rings, which are the same as those seen in the (111), (220), and (311) diffraction of bulk ZnS (Hanifehpour *et al.*, 2016). From the selected area electron diffraction (SAED) pattern, the d-spacing is calculated. The first ring is 2.0Å, the second is 1.6Å, and the third is 1.2 Å.

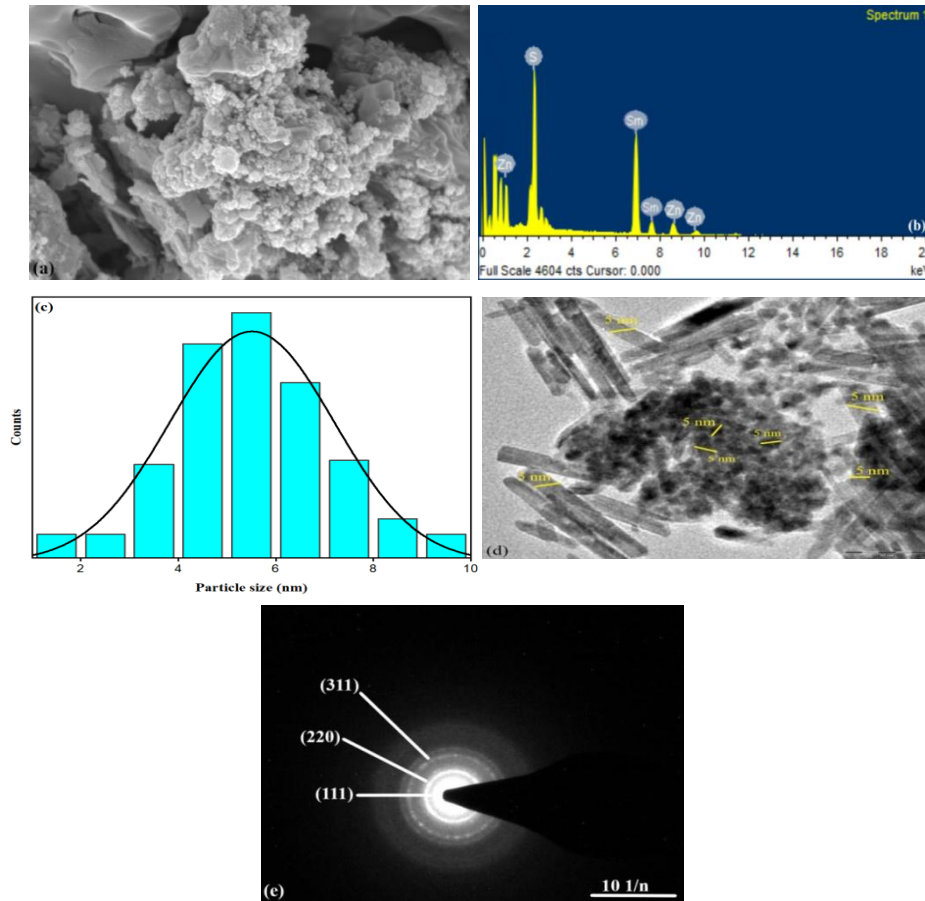


Figure 5.2: (a) SEM image of Sm³⁺-doped ZnS 9at. % (b) Corresponding EDX spectra and (c) Average particle size of Sm³⁺-doped ZnS 9at. %. (d) TEM image of Sm³⁺-doped ZnS 9at. % and (e) SAED patterns of Sm³⁺-doped ZnS 9at. %.

Table 5.2: Atomic and weight percentages from the EDX.

Element	Weight	Atomic %
S	27.41	41.41
Sm	59.33	48.76

Zn	13.26	9.83

5.3.3 Brunauer Emmett Teller (BET)

The Brunauer Emmett Teller (BET) method is popular for calculating a particular surface area. The two primary factors in photodegradation are the vast surface area and the small particle size. Figure 5.3. shows the Sm^{3+} -doped ZnS N2 absorption-desorption observations at 1, 3, 5, 7, and 9 at.%. The produced samples displayed type-IV H1 hysteresis loop isotherms, indicating mesoporous. Mesoporous (2 nm < pore size <50 nm) materials produce a type IV isotherm (Chang *et al.*, 2009). The BET-specific surface areas were 54 m² /g, 72 m² /g, 88 m² /g, 113 m² /g, and 129 m² /g for 1, 3, 5, 7, and 9 at.% samples, respectively. The results of this BET analysis showed that Sm^{3+} -doped ZnS 9at. % nanoparticles with large surface areas could efficiently promote electron and ion movement at the interface to improve dye degradation performance. This is a crucial observation because more active areas for chemical reactions exist when a surface area is more significant. The increased surface area of the Sm^{3+} -doped ZnS nanoparticles promotes effective electron and ion transport at the interface between nanoparticles and dye molecules. The performance of dye degradation is improved due to the higher electron and ion movement (Kannan *et al.*, 2020). The electrical structure and surface characteristics of the ZnS nanoparticles are probably affected by the Sm^{3+} -dopant, which makes them better suited to enhanced electron transfer and facilitates the degrading process. Overall, the BET study shows that Sm^{3+} -doped ZnS nanoparticles have properties that make them suitable catalysts for dye degrading. Nanoparticles have proven to be highly effective in various applications, including dye degradation. This is mainly because nanoparticles possess a large surface area, enabling more efficient reactions. In addition, dopants like Sm^{3+} further enhance their performance, leading to superior results.

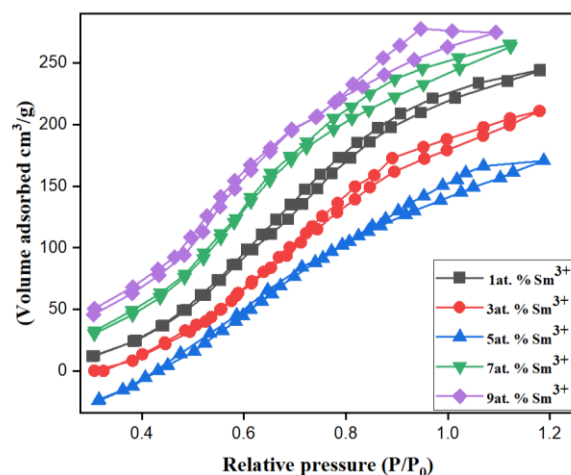


Figure 5.3: BET study of Sm^{3+} doped ZnS 1, 3, 5, 7, 9at. %.

5.3.4 Photoluminescence and CIE study

Figure 5.4 (a) shows Sm^{3+} - doped ZnS 1, 3, 5, 7, 9at. % emission peaks for photoluminescence spectra, which were measured between 500 and 700 nm. When excited at 395nm, the peak positions are found to increase with an increase in Sm^{3+} concentrations up to 5 at. % and then decrease with a further increase in Sm^{3+} concentration, caused by the concentration quenching effect of Sm^{3+} induced by cross-relaxation. With increasing dopant concentration, there are more non-radiative transition events where energy is transferred from the initially absorbing impurity ions to comparable ions. A transfer to a quenching site (defect) may be implicated after many of these steps, further reducing the radiative process. Significant peaks in the emission spectra can be observed at wavelengths 559 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$), 595 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$), and 642 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$), corresponding to the f-f transitions of Sm^{3+} in the $4f^5$ configuration, respectively. According to the selection rule, the peak at 559 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$) resulted from a pure dipole transition between an electric dipole ($\Delta J = \pm 2$) and a magnetic dipole ($\Delta J = 0$ and ± 1). While the transition ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$) observed at 595 nm satisfies the selection rule for a magnetic dipole transition, it is attributed to a combination of partially electric dipole and partially magnetic dipole transitions, with the electric dipole transition predominating. The peak ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$) at 642 nm results from an electric dipole transition (Seeta Rama Raju *et al.*, 2012), (Ratnam *et al.*, 2014), (Yu *et al.*, 2014). The impact of the crystal

field on the transition between pure electric dipoles is significant indeed. It is also fascinating how it affects the transition between two pure electric dipoles. The Judd - Ofelt theory can be used to explain the local site symmetry around Ln^{3+} in a matrix (Jamalaiah *et al.*, 2009). Despite variations in their intensities, the peak profiles remained unchanged when Sm^{3+} concentrations were altered, indicating that Sm^{3+} exhibited the same site symmetry at all concentrations. Figure 5.4. (b) displays the excitation spectra for the as-prepared Sm^{3+} - doped ZnS 1, 3, 5, 7, and 9at. % obtained by monitoring when emitted at 615 nm. The spectra comprise a broad band between 350 and 550 nm. The electronic transition from Sm^{3+} ground state ($^6\text{H}_{5/2}$) to various excited energy levels produces spectra with sharp, narrow peaks. They can be positioned at 367 nm ($^6\text{H}_{5/2} \rightarrow ^6\text{P}_{7/2}$), 401 nm ($^6\text{H}_{5/2} \rightarrow ^4\text{F}_{7/2}$), 439 nm ($^6\text{H}_{5/2} \rightarrow ^6\text{P}_{5/2}$), 476 nm ($^6\text{H}_{5/2} \rightarrow ^4\text{G}_{9/2}$), and 501 nm ($^6\text{H}_{5/2} \rightarrow ^4\text{I}_{13/2}$). Due to Sm^{3+} f-f transitions, it can be seen that the broad absorption band's intensity is more significant than those narrow peaks, indicating that energy has been transferred from the host lattice to Sm^{3+} (Blasse & Grabmaier, 1994). These results agree with the earlier publications on the photoluminescence features of Sm^{3+} (Singh *et al.*, 2018), (Singh *et al.*, 2017). The luminescence properties of ZnS are changed by doping with Sm^{3+} ions, which introduce luminous centers into the crystal structure. The characteristic energy level transition in Sm^{3+} ions result in luminescence at particular wavelengths. The excitation wavelength, Sm^{3+} doping concentrations, and luminescence intensity of Sm^{3+} doped ZnS will all affect the emission spectra and luminescence intensity. Applications for the luminescence produced by Sm^{3+} doped ZnS include optoelectronics, display technology, luminescence devices, etc.

For applications involving photoluminescence, CIE colour coordinates are important. Figure 5.4. (c) displays the CIE chromaticity curve for synthesized Sm^{3+} - doped ZnS at 1, 3, 5, 7, and 9 at. %. This diagram shows that when triggered at 395 nm, the generated samples emit a hue that is almost entirely white hue. Figure 5.4. (d) shows the emission decay curves for Sm^{3+} - doped ZnS samples at 1, 3, 5, 7, and 9at. %. The bi-exponential function can be used for precisely fitting the entire decay curve as given in equation 5.7 (Naorem *et al.*, 2022a):

$$I = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2) \quad (5.7)$$

I_1 and I_2 represent the equivalent decays of intensities at two different points in time 't'. It displays the values of two lifetimes: slow time τ_2 and quick time τ_1 . The key variables influencing the behavior of bi-exponential decay are the number of luminescence centers, energy transfer from the donor, the unequal distribution of dopant ions on the host lattice, and impurities. Factors such as the number of luminescence centers, energy transfer from the donor, unequal distribution of dopant ions on the host lattice, and impurities can also impact the behavior of bi-exponential decay. The typical luminescence lifespan can be calculated using the following equation 5.8: (Premjit Singh *et al.*, 2019).

$$*\tau = I_1\tau_1^2 + I_2\tau_2^2 / I_1\tau_1 + I_2\tau_2 \quad (5.8)$$

The calculated average life times of Sm^{3+} -doped ZnS at concentrations 1, 3, 5, 7, 9at. % was found to be 1.88, 1.71, 1.89, 1.52, 1.49 ms, respectively. According to speculation, the concentration quenching effect is what causes the lifetime value to decrease with increasing Sm^{3+} concentration.

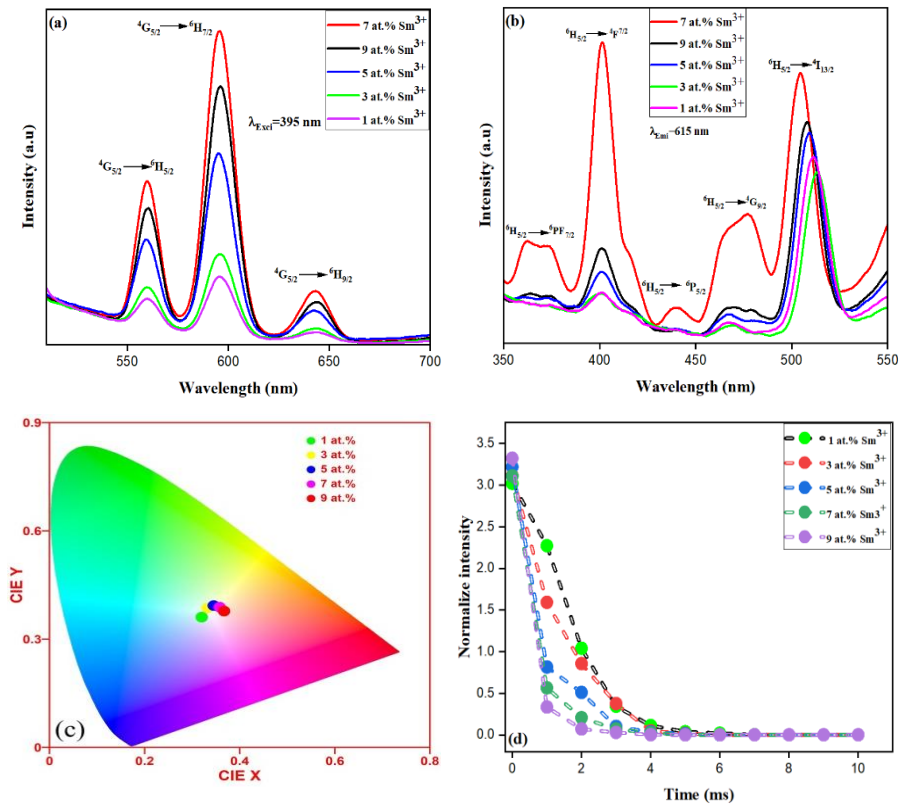


Figure 5.4: (a) Emission and (b) excitation spectra of Sm³⁺-doped ZnS 1, 3, 5, 7, 9at. %. (c) CIE analysis (d) Lifetime decay of Sm³⁺-doped ZnS 1, 3, 5, 7, 9at. %.

5.3.5 UV-optical study

Nanocatalyst doses ranging from 5 to 30 mg/L are exposed to light for 210 minutes. Due to an increase in active sites, the rate of decolourization increases to its maximum degrading efficiency in the presence of 15 mg/L of nano-photocatalyst. However, as the loading was increased above the optimal level, the decolourization rate decreased due to the increased opacity of the suspension samples, resulting in increased light scattering, as shown in Figure 5.5(a). The pH range where the solution can degrade Indigo Carmine was found to be 5.3. A diluted hydrochloric acid or potassium hydroxide solution was used to modify the pH value when necessary. Different solutions were created with pH values ranging from 1, 3, 5, 7, 9, and 11. Following 210 minutes of photocatalytic irradiation, the degradation efficiencies were examined. The effectiveness of the Indigo Carmine solution's degradation decreased as the pH level of the reaction solution increased, as shown in Figure 5.5 (b). When the pH was 5, degradation efficiency was higher, but when it was 11, it reduced to 30.45%, indicating that the optimal pH for degradation was found to be pH 5. Since Indigo Carmine is a synthetic dye, its stability and chemical properties, like those of many other dyes, may be pH-dependent. Dye molecule may be more vulnerable to breakdown at pH 5 due to several mechanisms, including hydrolysis, oxidation, or reduction. Dye molecule may be more likely to degrade at this ideal pH. Indigo Carmine can be broken down more quickly at pH 5 because some enzymes or catalysts may be more active at that level. Dye may be more soluble or more likely to form aggregates more vulnerable to deterioration processes. The molecule may be more prone to photodegradation, where light energy triggers chemical processes that result in dye deterioration.

Dye solutions have been produced in concentrations ranging from 10 to 40 (ppm). 10 ppm shows the best degradation percentage. The decreasing efficiency decreased as the starting concentration rose, as indicated in Figure 5.5(c), and the tendency accelerated as the concentration increased. As the concentration increased, more

photons would be absorbed, limiting light transmission. As a result, less light was able to penetrate deeply, limiting nanoparticle's potential to catalyze the processes. The ability of a chemical to deteriorate at varied doses over time was investigated. Figure 5.5(d) shows the degradation of Indigo Carmine over 210 minutes at pH 5 with catalytic doses of 10 ppm and 15 mg/L. Indigo Carmine absorbs the lightest in the visible spectrum at a wavelength peak of 615 nm. Indigo Carmine absorbs some wavelengths of visible light and reflects or transmits others when it is in contact with the light. The absorption at 615 nm is defined by the conjugated system of aromatic rings' molecular structure and electronic transitions. The energy needed to move electrons from their lower-energy (ground) states to their higher-energy (excited) states is represented by this absorption peak. Figure 5.5(e) provides information on the structure of Indigo Carmine and the potential degradation mechanism. The photocatalytic performance of ZnS for the degradation of dyes concerning this work is given in Table 5.3. Dye degradation is a systematic process with a well-defined course and intuitive mechanism. ZnS has an energy band structure with a low valence band (VB) filled with electrons and a high empty energy conduction band (CB). It has been demonstrated that when the energy of the radiation exceeds the band gap width of ZnS, matched holes (h^+) grow in the valence band (VB), creating an "electron hole" pair. In contrast, excited electrons in the valence band (VB) can jump into the conduction band (CB). According to equations (5.9-5.15), superoxide ions ($O_2\cdot^-$) are created when absorbed oxygen (O_2) and conduction band electrons (CB) interact under the conditions of irradiation. These reactive oxygen species ($O_2\cdot^-$, $OH\cdot$, and H_2O_2) have an exceptionally high redox capacity along the whole photocatalytic reaction pathway. They are capable of breaking down large organic molecules into smaller molecules, more environmentally friendly molecules like CO_2 and H_2O . In order to speed up chemical reactions that break down dye molecules, photocatalytic degradation of dyes uses light to activate catalyst materials. The bandgap energy of the catalyst material may change due to doping. Doping enables the material to absorb a wider range of light, including visible light, by reducing the bandgap. The photocatalytic process depends on the photogenerated electron-hole pairs' recombination rate, which doping can

lower. Reduced recombination means that more of these charge carriers can interact with dye molecules in redox processes, which increases the effectiveness of dye degradation. Dopant atoms can increase the number of active sites and alter the catalyst's surface characteristics, thereby facilitating the adsorption of dye molecules and subsequent reactions. More dye molecules may interact with the catalyst's active sites, resulting in increased catalytic activity. The degradation of Indigo Carmine using pure, 1, 3, 5, 7, and 9 at.% is shown in Figure 5.5(f), demonstrating that 9 at.% was the most effective for dye degradation, highlighting the significant influence that doping has on photocatalytic activity. Doping a catalyst can considerably enhance its performance in dye degradation, particularly in photocatalysis, by extending its light absorption range, improving charge separation and transport, increasing the number of active sites for adsorption, and fine-tuning its properties. These advancements are essential for wastewater treatment and environmental remediation procedures that are more effective and sustainable. The percentage of nanoparticles yielded was above 88%. The highest yield is achieved at 9 at.%; it also demonstrates a greater advantage in the degradation of nanoparticles and is most effective in degrading Indigo Carmine. The purity of the starting ingredients, the effectiveness of the synthesis process, and the methods used for purification can all impact the yield of nanoparticles. Due to the difficulties in regulating and isolating nanoparticles in a highly pure state, nanoparticles frequently have lower yields than bulk materials. The abovementioned processes demonstrate that photocatalytic degradation is possible when soluble oxygen and H₂O are present. There have been other reports of similar methods for the photocatalytic destruction of dyes (Koe *et al.*, 2019). As a result, ZnS nanoparticles have the potential to purify them, which causes photocatalysis to destroy Indigo Carmine dye. The following steps represent the photodegradation mechanism:



Zinc sulfide (ZnS) absorbs light energy ($h\nu$) and undergoes photoexcitation. This process generates an electron (e^-) and a positive hole (h^+).



The generated electron (e^-) reacts with oxygen (O_2) to form superoxide anion ($\text{O}_2^{\cdot -}$).



The positive hole (h^+) reacts with superoxide anion ($O_2^{\cdot-}$) to form hydroperoxyl radical ($HO_2^{\cdot}$).



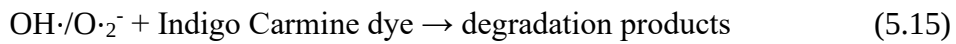
The hydroperoxyl radical ($HO_2^{\cdot}$) reacts with the generated electron (e^-) to form a positive hole (h^+), leading to the production of hydrogen peroxide (H_2O_2).



Water (H_2O) reacts with the generated electron (e^-) to produce hydroxyl radical ($OH^{\cdot}$) and hydroxide ion (OH^-).



The positive hole (h^+) reacts with hydroxide ion (OH^-) to form hydroxyl radical ($OH^{\cdot}$).



Hydroxyl radicals ($OH^{\cdot}$) or superoxide anions ($O_2^{\cdot-}$) react with Indigo Carmine dye, leading to the degradation of dye and the formation of various degradation products. Figure 5.5 (g). shows the UV-Vis absorption spectra of different atomic percentages. The energy of the band gap (E_g) of ZnS nanoparticles can be calculated from the UV-Vis spectra by creating a Tauc plot of $(h\nu\alpha)^2$ versus $(h\nu)$ and extrapolating the linear portions of the curves to the energy axis: $ah\nu = B(h\nu - E_g)^{1/2}$, where E_g is the direct band gap energy, $h\nu$ is the photon energy, α is the absorption coefficient, and B is a constant. The calculated bandgaps were found to be 4.25, 4.01, 3.90, 3.78 and 3.72 eV for 1, 3, 5, 7, and 9 at.%, respectively. Depending on the concentration and type of doping, adding samarium (Sm^{3+}) to zinc sulfide (ZnS) might change its bandgap. Samarium can introduce energy levels within the bandgap by increasing doping concentrations, effectively reducing the bandgap. This process is referred to as "bandgap narrowing." Samarium introduces impurity states in these conditions, decreasing the energy required for electron excitation and facilitating electron migration from the valence band to the conduction band. The concentration of samarium and the material's crystal structure will determine the exact impact on the bandgap.

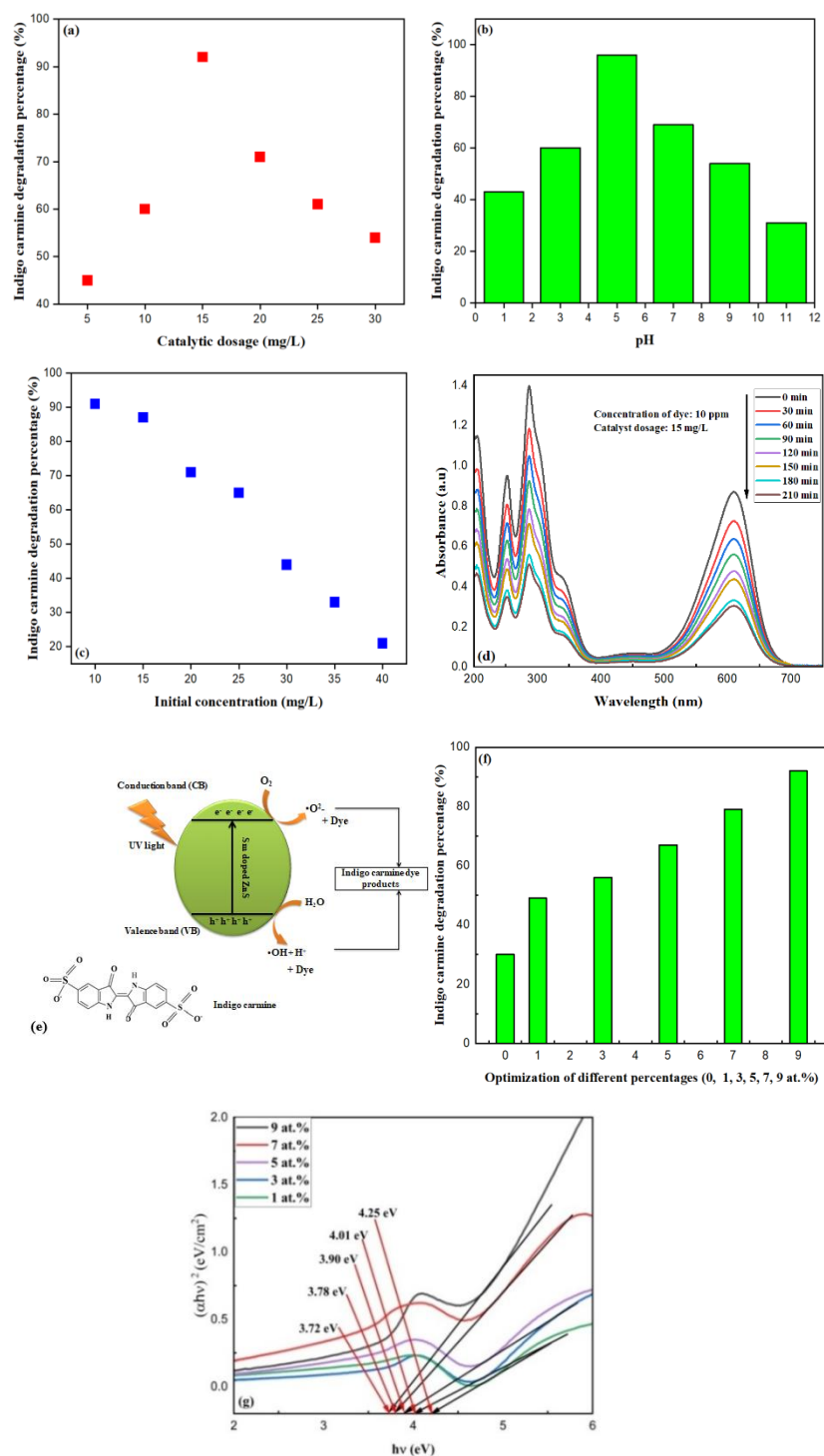


Figure 5.5: (a) Amount of catalytic dosage on the degradation of Indigo Carmine (b) Effect of different pH concentration on the degradation of Indigo Carmine (c) Initial concentration study on the degradation of Indigo Carmine (d) Degradation of Indigo Carmine within 210 minutes (e) Structure of Indigo Carmine and photocatalytic

degradation. (f) Optimization of different atomic percentage concentration on the degradation of Indigo Carmine (g) Tauc plot of Sm^{3+} -doped ZnS different percentage.

Table 5.3: Comparison of the photocatalytic performance of ZnS for the degradation of dyes with reference to this work.

Sample	Light	Catalyst	Time (min)	Dye	Degradation %	Reference
ZnS 1 ZnS 2	Mercury lamp (70W)	5 mg	180	Methylene Blue	55.97 % 65.92 %	(Ajibade <i>et al.</i> , 2022)
Chitosan-ZnS	UV lamp	30 mg	100	Acid black-234	96%	(Aziz <i>et al.</i> , 2020)
Chitosan-ZnS	UV lamp	30 mg	165	Acid brown-98	92%	(Ajibade & Oluwalana, 2021)
ZnS 1	Sodium lamp OSRAM VIALO X (80W)	5mg	180	Green Rhodamine B	70.60 %	(Ajibade & Oluwalana, 2021)
ZnS 2	Sodium lamp OSRAM VIALO X (80W)	5mg	180	Green Rhodamine B	88.80 %	(Ajibade & Oluwalana, 2021)
ZnS 3	Sodium lamp OSRAM VIALO X (80W)	5mg	180	Green Rhodamine B	98.51 %	(Ajibade & Oluwalana, 2021)
ZnS:Sm ³⁺	UV light	15mg	210	Indigo Carmine	93%	This work

5.3.6 Isotherm study

An adsorption isotherm describes the relationship between the amount of dye adsorbed by the adsorbent at equilibrium and the equilibrium dye concentration in the solution. For assessing the viability of the adsorption process as a single operation, adsorption equilibrium provides essential physiochemical information. This isotherm accounts for the effects of numerous dye/adsorbent interactions that are indirect, and it predicts that these interactions will cause a linear reduction in the heat of adsorption with increasing molecule-by-molecule coverage of the layer. Adsorption equilibrium gives critical physicochemical data for assessing the adsorption process's applicability as a single operation. The Freundlich and Langmuir isotherm models examined the relationship between solution concentration and dye adsorption. The isotherm's best fit was determined using a linear regression value (Sathishkumar *et al.*, 2018).

Freundlich Isotherm:

The adsorption on heterogeneous surfaces is explained by this isotherm, and the data frequently suit the provided equation 5.16 (Valizadeh *et al.*, 2016) (W. H. Xu *et al.*, 2013).

$$q_e = K_f C_e^{\frac{1}{n}} \quad (5.16)$$

The Freundlich isotherm has the following logarithmic form:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5.17)$$

The equilibrium amount of dye adsorbed per gram of adsorbent is indicated by q_e (mg/g), and the equilibrium adsorbate concentration is denoted by the symbol C_e (mg/L). The slope and intercept of the line shown in Figure 5.6(a) can be used to determine the sorption intensity (g/L), or $1/n$ and K_f (Freundlich constant) where R^2 was found to be 0.922.

Langmuir Isotherm:

The equation can be used to calculate this isotherm, which provides data on the production of monolayers on homogeneous surfaces:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (5.18)$$

The equation can be written as follows in linearized form:

$$\frac{1}{q_e} = \frac{1}{K_L C_e} + \frac{a_L}{K_L} \quad (5.19)$$

Langmuir isotherm constants are K_L and a_L ; the concentration at equilibrium (mg/L) is represented by C_e ; q_e , which is the adsorbed amount (mg/g), K_L/a_L is the numerical equivalent of the theoretical monolayer capacity (Q_0). C_e/q_e versus C_e was used to depict the Langmuir adsorption isotherm and a line with a 0.998 R^2 correlation coefficient was found, as given in Figure 5.6 (b). Table 5.4. shows the calculated parameters for the Langmuir and Freundlich isotherm models. The Langmuir isotherm model may be the best-fitting model for the sorption of Indigo Carmine dye, based on the estimated correlation value R^2 .

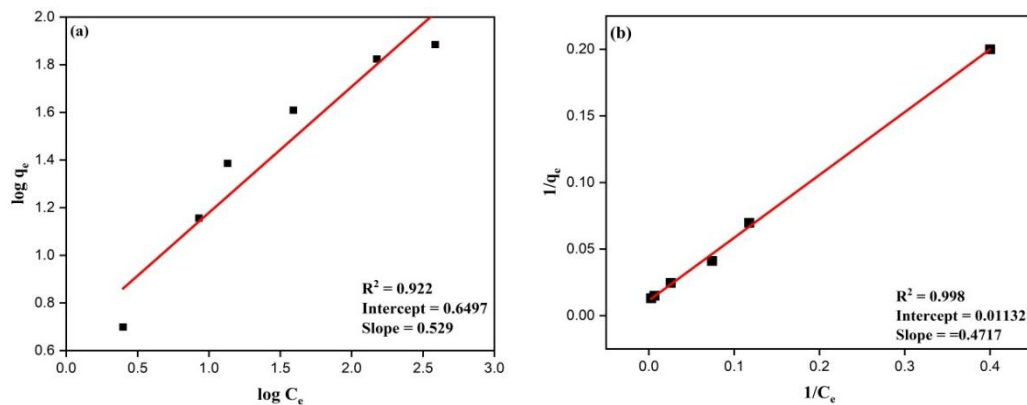


Figure 5.6: (a) Freundlich isotherm model and (b) Langmuir isotherm model of degradation of Indigo Carmine.

Table 5.4: Calculated parameters for Langmuir and Freundlich isotherm models for degradation of Indigo Carmine dye at 10ppm concentration.

Isotherm models	Parameters	Values
Langmuir isotherm	$q_{\max}$ (mg/g)	88.339
	K_L (L/g)	2.119
	R	106.99

	R^2	0.998
Fruendlich isotherm	$1/n$	0.529
	K_f $(\text{mg/g})^{1/n}$	4.463
	R^2	0.922

5.3.7 Kinetic Study

The primary step in many separation and purification procedures is adsorption. The molecules or ions from a solution adhere to the surface of a solid or liquid adsorbent. Mathematical representations known as kinetic models are used to explain the adsorption rate. It is predicated on the idea that the rate of adsorption is inversely proportional to the solute concentration. In other words, the rate of adsorption increases with increasing solute concentration. The pseudo-first-order model may not be applicable in all situations but is appropriate for systems where adsorption is largely a physical process. Another kinetic model used to describe adsorption is the pseudo-second-order model. It is predicated on the idea that the adsorption rate is inversely proportional to solute concentration squared. This model can better fit systems where adsorption involves chemical interactions between the solute and the adsorbent when dealing with heterogeneous sorbents and chemical sorption. Experimental data on the degradation of Indigo Carmine are gathered and analyzed using these models to shed light on the adsorption mechanism and validate the kinetic models. The system will influence model selection under study, the type of adsorption, and the adsorbent's characteristics. The pseudo-first-order equation 5.20 is expressed as (Chakrabarti & Dutta, 2004):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5.20)$$

q_e is the catalyst amount (mg/g) at equilibrium. q_t is the catalyst quantity (mg/g) at any given time (min^{-1}), q_e is the catalyst quantity (mg/g) at equilibrium, and k_1 is the first-order reaction rate constant.

The pseudo-second-order model is based on the hypothesis that chemisorption, which involves valence forces through the sharing or exchange of electrons between the adsorbent and the adsorbate, may be the rate-limiting step. The pseudo-second-

order equation is represented as follows: (Chiou *et al.*, 2004), (Salama *et al.*, 2018):

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{kq_e^2} \quad (5.21)$$

The catalyst amount (mg/g) at a specific time (min^{-1}) is given by q_t , q_e is the catalyst amount (mg/g) at equilibrium, and k_2 is the pseudo-second-order reaction rate constant. The rate constant for the first-order-kinetic (k_1) was calculated using a linear plot of time (t) vs. $\log (q_e - q_t)$, where q_e and q_t represent the quantity of dye adsorbed (mg/g) at equilibrium and time (t), respectively. The second-order kinetic (k_2) rate constant was calculated using the linear time vs. t/q_t plot shown in Figure 5.7. (a) and (b). Table 5.5 represents the rate constant and R^2 values, which follow pseudo-first-order kinetics. The pseudo-first-order kinetic model's R^2 value is considerably more significant than that of second-order kinetic model. As a result, the adsorption of Indigo Carmine dye using Sm^{3+} -doped ZnS nanoparticles is well correlated using the pseudo-first-order kinetic model.

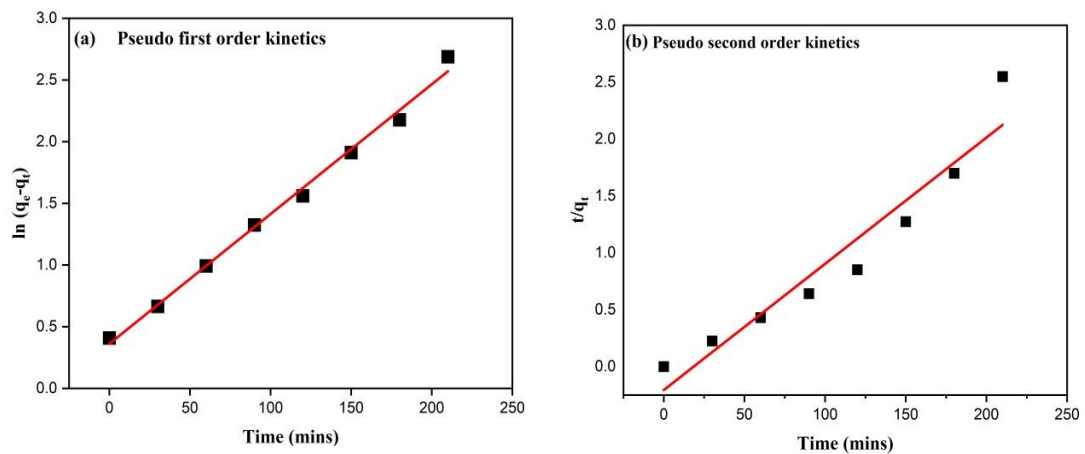


Figure 5.7: (a) Pseudo first kinetic order model (b) Pseudo second order kinetic model.

Table 5.5: Calculated values of R^2 and rate constant for pseudo first and second kinetics models for the degradation of Indigo Carmine dye at a concentration of 10ppm.

Models	R ² value	Rate constant
Pseudo first order	0.992	$k_1 = 0.0261 \text{ min}^{-1}$
Pseudo second order	0.913	$k_2 = 0.0122 \text{ g/mg} \times \text{min}$

5.3.8 Reusability

As a result of the repeated usage of nano-photocatalysts for the degradation of Indigo Carmine dye, the reusability of the catalysts has been studied, as shown in Figure 5.8. The results show that reusability is good for up to five consecutive cycles. The nanophotocatalyst was collected by filtration after the first photodegradation cycle. After being thoroughly cleaned with deionized water, it was dried in an oven overnight at room temperature. The experiment was conducted in both the presence and absence of UV and visible light. It clearly shows that in UV light, photocatalytic degradation decreases from 93% to 65%, and in visible light, it decreases from 89% to 64%. The photocorrosion effect is the cause of this decline in photocatalytic effectiveness. A material oxidatively degrades in the presence of light, which is known as the photocorrosion effect. Under UV light and sunlight, ZnS undergoes photocorrosion.

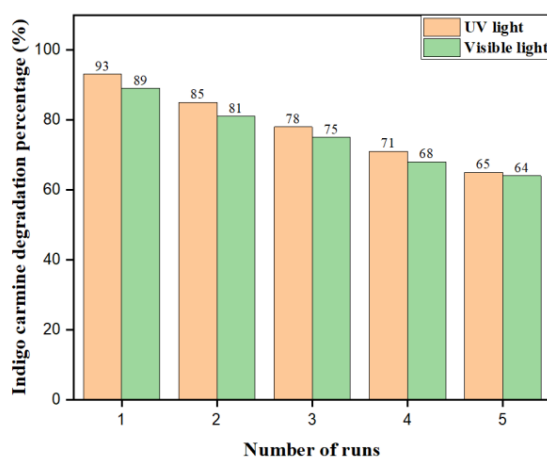


Figure 5.8: Reusability of a catalyst.

5.4 Conclusion

In this study, the focus was on the synthesis and characterization of Sm^{3+} -doped ZnS nanoparticles using the reflux method. The research team investigated several properties of nanoparticles, including kinetics, structural, chemical, optical, isotherms, luminescence, and photocatalytic properties. The results indicated that Sm^{3+} -doping had a positive impact on the luminescence and photocatalytic properties of the ZnS nanoparticles. The maximum photocatalytic activity has been observed in 9 at% Sm^{3+} -doped ZnS nanoparticles, which were used for further evaluation. The best optimum parameters for removing dye were found to be 15 mg/L of catalyst, 210 minutes of reaction time, pH 5, and an initial concentration of 10 ppm. All the synthesized samples exhibited a cubic zinc phase, as observed in the XRD pattern. The average particle size calculated from SEM image was found to be 5.15 nm. According to photoluminescence studies, when excited at 395 nm, the emission spectra are observed at wavelengths of 559 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$), 595 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$), and 642 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$), corresponding to the f-f transitions of the Sm^{3+} in the $4f^5$ configuration, respectively. The results of CIE diagram showed that nanoparticles can be highly useful for photonic applications. Five catalyst runs could be successfully retrieved without the catalyst experiencing a significant loss of activity. The reaction exhibited pseudo-first-order kinetics, and the Langmuir model provided the best fit to the isotherm data. As a result of improved charge separation and decreased recombination, Sm^{3+} -doped ZnS can increase the photocatalytic degradation efficiency of Indigo Carmine. Overall, the study suggests that Sm^{3+} -doped ZnS nanoparticles can be an effective and promising method for removing coloured effluents, with significant potential for reuse and luminescent applications.

CHAPTER 6

Effect of additives on the photocatalytic degradation of Malachite Green using NiS:Tb³⁺ Nanoparticle and their photoluminescence properties

6.1 Introduction

Water contamination in the biosphere has increased due to quick urbanization, changing consumption habits, population growth, and quickening socioeconomic development rates (Cheriyamundath & Vavilala, 2021). Heavy metals, dyes, toxic organic compounds, and phenols, etc., are all significant pollutants from residential and commercial activities that can alter natural water colour (Singh & Susan, 2018). This pollution load poses a significant challenge for wastewater management, as it increases treatment costs and introduces a range of chemical and microbiological contaminants into water sources (Yagub *et al.*, 2014). Water-dye pollution prevents sunlight from penetrating the surface and causes photosynthesis to proceed more slowly (Al-tohamy *et al.*, 2022). Also, colourants disrupt gas solubility, impacting the development of aquatic vegetation and animal life. The colours used in textiles can be highly toxic and carcinogenic. The wastewater's multicoloured discharge also has an adverse visual effect because human eyes can sense colour at quantities as low as 1 ppm (Rashed *et al.*, 2022). Water clarity and gas solubility are impacted by the coloured effluent's ability to absorb and reflect sunlight. The increasing water contamination due to various pollutants has made wastewater management a significant challenge. Treatment costs have increased significantly, and the presence of chemical and microbiological contaminants in water sources has raised concerns about public health and safety (Halmann, 1995). UV energy and photocatalysis are both crucial for heterogeneous photocatalysis to occur, and metal oxide/ metal sulfides (such as CoS, CdS, ZnO, ZnS, TiO₂, NiS, and others) are one of the advanced oxidation processes that offer a fascinating approach to the destruction of numerous organic molecules. Metal sulfides have garnered considerable attention as photocatalysts. Researchers have been drawn to metal sulfides due to their chemical stability, accessibility, non-toxicity, and outstanding photocatalytic activity (Huang *et al.*, 2023), (Ullah *et al.*, 2021).

Particle size, crystallinity, surface properties, and other factors influence photocatalytic activity. Adding a foreign element to the photocatalyst is one method for changing the morphology (particle size and structure) of photocatalyst particles. Doping is inadequate since photocatalytic efficiencies drop in many circumstances, even when visible light absorption bands are obtained. Lanthanide-doped nanoparticles exhibit remarkable luminous properties, including restricted emission bandwidth, substantial Stokes shift, and the ability to transform long-wavelength excitation into short-wavelength emission (B. Chen & Wang, 2020), (F. Wang & Liu, 2014). The catalyst surface of heterogeneous photocatalytic reactions primarily acts as a scavenger for photo-generated electrons, preventing them from recombining with photo-generated holes and raising the reaction's efficiency. Inorganic oxidants improve photocatalytic activity in photocatalytic reactions by absorbing conduction band electrons generated by catalyst irradiation and reducing the electron-hole separation time. Most often, organic pollutants and inorganic anions (such as nitrates, carbonates, phosphates, and sulphates) coexist in wastewater. Inorganic oxidants can affect heterogeneous photocatalytic processes, but their impacts go beyond changing the reaction fluid's ionic composition and the photocatalyst's catalytic activity. The usage of particular oxidants, the photocatalyst, and the reaction conditions all affect how inorganic oxidants affect photocatalysis (Reza *et al.*, 2017), (Ravichandran *et al.*, 2007). As a result, it is critical to understand how transition metal ions, inorganic anions, and inorganic oxidants influence the effectiveness of heterogeneous photocatalytic processes.

6.2 Experimental details

6.2.1 Sample preparation

The commercial reagents specified were bought from Alfa Aesar: Nickel(II) nitrate hexahydrate, 98%, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Terbium(III) nitrate hydrate, 99.9% (REO), $\text{Tb}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sodium sulfide, anhydrous, Na_2S , Malachite Green oxalate, $\text{C}_{52}\text{H}_{54}\text{N}_4\text{O}_{12}$ were used without further purification.

Nanoparticle preparation

The synthesis of nickel sulfide-doped Tb^{3+} nanoparticle was carried out using

the reflux technique. This method allows for precise control of reaction conditions such as temperature and time, which is crucial in the production of nanoparticles where even small changes can have a significant impact on their properties. By using reflux method, it is possible to maintain stable reaction conditions for an extended period, which is particularly important for lengthy reactions required to obtain nanoparticles. The process involved stirring nickel (II) nitrate hexahydrate and terbium (III) nitrate hydrate at room temperature for 1 hour, followed by the gradual addition of sodium sulfide with continuous stirring. The mixture was then heated at 150°C for two hours and centrifuged at 8500 rpm. The resulting product was washed with acetone and alcohol, dried, heated at 170°C for 2 hours, and then subjected to characterization. The molecularity of the synthesized nickel sulfide-doped Tb³⁺ nanoparticle was determined to be 86.45%.

6.2.2 Sample characterization

At room temperature, X-ray diffraction (XRD) tests were done using Siemens X-ray diffractometer with Cu K α radiation. The average crystalline size of the samples was calculated using equation 1 of the Debye-Scherrer formula. $D = 0.9\lambda/\beta\cos\theta$, where D is the average crystallite size, β is the total width at half the peak's maximum intensity, and θ is the diffraction angle. The wavelength of X-ray radiation is given by Cu K α , which is 1.541 Å. Transmission electron microscopy (TEM, Philips Model EM 208) was used to determine the size of nanoparticles. The surface morphology was investigated using a scanning electron microscope (KYKY-EM3200). Energy-dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) were used to analyze the chemical composition of nanoparticles. Photoluminescence (PL) emission spectra were obtained at 220-240 volts and 50-60 hertz using an F-7000 HITACHI fluorescence spectrophotometer. A Thermo Scientific Evolution 220 (UV-visible spectrophotometer) was used to obtain UV-visible spectrum.

Photocatalytic experiments

The efficiency of nickel sulfide-doped Tb³⁺ nanoparticle in degrading malachite

green in an aqueous solution at room temperature was evaluated. To achieve equilibrium between the photocatalyst, and the pollutant prior to radiation exposure, the solutions were magnetically stirred in the dark for 1 hour. Various amounts of catalyst, starting concentrations, and pH levels were tested for the degradation of malachite green. The samples were collected at regular intervals and the catalyst was removed by centrifugation. The removal was determined using a UV-vis spectrophotometer by measuring the absorption at 617 nm. The decolourization and photocatalytic degradation efficiency were calculated using equation 6.1:

$$\text{Efficiency \%} = (C_e - C)/C_0 \times 100 \quad (6.1)$$

Where C_0 and C_e represent the initial and final dye concentrations before and after photo-irradiation. E% in this equation is dye photocatalyst degradation percentage.

6.3 Results and discussion

6.3.1 X-ray diffraction

The average crystallite size and phase composition of nickel sulfide-doped Tb^{3+} nanoparticles were determined by XRD analysis, as shown in Figure 6.1. According to JCPDS Card No. 12-0041, nanoparticles have a rhombohedral crystalline structure with a space group of $R\bar{3}m$, as indicated by the reflections at 2θ values of 18.98, 30.48, 32.28, 35.71, 40.98, 48.17, 50.19, 52.33 and 56.64 having planes (110), (101), (300), (021), (220), (211), (131), (410), (401) and (321) respectively (Niasari *et al.*, 2010). Nanoparticles average crystallite size and phase content were calculated using the Scherrer equation, the average crystallite size was determined to be 12 nm and 16 nm, respectively, which were found to be in agreement with the theoretical lattice constants listed in Table 6.1. The crystallinity of nickel sulfide doped Tb^{3+} was found to be higher than that of nickel sulfide powder, which could be attributed to terbium doping. Terbium (Tb^{3+}) doping has the potential to influence the crystalline structure and properties of materials, resulting in improved crystal alignment and growth, as well as larger crystallite sizes.

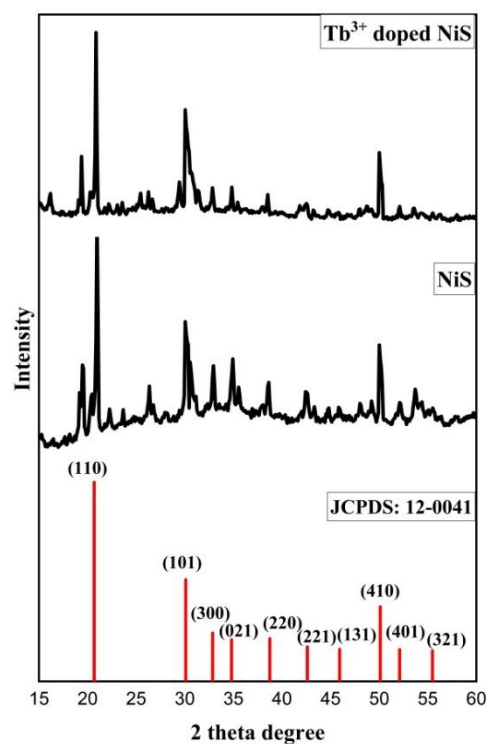


Figure 6.1: XRD pattern of NiS and nickel sulfide doped Tb³⁺ nanoparticle.

Table 6.1: Comparisons of standard values and observed values for cell parameters and volumes.

Parameter	Standard value	Observed value	Observed value	Reference JCPDS card number
		NiS	NiS:Tb ³⁺	
a (Å)	9.620	9.64Å	9.69Å	12-0041
c (Å)	3.149	3.13Å	3.16Å	
Unit cell volume (Å) ³	252.38 (Å) ³	252.54(Å) ³	252.78(Å) ³	

6.3.2 Scanning electron microscopy (SEM) and Transmission Electron Microscopy (TEM)

The morphologies and microstructures of the as-prepared materials were examined using SEM and TEM. Figure 6.2 (a) displays a typical SEM image of nickel sulfide-doped Tb^{3+} nanoparticle, which exhibits a spherical agglomerated structure composed of individual nanoparticles. Van der Waals forces, electrostatic interactions, and solvent evaporation during sample preparation are among the reasons that may cause agglomeration. Depending on the extent of agglomeration and the distribution of nanoparticle sizes, the agglomerates may exhibit variances in size (Hermann *et al.*, 2017). The average particle size of nanoparticles was calculated to be 19 nm using J image software, as shown in Figure 6.2 (b). Energy-dispersive X-ray spectroscopy (EDX) revealed the chemical composition of nanoparticles, which comprises terbium, nickel, and sulfide, as shown in Figure 6.2 (c). The TEM micrograph of the synthesized nanocrystalline samples provided immediate information about the particle size and morphology of the samples. Figure 6.2 (d) shows a typical TEM image of nickel sulfide-doped Tb^{3+} nanoparticle, revealing monodispersed spherical crystallites (Poornaprakash *et al.*, 2018). The calculated particle size was determined to be 13 nm, which was supported by the XRD data. Figure 6.2 (e) shows the SAED rings of nickel sulfide doped Tb^{3+} nanoparticle, which exhibit concentric rings. The considerable ring pattern of this compound enables the formation of highly crystalline nanoparticles and exhibits polycrystalline behaviour. The rings have been indexed to ZnS phases with rhomb centers in the (110), (101), (300), and (021) planes. The crystalline nanoparticles or polycrystalline portions of the sample show a high degree of crystallinity, as shown by the concentric rings seen in the SAED pattern. The electron waves diffracted by the material's crystal lattice planes constructively interfere to produce the rings.

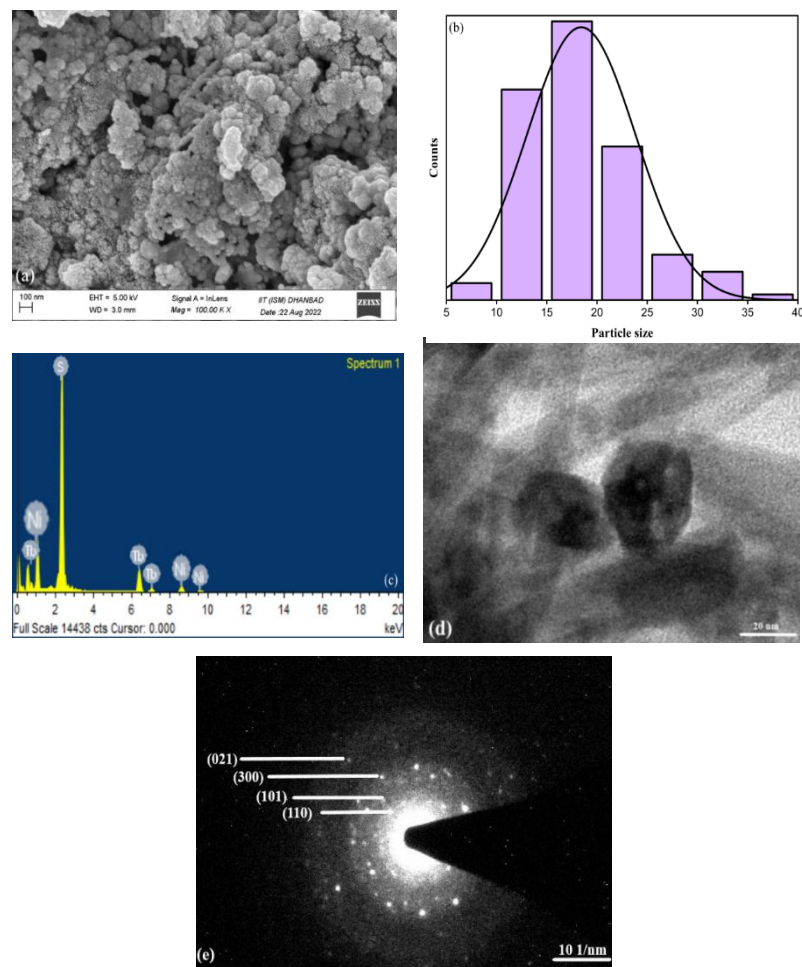


Figure 6.2: SEM image of (a) Nickel sulfide doped Tb^{3+} nanoparticle (b) Average particle size of Nickel sulfide doped Tb^{3+} nanoparticle (c) EDX spectra of Nickel sulfide doped Tb^{3+} nanoparticle (d) TEM image of Nickel sulfide doped Tb^{3+} nanoparticle (e) SAED rings of Nickel sulfide doped Tb^{3+} nanoparticle.

6.3.3 Photoluminescence spectroscopy (PL)

The photoluminescence emission spectrum is shown in Figure 6.3(a). With an excitation wavelength of 351 nm, the spectra were obtained. The presence of four emission peaks at 488, 543, 584, and 620 nm indicates the presence of trivalent Tb^{3+} ions, corresponding to the electron transitions $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$, and $^5\text{D}_4 \rightarrow ^7\text{F}_3$. Recombination of electron-hole pairs at defect sites can drastically change the local charge distribution, frequently modifying the equilibrium bond length and

affecting the strong vibration, resulting in a broad emission band in photoluminescence spectra (Naorem *et al.*, 2022a), (Premjit Singh *et al.*, 2019). In order to assess the impact on the optical absorption characteristics of nanoparticles, the band gap energy (E_g) values were derived from the Tauc plot. The results are shown in Figure 6.3(b), where the bandgap values were found to be 3.47 and 3.67 eV, respectively. According to the findings, nickel sulfide doped Tb^{3+} nanoparticle increased optical band gap energy, which caused the doped nanoparticles to have a wider electron-hole separation. This phenomenon may have consequences in several areas where managing electron-hole separation is crucial, including optoelectronics, photocatalysis, and sensing applications. This shift suggests that terbium dopants modify the electrical structure of nanoparticles, changing their optical absorption properties. The larger band gap implies that doping with terbium affects the energy levels accessible for electron transitions, leading to a greater distance between electron and hole states (Zanatta, 2019).

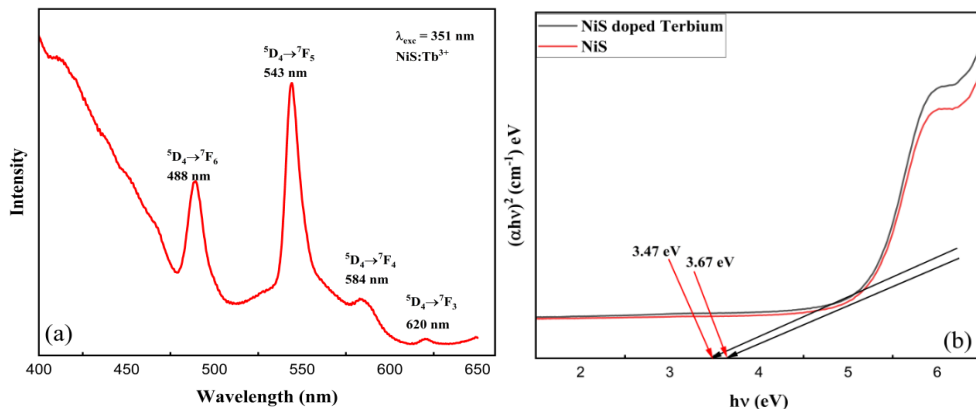


Figure 6.3: (a) Photoluminescence spectra of Nickel sulfide doped Tb^{3+} nanoparticle (b) Plot of $(\alpha h\nu)^2$ vs. $h\nu$ of NiS and Nickel sulfide doped Tb^{3+} nanoparticle.

6.3.4 Photocatalytic Activity of Nickel sulfide doped Tb^{3+} nanoparticle

Figure 6.4. (a) shows the deterioration percentage peaked at 30 ppm and thereafter declined progressively. The degradation efficiency controls the probability of an interaction between dye molecules and the catalyst for a given sample amount, which

increases with dye concentration. When dye concentration exceeds a particular limit, additional dye molecules cover the catalyst molecules, preventing light from reaching the sample and creating a screening effect. As a result, the photocatalytic activity increases initially and then decreases as dye concentration increases. The effect of pH in the range of 1-10 was tested to determine the capability of the prepared photocatalyst at various acidic and basic conditions, as shown in Figure 6.4 (b). The degradation percentage was highest at pH 3. Malachite green degradation at different pH levels is influenced by various factors, including dye's chemical characteristics and the environment in which it is present. Under acidic conditions, malachite green may hydrolyze. A chemical reaction in which water molecules break down bigger molecules is known as hydrolysis. In the case of malachite green, hydrolysis under acidic circumstances may result in dye degradation. Malachite green includes amine groups that can be protonated in acidic environments. The protonation of these groups may modify dye's chemical structure, making it more prone to degradation (Yong *et al.*, 2015). One of the most important elements influencing photocatalytic efficiency is catalyst dosage Figure 6.4 (c). The trials were carried out with different dosages ranging from 10 mg to 50 mg. The catalyst with 20 mg/L dosage showed the highest degradation percentage. The photocatalytic action was initially shown to increase with increasing catalyst amount, possibly due to higher photocatalyst quantities having more active sites available. Furthermore, increasing the amount of catalyst resulted in lower photocatalytic activity due to nanoparticle agglomeration, which may have generated turbidity, limiting light penetration due to scattering. Malachite green dye degradation was investigated using the catalyst's photocatalytic activity within 90 minutes, where the degradation percentage was found to be 94%, respectively, as shown in Figure 6.4 (d). Due to their ability to act as catalysts in various oxidation reactions, transition metals are often added to organic dye solutions during degradation processes. These metals, such as iron, manganese, and titanium, can facilitate the breakdown of organic molecules through processes like Fenton or photo-Fenton reactions (Y. Li *et al.*, 2021).

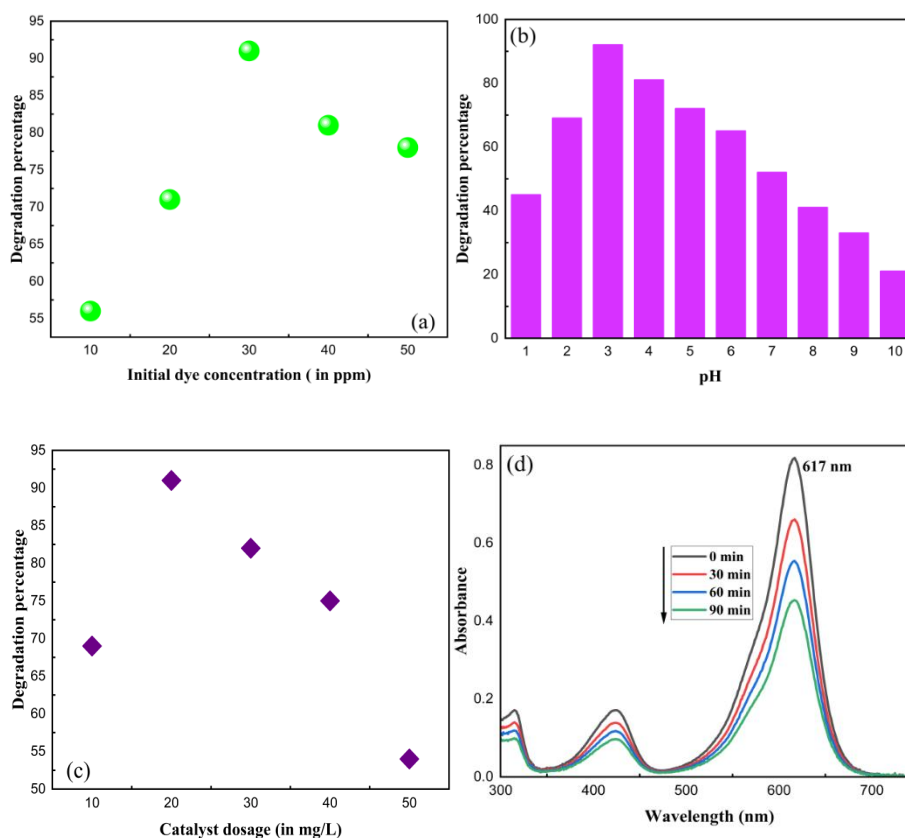
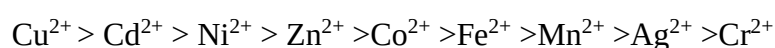


Figure 6.4: (a) Initial dye concentration (in ppm) (b) Effect of pH concentrations (c) Different catalytic dosage (d) Degradation of malachite green within 90 minutes.

6.3.5 Influence of Transition-Metal Ions on Malachite Green

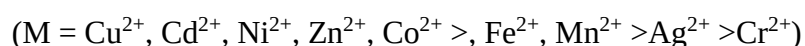
Photodegradation Dye

Figures 6.5 (a) and (b) show how different transition-metal ions affect the malachite green's photocatalytic decomposition rate. The introduction of transition-metal ions has a beneficial effect on the rate of photocatalytic dye degradation of malachite green. The following metal ions were found to have potential effects (Seyed-Dorraj et al., 2009):



The outcomes demonstrate that the rate of malachite green adsorption onto the catalyst increases due to the common anion (Cl^-) being inert in the presence of additional metal ions. There may be an increase in the surface area accessible for malachite green adsorption as a result of the interactions between the metal ions and

the catalyst (Chen *et al.*, 2002). As a result, more malachite green molecules can bind to the catalyst surface in a given amount of time, increasing the rate of adsorption. As a result, the considerable adsorption of malachite green molecules on the catalyst surface may be associated with an increased photocatalytic degradation rate in the environment (Bhandari *et al.*, 2006). Transition-metal ions act as electron scavengers, preventing electron-hole recombination and boosting the possibility of $\cdot\text{OH}$ production on the catalyst surface equation 6.2. The co-catalytic action of transition-metal ions can enhance the photocatalytic activity of photocatalyst (Brezová *et al.*, 1995).



In order to facilitate the photodegradation process, they assist in increasing the separation of electron-hole pairs when exposed to light. A few transition-metal ions can change SEMiconductor's electrical structure, increasing the range of light that can be absorbed. The charge-carrying and center-trapping abilities of transition-metal ions can minimize the recombination of electrons and holes produced by photosynthesis (Brezová *et al.*, 1995). As a result, more photogenerated charge carriers will actively contribute to the degradation of malachite green. Transition-metal ions may assist in the formation of highly oxidative reactive oxygen species such as hydroxyl radicals ($\cdot\text{OH}$) and superoxide radicals ($\cdot\text{O}_2^{-}$), which can efficiently oxidize and destroy organic compounds such as malachite green (Brezová *et al.*, 1995), (Chen *et al.*, 2002). The photocatalytic degradation of dye becomes faster as the concentration of dissolved transition-metal ions increases. However, as the concentration of metal ions in the reaction media increases, the photocatalytic degradation rate decreases. This fact explains the negative repercussions of high metal ion concentration; high metal ion concentration has a filtering effect due to UV light absorption, reducing the light intensity in the reaction medium and thereby lowering the photocatalytic degradation rate (Asiltürk *et al.*, 2009). As the concentration of dissolved transition-metal ions increases, the M^{+} ion created by electrons becomes the dominant ion in the reaction media, and the M^{+} ions are

oxidized to M^{2+} on the catalyst's surface by photo-induced h^+ equation 6.3.(D. P. Dutta *et al.*, 2017).



The reduction potential of the Cu^{2+}/Cu pair is provided as 0.1 eV, which is connected to the standard hydrogen electrode (NHE), which requires relatively minimal energy for the reduction to proceed. A high concentration of Cu^{2+} ions may have an unfavorable effect because Cu^{2+} ions with a low reduction potential are rapidly reduced to Cu^+ ions. Cu^{2+} ions have previously been reduced to Cu^+ , which could divert electrons from other reactions, influencing superoxide generation. Cu^{2+} ion reduction competes with O_2 production. Photo-induced electrons can participate in reduction processes when they are present. Dye deterioration is frequently faster in mixed systems than in single systems because dye oxidation uses photo-excited holes quickly and efficiently, reducing electron-hole recombination(Rajabi & Farsi, 2015), (Brezová *et al.*, 1995).

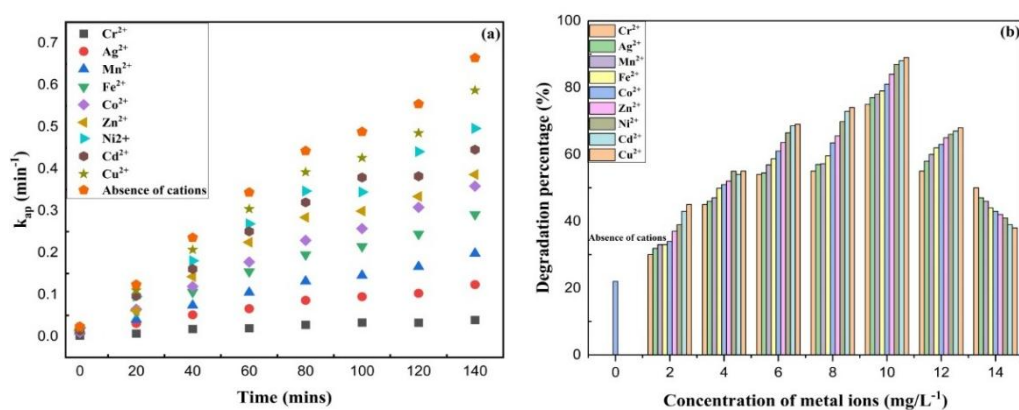


Figure 6.5: (a) Transition metal ion's impact on the rate of photocatalytic degradation (b) Degradation percentage of concentration of metal ion.

6.3.6 Influence of Inorganic oxidants on Malachite Green Photodegradation Dye

Adding all inorganic anions benefited the photocatalytic procedure and accelerated the rate at which the malachite green dye degraded through photocatalysis. By accepting conduction band electrons produced by catalyst irradiation, oxidants accelerate the photocatalytic degradation of dyes. Inorganic oxidants also play a crucial role in the photocatalytic process, as their interaction with UV radiation generates robust oxidant systems through the formation of additional oxidizing species (Ravichandran *et al.*, 2007). As an alternate approach for removing organic contaminants from aqueous solutions, UV/inorganic oxidants are often utilized. The oxidants that were found to have the biggest positive effects on the system's photocatalytic efficiency are as follows (Wang & Hong, 1999), (Sadik, 2007):

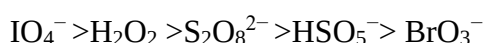
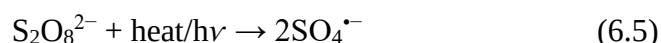


Figure 6.6 (a) and (b) show that increasing the concentration of oxidants promotes photocatalytic degradation of malachite green dye. This higher photocatalytic efficacy could be attributed to the generation of additional oxidizing species. However, using a higher concentration of oxidants may generate excess $\cdot\text{OH}$ radicals, which recombine to form less-reactive molecules. In addition, using a higher concentration of particular oxidants may cause some anions to bind to the catalyst surface, slowing the rate at which malachite green dye is broken down through photocatalysis (Selvam *et al.*, 2007), (Seyed-Dorraji *et al.*, 2009). In photocatalytic processes, inorganic oxidants such as hydrogen peroxide (H_2O_2) and persulfate ($\text{S}_2\text{O}_8^{2-}$) can be electron acceptors. As a result, more reactive oxygen species (ROS) are generated, including hydroxyl radicals ($\cdot\text{OH}$), which are very effective at dissolving malachite green molecules (Sadik, 2007). Inorganic oxidants can speed up the rate of degradation reactions by providing the necessary oxidation potential to initiate and propagate degradation pathways. As a result, Malachite Green may be eliminated from the aqueous solution more quickly. All of the added inorganic anions benefit the photocatalytic process, increasing the rate of photocatalytic dye degradation (Modirshahla & Behnajady, 2006). By accepting the conduction band electrons produced by catalyst irradiation, oxidants improve photocatalytic dye

degradation. Strong oxidant systems are formed when inorganic oxidants and UV light are mixed. In photocatalytic processes, this combination serves a twofold purpose. Periodate photolysis occurs in an aqueous solution, resulting in the degradation of periodate into different highly reactive radicals and non-radical intermediates given in equation 6.4 (Lau *et al.*, 2007):

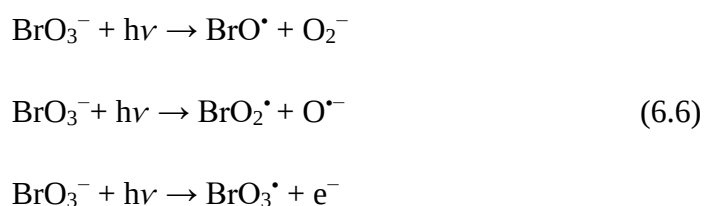


The photolysis of periodate (IO_4^-) under UV light results in the formation of different reactive species, both radical and non-radical. The iodate radical ($\text{IO}_3^\bullet$) species can react with other species in the system or undergo additional reactions that result in the generation of other intermediates, whereas the oxygen radical ($\text{O}^{\bullet-}$) is extremely reactive and can participate in a variety of reactions. The highly reactive species can then participate in radical reactions, adding to the system's total chemical changes. Non-radical intermediates may also undergo numerous reactions, altering the system's composition and behavior. Peroxydisulfate is a thermodynamically powerful oxidizing compound (redox potential 2.05 V) that has been utilized as a sacrificial reagent and alternate oxidant in the chemical oxidation of organic pollutants (Chen *et al.*, 2002), (Asiltürk *et al.*, 2009). When $\text{S}_2\text{O}_8^{2-}$ decomposes in an aqueous solution due to photolysis or thermolysis, free sulphate ($\text{SO}_4^{\bullet-}$) is produced equation 6.5 (Liang *et al.*, 2003). This radical, as a strong oxidizing agent (with a redox potential of 2.6 V), can accelerate the reaction by rapidly attacking any oxidizable component. The sulphate radical is a highly reactive species with a high oxidizing potential (as previously indicated, redox potential of 2.6 V). It can quickly attack and oxidize organic and inorganic molecules in its proximity. Sulphate radicals are potent oxidants that promote the breakdown of complex chemical compounds into more straightforward and less damaging products (Ali *et al.*, 2020).



Bromate is an inorganic disinfectant that mineralizes and has an oxidation potential of 1.4 V in acidic environments. Bromate photolyzes and decomposes in aqueous solution to yield a range of radical species ($\text{BrO}_3^\bullet$, $\text{O}^{\bullet-}$, O_2^- , etc.) equation 6.6.

Bromate's photo-oxidative activity is due to the production of these reactive species. These reactions collectively demonstrate bromate photo-oxidative activity, in which light energy absorption initiates the breakdown of bromate into reactive species. Bromate's oxidative potential and the generation of these reactive species add to its disinfection efficiency and emphasize its capacity to induce oxidative conditions in water treatment applications (Zuo & Katsumura, 1998), (Hu *et al.*, 2003).



When integrated with UV light (UV/H₂O), hydrogen peroxide serves as a potent oxidant with a high active oxygen content, making it a well-known advanced oxidation approach for the breakdown of organic compounds. The reaction depicted below demonstrates the breakdown of H₂O₂ in the presence of UV radiation. This reaction is a component of advanced oxidation processes (AOPs), notably the UV/H₂O₂ system, which is widely used in water treatment to destroy numerous organic contaminants (Yang *et al.*, 2013). The generated hydroxyl radicals can effectively oxidize and degrade organic compounds, transforming complex molecules into simpler and less hazardous ones. The overall reaction mechanism involves hydroxyl radicals attacking organic molecules, leading to a cascade of radical reactions and the subsequent destruction of organic contaminants. Because the combination of hydrogen peroxide and UV radiation enhances the generation of hydroxyl radicals, this system is an effective and ecologically acceptable method for wastewater treatment and the elimination of organic pollutants (Masoudian *et al.*, 2011). When paired with ultraviolet radiation (UV/H₂O₂) and hydrogen peroxide with potent antioxidant with high active oxygen content, is a well-known advanced oxidation process for breaking down organic molecules. The following reaction illustrates how H₂O₂ breaks down when exposed to UV rays equation 6.7 (Saien *et al.*, 2011), (Riga *et al.*, 2007).



Using oxidants at concentrations ranging from 1-5 mg L⁻¹, the experiments were conducted to determine the impact of these oxidants on the photocatalytic efficiency of Tb³⁺ doped nickel sulfide nanoparticles. The photocatalytic degradation is enhanced by an increase in the concentration of oxidants, as seen by Figure 6.6 (a) and (b). The formation of more oxidizing species may lead to an increase in photocatalytic efficiency. Higher concentrations of oxidants, however, may produce more excessive [•]OH radicals, which can then recombine to form less reactive molecules. Moreover, higher concentrations of some oxidants may cause some anions to adsorb onto the catalyst surface, which would reduce the rate of dye photocatalytic degradation (Li *et al.*, 2021), (Dorraj *et al.*, 2009).

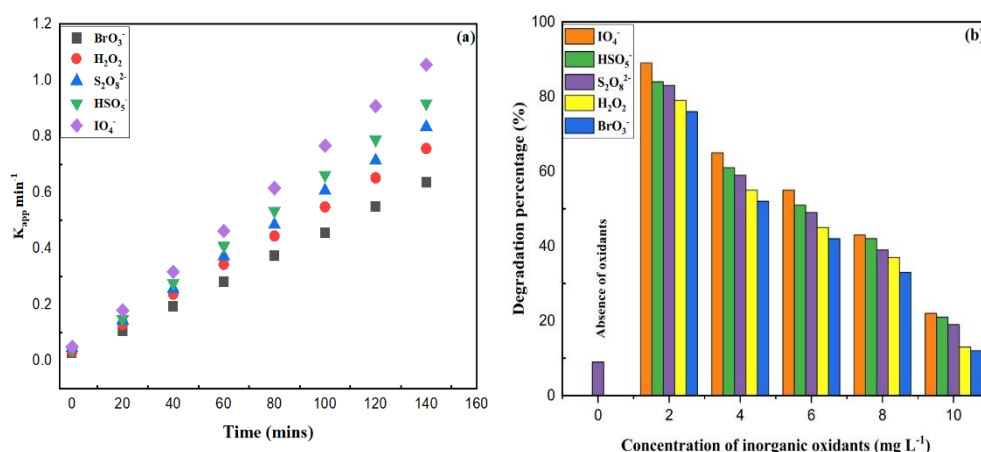
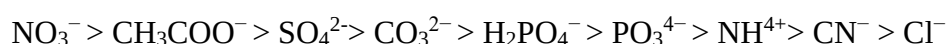


Figure 6.6: (a) Inorganic oxidants impact on the rate of photocatalytic degradation
(b) Degradation percentage of concentration of inorganic oxidants.

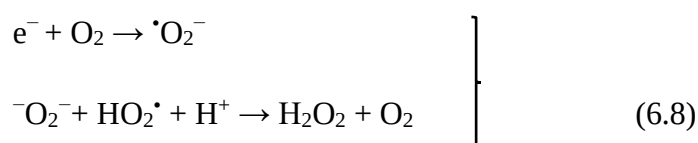
6.3.7 Influence of Inorganic anions on Malachite Green Photodegradation Dye

Figures 6.7 (a) and (b) show the effect of different inorganic anions on the photocatalytic degradation rate at different concentrations. The photocatalytic process of malachite green dye is inhibited by all excess inorganic anions, which also slows down the rate of decomposition. These inorganic anions were discovered to have the following detrimental effects (Seyed-Dorraj *et al.*, 2009):

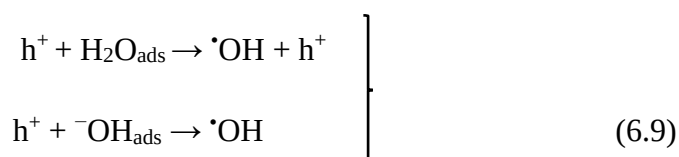


Only anions are involved in the inhibitory action because Na^+ is the primary cation of all the additional anions (Sökmen & Özkan, 2002). Additionally, as the concentration of inorganic anions increases, the photocatalytic degradation of malachite green accelerates. Inorganic anions have an adverse impact because they compete with the intended organic substance for space on the catalyst's surface, hindering the active sites and preventing the oxidative species' ability to break down organic compounds via photocatalysis. Negatively charged inorganic anions, on the other hand, produced less reactive species when they interacted with positive holes (h^+) and hydroxyl radicals ($\cdot\text{OH}$) (Georgiou *et al.*, 2002). These inorganic anions also performed h^+ and $\cdot\text{OH}$ scavenger functions, which lowered the absence of photocatalytic degradation. Malachite green degradation procedures frequently use substances or environmental factors that encourage the breakdown of dye molecule. By competing for reactants or by impeding the degradation reactions, inorganic anions can obstruct these degradation processes (Pillai & Gupta, 2016). A few anions may compete with malachite green for catalyst-reactive sites or absorb UV light required for photodegradation. Complexes between malachite green and inorganic anions can result in the synthesis of long-lasting, inert substances. This may make the molecule of malachite green less prone to deterioration. Inorganic anions can change malachite green degradation's reaction kinetics. Depending on the circumstances, they may operate as degradation reaction promoters or inhibitors. Unpredictable outcomes may emerge from anions that speed up or slow the reaction pace. Only anions are involved in the inhibitory action because Na^+ is the common cation of all the added anions (Yang *et al.*, 2010). Furthermore, when the concentration of inorganic anions increases, the photocatalytic degradation of dyes slows. Anions aid in the inhibition of dye photocatalytic degradation. They could compete for active areas on the catalyst surface, scavenge reactive species, or interfere with producing reactive oxygen species (ROS) during the degradation process. Inorganic anions have a negative effect on the photocatalytic degradation of organic substances by oxidative species due to the competitive adsorption of anions and the target organic substance onto the surface of the catalyst (Hu *et al.*, 2003). The anions, as well as the target organic compound, have the ability to adsorb on the catalyst surface. Chemical reactions occur at active spots on the catalyst surface, such as photocatalytic

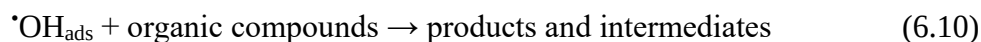
degradation of organic molecules. Stocking active sites on the catalyst surface lowers the efficacy of the photocatalytic degradation process. Active sites are essential for encouraging reactions involving the target organic material and generating oxidative species (such as reactive oxygen species) that cause degradation. If these sites are hindered by competing anion adsorption, the necessary processes may be hampered. $\cdot\text{OH}$ radicals are highly reactive molecules that play an essential part in the photocatalytic destruction of organic compounds. Inorganic anions with negative charges also react with hydroxyl radicals, resulting in less reactive species (B. Gao *et al.*, 2010), (Xiong *et al.*, 2013). Superoxide radical anion can be produced by reducing dissolved oxygen with electrons in the conduction band. Hydrogen peroxide could be produced by this radical equation 6.8.



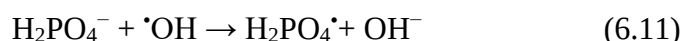
Hydroxyl radicals can be produced by oxidizing adsorbed water or hydroxide ions through the holes in the valence band equation 6.9.



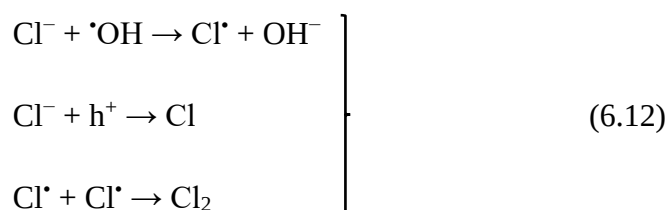
Hydroxyl radicals are highly reactive oxidizing species. They can participate in various processes, including the oxidation of organic and inorganic substances. The reactions show how these radicals are formed by mechanisms involving electrons, superoxide anions, and holes in the valence band. Hydroxyl radicals are highly reactive oxygenating species; they are potent oxidants due to their strong tendency to accept electrons. This property enables them to participate in redox reactions with organic molecules, ultimately breaking them down. Throughout the degradation process, hydroxyl radicals react with organic molecules to produce intermediate products. These intermediates could be more or less complex than the original organic compounds. The following reactions or transformations of these intermediates contribute to the overall degradation pathway equation 6.10 (El-Kemary *et al.*, 2010), (Sökmen & Özkan, 2002).



Positive holes are created when electrons in a semiconductor material's valence band are driven to the conduction band by light (photons). Positive holes (h^+) on the valence band are particularly reactive and are crucial in initiating oxidation processes during photocatalysis. Anions scavenge or react with positive holes and hydroxyl radicals. Scavenging shows that anions are capturing or neutralizing reactive species in this circumstance. Scavenger anions can hinder photocatalysis by reducing the availability of positive holes and hydroxyl radicals, which are necessary for the chemical processes. Hydroxyl radicals react faster than $\text{H}_2\text{PO}_4^\cdot$ radicals' equation 6.11. Overall, chemical pathways and the effectiveness of organic compound breakdown may be impacted by this decrease in reactivity (Hu *et al.*, 2003).



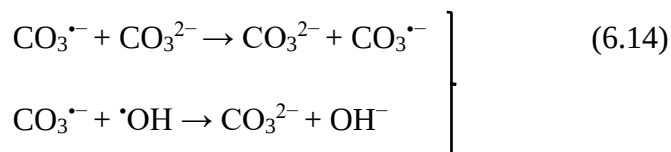
Chloride ions operate as a scavenger of h^+ and $\cdot\text{OH}$, and the recombination of two $\text{Cl}^\cdot$ will stop radical production equation. 6.12 (Gao *et al.*, 2010)



Bicarbonate also functions as an $\cdot\text{OH}$ scavenger, forming $\text{CO}_3^{\cdot-}$. A hydroxide ion (OH^-) and a carbonate radical ($\text{CO}_3^{\cdot-}$) are produced when the hydroxyl radical ($\cdot\text{OH}$) steals a hydrogen atom from one of the oxygen atoms in the carbonate ion (CO_3^{2-}) equation 6.13 (Selvam *et al.*, 2007)



The carbonate radical ($\text{CO}_3^{\cdot-}$) undergoes comparable hydrogen abstraction reactions to combine with another carbonate ion (CO_3^{2-}) or with a hydroxyl radical ($\cdot\text{OH}$), renewing the hydroxyl radical and making a new carbonate radical equation 6.14:



The radicals can interact with other species in the system or with one another in a variety of termination reactions to produce stable products. The role of NO_3^- could generate additional $\cdot\text{OH}$ as shown below (Kim & Zoh, 2013), (Oh *et al.*, 2011). The role of NO_3^- in the given reactions is to participate in a series of photochemical reactions that lead to the generation of hydroxyl radicals, which are highly reactive species involved in various chemical processes, including oxidation and degradation of organic compounds equation 6.15. However, NO_3^- , particularly at high concentrations, may function as an inner filter, preventing excess NO_3^- from absorbing UV radiation and reducing the rate of photocatalytic destruction. It is clear that NO_3^- 's harmful effect outweighed its beneficial effect (Zhang *et al.*, 2005).

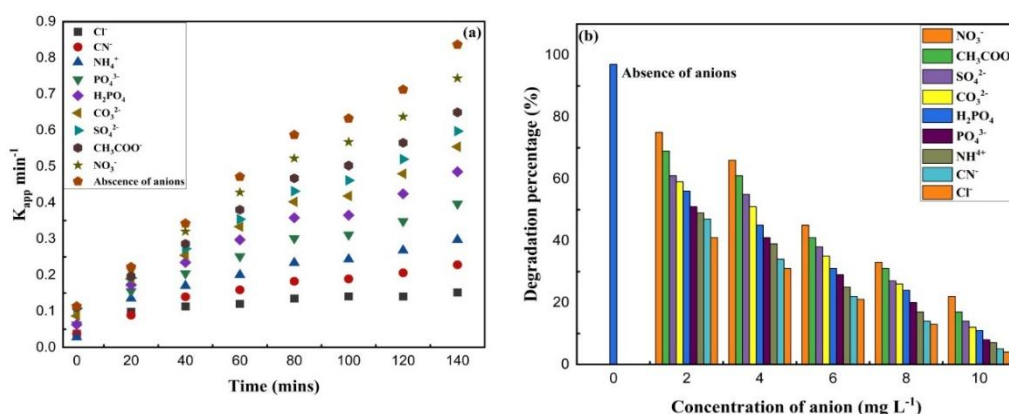
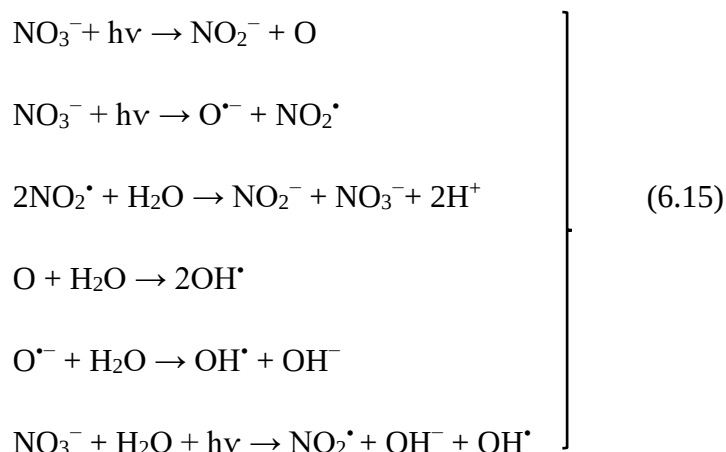


Figure 6.7: (a) Inorganic anions impact on the rate of photocatalytic degradation (b) Degradation of concentration of inorganic anions.

6.4 Conclusion

This study successfully investigated the photocatalytic degradation of malachite green using Nickel sulfide-doped Tb^{3+} nanoparticle and various additives, including inorganic oxidants, transition metal ions, and inorganic anions. The originality of this study lies in highlighting the research work on doping with lanthanide ions for the degradation of dyes, which affects the synthesis and applications of organic dyes. With a space group of R3m and a rhombohedral crystalline structure, nanoparticles average crystallite sizes were found to be 12 and 16 nm. The characteristics and crystalline structure of materials can be affected by terbium (Tb^{3+}) doping. Using J imaging software, it was determined that nanoparticles' average particle size was 19 nm. With an excitation wavelength of 351 nm, the europium spectra were obtained. The presence of four emission peaks at 488, 543, 584, and 620 nm indicates the presence of trivalent Tb^{3+} ions, $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$, and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ electron transitions. Nickel sulfide doped Tb^{3+} nanoparticle increased optical band gap energy, which caused the doped nanoparticles to have a wider electron-hole separation. The greater band gap indicates that terbium doping modifies the energy levels available for electron transitions, resulting in a greater separation between the electron and hole states. The photocatalytic activity of the Nickel sulfide-doped Tb^{3+} nanoparticle was used for investigating the breakdown of malachite green dye within 90 minutes, and the degradation percentage was found to be 94%. Malachite green dye is favorably affected by transition-metal ions and inorganic oxidants, but negatively impacted by inorganic anions. Overall, these findings clearly demonstrate Nickel sulfide-doped Tb^{3+} nanoparticle can be effectively utilized as photocatalysts for the degradation of malachite green in the presence of various additives.

CHAPTER 7

Photocatalytic Degradation of Rhodamine B Dye using PEG@ZnS:Au and PVP@ZnS:Au Nanoparticles

7.1 Introduction

The persistence of organic dyes in water bodies constitutes a critical environmental and public health issue, owing to their recalcitrant characteristics and toxicological properties. Consequently, the need for efficacious water treatment solutions has become a pressing priority in the 21st century, underscoring the imperative for innovative and sustainable remediation technologies to mitigate these hazards. The textile industry is a significant sector globally, employing approximately 35 million people and generating annual revenues of around \$1 trillion, accounting for 7% of global exports. However, this industry is also a substantial contributor to environmental pollution, relying heavily on fuels and chemicals in its production processes. Heavy metal pollution from wastewater constitutes a major environmental and health hazard. The release of toxic elements like lead, mercury, cadmium, and arsenic can degrade aquatic ecosystems and contaminate the food chain. Human exposure to these pollutants is associated with severe health outcomes, including organ damage, neurological disorders, developmental impairments, and carcinogenesis. The removal of food dye from wastewater is vital due to health and environmental concerns (Khan *et al.*, 2019). A critical aspect of the textile industry's environmental footprint is its water usage, particularly in the washing, bleaching, and dyeing stages of its production cycle (Phyllis *et al.*, 2022). The multifaceted utility of synthetic dyes has led to their pervasive adoption in diverse industries, notably textile, leather, pharmaceutical, and paper production, driven by their ability to impart vibrant colours and functional properties. The textile industry generates significant amounts of solid waste, comprising discarded fabric, broken yarn, and packaging materials, presenting both opportunities for recycling and waste reduction, as well as serious environmental challenges. Pesticide pollution of water resources constitutes a major environmental and public health concern. The infiltration of pesticides into aquatic systems through non-point sources, such as agricultural

runoff, can have far-reaching consequences, including human health impairments and ecological degradation (Malik & Grohmann, 2012a). Furthermore, the complex composition of textile sludge, a byproduct of wastewater treatment in the textile industry, poses a substantial environmental risk, with high concentrations of micronutrients, heavy metal cations, organic compounds, and pathogenic microorganisms (Bala *et al.*, 2017). The textile industry is a significant contributor to global pollution, with approximately 80% of its environmental emissions stemming from untreated wastewater discharged into water bodies (Sridewi *et al.*, 2011). Textile dyes have a profound impact on aquatic environments, altering biological processes and aesthetic water quality. The diminished light penetration resulting from the presence of dye impairs photosynthesis, leading to decreased oxygen production and detrimental effects on aquatic life (Al-Tohamy *et al.*, 2022).

Sustainable ecosystem management necessitates comprehensive textile effluent treatment methods that integrate physical, chemical, and biological technologies (Patra & Baek, 2014). While physical-chemical methods are effective, they have drawbacks, including sludge disposal difficulties and high operational costs (Niculescu *et al.*, 2022). Recent advances have highlighted the potential of metal oxide nanostructures, notably titanium dioxide (TiO₂) and zinc oxide (ZnO), as promising photocatalysts for wastewater treatment applications, garnering significant attention in the field of environmental remediation (Saeed *et al.*, 2022). These nanostructures exhibit outstanding performance due to their tunable optical band structure, morphological control, surface textural properties, and tunable surface area and surface chemistry (Anandan *et al.*, 2020). Metal sulfides, particularly cadmium sulfide (CdS), have also shown promise as photocatalysts due to their favorable band gap characteristics (Lianmawii & Singh, 2024). CdS exhibits excellent photocatalytic efficiency under solar radiation, with a direct band gap of approximately 2.4 eV. Zinc sulfide (ZnS) has notable optoelectronic properties, with direct band gaps of 3.54 eV (zinc blende) and 3.91 eV (wurtzite), making it an effective absorber of visible and UV light (Prabhu & Abdul Khadar, 2005), (Vijayalakshmi, 2017), (Jrad *et al.*, 2021). Over the past twenty years, semiconductor nanoparticles have emerged as a fascinating realm of research, attributable to their distinctive characteristics and

prospective utility in various domains, prompting considerable scientific interest and investigation (Lianmawii *et al.*, 2024). Zinc sulfide (ZnS), a wide bandgap semiconductor, has been widely used in industry as a phosphor and thin-film electroluminescent material (Isac & Enesca, 2022). This is especially the case when it is doped with different transition metals or rare earth elements that operate as luminescent centers. Doping ZnS with transition metals or rare earth elements can introduce luminescent centers, enabling nanoparticles to exhibit full-colour luminescence in the UV-visible spectrum (Melendres-Sánchez *et al.*, 2021). Zinc sulfide (ZnS), a prominent member of the II-VI semiconductor group, has garnered substantial interest in recent years due to its exceptional optical and electrical characteristics. Notably, ZnS exhibits outstanding physical properties and remarkable photocatalytic activity at the nanoscale, attributed to its wide bandgap energy (ranging from 3.2 to 4.4 eV), small Bohr radius, and high exciton binding energy. Furthermore, its high activity under ultraviolet (UV) irradiation renders it an attractive material for various applications. The unique properties of ZnS, particularly its wide bandgap energy of 3.6 eV at ambient temperature, have sparked significant research interest. ZnS has emerged as a promising candidate for diverse optoelectronic applications, including ultraviolet light-emitting diodes, electroluminescence, photocatalysis, and other photonic devices.

Additionally, its high refractive index and exceptional optical transmission make ZnS an ideal material for dye-sensitized devices, infrared (IR) windows, and innovative photonic devices operating across the visible to near-infrared spectrum. ZnS, a non-toxic semiconductor, possesses a substantial band gap energy of 3.6 eV, offers attractive prospects for optoelectronic device fabrication and related technological advancements, can be synthesized through various techniques, including solid-state methods, solvothermal techniques, one-pot chemical processes, sol-gel procedures, and chemical precipitation techniques (Kumar *et al.*, 2015), (Naorem *et al.*, 2022b), (Rajabi *et al.*, 2018). ZnS has found widespread application in photocatalytic applications and electronic and optoelectronic devices, including solar cells, LEDs, and luminous devices (Smet *et al.*, 2010). However, its performance is limited due to its sole response in the UV range, necessitating the need for efficient synthesis

techniques to alter its band structure and enhance its performance (Othman *et al.*, 2019). Surface functionalization of ZnS nanoparticles through organic capping agents significantly modifies their band structure and improves their photocatalytic performance (Niu *et al.*, 2006). Capping agents prevent nanoparticle accumulation, preserve their high surface area and tiny size, and provide potential interactions with pollutant molecules, enhancing photocatalytic activity (Ajibade *et al.*, 2022), (Othman *et al.*, 2019). ZnS nanoparticles, nanorods, and nanocrystals have demonstrated high efficiency in breaking down hazardous dyes upon UV radiation, with reactive species such as superoxide ions and hydroxyl radicals forming on the surface and degrading adsorbed dye molecules into smaller, less harmful fragments (Mummadi & Shaik, 2024).

This study presents a groundbreaking approach to photocatalytic nanotechnology, introducing several innovative advancements. Notably, the co-precipitation synthesis of PEG@ZnS:Au and PVP@ZnS:Au nanoparticles present a novel method, yielding exceptional photocatalytic efficiency with degradation efficiencies of 94.25% and 91.45% for Rhodamine B dye under UV irradiation. The tailored surface modification using PEG and PVP enhances nanoparticle stability and adsorption capacity, while adhering to the Langmuir model and pseudo-first-order kinetics. By addressing the critical environmental concern of textile industry effluent remediation, this research bridges materials science, nanotechnology, and environmental engineering. Overall, this work contributes significantly to the advancement of photocatalytic technology, offering a unique combination of innovative synthesis methods, enhanced photocatalytic performance, and environmental relevance, paving the way for efficient wastewater treatment strategies leveraging nanoscale materials.

7.2 Experimental details

7.2.1 Sample preparation

All reagents were obtained from Alfa Aesar and used as received, without additional purification or modification. The chemicals included Zinc acetate dihydrate, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2(\text{H}_2\text{O})$, 219.50 g/mol, sodium sulfide, Na_2S , 56.06 g/mol, gold(III) chloride (AuCl_3), Polyvinylpyrrolidone (PVP), $\text{C}_6\text{H}_9\text{NO}$, 111.14 g/mol, and

polyethylene glycol 6000 (PEG), C_2H_4O . Laboratory-prepared deionized (DI) water was used for both photocatalytic experiments and synthesis of photocatalysts. Zinc acetate dihydrate and Gold(III) chloride were mixed and stirred at room temperature for 1 hour. Na_2S was added dropwise to the solution with continuous stirring. The mixture was stirred for 48 h, and then PVP and PEG were added sequentially. The resulting precipitate was washed with alcohol and ethanol at 7500 rpm and dried at $130^{\circ}C$ for 1 hour, and used for characterization.

7.2.2 Sample characterization

The synthesized materials were comprehensively characterized using a range of analytical techniques. X-ray diffraction (XRD) analysis was performed on a JEOL JDX-3532 diffractometer, yielding patterns over a 2θ range of 20° - 70° , from which crystallite sizes were determined using the Debye-Scherrer equation. Morphological examination was conducted via field emission scanning electron microscopy (FESEM) on a Zeiss Ultra Plus instrument, equipped with an energy dispersive X-ray (EDX) detector, operating at 5 kV. Transmission electron microscopy (TEM) imaging, selected area electron diffraction (SAED) pattern acquisition, and high-resolution TEM (HRTEM) imaging were performed on a JEOL JEM-2100 transmission electron microscope. Fourier transform infrared (FT-IR) spectroscopy was carried out on a Thermo Scientific Evolution 220 spectrophotometer, spanning the wavenumber range of 500 - 4000 cm^{-1} , employing KBr pellet techniques. The surface area and pore size distribution were determined using the Brunauer-Emmett-Teller (BET) method on a Microtrac BEL Corp BELSORP-maxII surface area analyzer. Photoluminescence excitation, emission, and decay time measurements were performed using a Hitachi F-7000 fluorescence spectrophotometer, with a xenon discharge lamp as the excitation source. UV-vis absorption spectroscopy was performed on a Thermo Scientific Evolution 220 spectrophotometer.

7.3 Results and discussions

7.3.1 X-ray diffraction (XRD)

The phase composition and crystal structure of the synthesized PEG@ZnS:Au and PVP@ZnS:Au nanoparticles were investigated using X-ray diffraction (XRD) over a

2 θ range of 20°-70°. The XRD patterns Figure 7.1. (a) reveals the cubic phase of ZnS (space group F43m), with diffraction peaks indexed to specific crystallographic planes, namely (111), (220), and (311), based on the JCPDS card No. 05-0566. The prominent diffraction intensity of the (111) plane confirms the cubic crystal structure of ZnS (Daskalakis *et al.*, 2020), (Sánchez *et al.*, 2021). The XRD patterns also exhibit peak broadening, indicative of small-sized nanocrystals, and a polycrystalline nature with a cubic zinc blende lattice structure. The presence of gold (Au) nanoparticles is evident from distinct peaks at 2 θ values of 38.71°, 44.54°, and 64.31° for PEG@ZnS: Au and 38.66°, 44.31°, and 64.24° for PVP@ZnS: Au, respectively. These peaks are indexed to the (111), (200), and (220) lattice planes of the cubic phase of gold nanoparticles (space group Fm-3m, lattice parameter $a = 4.070 \text{ \AA}$), exhibiting excellent agreement with the reference pattern (JCPDS No. 65-2870). The high crystallinity of the synthesized nanoparticles is evident from the sharp and intense XRD peaks, indicating no heat treatment is required during post-synthesis. The addition of PEG and PVP modifies the XRD peaks and intensities, suggesting a change in the crystalline structure of the nanoparticles (Fkiri *et al.*, 2018). The interplanar spacing (d_{hkl}) between successive crystallographic planes was calculated using the Bragg equation 7.1. The calculated interplanar spacing confirms the cubic lattice structure of the synthesized nanoparticles, supporting their polycrystalline nature (Singh *et al.*, 2016).

$$2d_{hkl}\sin\theta = n\lambda, \quad (7.1)$$

where n is the order of diffraction, λ is the wavelength of the X-ray radiation, d_{hkl} is the interplanar spacing, and θ is the angle of incidence. The XRD patterns confirm the successful synthesis of ZnS nanoparticles with a cubic crystal structure, which is essential for their optical and electronic properties. The lattice constant ' a ' of the synthesized crystallites was calculated from the XRD patterns using equation 7.2.

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} \quad (7.2)$$

The values obtained for the as-prepared particles show good agreement with the standard value for the ZnS cubic (zinc blende) lattice structure phase ($a = 5.398 \text{ \AA}$).

The diffraction peak, lattice parameters, and corresponding *hkl* planes are listed in Table 7.1. The XRD line broadening was used to determine the crystallite size (*D*) and internal strain of the ZnS nanoparticles using the Williamson-Hall equation Figure 7.1 (b). The Williamson-Hall equation 7.3 was used to determine the crystallite size (*D*) and internal strain (ϵ) from the XRD data. The fitted equation revealed a relationship between the line broadening and both the crystallite size, as well as the internal strain in the sample (Mummadi & Shaik, 2024). The crystallite size (*D*) was determined to be 22.77 nm and 17.56 nm for PEG @ ZnS: Au and PVP @ ZnS: Au.

$$\beta \cos \theta = \frac{K\lambda}{D} + 2\epsilon \sin \theta \quad (7.3)$$

where *D* is the internal strain (in %), λ is the wavelength ($\lambda = 1.54\text{\AA}$), *D* is the coherent scattering length (crystallite size), and θ is the Bragg angle and *K* is a constant equal to 0.9. The line-broadening analysis was conducted using the dominant reflection peaks of the XRD pattern. The Scherrer formula equation 7.4 was also used to determine the crystallite size (*D*), which was found to be 19.44 nm and 14.65 nm for PEG@ZnS: Au and PVP@ZnS: Au, respectively (Lianmawii & Singh, 2023).

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (7.4)$$

The crystallite sizes calculated using the Williamson-Hall equation and Scherrer formula are in good agreement, indicating that the nanoparticles have a size range of 15-23 nm. This result demonstrates the effective synthesis of ZnS nanoparticles with a cubic crystal structure, and containing gold nanoparticles, which is essential for their optical and electronic properties.

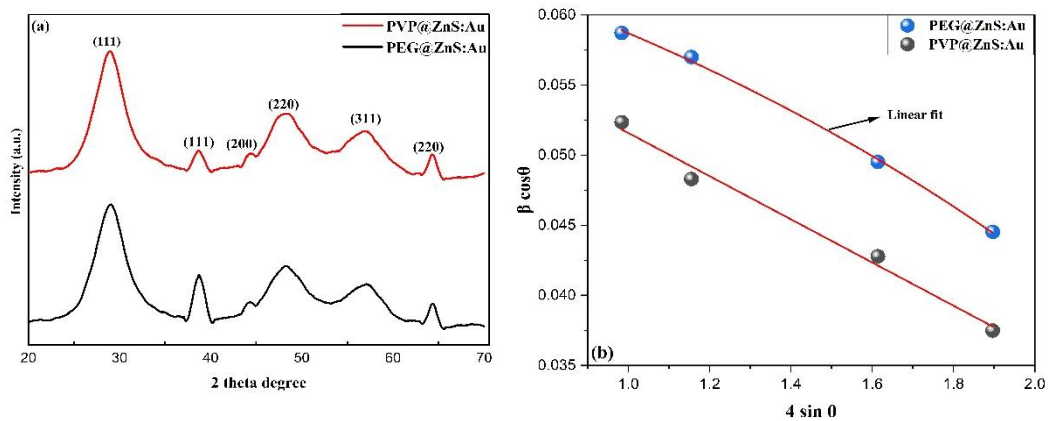


Figure 7.1: (a) X-ray diffraction pattern of PEG@ZnS:Au and PVP@ZnS:Au nanoparticles. (b) Williamson-Hall plot of PEG@ZnS:Au and PVP@ZnS:Au nanoparticles.

Table 7.1: Lattice parameters and cell volumes for PEG@ZnS:Au and PVP@ZnS:Au nanoparticles.

Sample	2 theta degrees	Plane (hkl)	$d_{hkl}(\text{\AA})$	Lattice parameters a($\text{\AA}$)	Cell volume ($\text{\AA}^3$)
PEG@ZnS:Au	28.17	(111)	2.06	5.34 $\text{\AA}$	157.45
	56.21	(311)			
	47.21	(220)			
PVP@ZnS:Au	28.56	(111)	3.01	5.31 $\text{\AA}$	157.21
	47.79	(220)			
	56.39	(311)			

7.3.2 Scanning Electron Microscopy (SEM) study

The nanoparticles morphology was characterized using SEM, revealing their shape, size, and surface features. As shown in Figure 7.2 (a) and (b), the SEM images reveal a diverse range of particle shapes, including radial cubic, spherical, and rod-like forms, with hexagonal particles observed on certain surface areas. The nanoscale ZnS grains exhibit a significant surface area and distinct mesopores. Moreover, a uniform distribution of particles is evident, comprising both single particles and clusters. EDX analysis, Figure 7.2 (c) and (d) confirmed the presence of Zn, S, Au, and P elements, indicating the formation of a ZnS matrix composed of zinc (Zn), sulfide (S), gold (Au). These results demonstrate the successful synthesis of ZnS nanoparticles with a diverse range of morphologies and a uniform distribution. The atomic and weight percentages of the synthesized nanoparticles are presented in Table 7.2. The average particle size was determined using J Image software, yielding values of 42 ± 5 nm and 36 ± 4 nm for PEG@ZnS:Au and PVP@ZnS:Au, respectively inset of Figure 7.2 (c) and (d).

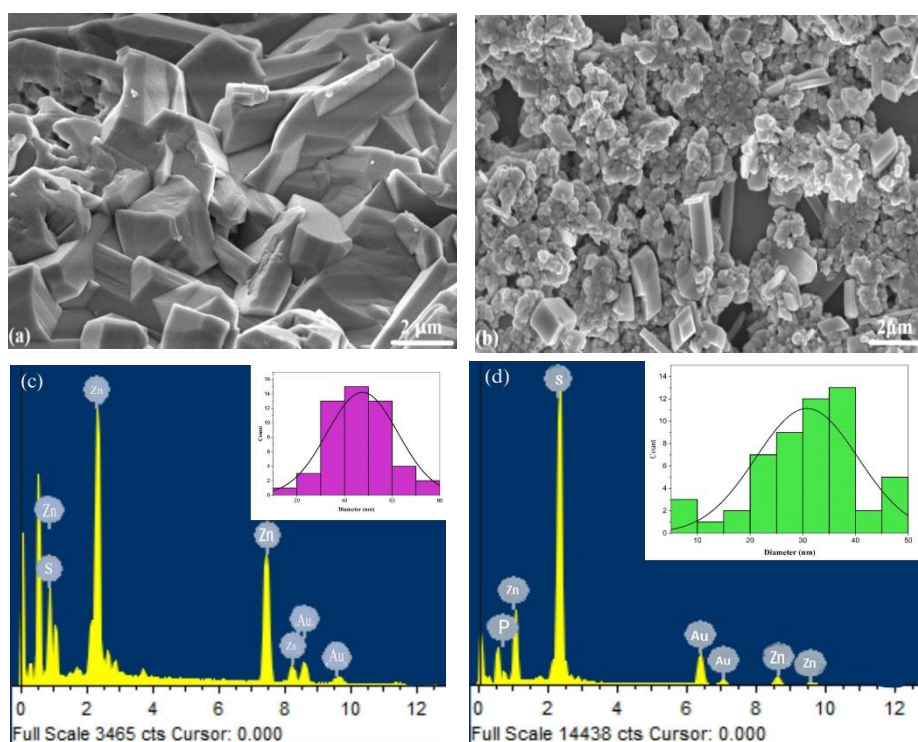


Figure 7.2: (a) and (b) SEM image of PEG@ZnS:Au and PVP@ZnS:Au. (c) and (d) EDX analysis of PEG@ZnS:Au (inset average particle size) and PVP@ZnS:Au (inset average particle size).

Table 7.2: Atomic and weight percentage of the synthesized nanoparticles of PEG@ZnS:Au and PVP@ZnS:Au.

Element	PEG@ZnS:Au		PVP@ZnS:Au	
	Weight %	Atomic %	Weight %	Atomic %
Zn	56.71	47.99	44.98	57.35
S	25.98	39.89	37.36	28.39
Au	17.31	12.12	17.66	14.26

7.3.3 Transmission Electron Microscopy (TEM) study

The size distribution histograms and TEM images of PEG@ZnS:Au and PVP@ZnS:Au are displayed in Figure 3. A morphological analysis of the TEM images, Figures 7.3. (a) and (b) reveal a mixed morphology comprising rod-shaped nanostructures and a minority of spherical particles, with some agglomeration and narrow size distributions. The concentration of PVP and PEG significantly impacts the size distribution and dispersion of the resultant nanoparticles (Soltani *et al.*, 2012). High-Resolution TEM (HR-TEM) images, Figure 7.3. (c) and (d) exhibit well-defined lattice fringes, confirming the resilient crystallinity of the samples. The interplanar distances were calculated to be 1.29 Å, 1.69 Å, and 1.84 Å for PEG@ZnS:Au, corresponding to the (111), (220), and (311) lattice planes, and 2.34 Å, 2.02 Å, and 2.45 Å for PVP@ZnS:Au, corresponding to the (111), (220), and (311) lattice planes, respectively. Selected Area Electron Diffraction (SAED) patterns Figure 7.3 (c) and (d) inset display a ring pattern, indicating the polycrystalline nature of the samples, consistent with the XRD results and indexed to JCPDS 05-0566. Gaussian fit analysis (Li, 2006), (Murray *et al.*, 2017).

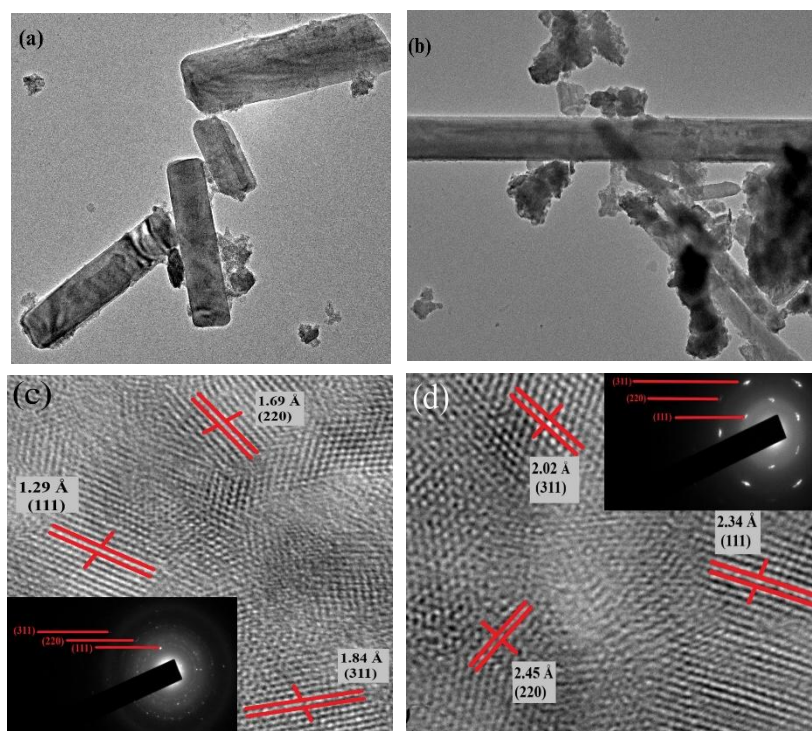


Figure 7.3: (a) and (b) TEM image of PEG@ZnS:Au and PVP@ZnS:Au. (c) and (d) HR-TEM of PEG@ZnS:Au (inset SAED pattern) and PVP@ZnS:Au (inset SAED pattern).

7.3.4 Fourier-transform infrared spectroscopy (FTIR)

Figure 7.4 presents the FTIR spectra of PEG@ZnS:Au and PVP@ZnS:Au, revealing characteristic absorbance peaks within 500-4000 cm^{-1} range. The broad peaks at 3384 cm^{-1} (PEG@ZnS:Au) and 3794 cm^{-1} (PVP@ZnS:Au) correspond to O-H stretching, while the peaks at 1416 cm^{-1} (PEG@ZnS:Au) and 1431 cm^{-1} (PVP@ZnS:Au) are attributed to C=O stretching from carboxylic acid. The Zn-S water molecular stretching is observed at 745 cm^{-1} (PEG@ZnS:Au) and 779 cm^{-1} (PVP@ZnS:Au) (Sathishkumar *et al.*, 2018), (Kashinath *et al.*, 2017), (Malarkodi & Annadurai, 2013). Additional peaks are assigned to alkyl halides (589 cm^{-1} , 550 cm^{-1} , 859 cm^{-1} , and 877 cm^{-1}), C-H stretching of aliphatic CH_3 and CH_2 (2345 cm^{-1} and 2436 cm^{-1}), and C-N stretching vibrations of aromatic and aliphatic amines (1103 cm^{-1} and 1123 cm^{-1}) (Malarkodi *et al.*, 2014), (Xin *et al.*, 2013), (Dhanasekar *et al.*, 2015). The PVP spectrum exhibits characteristic peaks at 1623 cm^{-1} (C=O) and 1223

cm^{-1} (C-N), while the PEG diacrylate shows an absorption band at 1689 cm^{-1} (C=O) and 1223 cm^{-1} (C-N). The shift in C=O stretching in PVP-@ gold nanoparticles indicates intermolecular hydrogen bonding (Dhumale *et al.*, 2012), (Deepa *et al.*, 2012).

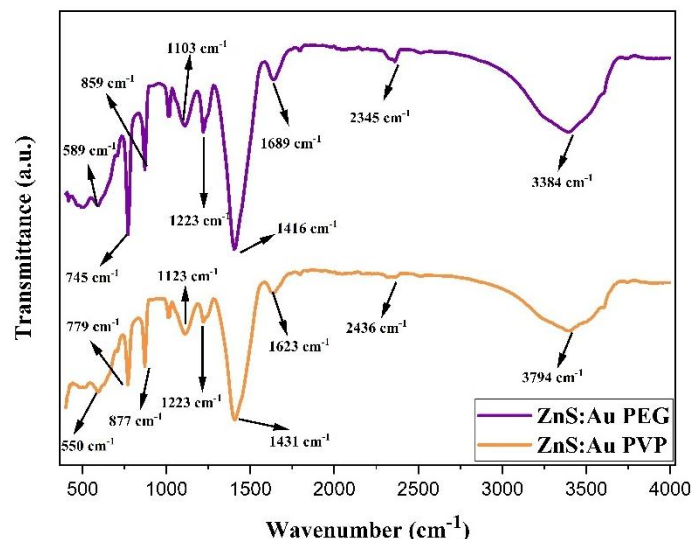


Figure 7.4: FTIR spectra of PEG@ZnS:Au and PVP@ZnS:Au.

7.3.5 Brunauer–Emmett–Teller (BET) surface analysis

The nitrogen adsorption-desorption isotherms and pore size distribution of ZnS nanoparticles are shown in Figure 7.5 (a) and (b) for PEG@ZnS:Au and PVP@ZnS:Au, respectively. The nitrogen adsorption-desorption isotherms exhibited H3-type hysteresis loops, indicative of their mesoporous nature with pore sizes ranging from 2-50 nm (Kannan *et al.*, 2020). The hysteresis loop suggests the interconnectivity of pores of different sizes, and the adsorbent generates significant micropore and mesopore volumes. The specific surface areas, determined using the Brunauer-Emmett-Teller (BET) method, were found to be $54 \pm 2\text{ m}^2/\text{g}$ for PEG@ZnS:Au and $36 \pm 2\text{ m}^2/\text{g}$ for PVP@ZnS:Au. Moreover, the observed hysteresis loop indicates the interconnectivity of pores of different sizes, and the adsorbent generates significant micropore and mesopore volumes. The enhanced surface area of PEG@ZnS:Au nanocomposites, as revealed by BET analysis, facilitates improved dye degradation performance by facilitating electron and ion

transportation at the interface (Y. Zhang *et al.*, 2016). The large surface area of PEG@ZnS:Au nanocomposites, as revealed by BET analysis, can enhance dye degradation performance by facilitating electron and ion transportation at the interface. This highlights the potential of these materials for improved photocatalytic applications (Wani *et al.*, 2024). The pore size distribution analysis revealed distinct differences between PEG@ZnS:Au and PVP@ZnS:Au nanocomposites. Notably, PEG@ZnS:Au exhibited a larger proportion of mesopores, which contributed to its significantly higher surface area of 54 m²/g. PVP@ZnS:Au had a smaller proportion of mesopores, resulting in a lower surface area of 36 m²/g. This variation in pore size distribution and surface area has important implications for photocatalytic applications, where enhanced surface area and pore connectivity can facilitate improved electron and ion transportation, ultimately leading to enhanced dye degradation performance.

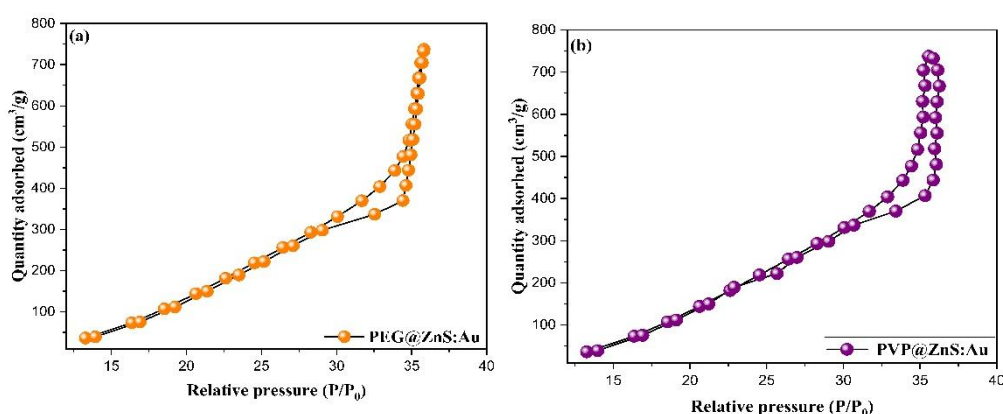


Figure 7.5: (a and b) Brunauer–Emmett–Teller (BET) surface analysis of PEG@ZnS:Au and PVP@ZnS:Au.

7.3.6 Photoluminescence studies

The incorporation of PEG and PVP capping agents on ZnS nanoparticles, forming PEG@ZnS:Au and PVP@ZnS:Au, significantly enhances photoluminescence (PL) emission intensity compared to pure ZnS given in Figure 7.6 (a). This improvement is attributed to the passivation layer provided by PEG and PVP, which effectively reduces surface defects and non-radiative recombination centers, thereby boosting

radiative recombination and PL intensity. The samples were prepared in aqueous solution and placed in a quartz cuvette (10 mm path length) for spectroscopic measurement. An excitation wavelength of 321 nm was used. The electronic transitions observed in the spectra are attributed to surface vacancies and defect states, which are prevalent in ZnS nanoparticles due to their high surface-to-volume ratio. The concentration of surface states on ZnS nanoparticles enhances non-radiative recombination, leading to a decrease in radiative recombination (Kole & Kumbhakar, 2012). The defect states can be classified into shallow and deep levels. Shallow levels, located near the valence band or conduction band edge, facilitate radiative recombination, whereas deep levels promote non-radiative recombination, releasing photons as a byproduct. Thermal activation of carriers at higher temperatures can reduce radiative recombination (Shahi *et al.*, 2011). The CIE chromaticity diagram Figure 7.6 (b) displays the colour coordinates (x , y) of the as-prepared PEG@ZnS:Au and PVP@ZnS:Au nanoparticles, which are (0.350, 0.456) and (0.321, 0.413), respectively. These coordinates were determined using an excitation wavelength of 321 nm, indicating that all samples fall within the white colour region. The bi-exponential equation 7.5 can be used to fit all decay curves as follows (N. P. Singh *et al.*, 2018):

$$\tau_{ave} = \frac{I_1\tau_1^2 + I_2\tau_2^2}{I_1\tau_1 + I_2\tau_2} \quad (7.5)$$

The average lifetimes of the as-prepared PEG@ZnS:Au and PVP@ZnS:Au samples were calculated to be 0.984 ± 0.001 ms and 0.971 ± 0.001 ms, respectively Figure 7.6. (c). These values indicate the radiative relaxation dynamics of the nanoparticles and are consistent with the observed photoluminescence properties.

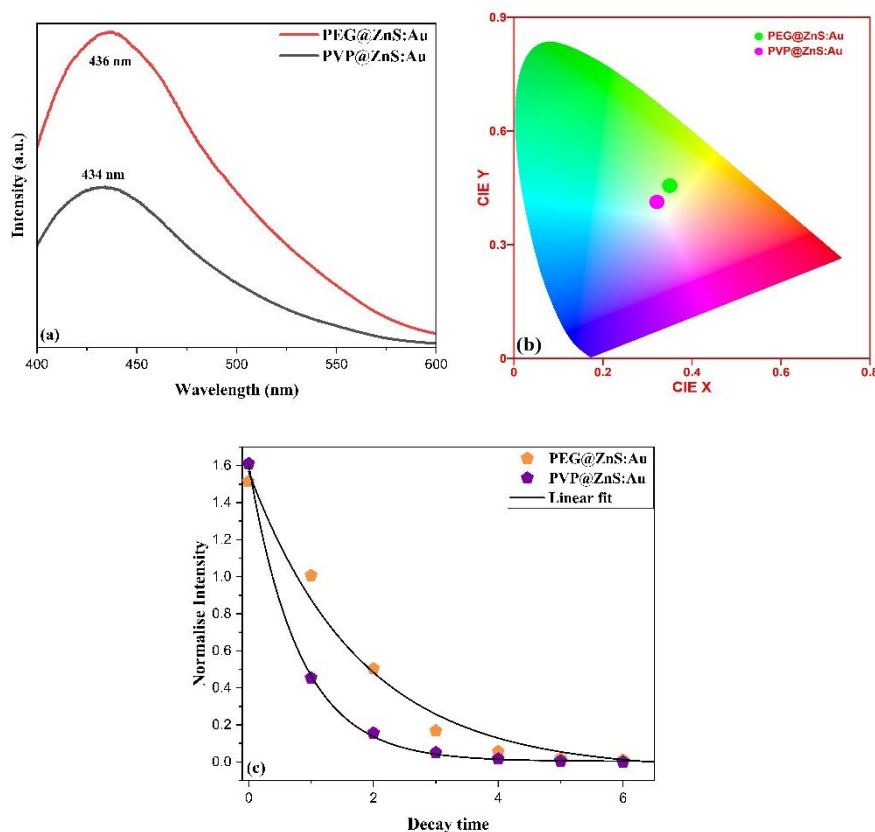


Figure 7.6: (a) Photoluminescence spectra of PEG@ZnS:Au and PVP@ZnS:Au. (b) CIE diagram of PEG@ZnS:Au and PVP@ZnS:Au (c) Decay lifetime of PEG@ZnS:Au and PVP@ZnS:Au.

7.3.7 Optical study

The UV-visible absorption spectra of PEG@ZnS:Au and PVP@ZnS:Au nanoparticles were measured in the range of 250-600 nm Figure 7.7 (a). The spectra show broad absorption in the UV region and reduced absorption in the visible range, attributed to the wide forbidden bandgap transition and ZnS surface defects (Palanisamy *et al.*, 2020). Notably, PEG@ZnS:Au exhibits a prominent absorption peak at 226 nm, blue-shifted compared to bulk ZnS (340 nm), due to quantum confinement phenomena. The absorption peak shifts to lower energy with increasing PEG concentration, likely due to the formation of zinc hydroxide, reducing Zn^{2+} ion concentration and ZnS particle yield (Abed *et al.*, 2022), (Y. Chen *et al.*, 2012). The observed blue shift is attributed to the synergistic effects of quantum confinement and exciton transitions. As the nanoparticle size decreases below the exciton Bohr

radius, the electronic properties diverge from those of bulk materials, leading to a shift in the optical transition from the valence band to the conduction band or to the exciton state. This phenomenon results in a notable blue shift, characteristic of nanocrystalline materials (Murugadoss, 2013). The surface plasmon resonance (SPR) band of gold nanoparticles appears at 425 nm, indicating their successful synthesis (Qayyum *et al.*, 2019), (Balamurugan & Maruyama, 2005). Figure 7.7(b) presents the UV-Vis diffuse reflectance spectra of PEG@ZnS:Au and PVP@ZnS:Au nanocomposites, which were utilized to determine their optical band gaps. The band gap energies were calculated using the Kubelka-Munk transformation, a widely accepted method for estimating the band gap of materials from diffuse reflectance spectra. Notably, the calculated band gaps of PEG@ZnS:Au and PVP@ZnS:Au were found to be 3.15 eV and 3.45 eV, respectively. These values indicate that both nanocomposites exhibit wide band gaps, characteristic of semiconductor materials with potential applications in optoelectronic devices. The difference in band gap energies between the two nanocomposites suggests that the capping agents, namely polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP), influence the electronic structure of the ZnS:Au nanocrystals. The slightly lower band gap of PEG@ZnS:Au may be attributed to the stronger interaction between PEG and the ZnS surface, leading to a greater degree of electronic coupling and a consequent reduction in the band gap energy. PVP capping agent results in a slightly wider band gap, potentially due to its weaker interaction with the ZnS surface.

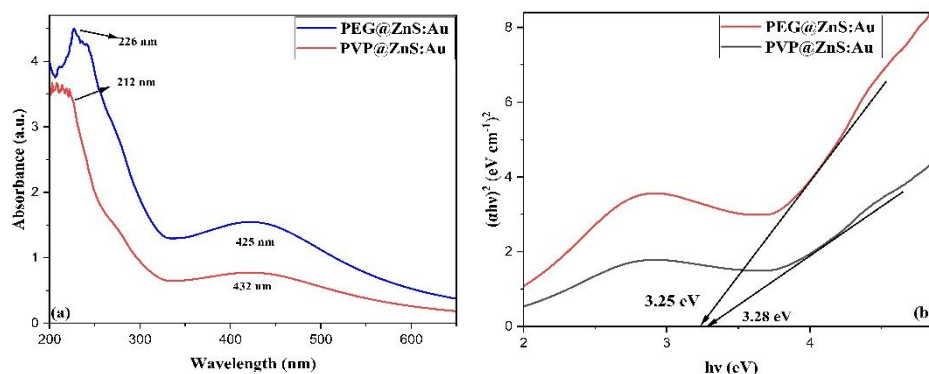


Figure 7.7: (a) UV-absorbance of PEG@ZnS:Au and PVP@ZnS:Au. (b) UV-vis. diffuse reflectance spectra and band gap of PEG@ZnS:Au and PVP@ZnS:Au.

Effect of temperature on the degradation of dye

The catalytic activity of PEG@ZnS:Au and PVP@ZnS:Au was investigated for the degradation of Rhodamine B at temperatures ranging from 293 to 318 K for 2 h. A dye solution concentration of 10 ppm and a catalyst of 15 mg/L were employed. The degradation efficiency increased significantly with temperature, reaching 92.34% and 93.66% at 318 K for PEG@ZnS:Au and PVP@ZnS:Au, respectively Figure 7.7 (c). The temperature-dependent degradation profile reveals a consistent enhancement in degradation efficiency with increasing temperature, highlighting the potential of these catalysts for efficient dye degradation (Jabeen *et al.*, 2021).

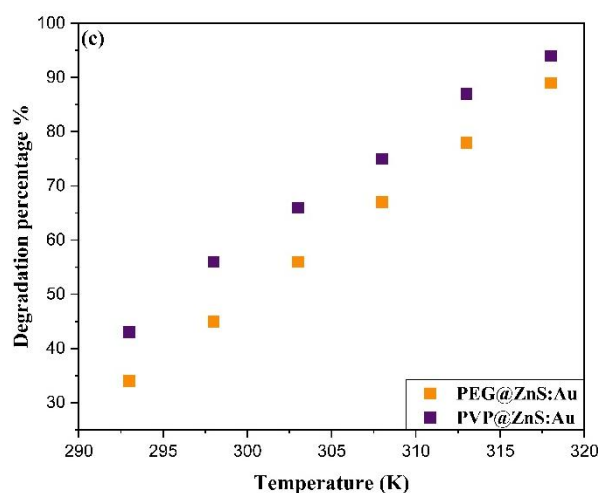


Figure 7.7: (c) Effect of temperature on degradation of Rhodamine B.

Effect of light on degradation of Rhodamine B

The rate of photodegradation increases with light intensity, as more photons enter the system, accelerating reaction rates and efficiencies (Ahmad *et al.*, 2006). This correlation is also observed in photocatalytic photofading. Higher light intensities cause more photons to enter the system, accelerating reaction rates and increasing photodegradation (Neppolian *et al.*, 2002), (Liu *et al.*, 2006). At low intensities, the photodegradation rate varies with intensity, while at intermediate intensities, it depends on the square root of the intensity (Ollis *et al.*, 1991). Figure 7.7 (d)

compares the degradation of Rhodamine B in the presence of PEG@ZnS:Au and PVP@ZnS:Au catalysts under artificial UV lamps and sunlight. The artificial UV lamp degraded 94.72% of the dye in 50 minutes, while sunlight degraded 48.19%. The stronger UV light from artificial lamps accelerates degradation, resulting in a decrease in colour intensity as the compound breaks down.

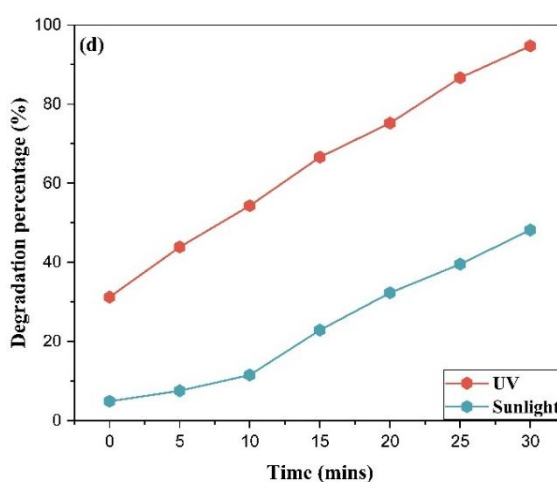


Figure 7.7: (d) Effect of light on the degradation of Rhodamine B within 30 minutes.

Effect of pH on degradation of Rhodamine B

pH levels and reducing agents can significantly impact photodegradation in solutions. Acidic or alkaline conditions can alter redox active groups, making them less susceptible to photodegradation. Different colours react differently to pH changes, depending on their pKa values and chemical compositions. Charged molecules are more likely to undergo photodegradation reactions (Mzimela *et al.*, 2022), (Groeneveld *et al.*, 2023). The influence of pH on the degradation rate of Rhodamine B was investigated under basic conditions using PEG@ZnS:Au and PVP@ZnS:Au catalysts. The pH range of 1-13 was achieved by adding 0.1 M NaOH and 0.1 M H₂SO₄ to the solution. The results showed that the ultrasonic degradation rates were significantly higher in strongly acidic water (pH 1-3) compared to pH 4-13 solutions. The degradation rates remained relatively constant between pH 4-9, with a slight decrease from pH 1 to 3 Figure 7.7 (e). At pH 10, the degradation rate was relatively slow, while strong basic water (pH 11-13) exhibited higher initial

degradation rates. Notably, the dye's maximum absorption wavelength remained consistent across the pH range of 1-13. Rhodamine B exhibited maximum absorption wavelengths of 554 nm at pH 1-3, 553 nm at pH 4, and 552 nm at pH 5-13. In polar solvents, Rhodamine B exists in two primary forms: cationic and Zwitterion Figure 7.7. (f) (Merouani *et al.*, 2010). The dye undergoes deprotonation of its carboxyl group, converting from the cationic to zwitterion form, when the pH exceeds its pKa value (Serpone *et al.*, 1994). The absorption spectra of these forms are virtually identical. At low pH, RhB's cationic form exhibits minimal hydrophobicity and maximum degradation rate. In contrast, high pH solutions, where RhB exists in its zwitterion form, exhibit slower sonolytic decomposition rates due to reduced accumulation at the bubble interface. However, the increased hydrophobicity of RhB at high basic conditions (pH 11-13) may enhance its breakdown rate.

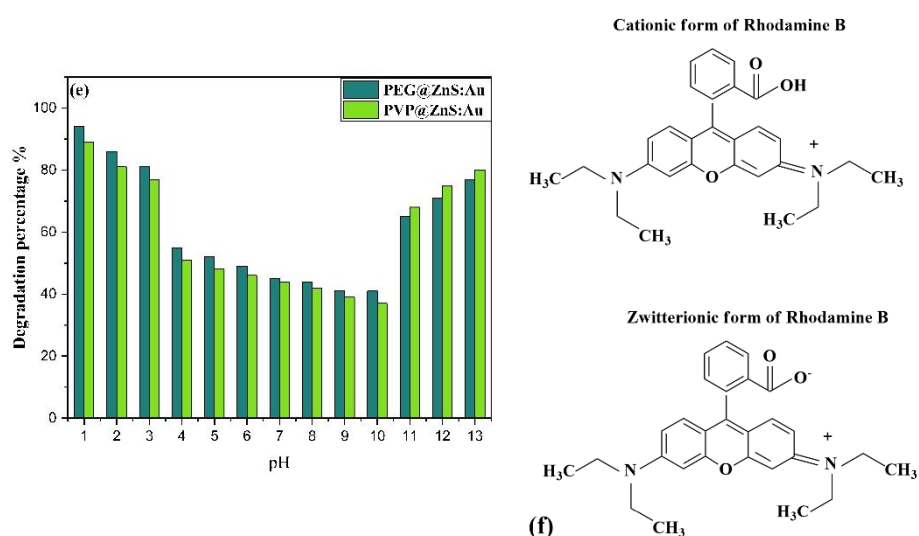


Figure 7.7: (e): Effect of pH levels on the degradation of Rhodamine B. (f): Rhodamine B in water (cationic and zwitterion form).

Point of zero charge

The Point of Zero Charge (PZC) is where the pH at which the surface charge of a material or molecule is neutral, thereby possessing no net positive or negative charge given in Figure 7.7 (g). The relationship between initial pH (pHi) and Δ pH reveals crucial information about the surface charge properties, particularly the Point of Zero

Charge (PZC). At $pH_i = 5$, ΔpH equals 0, indicating the PZC. pH-dependent surface charge interactions significantly influence the degradation of Rhodamine B (RhB). At acidic pH ($pH < PZC$), the catalyst surface exhibits a positive charge, facilitating coulombic attraction with negatively charged RhB molecules, thereby enhancing degradation rates. Unexpectedly low Rhodamine B (RhB) degradation rates near the point of Zero Charge (PZC, pH 4-6), where the catalyst surface is electrically neutral. This discrepancy may be attributed to catalyst surface modifications, competing reactions, or mass transport limitations, which hinder effective RhB-catalyst interactions. Alternatively, pH-dependent speciation changes or residual electrostatic interactions might reduce RhB reactivity. Contrary to expectations, our results show an increase in Rhodamine B (RhB) degradation rate at basic pH ($pH > PZC$). This phenomenon can be attributed to alternative degradation mechanisms, such as hydroxyl radical ($\cdot OH$) mediated degradation, which becomes more prevalent at basic pH. Additionally, the catalyst surface may undergo modifications, create new active sites or enhance existing ones, leading to increased degradation rates. Furthermore, increased RhB solubility at basic pH may facilitate better interaction with the catalyst, overcoming electrostatic repulsion. These factors suggest that, despite the negative surface charge at basic pH, other forces such as hydrogen bonding or π - π interactions may dominate, enabling effective RhB adsorption and degradation.

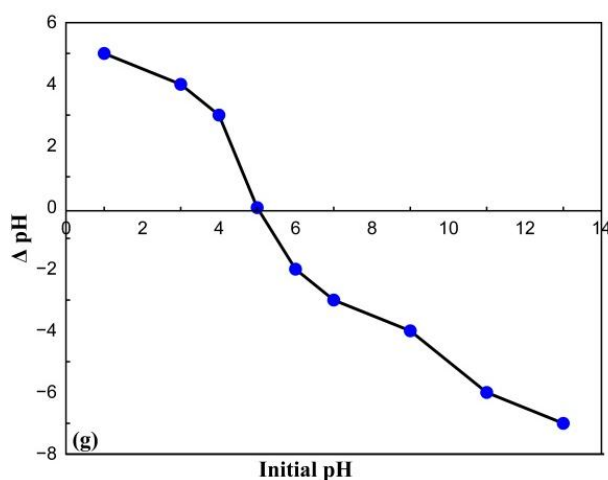


Figure 7.7 (g): Point of zero charge ΔpH vs. initial pH.

Effect of catalyst loading

We investigated the effect of catalyst loading (5-25 mg/L) on Rhodamine B degradation using PEG@ZnS:Au and PVP@ZnS:Au Figure 7.7 (h). Increasing the amount of catalyst boosts photodegradation efficiency and reaction rate, as more active sites become available for dye molecule adsorption, enhancing the overall photocatalytic performance. Our results show that increasing catalyst loading enhances photodegradation efficiency and reaction rate, but only up to a critical point (15 mg/L). Beyond this point, efficiency and rate plateau or even decline due to increased turbidity, light scattering, and catalyst agglomeration, reducing the effective surface area for reaction. Our findings highlight the importance of optimal catalyst loading (15 mg/L) for maximizing photodegradation efficiency and reaction rate. At higher concentrations, the suspension's turbidity increases, leading to enhanced light scattering, which reduces the amount of light absorbed by the photocatalyst surface. Additionally, catalyst particles may agglomerate or cluster, rendering interior surfaces inaccessible to reactants and decreasing the effective surface area for reaction. Consequently, the optimal catalyst loading for Rhodamine B degradation was found to be 15 mg/L for both PEG@ZnS:Au and PVP@ZnS:Au, striking a balance between catalyst activity and adverse effects.

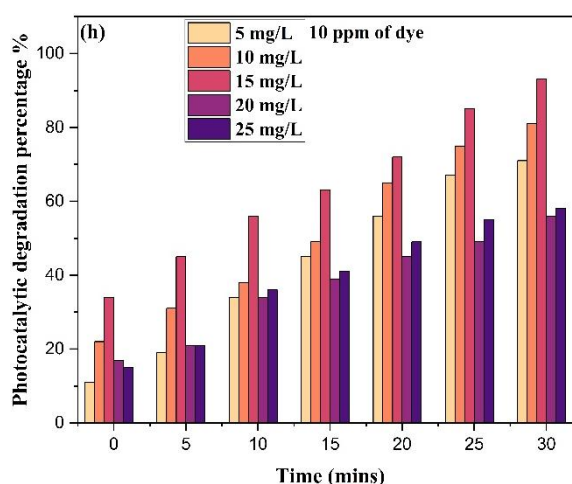


Figure 7.7 (h): Effect of catalyst loading on degradation of Rhodamine B.

Effect of initial concentration of Rhodamine B dye

Increased dye concentrations lead to the formation of larger aggregates, reducing the available surface area for photofading. Consequently, higher dye concentrations result in decreased photofading rates due to enhanced aggregation, which limits the exposure of dye molecules to environmental factors that promote photodegradation. The impact of dye concentration on photodegradation efficiency was investigated, revealing that higher concentrations lead to reduced degradation rates due to increased aggregation, stronger substrate-organic colourant interactions, and enhanced surface absorption Figure 7.7 (i). As the RhB dye concentration increased from 10 to 50 ppm, the decolourization rate decreased, with a degradation efficiency of 94.15% at 10 ppm for both PEG@ZnS:Au and PVP@ZnS:Au. The reduction in photodegradation efficiency at higher dye concentrations is attributed to light shielding and a decrease in active sites on the composite surface. As dye concentration increases, less light penetrates the solution, reducing competition for active sites and slowing down degradation. This highlights the significant impact of initial dye concentration on photodegradation mechanisms in heterogeneous photocatalytic systems. Increased dye concentration leads to a decrease in photodegradation efficiency and reaction rates, due to the rate-limiting step in hydroxyl radical production on the photocatalytic surface. With constant irradiation intensity, dye molecules absorb more photons, resulting in fewer reactive radicals and a slower photodegradation rate, ultimately reducing photon absorption by the catalyst surface (Rashed *et al.*, 2022).

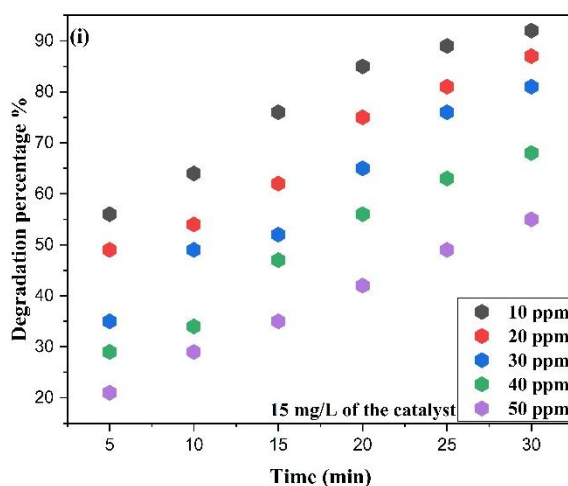


Figure 7.7 (i): Effect of initial concentration of Rhodamine B (in ppm).

7.3.8 Effect of additives and kinetic studies

The addition of H_2O_2 as an oxidant to the solution system enhanced the photodegradation process by accepting electrons from the conduction band to form $\cdot\text{OH}$ radicals, which accelerated the degradation of Rhodamine B (RhB). The presence of H_2O_2 significantly increased the rate of RhB degradation, with degradation percentages of 93.85% and 94.65% for PEG@ZnS:Au and PVP@ZnS:Au, respectively, compared to 82.11% and 81.21% in the absence of H_2O_2 Figure 7.8. (a). The increased availability of hydroxyl radicals in the presence of H_2O_2 accelerated the rate of RhB breakdown, leading to rapid decolourization and dye degradation. The chromophoric structure of RhB was targeted by these radicals, highlighting the essential role of hydrogen peroxide in the photodegradation process. The presence of H_2O_2 enhanced the formation of hydroxyl radicals, which are potent agents in destroying the dye, making it an indispensable component for the photodegradation of Rhodamine B (AlHamedi *et al.*, 2009). The discolouration of the dye solution is attributed to the reaction of hydroxyl radicals ($\cdot\text{OH}$) generated by the photolysis of hydrogen peroxide (H_2O_2) under UV irradiation (P. K. Malik & Sanyal, 2004).



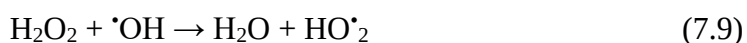
These highly reactive oxidizing agents react with dye molecules, forming intermediates that subsequently lead to the discolouration of the original solution.



The self-quenching process at higher concentrations involves the reaction of excess H_2O_2 with $\cdot\text{OH}$ radicals, yielding $\text{HO}\cdot_2$ radicals and H_2O as products.



The solution self-quenches $\cdot\text{OH}$ radicals at high concentrations by adding excess H_2O_2 , which converts $\cdot\text{OH}$ to $\text{HO}\cdot_2$, thereby maintaining an optimal level of H_2O_2 .



The reaction described above can also yield peroxy radicals, which can enter additional reaction pathways. Therefore, it may be assumed that in this instance, H₂O₂ functions as a pseudo catalyst (Neamtu *et al.*, 2002), (Ince & Gönenç, 1997).

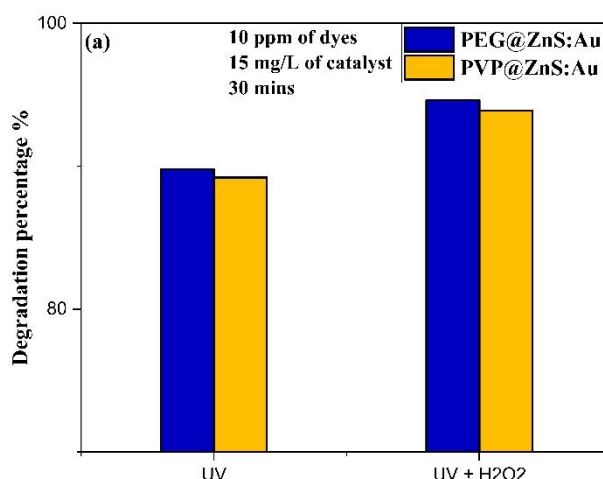
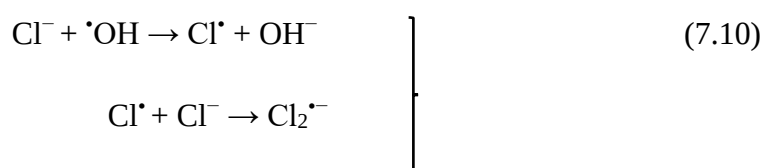


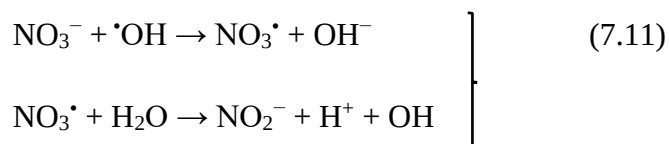
Figure 7.8: (a) Effect of H₂O₂ on degradation of Rhodamine B.

Effect of additives on the degradation of Rhodamine B

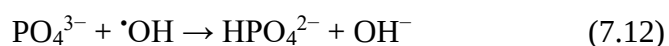
We explored the impact of various anions (Cl⁻, PO₄³⁻, SO₄²⁻, and NO₃⁻) on the photolytic decolourization of Rhodamine B in the presence of PEG@ZnS:Au and PVP@ZnS:Au as catalysts. Figure 7.8 (b) illustrates the results, which show that all the investigated anions inhibited the decolourization process to some extent. Notably, nitrate and phosphate ions exhibited comparable decolourization percentages, while the inhibitory effect was less pronounced for chloride ions. A proposed reaction mechanism suggests that chloride ions can react with hydroxyl radicals ([•]OH) to form less reactive species such as Cl[•], Cl₂^{•-}, and HOCl. This reduces the effective concentration of [•]OH available for RhB degradation, thereby hindering the decolourization process (AlHamedi *et al.*, 2009). This lowers the effective concentration of [•]OH that is available for RhB degradation (Rauf *et al.*, 2007).



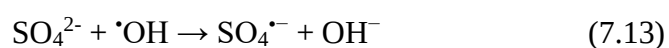
The inhibitory effects of anions on the photolytic decolourization of Rhodamine B are attributed to their reactions with hydroxyl radicals ($\cdot\text{OH}$). Chloride ions react with $\cdot\text{OH}$ to form less reactive species, ($\text{Cl}\cdot$, $\text{Cl}_2\cdot^-$), which slows down the degradation process. Nitrate ions also scavenge $\cdot\text{OH}$, producing less reactive nitrogen species, such as nitrite NO_2^- .



Similarly, phosphate ions scavenge $\cdot\text{OH}$, forming less reactive species equation 7.12. Additionally, phosphate ions can form stable complexes with metal ions, like Fe^{3+} , which may impact the Fenton process or other catalytic mechanisms.



Sulfate ions (SO_4^{2-}) can also interact with iron and other catalysts, potentially preventing the formation of hydroxyl radicals.



Sulfate anions exhibited the lowest extent of decolourization, and their presence was found to decrease Rhodamine B degradation (Muruganandham & Swaminathan, 2006). This phenomenon can be attributed to the reaction between sulfate anions and hydroxyl radicals ($\cdot\text{OH}$) in solution, leading to the depletion of $\cdot\text{OH}$ radicals. The primary mechanism by which anions like Cl^- , NO_3^- , SO_4^{2-} , and PO_4^{3-} inhibit Rhodamine B degradation is through scavenging hydroxyl radicals and obstructing their catalytic production. Chloride ions demonstrated a more pronounced effect due to their high reactivity with hydroxyl radicals, ability to form stable, less reactive species (such as chlorine), and tendency to complex with iron, thereby diminishing the efficiency of catalytic reactions like the Fenton reaction (Wang *et al.*, 2021). These findings highlight the significant impact of anions on the photocatalytic degradation of Rhodamine B, emphasizing the importance of considering anion-radical interactions in photocatalytic processes.

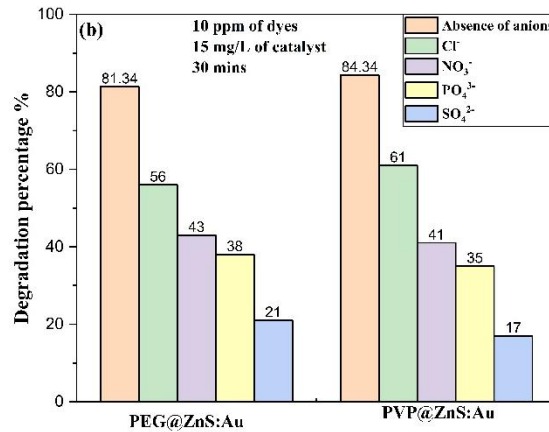


Figure 7.8: (b) Effect of additives on the degradation of Rhodamine B.

Kinetic study on the photocatalytic degradation of Rhodamine B

Figure 7.8. (c) displays the first-order kinetics of Rhodamine B degradation, allowing for a comparison of the photocatalytic activities of PEG@ZnS:Au and PVP@ZnS:Au. The initial (C_0) and final (C) concentrations of the colourant were determined from absorbance spectra. The photocatalytic activity was assessed by monitoring the degradation kinetics and colourant concentration as a function of exposure time, revealing first-order kinetics given in equation 7.14 (Lopes *et al.*, 2014).

$$V = \frac{dC}{dt}kC \quad (7.14)$$

k is the rate constant, by integrating the above equation:

$$\ln \frac{C}{C_0} = -kt \quad (7.15)$$

The linear correlation between $\ln(C/C_0)$ and time (slope = k) confirms first-order kinetics, with k and R^2 values of 0.0821 and 0.990 for PEG@ZnS:Au, and 0.0811 and 0.987 for PVP@ZnS:Au, respectively. The high R^2 values (>0.9577) indicate an excellent fit. The photocatalytic degradation of Rhodamine B under UV irradiation is shown in Figure 7.8 (d), demonstrating efficient degradation within 30 minutes (Paéz *et al.*, 2020). UV-vis spectrophotometry monitored the concentration change of Rhodamine B in the 400-700 nm range, revealing 94.25% and 91.45% photocatalytic

degradation for PEG@ZnS:Au and PVP@ZnS:Au, respectively. The presence of Polyethylene Glycol (PEG) significantly enhances the degradation of Rhodamine B compared to Polyvinylpyrrolidone (PVP) due to its unique properties. PEG's robust hydrogen bonding, solvent property alteration, and enhancement of photocatalytic activity contribute to its superior degradation efficiency. In contrast, PVP's bulkier structure, weaker hydrogen bonding, and lower photocatalytic activity hinder its interaction with Rhodamine B, resulting in reduced degradation. These findings highlight the importance of polymer selection in degradation processes and demonstrate PEG's potential as a suitable polymer for enhancing degradation efficiency.

The reusability of the heterogeneous catalysts was evaluated for six cycles, with intermediate washing and drying steps (ethanol, 20 min; 120°C, 6 h) to remove residual substances. This demonstrates the catalysts' stability and reusability. Figure 7.8 (e) reveals that the catalysts exhibit good reusability for the first four cycles. However, their efficiency drops significantly to 61% and 36% for PEG@ZnS:Au and 64% and 33% for PVP@ZnS:Au in the fifth and sixth cycles, respectively. This decrease may be attributed to structural changes, such as sintering, which reduces the available surface area for catalysis. Notably, the degradation efficiency of the catalyst remained remarkably consistent, exhibiting negligible decline even after six consecutive cycles. This outstanding stability was further corroborated by X-ray diffraction (XRD) analysis, which revealed no significant alterations in the crystal structure of the catalyst after repeated use Figure 7.8 (f). The consistent XRD pattern suggests that the catalyst's crystallinity and phase composition remain unaffected by repeated cycling, underscoring its excellent reusability and durability. PEG@ZnS:Au and PVP@ZnS:Au nanoparticles degrade Rhodamine B with excellent stability and no detectable ion leaching. The X-ray diffraction (XRD) patterns, which remain unaltered even after several reuse cycles, support this phenomenon and highlight the structural stability of the nanoparticles. The lack of ion leaching is explained by the stable construction of the nanoparticles; the encapsulation of ZnS:Au in PEG or PVP matrices acts as a barrier to prevent the release of metal ions. PEG and PVP functional groups establish robust coordination bonds with Zn and Au atoms,

effectively stabilizing them. Meanwhile, the ZnS:Au core itself possesses intrinsic chemical stability, which defies dissolution in degradation-prone environments. The stable and reusable nature of the nanoparticles is guaranteed by their synergistic combination, which also makes them effective catalysts for the degradation of Rhodamine B. The photocatalytic mechanism involves the formation of photo-induced electron-hole pairs on the ZnS surface, which are then utilized to generate hydroxyl radicals and superoxide radicals through the interactions with water and oxygen, respectively. The Au^+ doping enhances the photocatalyst reaction by creating a donor level above the valence band, facilitating the transfer of photogenerated holes to the Au level. The rhodamine dye molecules are readily oxidized by the hydroxyl radicals and superoxide radicals, leading to their degradation and mineralization into CO_2 , H_2O , and other degraded products, as shown in Figure 7.8 (g). This efficient oxidation process underscores the effectiveness of the PEG@ZnS:Au and PVP@ZnS:Au photocatalysts in promoting the degradation of Rhodamine B.

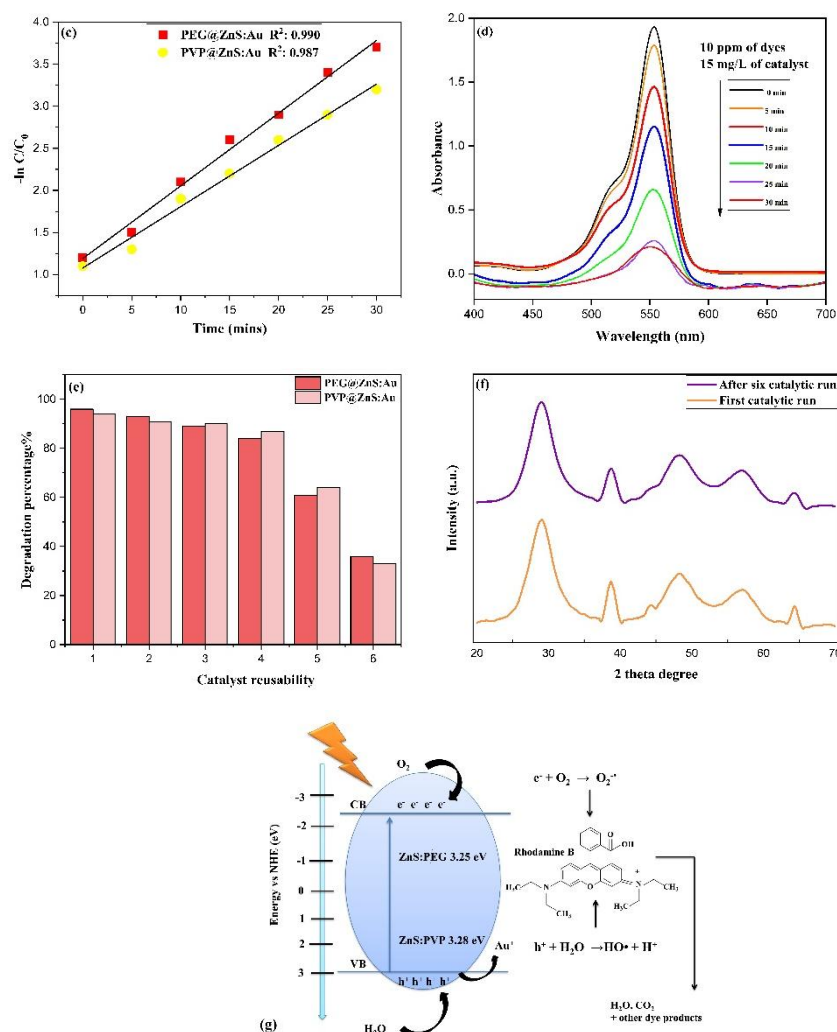


Figure 7.8: (c) Kinetic studies for degradation of Rhodamine B (d) Rhodamine B degradation within 30 minutes (e) Reusability of the catalysts (f) XRD of the catalyst before and after catalytic run (g) Possible mechanism for the degradation of Rhodamine B.

7.3.9 Isotherm study of Rhodamine B degradation

The Langmuir isotherm model was applied to determine the maximum adsorption capacity, assuming a uniform monolayer adsorption on a homogeneous surface, to elucidate the adsorption mechanism. The Freundlich isotherm model posits a heterogeneous surface with a non-uniform distribution of energy levels, providing an alternative framework for understanding adsorption phenomena. The Langmuir and

Freundlich models yield parameters that offer insights into surface characteristics, adsorbent-adsorbate interactions, and adsorption mechanisms, thereby facilitating a comprehensive understanding of adsorbent behavior. These findings have important implications for the design and optimization of adsorption systems. The general expressions for the Langmuir and Freundlich models are given in equations 7.16-7.19.

Langmuir isotherm: This isotherm can be obtained using the following equation, which provides information on the monolayer formation on the homogeneous surface (Jabeen *et al.*, 2021):

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (7.16)$$

This is the equation in linearized form:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L C_e}{K_L} \quad (7.17)$$

The Langmuir isotherm constants, K_L and a_L , represent the maximum sorption capacity (mg/g) and binding affinity, respectively. The equilibrium concentration (mg/L) and adsorbed amount (mg/g) are denoted by C_e and q_e , respectively. The theoretical monolayer capacity (Q_o) is calculated as K_L/a_L . The Langmuir adsorption isotherm is plotted as C_e/q_e vs C_e , yielding a linear correlation with R_2 values of 0.982 for PEG@ZnS:Au and 0.977 for PVP@ZnS:Au. The Freundlich isotherm is a mathematical model that describes the adsorption behavior on heterogeneous surfaces, where the adsorption sites have different energies. The model is expressed by the equation 7.18 (Lianmawii & Singh, 2023).

$$q_e = K_F C_e^{1/n} \quad (7.18)$$

The logarithmic form of the Freundlich isotherm is as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7.19)$$

The equilibrium concentration of the adsorbate (C_e) is expressed in mg/L, while the amount of dye adsorbed per gram of adsorbent at equilibrium is denoted by q_e . The

slope of the plot yields the sorption intensity ($1/n$), whereas the intercept corresponds to the Freundlich constant (K_F).

Figure 7.9. (a) and (b) display the Freundlich and Langmuir isotherm curves for PVP@ZnS:Au and PEG@ZnS:Au, respectively. The parameters of the Langmuir and Freundlich equations are summarized in Table 7.3. The adsorption of Rhodamine B on both catalysts is better described by the Langmuir isotherm, as evidenced by the higher correlation coefficients (R^2) between experimental data and adsorption isotherms for Langmuir (0.982 and 0.977) compared to Freundlich (0.934 and 0.922). This suggests that the adsorption of Rhodamine B by PEG@ZnS:Au and PVP@ZnS:Au nanoparticles occur on a homogeneous surface with a finite number of adsorption sites, consistent with the Langmuir model. The adsorbent surface is composed of multiple layered sections with varying adsorption capacities (Malakootian *et al.*, 2020). PEG@ZnS:Au has a higher Langmuir constant (a_L) value, indicating stronger adsorption affinity. PEG@ZnS:Au has a higher maximum adsorption capacity (Q_0) value, indicating higher adsorption capacity.

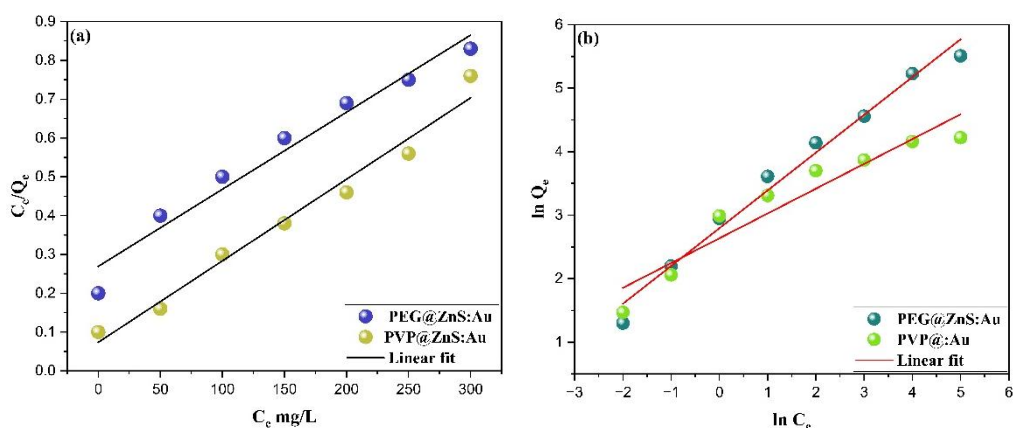


Figure 7.9: (a) and (b) Langmuir and Freundlich isotherm study.

Table 7.3: Calculated parameters for Langmuir and Freundlich isothermal models for PEG@ZnS:Au and PVP@ZnS:Au.

Sample	Model	Parameter	Values
PEG@ZnS:Au	Freundlich Isotherm	K_F	0.59
		N	-0.003
		R^2	0.934
PVP@ZnS:Au		K_F	0.76
		N	-0.012
		R^2	0.922
PEG@ZnS:Au	Langmuir isotherm	Q_0 (mg/g)	0.31
		aL	3.23
		R^2	0.982
PVP@ZnS:Au		Q_0 (mg/g)	0.26
		aL	2.12
		R^2	0.977

7.3.10 Thermodynamic study

Figure 7.10 shows the results of experiments conducted at various temperatures (303K, 313K, 323K, and 333K) to investigate the effect of temperature on Rhodamine B adsorption onto the catalyst at different concentrations. The thermodynamic parameters were determined using the following equations (Wani *et al.*, 2024):

$$\Delta G^\circ = -RT \ln K_c \quad (7.20)$$

The universal gas constant is R, the temperature in Kelvin is T, and the distribution coefficient is K_c . Using $\ln K_c$ values at different temperatures, the change in Gibbs free energy (ΔG°) was calculated. The following formula was used to get these K_c values.

$$K_c = \frac{q_e}{c_e} \quad (7.21)$$

The formula below was used to determine the enthalpy change (ΔH°) and entropy change (ΔS°) of adsorption:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7.22)$$

The variables in this equation are the standard entropy ($\Delta S^\circ = \text{Jmol}^{-1}\text{K}^{-1}$), standard enthalpy ($\Delta H^\circ = \text{kJmol}^{-1}$), distribution coefficient ($K_c = \text{Lg}^{-1}$), gas constant ($R = 8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature (K).

The thermodynamic parameters ΔS° and ΔH° were evaluated from the slope and intercept of the plot of $\ln K_c$ against $1/T$ shown in Figure 7.10. A comparative analysis of the thermodynamic parameters reveals that PEG@ZnS:Au exhibits slightly more favorable ΔG° values than PVP@ZnS:Au at all temperatures Table 7.4. Conversely, PVP@ZnS:Au displays higher ΔS° values at elevated temperatures (323 K and 333 K), suggesting an entropic advantage. The similarity in ΔH° values indicates equivalent energy requirements for the process. These findings suggest that PEG@ZnS:Au is more suitable for applications where spontaneity is desirable, whereas PVP@ZnS:Au may be more advantageous in high-temperature contexts where increased entropy is beneficial. The overall trend indicates that the degradation of Rhodamine B using these catalysts requires external energy input and is not thermodynamically favored.

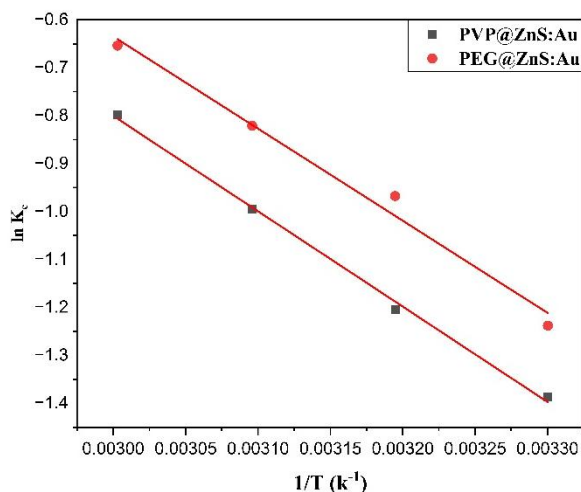


Figure 7.10: Thermodynamic study for Rhodamine B degradation.

Table 7.4: Calculated thermodynamic parameters for Rhodamine B degradation of PEG@ZnS:Au and PVP@ZnS:Au.

Sample	ΔH° (kJ mol ⁻¹)	ΔS° (JK ⁻¹ mol ⁻¹)	ΔG° (kJmol ⁻¹)			
			303 K	313 K	323 K	333 K
PEG@ZnS:Au	15.97	42.43	3.49	3.03	2.50	2.01
PVP@ZnS:Au	15.66	42.95	3.22	3.45	3.56	3.90

7.3.11 Adsorption kinetics study of Rhodamine B degradation

In the present study, the pseudo-first-order and pseudo-second-order models were employed to elucidate the kinetic parameters at a temperature of 303 K, facilitating the delineation of the underlying mechanisms governing the process. The kinetics parameters were calculated from the plots of the obtained values, as shown in Figure 7.11.

The following is an expression for the pseudo first order equation 7.23 (Jabeen *et al.*, 2021):

$$\log (q_i - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (7.23)$$

Where k_1 is the pseudo-first order reaction rate constant for sorption (min⁻¹), q_e is the catalyst amount (mg/g) at equilibrium, and q_t is the catalyst amount (mg/g) at any given time (min).

The expression for the pseudo-second-order equation 7.24 is as follows:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k q_e^2} \quad (7.24)$$

where k_2 is the pseudo-second order reaction rate constant for sorption, q_e is the catalyst quantity at equilibrium, and q_t is the catalyst amount at a specific time (min). The rate constant for first order kinetic (k_1) was found from the linear plot of time (t) versus $\log(q_e - q_t)$, where q_e and q_t are the amounts of dye adsorbed at equilibrium and time t , respectively Figure 7.11. (a). Similarly, the linear plot of time vs. t/q_t Figure 7.11. (b) was used to derive the 2nd order kinetic (k_2) rate constant. R^2 values and the kinetic constants are shown in Table 7.5. Notably, the pseudo-first-order model showed a higher regression coefficient ($R^2 = 0.981$ and 0.993) compared to the pseudo-second-order model ($R^2 = 0.943$ and 0.948) for both PEG@ZnS:Au and PVP@ZnS:Au. The rate constants (k_1 and k_2) are different for the two systems, indicating different reaction kinetics.

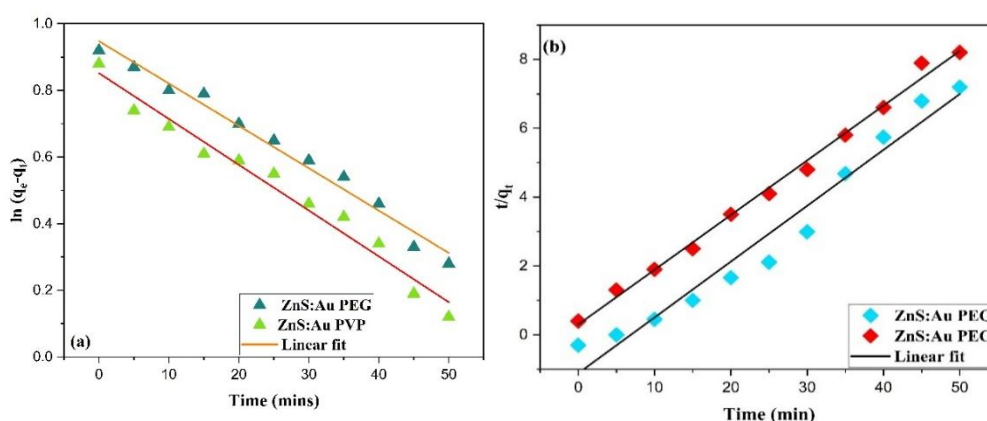


Figure 7.11: (a) Pseudo first order kinetic model (b)Pseudo second order kinetic model.

Table 7.5: Calculated values of R^2 and rate constant for pseudo first and second order kinetics models for PEG@ZnS:Au and PVP@ZnS:Au.

	Models	R^2 value	Rate constant
Pseudo- first-order	PEG@ZnS:Au	0.981	$k_1 = 0.0041213 \text{ (min}^{-1}\text{)}$
	PVP@ZnS:Au	0.993	$k_1 = 0.0039443 \text{ (min}^{-1}\text{)}$
Pseudo-	PEG@ZnS:Au	0.943	$k_2 = 0.01244 \text{ (L Mol}^{-1} \text{ min}^{-1}\text{)}$

second- order	PVP@ZnS: Au	0.928	$k_2 = 0.02210 \text{ (L Mol}^{-1} \text{ min}^{-1}\text{)}$

7.4 Conclusion

The findings of this research underscore the exceptional photocatalytic efficiency of these nanoparticles in degrading Rhodamine B dye under UV irradiation, with degradation efficiencies of 94.25% and 91.45%, respectively. The structural and morphological characterization revealed a cubic zinc blende lattice structure and diverse particle shapes, indicating mesoporous characteristics with pore sizes ranging from 2-50 nm. The temperature-dependent degradation profiles showed consistent enhancement with increasing temperature, and catalyst loading optimization revealed a critical point of 15 mg/L for efficient photodegradation. The presence of H₂O₂ enhanced hydroxyl radical formation, facilitating dye degradation, while investigated anions (Cl⁻, PO₄³⁻, SO₄²⁻, and NO₃⁻) inhibited decolourization to some extent. The adsorption of Rhodamine B on both catalysts was accurately described by the Langmuir isotherm, indicating homogeneous surface adsorption with finite sites.

The pseudo-first-order model best described the photocatalytic degradation kinetics. The study's findings have significant implications for environmental applications, particularly in wastewater treatment, and contribute to the understanding of photocatalytic nanotechnology. Future research should focus on optimizing catalyst synthesis, exploring large-scale applications, and investigating degradation mechanisms. Overall, this study provides a comprehensive understanding of PEG@ZnS: Au and PVP@ZnS: Au nanoparticles as efficient photocatalysts for the degradation of Rhodamine B, paving the way for future advancements in photocatalytic nanotechnology. The developed catalysts demonstrate potential for efficient dye degradation, highlighting the importance of continued research in photocatalytic nanotechnology for environmental remediation and sustainability.

CHAPTER 8

Photoluminescence and Photocatalytic Degradation of Organic Pollutants using CoS:Ce³⁺ Nanoparticles: Insights from Adsorption and Kinetic Studies

8.1 Introduction

The textile industry's persistent organic pollutants and effluents have been a longstanding research focus, with a particular emphasis on the remediation of harmful organic dyes that compromise water quality (Isac *et al.*, 2019), (Lam *et al.*, 2012). Studies indicate that up to 50% of dyes utilized in textile production remain unfixed to the fiber, contaminating water bodies (J. Sharma *et al.*, 2021). Untreated dye pollutants in aquatic ecosystems can harm water quality, leading to aesthetic degradation, reduced photonic transmission, inhibited photosynthetic activity, and depleted dissolved oxygen levels (Pereira & Alves, 2012), (Owa, 2014), (Lianmawii & Singh, 2025). Despite employing conventional treatment methods, including adsorption, coagulation, ion exchange, and enzyme degradation, complete mineralization of dye effluents remains an elusive goal, underscoring the need for novel and sustainable solutions to address this pressing environmental concern (S. Dutta *et al.*, 2021), (C. Mondal *et al.*, 2015).

Furthermore, conventional methods have been found to have significant limitations, including the generation of toxic byproducts such as gases and sludge, which require additional processing and preclude complete mineralization, necessitating innovative and sustainable remediation strategies (Thirumaran *et al.*, 2020). The contamination of water resources by textile dyes has evolved into a paramount global issue, transcending national boundaries and necessitating immediate attention (Tahir *et al.*, 2021). The proliferation of these dyes in aquatic ecosystems poses a profound threat to aquatic life, culminating in irreversible harm and far-reaching consequences for other organisms and human populations that depend on these ecosystems (Balcha *et al.*, 2016). The escalating use of reactive dyes across diverse industrial sectors exacerbates this environmental crisis, necessitating urgent action and sustainable

solutions to mitigate the detrimental impacts of dye pollution on the environment and human well-being (Yuan *et al.*, 2020). Alternative technologies, such as heterogeneous photocatalysis employing nano-semiconductors, have shown promise in mitigating the issue of dye pollutants in wastewater. Industrial effluents and waste contain a diverse range of dyes and pollutants, posing significant global environmental challenges (Lima *et al.*, 2017). These dyes are harmful to the environment exhibit carcinogenic properties, contaminating water bodies and forming a colourful, foam-like layer that impedes oxygen availability for aquatic flora and fauna (Julkapli *et al.*, 2014). Human society faces the dual challenges of reducing energy consumption and environmental pollution, exacerbated by the increasing number of industries generating waste, disrupting the environment (Koe *et al.*, 2019). Industrial effluents from diverse sectors, including textile, chemical, poultry, dairy, and pharmaceutical industries, contain toxic, carcinogenic, and non-biodegradable pollutants that are discharged directly into aquatic ecosystems, posing significant threats to human health, aquatic life, and livestock welfare (Bafana *et al.*, 2011). The textile industry, in particular, is a significant contributor to water pollution, utilizing various dye colourants that generate pollutants in water (Lianmawii *et al.*, 2024).

Heterogeneous photocatalysis, an advanced oxidation process, offers a promising solution for completely mineralizing recalcitrant organic pollutants present in textile dye effluents, converting them into CO₂ and H₂O non-selectively. Semiconductor metal oxides, such as TiO₂ and ZnO, have been extensively investigated as photocatalysts for this purpose (Lianmawii & Singh, 2023), (Bhatkhande *et al.*, 2002). However, TiO₂'s wide bandgap (~3.2 eV) and rapid recombination of photogenerated hole-electron pairs limit its industrial applicability. To address these limitations, researchers have sought to develop visible-light-driven semiconductors with narrow bandgaps capable of efficiently removing organic pollutants (Shanker *et al.*, 2017), (Cheng *et al.*, 2016), (Carp *et al.*, 2004). Despite considerable efforts, numerous photocatalysts are limited by low quantum efficiency, high production costs, rapid charge recombination rates, and ineffective utilization of photogenerated charge carriers, leading to inadequate photodegradation efficiency and hindering

their widespread adoption. Z-scheme heterojunction photocatalysts offer a promising solution, enabling charge separation mechanisms that leverage their exceptional light trapping, spatially distributed active sites, and high redox capacities (Yan *et al.*, 2016), (Isac & Enesca, 2022). Moreover, the substitution of noble metals with earth-abundant co-catalysts such as Cu, Ni, and Co-based sulfides or oxides is essential for the development of cost-effective photocatalytic systems, providing a viable alternative to noble metal-based catalysts and enhancing the economic viability of photocatalytic processes. Cobalt sulfide (CoS), a transition metal sulfide, is an attractive option due to its excellent visible light activity, chemical stability, reactivity, and high photocatalytic performance, making it a promising candidate for photocatalytic applications (Hosseinpour *et al.*, 2018), (Sohrabnezhad *et al.*, 2009). CoS nanostructures have been fabricated for various applications, including sensors, solar cells, water splitting, environmental remediation, electrocatalysis, and supercapacitors, and offer improved lifetimes of photogenerated charge carriers and enhanced charge separation efficiency (Mozafari & Hamidinezhad, 2019). The development of CoS-based photocatalysts could potentially overcome the limitations of traditional photocatalysts, enabling efficient and sustainable removal of organic pollutants from textile dye effluents (Lu *et al.*, 2016).

Advanced oxidation technologies (AOTs), particularly photocatalytic degradation, have become a vital method for removing dyes from water. This process involves the in-situ generation of oxidizing agents in water, triggering a photochemical reaction that degrades dyes (Prasanna & Rajagopalan, 2016). Photocatalysis offers a distinct advantage over conventional methods, which typically involve the transfer of pollutants from the liquid to the solid phase, necessitating additional treatment steps. In contrast, photocatalysis enables the near-complete mineralization of pollutants, achieving efficient degradation without generating secondary pollutants or hazardous byproducts. This makes photocatalysis a more eco-friendly and sustainable approach for dye removal (Banat *et al.*, 1996).

Photocatalysis can mineralize organic pollutants, converting them into harmless CO₂ and H₂O, making it a promising technology for wastewater treatment (Phyllis *et al.*, 2022). Rare earth oxalates, in particular, have garnered significant attention due to

their intriguing luminescent, electrical, and magnetic properties. Recent investigations have elucidated the fluorescent properties of rare earth oxalates, indicating their promising potential for various optical applications. The high-quality, defect-free single crystals of these compounds are crucial for unlocking their full potential in these fields (Wang *et al.*, 2021). Metal oxides, such as Fe_2O_3 and CeO_2 , have emerged as valuable tools for removing heavy metals and toxic pollutants, leveraging their properties for water decomposition and pollutant mineralization. Cerium oxide (CeO_2), a semiconductor, absorbs light in the UV and visible range, making it effective for degrading organic pollutants (Deus *et al.*, 2015). Its applications extend beyond environmental remediation to UV-blocking materials, polishing materials, ceramic additives, and optical materials (Dubey *et al.*, 2016). Cerium's versatility shines as an electronic promoter, three-way catalyst, and oxygen buffer, making it a vital heterogeneous catalyst in various industrial processes. The significance of metal oxides in environmental cleaning and maintenance is evident, and their potential applications continue to expand (Mary *et al.*, 2016).

This study reports the successful development of a facile and efficient hydrothermal method for synthesizing cobalt sulfide (CoS) nanocomposites doped with cerium ions (Ce^{3+}), achieving tunable concentrations of Ce^{3+} ions. The as-synthesized nanocomposites exhibit excellent degradation capabilities for various pollutants, including Congo Red, Methylene Blue dye, and Cefixime. The synthesis approach employs a one-step hydrothermal process with self-heating and secondary calcination using metal sulfides, yielding nanocomposites with enhanced pollutant degradation properties.

8.2 Experimental details

8.2.1 Sample preparation

Cerium(III) nitrate hexahydrate, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 434.22 g/mol, Cobalt(II) nitrate hexahydrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 291.03 g/mol, and Sodium sulfide hydrate -NaHS, 56.06 g/mol were procured from Alfa Aesar (Thermo Fisher Scientific) and utilized without further purification. A typical hydrothermal synthesis involved loading 60 mL of deionized water, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ into a 100 mL Teflon-

lined stainless-steel autoclave. Excess NaHS was subsequently added and dissolved, facilitating the incorporation of cerium at varying atomic percentages (at.%) of 0.20, 0.30, 0.40, and 0.50. The autoclave was sealed and subjected to a temperature of 200°C for 12 hours. The autoclave was permitted to cool to ambient temperature naturally after the reaction. The resultant product was isolated via centrifugation and subjected to repeated washing cycles with 100% ethanol and deionized water. The final sample was dried at 170°C for 1 hour to facilitate characterization and photocatalytic reaction studies.

8.2.2 Sample characterization

The sample's crystal structure and phase composition were investigated using XRD analysis on a Bruker D8 Advance diffractometer equipped with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Diffraction patterns were collected over a 2θ range of $[20^\circ\text{-}80^\circ]$ to elucidate the structural properties of the samples. The surface morphology SEM was examined using a JEOL JSM 6700F instrument operated at an accelerating voltage of 20 kV. The ultrastructure and morphology of the samples were investigated using a JEOL JEM 2010F instrument operated at an accelerating voltage of 200 Kv, both TEM and HRTEM imaging modes were employed to reveal fine structural details. FTIR spectra were acquired using a PerkinElmer Spectrum Two spectrophotometer with a spectral resolution of 4 cm^{-1} over the wavenumber range of $4000\text{-}500 \text{ cm}^{-1}$. This enabled the identification of functional groups and molecular vibrations in the samples. Fluorescence spectroscopy measurements were performed on a Hitachi F-7000 spectrophotometer using a xenon discharge lamp as the excitation source. Excitation and emission spectra, as well as decay time data, were acquired to provide insights into the fluorescent properties of the samples. The photocatalytic activity of the samples was evaluated using UV-Vis spectroscopy on a Thermo Scientific Evolution 220 spectrophotometer. This enabled the assessment of their ability to absorb light and generate reactive species. The specific surface area and porosity of the samples were determined by nitrogen adsorption-desorption isotherms at 77 K using a Micromeritics ASAP 2020 analyzer.

Photocatalytic Degradation of Organic Contaminants using CoS:Ce³⁺ as a Catalyst

In a typical experiment, 10 mg of CoS:Ce³⁺ nanocatalyst was added to 30 mL of aqueous solution containing the model contaminant. The mixture was magnetically stirred in the dark for 30 minutes to achieve adsorption-desorption equilibrium, ensuring optimal interaction between the nanocatalyst and contaminant. The effects of various parameters, including dye concentration, solution pH, irradiation time, temperature, and photocatalyst dose, were systematically optimized during light irradiation. Experiments were then conducted under the optimized conditions to achieve maximal photocatalytic efficiency. The photocatalytic degradation efficiency was calculated using the following formula:

$$\text{Degradation (\%)} = (A - A_0)/A_0 \times 100$$

A and A_0 represent the absorbance of the dye solution after and before irradiation, respectively.

8.3 Results and discussions

8.3.1 X-ray diffraction (XRD)

The XRD patterns in Figure 8.1(a) demonstrate the cubic spinel crystal structure of Co₉S₈, in good agreement with the reference pattern JCPDS 65-6801. The observed diffraction peaks are consistent with the space group Fm3m, confirming the crystal structure of the material. The diffraction peaks at 2θ values of 25.78°, 31.56°, 39.12°, 40.11°, 44.56°, 47.78°, 52.90°, 54.56°, 58.79° correspond to the (220), (222), (331), (420), (422), (511), (440), (531), and (620) planes, respectively. The X-ray diffraction (XRD) pattern reveals distinct peaks attributed to cerium, exhibiting diffraction peaks at 2θ values of 31.65°, 36.12°, and 41.90°. These peaks correspond to the (102), (103), and (104) crystal planes, respectively, indicating the presence of cerium in the material as confirmed by JCPDS 89-2728. The d_{hkl} values, representing the interplanar spacing of the as-prepared CoS:Ce³⁺ nanocrystals, were calculated using the Bragg equation 8.1 (Singh *et al.*, 2016):

$$2d_{hkl}\sin\theta = n\lambda \quad (8.1)$$

The X-ray radiation source wavelength is denoted by λ , the Bragg angle of incidence is represented by θ (theta), hkl (Miller indices): represent the interplanar spacing between successive lattice planes, specifically: h , k , and l are integers that define the spatial arrangement of the lattice planes. The lattice parameter " a " of CoS:Ce³⁺ crystallites was determined from the XRD patterns using the following equation 8.2:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (8.2)$$

The lattice parameters and unit cell volumes, calculated from the X-ray diffraction (XRD) data, are summarized in Table 8.1. The values reveal the structural characteristics of the CoS:Ce³⁺ nanocomposites, providing insight into the effects of Ce³⁺ doping on the crystal structure of CoS. The XRD pattern of CoS:Ce³⁺ shows peak broadening, confirming the formation of CoS nanocrystals. Sharp, narrow peaks in the XRD pattern indicate a high degree of sample quality, crystallinity, and fine grain size. The sharpness and narrowness of the peaks suggest a high level of structural order and a low degree of structural disorder or defects, confirming the excellent crystalline quality of the sample. The well-documented influence of crystallite size and internal strain on X-ray diffraction (XRD) line broadening was exploited to determine these parameters in as-prepared CoS:Ce³⁺ nanoparticles quantitatively. Application of the Williamson-Hall equation 8.3 to the XRD data enabled the calculation of crystallite size (D) and internal strain, providing valuable insights into the material's microstructural properties (Mercy *et al.*, 2013).

$$\beta \cos \theta = \frac{K\lambda}{D} + 2\epsilon \sin \theta \quad (8.3)$$

D represents the coherent scattering length (crystallite size), K denotes 0.9 (a constant), λ is the wavelength of the incident radiation (1.54 Å), β is the full width at half maximum (FWHM) in radians, θ is the Bragg angle, and ϵ denotes internal strain (%). The Williamson-Hall plot ($4\sin \theta$ vs. $\beta \cos \theta$) shown in Figure 8.1 (b and c) was fitted to a straight line, enabling the determination of crystallite size (D) via the intercept of the line. The Williamson-Hall equation was used to calculate the crystallite size (D) of the CoS:Ce³⁺ nanoparticles, providing insight into their structural properties. The analysis yielded a crystallite size in the 25-32 nm range,

indicating a relatively small crystallite size. The average crystallite size of the nanoparticles was calculated using the Debye-Scherrer equation 8.4, resulting in a range of 38-49 nm. This suggests that the synthesis procedure was effective in producing nanoparticles with a uniform size distribution (Lianmawii & Singh, 2023)

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (8.4)$$

D represents average crystallite size (nm), K is the shape factor (typically 0.9-1.0), λ is the wavelength of the X-rays (nm), β denotes full width at half maximum (FWHM) of the diffraction peak (radians), θ = Bragg angle (degrees).

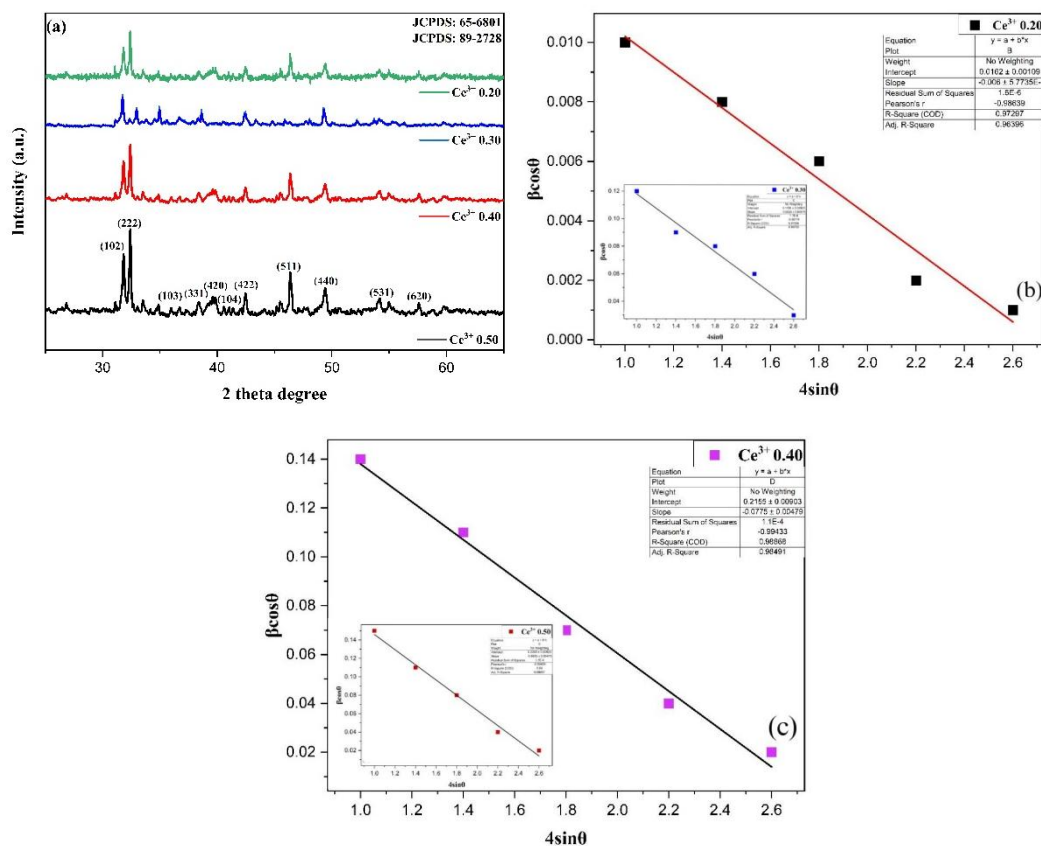


Figure 8.1: (a) X-ray diffraction (XRD) patterns of CoS:Ce³⁺ with varying concentrations (0.20-0.50 at.%). (b and c) Williamson-Hall plots of CoS:Ce³⁺ with varying concentrations (0.20-0.50 at.%).

Table 8.1: Calculated lattice parameters, cell volumes, and crystallite sizes of CoS:Ce³⁺ with varying Ce³⁺ concentrations (0.20-0.50 at.%).

Ce ³⁺ concentrations	Lattice parameters a (Å)	Cell volume (Å ³)	Crystallite size (nm)
Ce ³⁺ 0.20 at. %	9.786	978.45	38.44
Ce ³⁺ 0.30 at. %	9.721	978.66	43.89
Ce ³⁺ 0.40 at. %	9.654	978.72	46.66
Ce ³⁺ 0.50 at. %	9.609	978.88	49.22

8.3.2 Fourier Transform Infrared (FTIR)

The FTIR spectra provided valuable insights into the molecular bonding and structural arrangements of the CoS:Ce³⁺ system, enabling the identification of functional groups and their corresponding vibrational modes. This analysis aimed to elucidate the effects of Ce³⁺ doping on the molecular structure of CoS, shedding light on the potential changes in bonding configurations and molecular interactions. The FTIR spectra displayed in Figure 8.2 reveal seven distinct absorption peaks at 3334 cm⁻¹, 2357 cm⁻¹, 1651 cm⁻¹, 1388 cm⁻¹, 1077 cm⁻¹, 1024 cm⁻¹, 783 cm⁻¹, and 528 cm⁻¹, which are attributable to specific vibrational modes of the molecular structure. These peaks provide important information regarding the molecular geometry, functional groups, and bonding interactions (Abza *et al.*, 2020). The FTIR spectra of cobalt sulfide phases exhibit a series of absorption peaks assignable to specific molecular vibrations. The FTIR spectrum exhibits two distinct peaks at 3334 cm⁻¹ and 1651 cm⁻¹, which are assigned to the O-H stretching and bending vibrations, respectively. These peaks are characteristic of water (H₂O) absorption, suggesting the presence of hydrated species in the sample. The peak at 2357 cm⁻¹ comes from the stretching of C-H bonds. The 1388 cm⁻¹ and 1077 cm⁻¹ peaks come from stretching C-O-H and C-O bonds, respectively (Wan *et al.*, 2013). The strong peaks

at 1024 cm^{-1} and 528 cm^{-1} indicate the presence of sulfonated groups and polysulfide bonds. The FTIR spectrum shows a prominent peak at 783 cm^{-1} , which corresponds to the stretching vibration of Co-S bonds. This peak confirms the successful formation of cobalt sulfide (CoS) in the nanoparticles (P. Yin *et al.*, 2016).

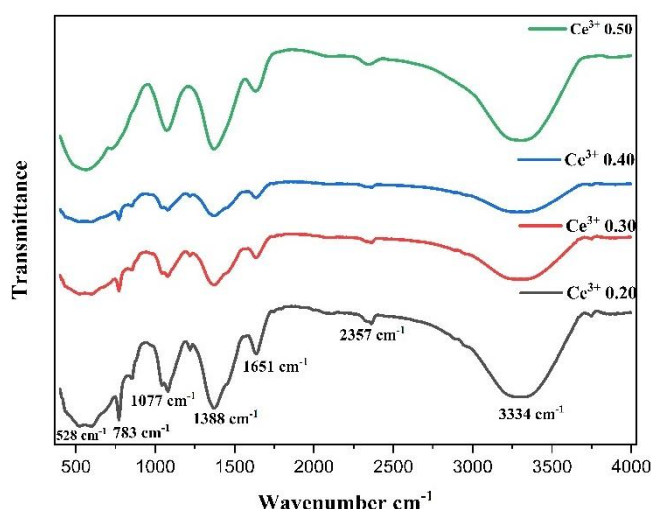


Figure 8.2: FTIR spectra of CoS:Ce³⁺ with varying concentrations (0.20-0.50 at.%).

8.3.3 Scanning Electron Microscopy (SEM)

The surface morphology, particle shape, and size of the CoS:Ce³⁺ nanoparticles were investigated using SEM. The corresponding micrographs, presented in Figure 8.3 (a–g), provide detailed insights into the structural and morphological features of the samples. A clear evolution in morphology was observed with varying Ce³⁺ concentrations. At 0.20 at.% Figure 8.3 (a), the nanoparticles displayed a relatively uniform morphology with slight agglomeration. When the Ce³⁺ concentration was increased to 0.30 at.% Figure 8.3 (c), a heterogeneous distribution emerged, consisting of smaller fused particles alongside larger discrete ones. At 0.40 at.% Ce³⁺ Figure 8.3 (e), the particles exhibited a mixed morphology, including cubic and spherical structures with distinct grain boundaries. Interestingly, the highest concentration (0.50 at.%) resulted in predominantly spherical nanoparticles with well-defined grain boundaries and a characteristic “grip-like” feature Figure 8.3 (f).

This progressive, concentration-dependent evolution led to the development of large plate-like grains composed of smaller granular nanoparticles, demonstrating a hierarchical structural arrangement. These results showed excellent agreement with particle size estimates obtained from X-ray diffraction (XRD) analysis, underscoring the consistency and reliability of both methods. Furthermore, energy-dispersive X-ray spectroscopy (EDX) confirmed the presence of Ce, Co, and S in the samples Figures 8.3 (b, d, f, h), thereby validating the successful synthesis of CoS:Ce³⁺ nanoparticles. Particle size analysis performed using J-image software indicated a positive correlation between Ce³⁺ concentration and particle size, with values ranging from 20 to 50 nm (inset).

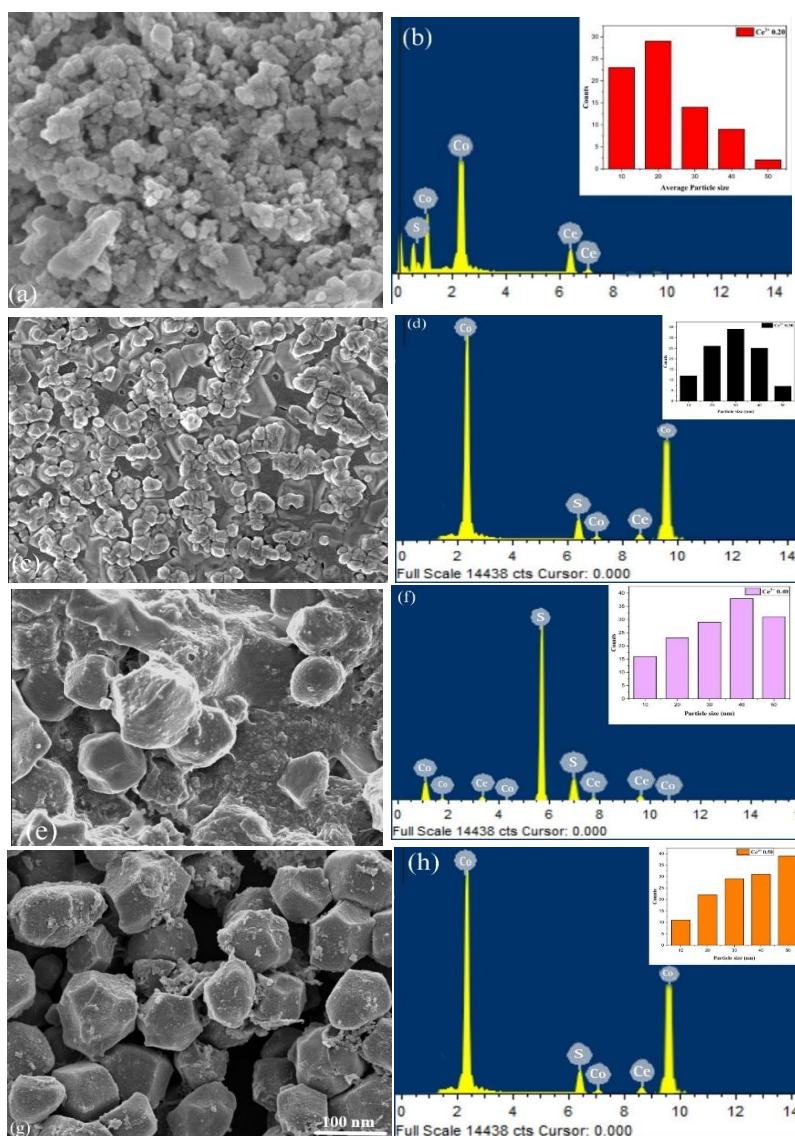


Figure 8.3: (a-d) SEM image, average particle size and EDAX of CoS:Ce³⁺ with varying concentrations (0.20-0.50 at.%).

8.3.4 Transmission electron microscopy (TEM)

TEM, HR-TEM, and SAED patterns of CoS:Ce³⁺ nanostructures with Ce³⁺ concentrations are presented in Figure 8.4. The images reveal agglomerated nanostructures with individual particle sizes ranging from 30-45 nm Figure 8.4 (a,c,e, and g). The size and shape of the nanocrystals are influenced by factors such as precursor concentration, growth temperature, and growth time. Notably, a low precursor concentration facilitates a slightly faster growth rate of nanocrystalline materials. In this study, the addition of Ce³⁺ to the solution during the reaction may have limited the growth rate of CoS, enhancing the confinement effect. Lattice fringes, and crystal planes, and selected area electron diffraction (SAED) patterns of CoS:Ce³⁺ nanostructures are also displayed.

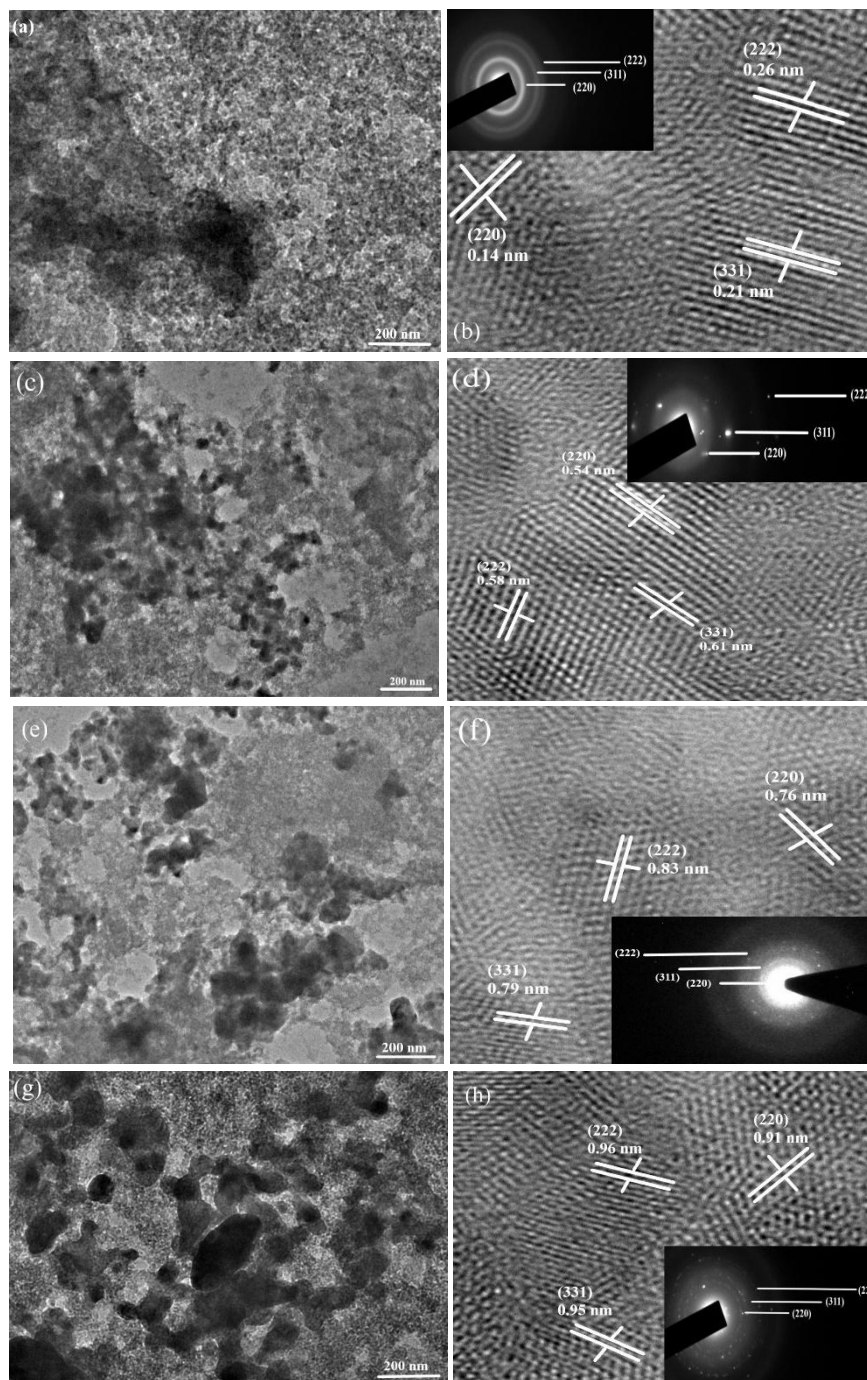


Figure 8.4: (a-d) TEM, HR-TEM and SAED patterns of CoS:Ce³⁺ with varying concentrations (0.20-0.50 at.%).

8.3.5 Brunauer-Emmett-Teller (BET)

The N₂ adsorption-desorption isotherm curves, presented in Figure 8.5, exhibit hysteresis loops between 0.4 - 1.2 relative pressure, indicating the presence of porosity in the samples. This behavior is characteristic of H3-type isotherms, which suggest the filling and emptying of pores through condensation (Donohue & Aranovich, 1998). The specific surface area of CoS:Ce³⁺ ranges from 45.08 to 60.12 m² g⁻¹, indicating a high surface area that can provide abundant surface reaction sites, thereby enhancing electrochemical performance. The nitrogen sorption isotherms exhibit a transition from monolayer to multilayer adsorption, indicative of a continuous pore system with a wide range of pore diameters, spanning from molecular to macroscopic scales. The observed H3 hysteresis loops are characteristic of slit-like pores with variable sizes, resulting from particle aggregation and subsequent formation of interconnected pores. This pore structure gives rise to a complex adsorption behavior, with both microporous and mesoporous regions contributing to the overall sorption capacity (Donohue & Aranovich, 1998). Notably, an increase in surface area and pore volume is observed with increasing Ce³⁺ concentration. The observed enhancement in specific surface area can be attributed to the modified morphology resulting from Ce³⁺ loading. The increased surface area of nanostructures indicates higher surface activity, which is beneficial for various applications, including catalysis, sensing, and energy storage. The Ce³⁺ loading-induced morphology transformation leads to an increased exposure of active sites, potentially enhancing the material's performance in various fields (Xu *et al.*, 2020). The correlation between Ce³⁺ concentration, morphology, and surface area highlights the importance of tailored synthesis approaches to optimize the electrochemical properties of CoS:Ce³⁺ materials.

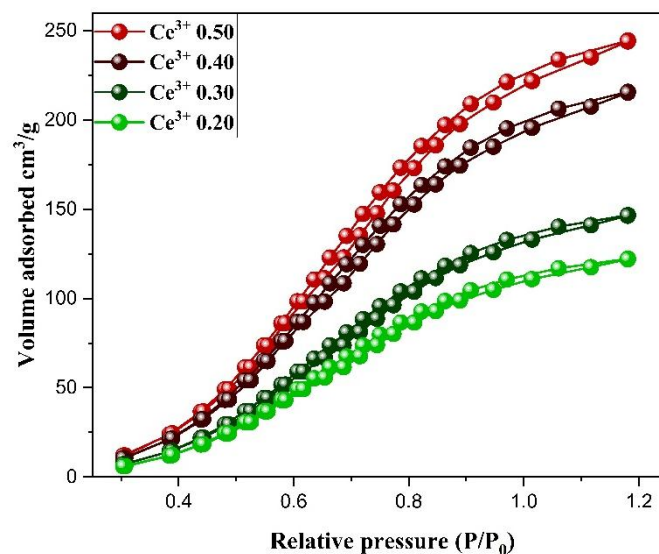


Figure 8.5: BET study of CoS:Ce³⁺ with varying Ce³⁺ concentrations 0.20-0.50 at.%.

8.3.6 Raman spectroscopy

Raman spectroscopy was used to analyze the composition and structure of the CoS:Ce³⁺ catalyst. The resulting spectrum, Figure 8.6, exhibits prominent peaks for the D bands at 1448 cm⁻¹, 1438 cm⁻¹, 1445 cm⁻¹, and 1440 cm⁻¹, and G bands at 1711 cm⁻¹, 1708 cm⁻¹, 1704 cm⁻¹, and 1701 cm⁻¹, for CoS: Ce³⁺ with varying concentrations (0.20-0.50 at.%). These peaks are attributed to the formation of carbon through pyrolysis and arise from the in-plane stretching of ordered sp²-bonded carbon atoms. The intensity ratio of the D band to the G band (ID/IG) indicates a higher defect level in the carbon material, suggesting that introducing defects depends on the sulfide source (Huang *et al.*, 2023), (Zhang *et al.*, 2017). Notably, the concentration of Ce³⁺ remains unchanged, indicating that the defects introduced by the sulfide source enhance charge transport.

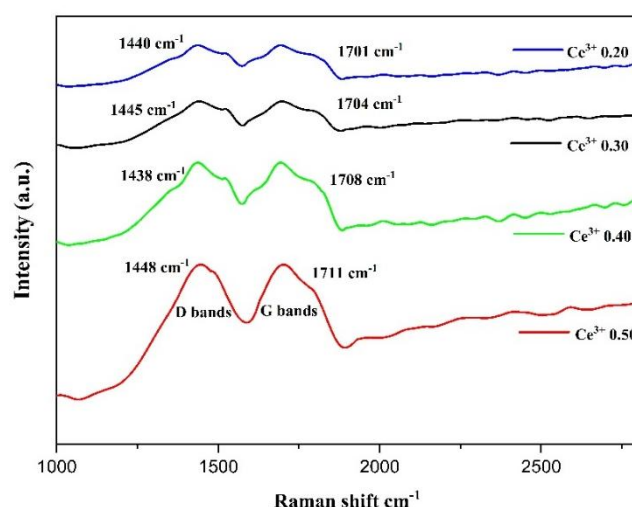


Figure 8.6: Raman spectra of CoS: Ce³⁺ with varying Ce³⁺ concentrations 0.20-0.50 at. %.

8.3.7 Photoluminescence studies

Figure 8.7 (a) displays the emission spectra of CoS:Ce³⁺ recorded at 310 nm excitation for concentrations of Ce³⁺ 0.20, 0.30, 0.40, and 0.50 at. %. The allowed electric dipole transitions of ions are responsible for the broad band observed in the spectra around 350–650 nm (Neto *et al.*, 2021), (Mary *et al.*, 2016). The observed enhancement in surface activity is attributed to the electronic transition from the lowest energy level of Ce³⁺, which is located at ⁵D₁ → ²F_{5/2} and ²F_{7/2} manifolds split by spin-orbit coupling. Emission from multiple energy levels is responsible for the emission peak's broadness (Wang *et al.*, 2021). The acquired spectra show that the only way to successfully regulate the reduction from Ce⁴⁺ to Ce³⁺ in an air atmosphere is to introduce carbon during the melting process (Omar *et al.*, 2018). It was associated with an ion-to-ion distance decrease that is favorable to the energy transfer (ET) process between neighbors of Ce³⁺. Then, the connected oxygen atoms raise the potential negative charge that the Ce³⁺ ion may acquire overall, and the decrease in binding lengths increases the covalent bond's nature, resulting in the nephelauxetic shift. Figure 8.7 (b) shows the normalized excitation spectra of the CoS:Ce³⁺ samples, which were obtained by emission at 445 nm. The asymmetric

broadband in the excitation spectra of Ce^{3+} ions has maximums at 261 nm, 258 nm, 257 nm, and 259 nm for Ce^{3+} concentrations of 0.20, 0.30, 0.40, and 0.50 at.%. In Ce^{3+} transitions, the oxygen ligand exerts influence and causes maximum displacement in the band. The results indicate a significant crystal field effect on the Ce^{3+} ions, leading to a substantial splitting of the 5d energy level. This suggests that the crystal field environment has a profound impact on the 5d electron configuration of the Ce^{3+} ions (Deus *et al.*, 2015).

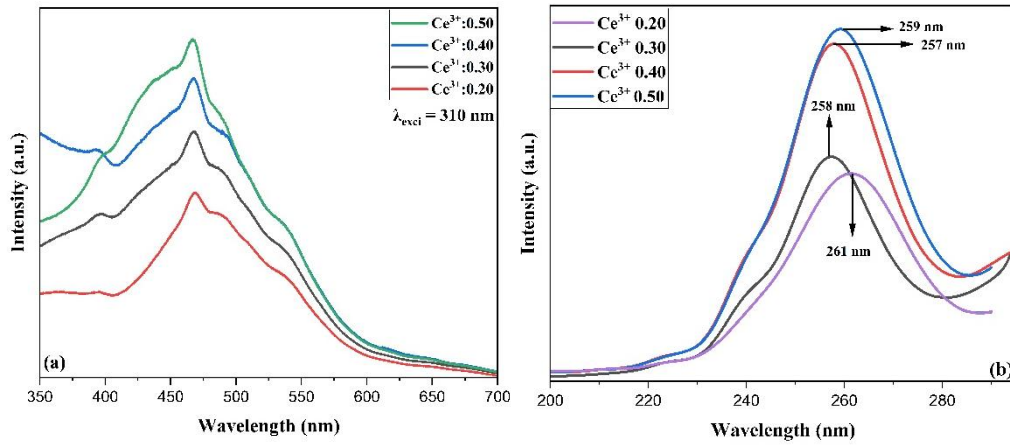


Figure 8.7: (a) Emission spectra of CoS: Ce^{3+} with varying Ce^{3+} concentrations 0.20-0.50 at.%. (b) Excitation spectra of CoS: Ce^{3+} with varying Ce^{3+} concentrations 0.20-0.50 at.%.

CIE chromacity and decay lifetime

Luminescent materials possess two crucial attributes: the associated colour temperatures (CCT's) and the CIE coordinates. Emission spectra can be used to determine the colour coordinates (Lu *et al.*, 2015). The corresponding colour temperature can also be determined using the approximation formula that McCamy developed, which is based on the CIE chromaticity coordinate given in equation 8.5 (McCamy, 1992), (Pollnau *et al.*, 2000).

$$\text{CCT}(x,y) = -437n^3 + 3.610n^2 - 6.861n + 5514.31 \quad (8.5)$$

Where the inverse slope line is given by $n = (x-x_e) / (y-y_e)$. The CIE chromaticity coordinates and correlated colour temperatures of CoS:Ce³⁺ have been calculated under different excitation wavelengths, as listed in Table 8.2. Figure 8.7(c) presents the CIE chromaticity coordinates (x,y) positions of CoS:Ce³⁺ in the Commission Internationale de l'Eclairage (CIE) 1931 chromaticity diagram. The samples excited at 310 nm are located in a blue region, which agrees with the previous literature reported (Wang *et al.*, 2021). The CoS:Ce³⁺ samples exhibit localized emissions in the blue region, as Figure 8.7(d). depicts. The material exhibits a light blue emission when excited at 310 nm, indicating its potential for use in optical applications, such as light-emitting diodes (LEDs). The photoluminescence properties of these materials make them suitable for use in blue light emission applications, including displays, lighting, and optical communication systems (Cui *et al.*, 2018), (Pimputkar *et al.*, 2009). The CoS:Ce³⁺ system exhibits a unique feature of tunable blue emission, where varying concentrations of Ce³⁺ ions enable the realization of different blue colour tones. Under an excitation wavelength of 445 nm, the CIE colour coordinates of the emission samples are situated in the cyan blue region, making them suitable for applications in lighting phosphors within this specific colour range. Notably, the Ce³⁺ doping concentration has a minimal impact on the emitting colour, suggesting a high colour stability (Pollnau *et al.*, 2000), (McCamy, 1992). The sample's CIE colour coordinates exhibit a shift from intense blue to light cyan blue, rendering it a promising candidate for blue phosphor applications, as previously reported. Given its favorable fabrication costs and high luminous efficiency, CoS:Ce³⁺ emerges as a viable material for white light generation, offering a valuable contribution to the development of advanced lighting technologies (Neto *et al.*, 2021). The decay curves for the synthesized CoS:Ce³⁺ nanoparticles at concentrations of Ce³⁺ 0.20, 0.30, 0.40, and 0.50 at.% are displayed in Figure 8.7(e), along with a conventional bi-exponential fitting. The following bi-exponential equation can be used to fit all decay curves given in equation 8.6 (N. P. Singh *et al.*, 2017):

$$I = I_1 \exp (-t/\tau_1) + I_2 \exp (-t/\tau_2) \quad (8.6)$$

Where I_1 and I_2 represent the intensities at periods "0" and "t" and τ_1 and τ_2 stand for the respective decay times. Using the formula below, one can determine the average lifespan given in equation 8.7:

$$\tau_{ave} = \frac{I_1\tau_1^2 + I_2\tau_2^2}{I_1\tau_1 + I_2\tau_2} \quad (8.7)$$

As-prepared CoS:Ce³⁺ nanoparticles average lifetime for concentrations of Ce³⁺ 0.20, 0.30, 0.40, and 0.50 at.% is determined to be 0.995, 0.989, 0.993, and 0.990. Non-exponential decay suggests an energy transfer from active ions to quenching sites that are not radiative. As different forms of Ce³⁺ coexist, there is a greater chance of Ce³⁺→Ce³⁺ energy migration, which is followed by energy transfer (loss). Additionally, one should consider the interaction between Ce⁴⁺ and Ce³⁺ ions. With an increase in cerium, it is observed that the overall abundance of cerium ions increases, and the spacing between them decreases (Neto *et al.*, 2021).

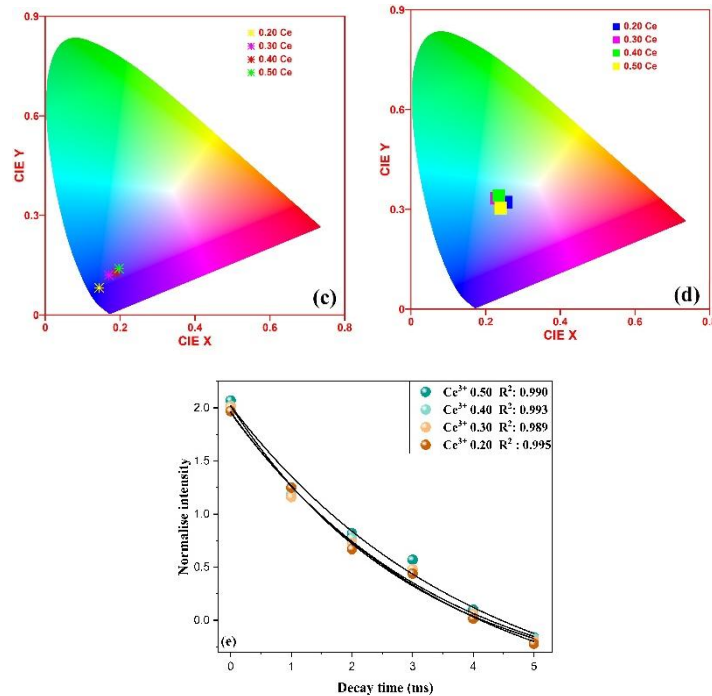


Figure 8.7: (c) and (d) CIE chromacity diagram of CoS:Ce³⁺ with varying Ce³⁺ concentrations 0.20-0.50 at.%. (e) Lifetime decay of CoS:Ce³⁺ with varying Ce³⁺ concentrations 0.20-0.50 at.%.

Table 8.2: The colour temperature and CIE chromaticity coordinates of CoS:Ce³⁺ excited at 310 and 445 nm, respectively.

Sample	Ce ³⁺ Concentration	Excitation wavelength (λ)	Coordinates of CIE chromaticity		Colour temperature (K)	Colour
			x	y		
	x = 0.20 at. %	310	0.144	0.082	2307	Blue
		445	0.255	0.321	10673	Cyan blue
CoS: Ce ³⁺	x = 0.30 at. %	310	0.166	0.118	3891	Blue
		445	0.230	0.333	12146	Cyan blue
	x = 0.40 at. %	310	0.189	0.127	3844	Blue
		445	0.235	0.341	11318	Cyan blue
	x = 0.50 at. %	310	0.197	0.140	5389	Blue
		445	0.240	0.304	13245	Cyan blue

8.3.8 Photocatalytic studies

The optical properties of CoS:Ce³⁺ at various concentrations were investigated by measuring absorbance in the 200-700 nm wavelength range Figure 8.8 (a). The Stern relationship (Equation 8.8) determined the energy band gaps and transition types.

$$A = \frac{[k(h\nu - E_g)]^{n/2}}{h\nu} \quad (8.8)$$

A is the absorbance, k is a constant, ν is the frequency of the radiation, h is Planck's constant, n is the transition type (1 for direct transition, 4 for indirect transition), E_g is the band gap energy. The analysis revealed a direct transition ($n=1$) in all samples, as evidenced by the linear relationship between $(Ah\nu)^2$ and $h\nu$ given in Figure 8.8 (b).

The band gap energy (E_g) was extrapolated by linearly fitting the $(Ah\nu)^2$ vs $h\nu$ curve and intercepting the $h\nu$ axis. The results showed a decrease in band gap energy with increasing Ce^{3+} concentration, with values ranging from 1.49 to 1.31 eV at Ce^{3+} concentrations of 0.20-0.50 at.%. This decrease in band gap energy may be attributed to the increase in thickness and crystallite size with deposition time, as these parameters significantly influence the band gap of particles (Abza *et al.*, 2020). Notably, the band gap values obtained in this study are relatively higher than commonly reported values, which may be attributed to the presence of excess sulfur, leading to high absorbance in the visible light region.

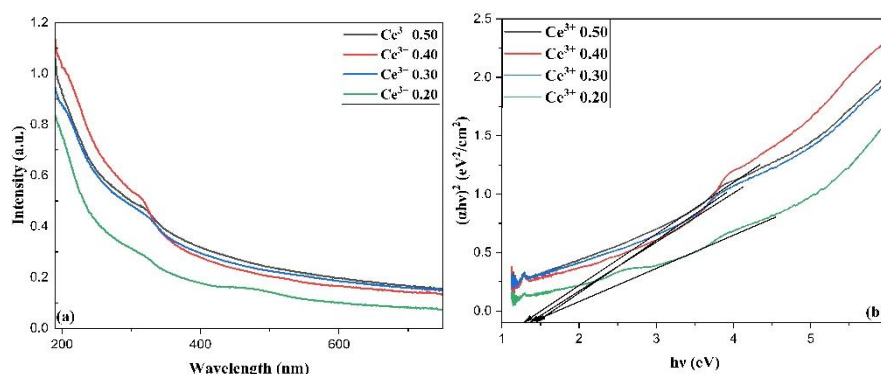


Figure 8.8: (a) UV absorption spectra of CoS:Ce³⁺ with varying Ce³⁺ concentrations 0.20-0.50 at.%. (b) Band gap of CoS:Ce³⁺ from $(ah\nu)^2$ and $h\nu$ plots with varying Ce³⁺ concentrations 0.20-0.50 at.%.

Evaluation of CoS:Ce³⁺ Catalysts with Varying Ce³⁺ Concentrations for Efficient Degradation of Pollutants

A series of CoS:Ce³⁺ catalysts were synthesized with varying Ce³⁺ concentrations (0.20, 0.30, 0.40, and 0.50 at.%) to investigate their efficacy in degrading selected pollutants. The degradation experiments were performed within a timeframe of 25 minutes, and the results revealed that the catalyst with the highest Ce³⁺ concentration (0.50 at.%) exhibited the most impressive degradation performance for Congo Red, Methylene Blue, and Cefixime given in Figure 8.8 (c). Notably, a direct correlation was observed between the Ce³⁺ concentration and degradation percentage, indicating

an enhancement in catalytic activity with increasing Ce^{3+} content. This suggests that the synthesized $\text{CoS}:\text{Ce}^{3+}$ catalysts possess excellent potential for the efficient degradation of pollutants, making them a promising candidate for environmental remediation applications. The optimal performance of Ce^{3+} 0.50 at.% concentration catalysts can be attributed to the enhanced optical and electronic properties imparted by the increased Ce^{3+} content, facilitating improved charge carrier generation and separation. The degradation profiles of Congo Red, Methylene Blue, and Cefixime Figure 8.8 (d-f) show a significant enhancement in photocatalytic degradation efficiency within 25 minutes, achieving 94% degradation of Congo Red, 96% degradation of Methylene Blue and 89% degradation of Cefixime. These results highlight the excellent photocatalytic activity of $\text{CoS}:\text{Ce}^{3+}$ catalysts, particularly at higher Ce^{3+} concentrations, demonstrating their potential for efficient pollutant degradation in environmental remediation applications (Chen *et al.*, 2023). Table 8.3 shows the degradation percentages of varying Ce^{3+} concentrations.

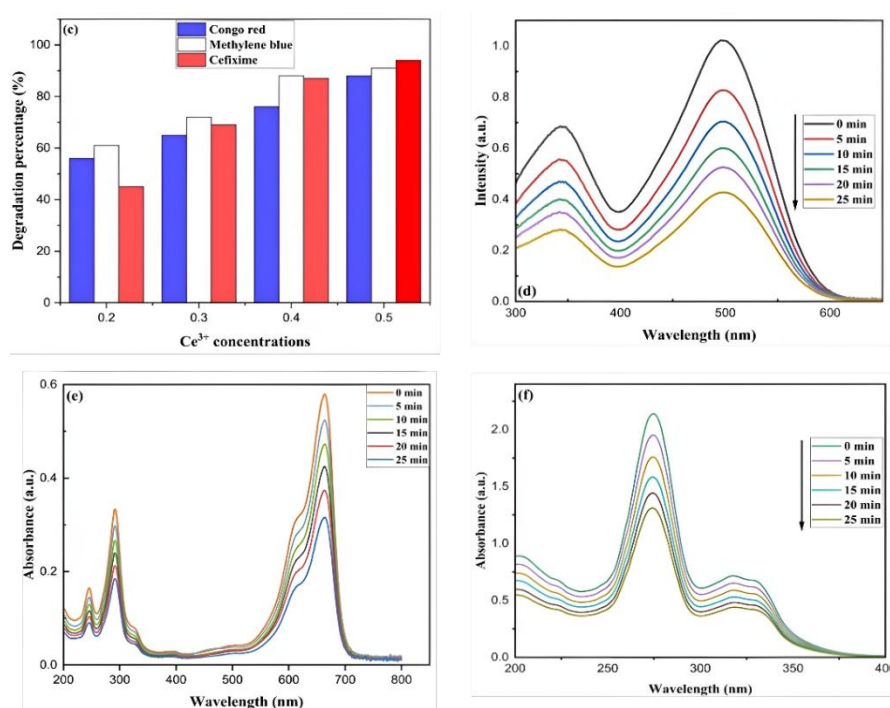


Figure 8.8: (c) Comparison of concentration of Ce^{3+} for degradation of dyes (d-f) Degradation of Congo Red, Methylene Blue and Cefixime within 25 minutes.

Table 8.3: The degradation percentages of the different pollutants using the CoS:Ce³⁺ catalysts with varying Ce³⁺ concentrations.

Ce ³⁺ concentrations	Degradation percentages		
	Congo Red	Methylene Blue	Cefixime
0.20 at. %	55.29%	67.22%	44.56%
0.30 at. %	65.60%	78.21%	65.76%
0.40 at. %	78.88%	86.66%	78.88%
0.50 at. %	94.44%	96.01%	89.78%

pH study

The impact of initial pH on the photocatalytic degradation of pollutants using CoS:Ce³⁺ 0.50 at. % was studied, and the results are shown in Figure 8.8 (g). For Congo Red, the findings reveal that the decolourization process is significantly enhanced at lower pH levels, attributable to the protonation of negatively charged sulfonate groups (-SO₃⁻). This protonation renders the molecules highly hydrophobic, thereby augmenting their reactivity. In contrast, the loss of hydrogen from the protonated sites in alkaline media confers a hydrophilic character to the molecules, leading to diminished decolourization efficiency (Gopinath *et al.*, 2010). The optimum pH level for degradation of Congo Red was found to be pH 2. The adsorptive removal of Methylene Blue was found to be optimal within a pH range of 9-10. pH influenced the chemical properties of the solution, affecting the behavior of the pollutants and the photocatalyst. It altered the surface properties of the adsorbents, affecting their ability to bind with pollutants and the photocatalyst. The adsorbent and adsorbate molecules interact through electrostatic forces, and This change in surface charge affects the adsorption process, influencing the interactions between the adsorbent and adsorbate molecules (Malaika & Kozłowski, 2011). As the pH increases, the solution's hydroxyl ion (OH⁻) concentration rises, causing the

adsorbent surface to become more negatively charged. This enhances the electrostatic attraction between the positively charged dye molecules and the adsorbent surface (Dolas *et al.*, 2011). The degradation of Cefixime was investigated under various pH conditions, revealing a significant impact of pH on the degradation efficiency of the CoS:Ce³⁺ catalyst. Optimal degradation efficiencies were achieved at pH 2 (89%) and pH 9 (91%), with a notable decrease in efficiency between pH 3 and 5. However, a subsequent increase in pH to 9 resulted in improved degradation efficiency, comparable to that observed at pH 3. The degradation efficiency varies with pH due to electrostatic interactions between the charged particles of CoS:Ce³⁺ and the contaminants. The pH of the solution controls the degree of dissociation of the pollutant (Cefixime), which is related to its pKa value (Nazir *et al.*, 2022).

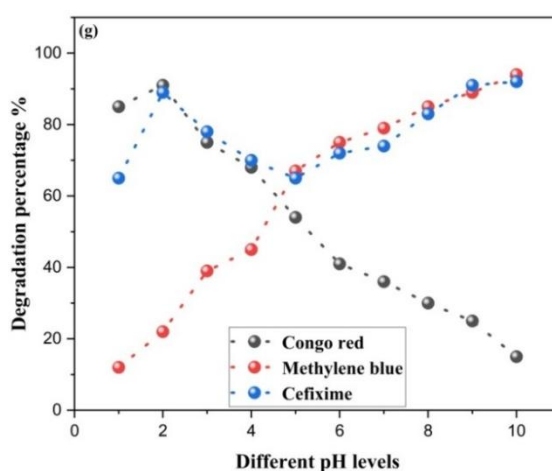


Figure 8.8: (g) Effect of pH on the degradation of Congo Red, Methylene Blue and Cefixime.

Light-Dependent Degradation of Congo Red, Methylene Blue, and Cefixime

The degradation of Congo Red, Methylene Blue, and Cefixime was systematically investigated under various light conditions, including ultraviolet (UV) light, visible light, sunlight, and darkness. The results revealed that UV light facilitates the highest degradation efficiencies for all three pollutants, with a degradation order of UV light > visible light > sunlight > darkness Figure 8.8 (h). The enhanced degradation under UV light is attributed to the increased formation of reactive species, including hydroxyl radicals ($\cdot\text{OH}$), hydrogen peroxide (H_2O_2), and superoxide ions ($\text{O}_2^{\cdot-}$).

These reactive species play a crucial role in the degradation process, as they are highly reactive and can attack dye molecules, leading to degradation. The UV light-mediated degradation process exhibits faster degradation rates compared to other light sources, making it a more efficient option for dye degradation (Reza *et al.*, 2017). This study highlights the potential of UV light as a viable approach for degrading organic pollutants, particularly dyes. UV light's high energy excites catalyst electrons and generates electron-hole pairs, enhancing ROS formation and degradation.

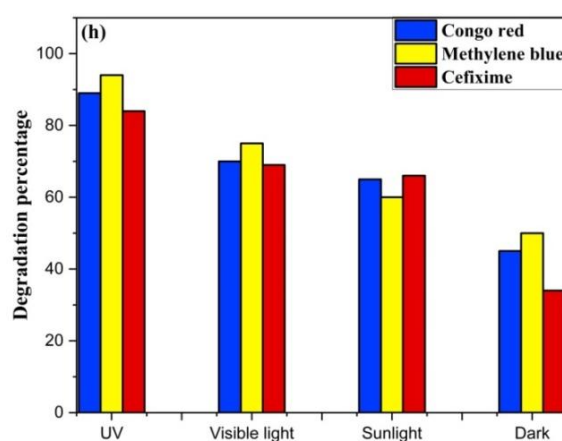


Figure 8.8: (h) Effect of light on the degradation of Congo Red, Methylene Blue and Cefixime.

Congo Red, Methylene Blue, and Cefixime degradation were investigated as a function of pollutant concentration (10-50ppm) given in Figure 8.8 (i). A statistically significant concentration-dependent relationship was observed for the degradation efficiency, wherein higher contaminant concentrations (50ppm) yielded lower degradation percentages. In contrast, lower concentrations (10 ppm) resulted in significantly higher degradation percentages, indicating an inverse correlation between contaminant concentration and degradation efficiency. The observed decrease in degradation efficiency at higher concentrations can be attributed to the saturation of active sites on the catalyst surface, thereby reducing the availability of reactive species. In contrast, at lower concentrations, the active sites remain unsaturated, facilitating more efficient degradation. Furthermore, the increased competition for reactive species (e.g., hydroxyl radicals) among dye molecules at

higher concentrations may also contribute to the decreased degradation efficiency. Additionally, aggregating dye molecules at higher concentrations may reduce their accessibility to reactive species, thereby decreasing degradation (Zhou *et al.*, 2024). Conversely, the more dispersed nature of dye molecules at lower concentrations enhances their accessibility to reactive species, leading to increased degradation.

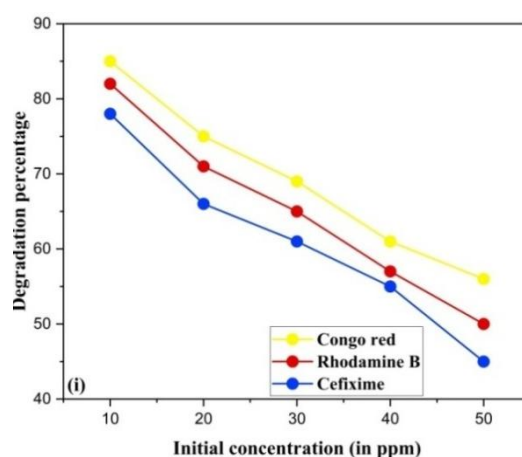


Figure 8.8: (i) Effect of initial concentrations on the degradation of Congo Red, Methylene Blue and Cefixime.

Effect of catalyst dosage

The degradation of Congo Red, Methylene Blue, and Cefixime was investigated as a function of catalyst concentration (5-30 mg/L). The results revealed a positive correlation between catalyst concentration and degradation efficiency, but only up to a critical point. The optimal catalyst concentration for maximum degradation was found to be 20 mg/L, beyond which the degradation efficiency decreased. This decrease in degradation efficiency at higher catalyst concentrations (above 20 mg/L) can be attributed to the aggregation of catalyst particles, resulting in a reduction in their surface area and, consequently, a decrease in degradation efficiency. This phenomenon highlights the importance of optimizing catalyst concentration for maximum degradation efficiency. The findings of this study demonstrate that the optimal catalyst concentration for the degradation of Congo Red, Methylene Blue, and Cefixime is 20 mg/L. The decline in degradation efficiency at higher catalyst concentrations (>20 mg/L) can be attributed to high catalyst loadings, which lead to

particle agglomeration, reducing the effective surface area and active sites. This decrease in surface area-to-volume ratio hinders contaminant adsorption and degradation. Higher catalyst concentrations enhance light scattering, diminishing the intensity of incident radiation and compromising degradation efficiency Figure 8.8 (j).

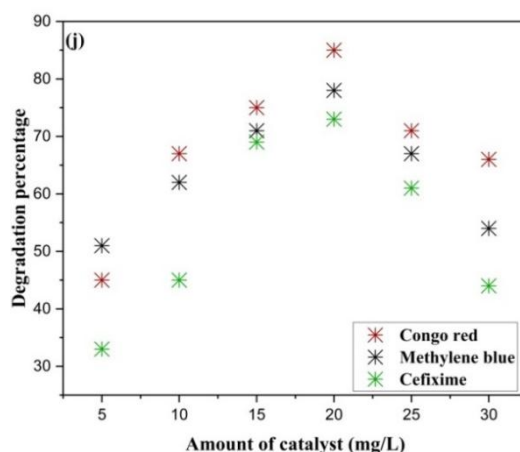


Figure 8.8: (j) Effect of amount of catalyst on degradation of Congo Red, Methylene Blue and Cefixime.

Kinetic Study

A kinetic study was conducted to elucidate the order of the photocatalytic degradation reaction, and the results revealed that the degradation of the dye conforms to first-order kinetics using equation 8.9 (Gautam *et al.*, 2016):

$$C = C_0 e^{-kt} \quad (8.9)$$

C_0 is the initial dye concentration (ppm), C is the concentration at time (ppm), ' k ' is the first-order rate constant (min^{-1}), ' t ' is time (min), equation 8.10:

$$-\ln \frac{C}{C_0} = kt \quad (8.10)$$

The rate constants (k) for the photocatalytic degradation of Congo Red, Methylene Blue, and Cefixime were calculated using equations 8.9 and 8.10 and found to be Congo Red: $k = 0.04133 \text{ min}^{-1}$ ($R^2 = 0.983$), Methylene Blue: $k = 0.04451 \text{ min}^{-1}$ ($R^2 = 0.991$) and Cefixime: $k = 0.05122 \text{ min}^{-1}$ ($R^2 = 0.980$). The high R^2 values indicate a

strong correlation between the experimental data and the first-order kinetic model, confirming that the degradation reactions follow first-order kinetics. The rate constants and R^2 values are presented and can be used to compare the degradation rates and efficiencies of the different pollutants, Figure 8 (k).

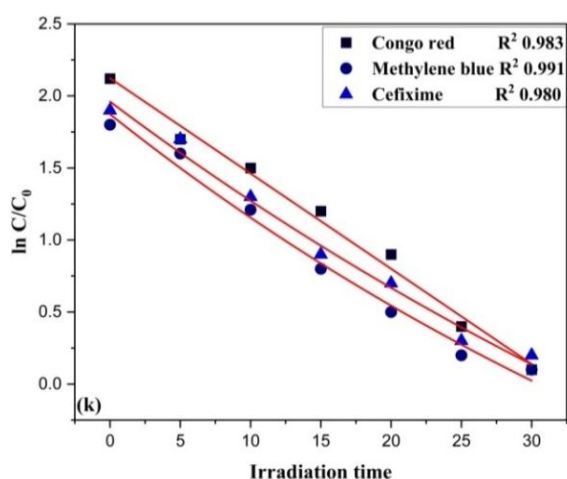


Figure 8.8: (k) Kinetic studies on the degradation of Congo Red, Methylene Blue and Cefixime.

8.3.9 Adsorption isotherm study

This study employed four well-known isothermal models: Freundlich, Temkin, Dubinin-Radushkevich (D-R), and Langmuir to examine the dye's adsorption behavior. These models provide valuable information on the adsorption mechanism, capacity, and affinity, which are essential for designing efficient adsorption systems for dye removal (Handayani *et al.*, 2024).

Langmuir isotherm

According to the Langmuir isotherm model, adsorption can only occur in a saturated monolayer with a finite number of equivalent-energy adsorption sites on the adsorbent surface Figure 8.9 (a). In contrast, the Freundlich isotherm model assumes that multilayer adsorption occurs on a heterogeneous surface with a variable energy distribution (Shahbazkhany *et al.*, 2022). The Temkin isotherm model, derived from a different perspective, assumes a linear decrease in heat of sorption with coverage, unlike the logarithmic relationship implied in the Freundlich equation. This model accounts for indirect dye-adsorbent interactions, which reduce the heat of adsorption

linearly as the molecular layer forms (Bameri *et al.*, 2022). The linear form of the Langmuir isotherm is expressed as equation 8.11 (Lianmawii & Singh, 2023):

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (8.11)$$

C_e/q_e is plotted against C_e , resulting in a linear relationship, where: C_e = equilibrium concentration of dye, q_e = amount of dye sorbed per gram of sorbent, q_m = maximum amount of dye sorbed per gram of sorbent, b = constant related to adsorption energy.

Freundlich Isotherm

The Freundlich isotherm model, widely recognized for describing multilayer formation and surface heterogeneity of sorbents, was also applied in this study Figure 8.9 (b). This model accounts for heterogeneous adsorption, where the adsorption capacity increases, but the binding surface energy decreases exponentially, indicating multilayer adsorption. The Freundlich model is frequently employed to describe the adsorption of organic compounds and dyes onto heterogeneous surfaces, including activated carbon and other porous materials. This model can optimize adsorption operations since it improves understanding of the sorbent's surface characteristics and adsorption behavior. The linear form is given by equation 8.12 (Naghizade Asl *et al.*, 2016):

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (8.12)$$

The Freundlich model fits the data, with K_f (L/g) representing the adsorption capacity and bonding energy. $1/n$ indicating the adsorption type: Favorable: $0 < 1/n < 1$, Irreversible: $1/n = 0$, Unfavorable: $1/n > 1$, the values of K_f and $1/n$ were determined from the plot of $\ln(q_e)$ vs $\ln(C_e)$.

Temkin isotherm

Additionally, the equilibrium data were fitted to the Temkin isotherm Figure 8.9 (c), which considers two important factors: a direct decrease in the adsorption temperatures of all adsorbate molecules as coverage increases as a result of interactions between the adsorbent and the adsorbate. An analogous distribution of

binding energies at the sorbent surface implies a uniform distribution of adsorption sites. The Temkin isotherm accounts for the interactions between the adsorbent and adsorbate by assuming that the adsorption heat reduces linearly as the surface coverage rises. This indicates a homogenous distribution of binding energies. This model offers an insight into the sorbent's surface characteristics and the adsorption mechanism. This relation provides a mathematical statement for this model equation 8.13 (Ayawei *et al.*, 2017), (Alkaim *et al.*, 2015):

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (8.13)$$

$B_T = (R_T/b_T)$, where R is the gas constant ($8.314 \text{ J/mol}^{-1}\text{K}^{-1}$) and T is the absolute temperature, b_T (unitless) and B_T (J/mol^{-1}) are related to the heat of adsorption, A_T is the equilibrium binding constant, representing the maximum binding energy. The linear plot of q_e vs $\ln(C_e)$ allows the determination of the constants A_T and B_T .

Dubini- Radushkevich (D-R) isotherm

The Dubinin-Radushkevich (D-R) isotherm, which assumes a heterogeneous surface and non-uniform biosorption potential, was applied to the equilibrium data to determine the adsorption type (physical or chemical), Figure 8.9 (d). The linearized form of the isotherm is expressed as equation 8.14 (A. E. A. A. Said *et al.*, 2020):

$$\ln q_e = \ln Q_m - \beta \varepsilon^2 \quad (8.14)$$

in this equation, q_e and Q_m were specified as in the former isotherms. β is a constant and linked to mean free energy of adsorption, and ε is the Polanyi potential and can be mathematically represented as equation 8.15:

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \quad (8.15)$$

However, the mean free energy (E), "which is the free energy when one mole of dye transferred from infinity in the solution to the surface of the adsorbent", can be evaluated as equation 8.16:

$$E = -(2\beta)^{1/2} \quad (8.16)$$

The calculated E value of 9.43 kJ/mol falls within the 8-16 kJ/mol range, indicating that the adsorption process is primarily chemisorption. This suggests that the pollutants form chemical bonds with the adsorbent surface, producing more robust and specific interactions. Therefore, the results imply that the adsorbent surface exhibits chemical reactivity towards the pollutants, leading to a chemisorption mechanism.

The adsorption data for Congo Red, Methylene Blue, and Cefixime are optimally described by the Langmuir isotherm model, as evidenced by the high coefficient of determination (R^2) values of 0.986, 0.991, and 0.979, respectively, and favorable separation factor (R_L) values of 0.956, 0.977, and 0.949, indicative of a monolayer adsorption process. This suggests that the adsorbent exhibits a high affinity for these compounds, thereby demonstrating its potential efficacy in removing these pollutants from wastewater through a monolayer adsorption mechanism characterized by a high adsorption capacity (Q_m).

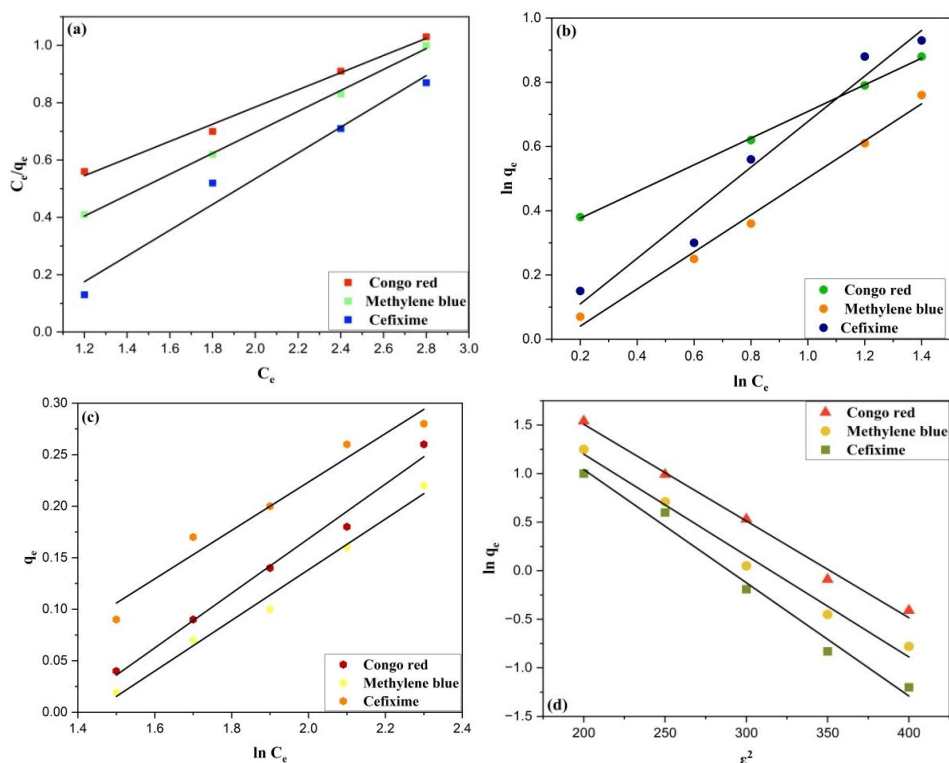


Figure 8.9: (a-d). Langmuir, Freundlich, Temkin and Dubbin-Radushkevich adsorption isotherms of Congo Red, Methylene Blue and Cefixime.

Table 8.4: Parameters of the applied isotherms for the adsorption of Congo Red, Methylene Blue and Cefixime.

Isotherm model	Parameters	Congo Red	Methylene Blue	Cefixime
Langmuir	Q_m	176.66	189.90	178.61
	R_L	0.956	0.977	0.949
	R^2	0.986	0.991	0.979
Freundlich	K_F (mg g ⁻¹)	5.076	5.129	5.288
	1/n	0.971	0.966	0.953
	R^2	0.958	0.948	0.959
Temkin	A_T (L mg ⁻¹)	4.033	4.671	4.648
	B_T (J mol ⁻¹)	3.245	2.908	3.224
	b_T	871.34	798.90	778.31
	R^2	0.941	0.952	0.948
Dubbin-Radushkevich	Q_m (mg g ⁻¹)	6.678	6.322	5.098
	B (mol ² (kJ) ⁻²)	0.008	0.007	0.019
	E (kJ mol ⁻¹)	7.433	8.430	9.412
	R^2	0.946	0.953	0.965

8.3.10 Kinetic Study

The adsorption kinetics was assessed in this study to identify the kind and rate of adsorption, among other adsorption behaviors. Four kinetic models were applied and studied; numerous factors related to the solid's state and the physicochemical conditions that allow for adsorption have a significant influence on the rate of adsorption (Valizadeh *et al.*, 2016), (Ayodhya & Veerabhadram, 2018b). Measurement of the photocatalysis rate is also crucial for developing and evaluating the catalyst's effectiveness in removing pollutants from solutions, as photocatalysis is

a time-dependent process. These include "pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models".

Linear form of Pseudo first order kinetic model (Ahmadi *et al.*, 2020):

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (8.17)$$

The quantity of dye adsorbed (mg g^{-1}) at a given time is denoted by q_t , while the particular rate constant of the first adsorptive step is represented by k_1 . It was possible to determine the k_1 and q_e values by examining the slope and intercept of $\log (q_e - q_t)$ vs t given in Figure 8.10 (a).

Pseudo-Second-Order Kinetic Model

According to the PSO kinetic model, the adsorption rate depends on the solute molecules and the adsorbent's adsorptive sites Figure 8.10 (b). It is calculated as the square of the difference between the number of occupied sites at equilibrium and the available sites on the adsorbent. The rate-limiting step occurs when a solute molecule and an adsorptive site establish a chemical bond. The following equation 8.18 can express the PSO kinetic model (Altaleb, 2024).

Linear form of Pseudo-second-order kinetic model (Naiya *et al.*, 2008):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8.18)$$

Plotting t/q_t versus t allowed for the estimation of k_2 and q_e values. At time $t = 0$, the initial sorption rate ($h = k_2 q_e^2$) was calculated using the pseudo-2nd order rate constant value, k_2 .

Linear form of Elovich kinetic model

An extra rate equation based on adsorption capacity is represented by this model Figure 8.10 (c). The linearized formula is provided by equation 8.19 (Handayani *et al.*, 2024), (Bedin *et al.*, 2016):

$$q_t = (\ln(\alpha\beta))/\beta + (\ln(t))/\beta \quad (8.19)$$

In terms of adsorption rate, α is measured in mg/g.min, while β is a constant in mg/mg.

Intraparticle Diffusion Model

Determining the rate-limiting phase in the kinetics of the adsorption cycle is a crucial step in the process. The following is how the experimental kinetic data were fitted to this model equation 8.20 (Qadeer, 2007), (Said *et al.*, 2020):

$$q_t = K_{id}t^{0.5} + C \quad (8.20)$$

where C is the intercept of the plot of q_t versus $t^{0.5}$, which gives an idea of the boundary layer's depth, and K_{id} is the intraparticle diffusion constant ($\text{mg g}^{-1} \text{min}^{0.5}$). The adsorption kinetics of the investigated compounds is most accurately described by the pseudo-first-order model, which indicates a rapid adsorption rate and suggests a strong affinity between the adsorbent and the adsorbates. Furthermore, the adsorption process appears to be governed by a synergistic mechanism involving surface adsorption and intraparticle diffusion, highlighting the adsorbent's potential efficacy for efficiently removing of these pollutants from aqueous solutions. Table 8.5 shows the values of the studied kinetic parameters. The adsorption of pollutants appears to be significantly influenced by intraparticle diffusion, as indicated by the plot in Figure 8.10 (d). Two diffusion linear regions comprise the intraparticle diffusion plot: the first linear region indicates the boundary layer effect (film diffusion) and is connected to the dye's adsorption on the sorbent's surface. The steadily spreading dye to the adsorption site (pore diffusion) is responsible for the second linear segment.

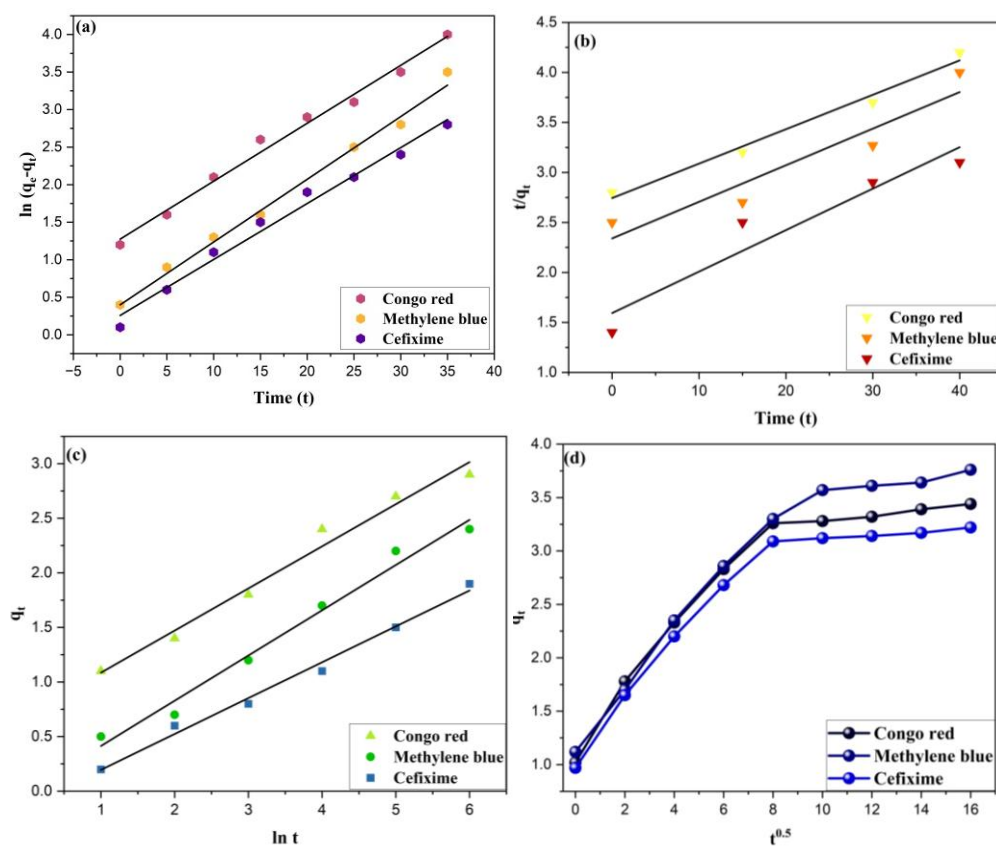


Figure 8.10: Adsorption kinetics of Congo Red, Methylene Blue and Cefixime.

Table 8.5: Kinetic parameter on the adsorption of Congo Red, Methylene Blue and Cefixime.

Kinetic model	Parameters	Congo Red	Methylene Blue	Cefixime
Pseudo first order	q_e (mg g ⁻¹)	2.5678	2.0998	2.4123
	k_1 (min ⁻¹)	0.0211	0.0276	0.0313
	R²	0.998	0.978	0.984
Pseudo second order	q_e (mg g ⁻¹)	4.0500	4.1897	5.2199
	k_2 (g mg ⁻¹ min ⁻¹)	0.0470	0.0499	0.0388

	$h \text{ (mg g}^{-1} \text{ min}^{-1}\text{)}$	0.2445	0.3892	0.3119
	R^2	0.932	0.897	0.901
Elovich	$\alpha \text{ (mg g}^{-1} \text{ min}^{-1}\text{)}$	1.688	1.791	1.888
	$\beta \text{ (mg g}^{-1} \text{ min}^{-1}\text{)}$	3.0877	2.0921	2.1299
	R^2	0.974	0.991	0.981
Intraparticle	Intercept C	0.0412	0.0599	0.0316
	$K_{id} \text{ (mg g}^{-1} \text{ min}^{-0.5}\text{)}$	0.3422	0.3877	0.0411
	R^2	0.971	0.979	0.994

8.3.11 Thermodynamic studies

The thermodynamic parameters of Congo Red, Methylene Blue, and Cefixime have been evaluated at various temperatures (298K, 308K, and 318K), revealing valuable insights into the spontaneity, exothermicity, and entropy changes associated with these reactions given, in Figure 8.11. The observation of uniformly negative ΔG° values across all three compounds at each temperature indicates that their degradation reactions are thermodynamically spontaneous, proceeding without external energy input (Handayani *et al.*, 2024). The negative ΔH° values corroborate the exothermic nature of these reactions, characterized by the liberation of heat energy into the surroundings given in Table 8.6. Furthermore, the positive ΔS° values provide evidence of an increase in molecular disorder or randomness attendant upon the degradation process. Notably, the ΔG° values exhibit a temperature-dependent trend, becoming increasingly negative with rising temperature, thereby underscoring the enhanced thermodynamic favorability of these degradation reactions at elevated temperatures. These findings conclusively demonstrate that the degradation reactions of Congo Red, Methylene Blue, and Cefixime are spontaneous, exothermic, and accompanied by an increase in molecular disorder.

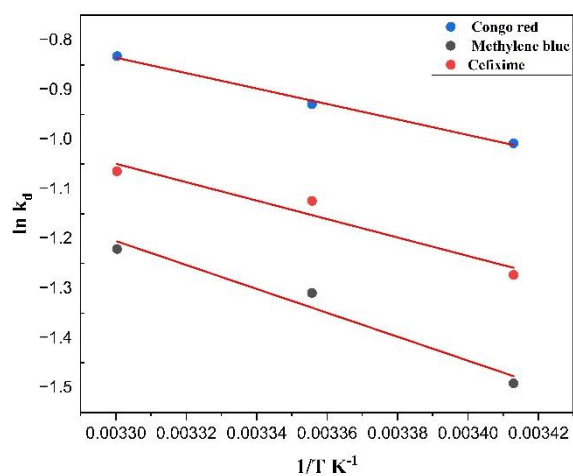


Figure 8.11: Thermodynamic parameters for Congo Red, Methylene Blue and Cefixime.

Table 8.6: Thermodynamic parameter on Congo Red, Methylene Blue and Cefixime.

Sample	Parameter	Temperature		
		298K	308K	318K
Congo Red	ΔG° (kJmol ⁻¹)	-0.548	-0.668	-0.743
	ΔH° (kJ mol ⁻¹)	-20.03		
	ΔS° (JK ⁻¹ mol ⁻¹)	56.036		
Methylene Blue	ΔG° (kJmol ⁻¹)	-0.685	-0.801	-0.866
	ΔH° (kJ mol ⁻¹)	-15.44		
	ΔS° (JK ⁻¹ mol ⁻¹)	42.24		
Cefixime	ΔG° (kJmol ⁻¹)	-0.889	-0.978	-1.095
	ΔH° (kJ mol ⁻¹)	-12.94		
	ΔS° (JK ⁻¹ mol ⁻¹)	35.75		

8.3.12 Reusability

The CoS:Ce³⁺ catalyst demonstrated exceptional reusability and stability over five consecutive cycles, maintaining a high catalytic activity level Figure 8.12. However, a notable decrease in transformation was observed after the fifth cycle, indicating a decline in catalytic performance. This decrease can be attributed to the cumulative effects of prolonged use and repeated washing, leading to the deactivation of active sites on the catalyst surface and the leaching of active species, such as Ce³⁺, from the surface. The excellent reusability of the CoS:Ce³⁺ catalyst over four cycles highlights its potential for sustainable and efficient esterification reactions. The slight decrease in activity after the fourth cycle suggests that the catalyst may require regeneration or replacement to maintain optimal performance. Further studies can focus on optimizing the catalyst's regeneration conditions to extend its lifespan and maintain its catalytic activity. This research demonstrates the feasibility of using CoS: Ce³⁺ as a reusable catalyst for esterification reactions, thereby contributing to the development of more sustainable and efficient chemical processes.

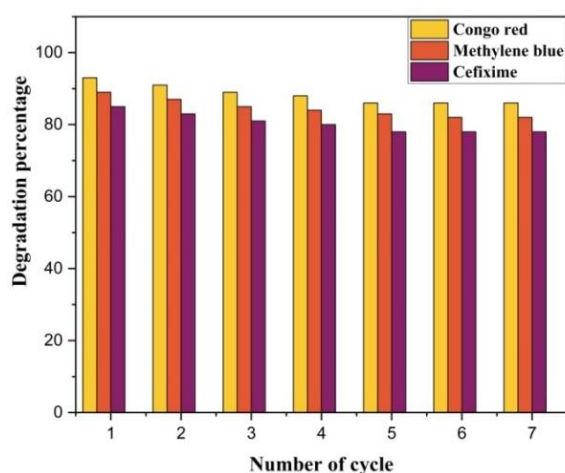


Figure 8.12: Reusability of Congo Red, Methylene Blue and Cefixime.

8.4 Conclusion

In this study, we demonstrated the photocatalytic activity of CoS:Ce³⁺ nanoparticles for the degradation of Congo Red, Methylene Blue, and Cefixime, achieving high degradation efficiencies within a short timeframe of 25 minutes. The optimal

performance was observed at a Ce^{3+} concentration of 0.50 at.%, which was attributed to the enhanced optical and electronic properties of the nanoparticles. Moreover, the catalyst exhibited excellent reusability and stability over four consecutive cycles, maintaining its high catalytic activity. The adsorption kinetics of the dyes onto $\text{CoS}:\text{Ce}^{3+}$ nanoparticles were found to follow both the first-order kinetic model. The $\text{CoS}:\text{Ce}^{3+}$ nanostructures exhibit a complex pore system, high surface area, and enhanced surface activity, making them suitable for various applications. The Langmuir model was also applicable, indicating monolayer adsorption. The findings of this investigation highlight the potential of $\text{CoS}:\text{Ce}^{3+}$ nanocomposites as a cutting-edge technology for the remediation of industrial wastewater. The nanoparticles exhibited remarkable degradation efficiency, unaffected by the complex water matrix, highlighting their potential for wastewater treatment applications. This suggests that the catalyst exhibits selectivity towards the degradation of these pollutants and has potential for real-world applications.

CHAPTER 9

Enhanced Photocatalytic and Photoluminescence Properties of NiS Doped with Pr³⁺ for Efficient Dye Degradation: Kinetics and Isotherm Studies

9.1 Introduction

The hazardous pollution of the aquatic environment is becoming a significant concern. Various chemicals, including colours, antibiotics, pesticides, steroid hormones, and others, have entered the aquatic environment due to fast development in the agricultural, pharmaceutical, and chemical industries. Pharmaceutical factories and hospitals generate substantial amounts of hazardous wastewater containing pigments, colours, pharmaceuticals, and chemical disinfectants (Ebert *et al.*, 2011). Pharmaceutical residues and metabolites can enter wastewater through manufacturing operations, research activities, and the excretion of unused medicines by patients. Even at low doses, some medications can be detrimental to aquatic life (Yagub *et al.*, 2014). Chronic exposure to these compounds may have negative environmental impacts. Due to their widespread use and large-scale global production, synthetic organic dyes have a significant impact on the environment. The paper, textile, and tannery industries consume substantial quantities of water and are responsible for its contamination by discharging large amounts of wastewater into aquatic environments (Liu *et al.*, 2020). Synthetic organic dye pollution from industries such as textiles, tanneries, and paper manufacturing is a major environmental concern. These industries frequently consume significant amounts of water and produce large volumes of effluent containing a variety of contaminants, including synthetic colours. Synthetic organic dyes are widely used for colouring and finishing items in the textile, tannery, and paper industries. Due to their complex chemical structures and brilliant colours, synthetic dyes can be challenging to remove from wastewater. The production of dye-containing wastewater is a significant environmental issue associated with various industrial operations, particularly in the textile industry. The extensive production and consumption of synthetic organic dyes result in a hazardous aquatic environment. A large amount of dye-containing industrial effluent (up to 50% in some situations) is frequently

dumped directly into water ecosystems without sufficient treatment (Kant, 2012). The wastewater generated by textile companies during the dyeing process is the most polluting agent in all water sources. Effluents containing dyes from the textile industry are brightly pigmented and thus immediately visible. Several dyes can be detected in water at concentrations as low as 1 mg/L (Å *et al.*, 2007). A wide range of hazardous chemicals are included in dye wastewater discharge. Azo dyes account for more than seventy percent of all dyestuffs by weight. Azo dye intermediates are exceedingly poisonous and mutagenic, providing a major health risk to people. Dyes and pigments are frequently used in a wide range of industries and a significant amount of these colouring compounds end up in effluent water during the dyeing process (Cheng *et al.*, 2018). Dyes can be hazardous to aquatic organisms, especially in more significant quantities. Some colours have the potential to bioaccumulate in organism tissues, resulting in contamination translocation via the food chain. This bioaccumulation can endanger higher trophic levels, such as those of predators and humans. Improper disposal of dye-containing effluents or garbage can pollute groundwater. Dyes and their breakdown products can leak into groundwater and contaminate it. Dyes can alter the colour of water, reducing light penetration and impacting the photosynthetic activity of aquatic plants. The carcinogenic and potentially hazardous nature of these chemicals poses an increasing threat to aquatic life.

As a result, numerous physicochemical methods for colour removal have been developed, including oxidation, precipitation, coagulation, adsorption, and filtering (Muthirulan *et al.*, 2017). Malachite green (MG) is a water-soluble cationic organic colour with the chemical formula $C_{52}H_{54}N_4O_{12}$. According to a specific source, MG has a variety of adverse effects on the human body due to its high toxicity, as well as being teratogenic, carcinogenic, and mutagenic. Side effects of intravenous Methylene Blue include nausea, vomiting, headaches, dizziness, and a blue staining of the urine and skin. Methylene Blue dye (MB) is a prevalent cationic dye, mutagenic, persistent, hazardous, and carcinogenic in the environment. MB is a synthetic dye that is commonly used in the garment and textile industries, as well as in colour papers and leathers (Murugadoss *et al.*, 2022). As a result, it is vital to

completely degrade these organic pollutants/dyes in wastewater while developing a semiconducting photocatalyst-mediated accelerated oxidation process. An innovative oxidation method used for degrading organic dyes has gained attention (Augugliaro *et al.*, 2006). AOPs (Advanced Oxidation Processes) are effective ways of degrading organic dyes and other contaminants in water and wastewater. Organic molecules can be effectively degraded and mineralized through the powerful action of hydroxyl radicals ($\cdot\text{OH}$) and other oxidizing species. These radicals are highly reactive and can start the oxidation of organic molecules. Hydroxyl radicals attack the organic molecules in dyes, breaking chemical bonds and forming intermediates. Hydroxyl radicals attack the organic molecules in dyes, breaking chemical bonds and forming intermediate intermediates. The mineralization of organic dyes by AOPs is advantageous to the environment since it lessens the dye components persistence and toxicity. End products are primarily non-toxic and pose little risk to aquatic ecosystems (Khan *et al.*, 2020). As a developing and efficient wastewater treatment approach, the advanced oxidation process has the advantages of no secondary contamination and high mineralization efficiency. The foundation for these reactions is the production of highly reactive hydroxyl radicals in response to light. Hydroxyl radicals fully oxidize organic compounds into water, CO_2 , and inorganic molecules. Dye degradation is influenced by factors including pH, catalyst concentration, substrate concentration, oxidant presence, temperature, and light intensity (Ramki *et al.*, 2020).

This study examines the degradation of RhB, MB, MO, and Congo Red organic dyes using NiS doped Pr^{3+} nanoparticles as a catalyst. Although praseodymium (the third member of the lanthanide series) is expensive to process, it has significant electrical, chemical, optical, and magnetic properties. Rare earth metals have been used to produce of medications, agricultural enhancements, and livestock feed. Lanthanide elements, such as praseodymium, are renowned for their distinct electrical characteristics, which could be useful in catalytic processes.

9.2 Experimental details

9.2.1 Sample preparation

NiS-doped Pr^{3+} nanoparticles were synthesized by dissolving nickel (III) nitrate hexahydrate, $\text{Ni}(\text{NO}_3)_3$, in 60 ml of distilled water and stirred for 1 hour at room temperature. Sodium sulfide was added to the preceding solution while stirring constantly. Drop by drop, praseodymium (III) chloride – PrCl_3 was added as a dopant. The entire solution was refluxed for 48 hours, constantly stirred throughout. The reflux method was used to keep the solution from evaporating. Reflux provides a controlled and steady temperature environment for the reaction. This is significant for nanoparticle synthesis, as temperature has a profound influence on particle size, shape, and crystallinity. The ability to maintain precise reaction conditions enhances the repeatability of synthesis. The precipitate was centrifuged at 7500 rpm in the presence of alcohol and acetone. Centrifugation efficiently separates nanoparticles from reaction mixtures or suspensions. This is especially significant when separating and purifying nanoparticles from unreacted precursors, byproducts, or contaminants, resulting in a more refined and purer nanoparticle product. After the nanoparticles had settled, the samples were dried and heated at 150 °C before use.

Solution preparation for adsorption tests, isotherm analysis, and adsorption kinetics: Following adsorption, the resultant supernatant was analyzed by measuring the adsorbate solutions' UV-vis absorption spectra at their maximum absorption wavelength. Rhodamine B (RhB), Methylene Blue (MB), Methyl Orange (MO), and Congo Red have maximal absorption wavelengths of 554 nm, 662 nm, 465nm, and 498 nm, respectively. A Ph metre and (0.1 M) HCl and (0.1 M) NaOH solutions were used to determine the Ph of the adsorption media. The maximum adsorption capacity of the adsorbents was measured by dispersing 10mg of catalyst in 30 Ml of various dye concentrations with continuous stirring for 2 hours.

Adsorption parameter calculation and statistical error analysis of isotherm and kinetic model data: Adsorption capacity denotes the amount of adsorbate adsorbed on the catalyst. The following formulas are used to compute the adsorption capacity (q_e) and adsorption efficiency (%) given in equations 9.1 and 9.2:

$$q_e \text{ (mg g}^{-1}\text{)} = \frac{C_0 - C_e}{M} \times V \quad (9.1)$$

$$\text{Adsorption efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (9.2)$$

C_0 : The initial concentration of the adsorbate in the solution, commonly measured in moles per litre (mol/L) or other concentration units. C_e : The equilibrium concentration of the adsorbate in the solution, measured in moles per litre or other concentration units. This is the concentration attained after the adsorption process has reached equilibrium. M : The mass of the dried adsorbent, usually measured in grams (g). V : The volume of the solution, which is commonly expressed in litres (L). Three statistical models were studied to identify the best-fit models for isotherm and kinetics experimental data: the chi-square test (χ^2), the sum of square error (SSE), and the coefficient of determination (R^2). A significantly lower value of SSE and χ^2 , and the highest R^2 indicates a higher agreement between computed and experimental data. χ^2 and SSE are given in equations 9.3 and 9.4:

$$\chi^2 = \sum_{i=1}^n \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \quad (9.3)$$

$$\text{SSE} = \sum_{i=1}^n (q_{e,exp} - q_{e,cal})^2 \quad (9.4)$$

Where $q_{e,cal}$ and $q_{e,exp}$ are the quantities of adsorbed adsorbate determined using computed values from the model equation and experiment values at equilibrium, respectively.

9.2.2 Sample characterization

For the synthesis of NiS doped Pr^{3+} nanoparticles nickel (III) nitrate hexahydrate $\text{Ni}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, sodium sulfide $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and praseodymium (III) chloride – PrCl_3 were purchased from Sigma-Aldrich (USA) and used without purification. The experiments were carried out with double-distilled water. An X-ray diffractometer (Rigaku Smart Lab 9Kw rotating X-ray diffractometer) in the range $10\text{--}70^\circ$ was used to study the structure of the synthesized nanoparticles. The phase of the nanoparticles was validated by comparing of main peak positions recorded in the standard JCPDS database. FTIR data was obtained using a Shimadzu scientific instrument. SEM was

performed using a Zeiss Gemini SEM. After preheating the samples for 6 hours at 130 °C, BET experiments were done to measure the specific surface area (BELSORP MINIX). Room temperature photoluminescence emission spectra were recorded using a Hitachi F-7000 fluorescence spectrophotometer with Xenon lamp excitation. The photocatalytic properties of the synthesized materials were evaluated using an Evolution 220 UV-Visible spectrophotometer, which covers a wavelength range of 190-1100 nm.

9.3 Results and discussions

9.3.1 X-ray diffraction (XRD)

Figure 9.1 illustrates the X-ray diffraction data sets of the powdered materials obtained at room temperature. The presence of (200), (210), (211), (220), (221), and (311) indicates the cubic shape of NiS nanoparticles from Joint Committee on Powder Diffraction Standards (JCPDS) No: 89-7142. The lattice parameters and atom arrangement in a cubic crystal structure are such that the unit cell has equal sides and all angles are 90 degrees. Miller indices (*hkl*) represent distinct crystallographic planes in a crystal structure. The existence of these planes in the XRD pattern indicates that the nickel sulfide nanoparticles have a cubic crystal structure. JCPDS No: 89-2921 confirms the presence of praseodymium at planes (100) and (101). The particle size was calculated using the Scherrer equation 9.5: (N.Singh *et al.*, 2020).

$$D = \frac{K\alpha}{\beta \cos \theta} \quad (9.5)$$

D is the average crystallite size, *K* is the Scherrer constant (0.9), *α* is the wavelength of the X-rays or neutrons, *β* is the full width at half maximum (FWHM) of the diffraction peak, and *θ* is the Bragg angle (the angle at which diffraction occurs). The Scherrer equation calculates average crystallite size and assumes crystallites have a spherical shape. The particle size calculated was found to be 12-19 nm. The values of lattice constants were derived using XRD data for all samples, and the values of lattice constants are reported in Table 9.1. XRD patterns from the (200) plane revealed that the diffraction peaks become broader as the Pr³⁺ level increases, as

shown in Table 9.2. This implies that the crystallite size grows as the dopant content increases.

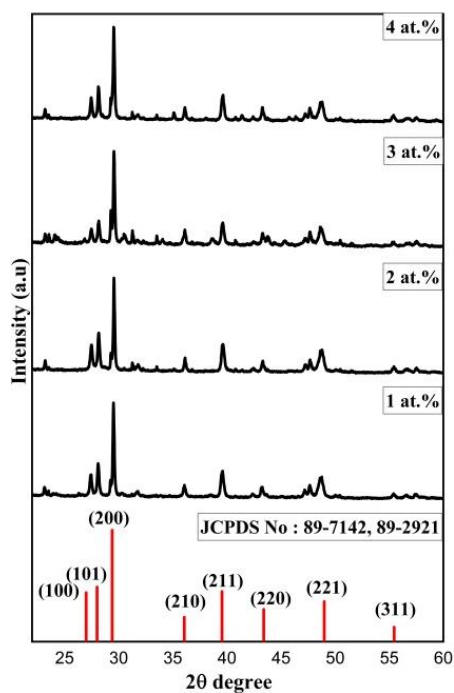


Figure 9.1: XRD pattern for NiS doped Pr^{3+} (1 at.%, 2 at.%, 3 at.%, 4 at.%).

Table 9.1: Lattice parameter, cell volume and particle size of NiS doped Pr^{3+} (1 at.%, 2 at.%, 3 at.%, 4 at.%).

Sample	Lattice parameter Å	Cell volume v (Å ³)	Particle size
	(Standard from JCPDS No. 89-7142) – 5.678	(Standard from JCPDS No. 89-7142) – 183.93	(nm)
1 at.%	5.632	183.66	12.12
2 at.%	5.671	183.50	14.89
3 at.%	5.552	183.88	17.33
4 at.%	5.598	183.90	19.45

Table 9.2: Comparison of 2θ values for Pr^{3+} for NiS doped Pr^{3+} (1 at.%, 2 at.%, 3 at.%, 4 at.%).

Nickel Sulfide (Cubic)			Standard	1 at. %	2 at. %	3 at. %	4 at. %
h	k	l	2θ	2θ	2θ	2θ	2θ
2	0	0	31.435	32.212	32.451	32.511	32.533

9.3.2 Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM)

SEM image of NiS doped Pr^{3+} 4 at. % is shown in Figure 9.2 (a). The non-spherical and irregular morphology of nanoparticles, coupled with their propensity to fuse into larger aggregates, can be attributed to kinetic and thermodynamic factors during synthesis, particularly rapid nucleation, inadequate growth control, or insufficient stabilization, which disrupt the equilibrium shape and facilitate the formation of anisotropic particles. Rapid particle aggregation can occur if the solvent evaporates too quickly. Electrostatic attractions may cause aggregation of nanoparticles with surface charges. The average particle size calculated using J imaging software was 25 nm, as shown in Figure 9.2 (b). Figure 9.2(c) presents the Energy-Dispersive X-ray (EDX) spectrum, which confirms the presence of nickel (Ni), sulfide (S), and praseodymium (Pr) elements in the sample, indicating a complex composition.

Transmission Electron Microscopy (TEM) is an excellent technique for characterizing and validating the properties of nanoparticles, including size, shape, and crystal structure. This is crucial for determining the intended size range of the synthesized particles. The nanoparticle size was determined from a 4 at.% TEM image, which was found to be 21 nm, as shown in Figure 9.2 (d). Figure 9.2€ presents the Selected Area Electron Diffraction (SAED) pattern, providing insight

into the crystal structure of the material. The SAED pattern exhibits distinct diffraction rings corresponding to specific crystallographic planes in the crystal lattice, characterized by Miller indices (hkl). These rings indicate the presence of a crystalline structure with well-defined lattice planes that diffract electrons. The HR-TEM image at high magnification shows that the distance between the atomic layers was 2.74 Å, corresponding to the d-spacing of the NiS phase's (200) plane, as shown in Figure 9.2 (f). The distance between crystal lattice planes is represented by d-spacing in crystallography. A single phase with good crystallinity was observed at 4 at.%. Praseodymium contributed to the uniformity of particle size distribution. The measured material's crystal lattice structure corresponds to the expected spacing for the NiS (200) plane.

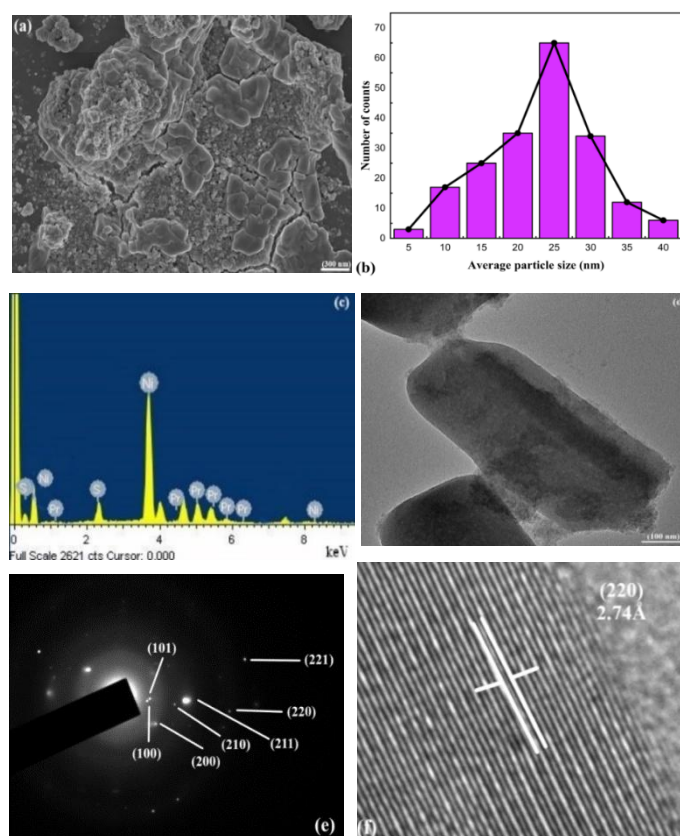


Figure 9.2: (a) SEM image of NiS doped Pr^{3+} 4 at. % (b) Average particle size of NiS doped Pr^{3+} 4 at. % (c) EDX image of NiS doped Pr^{3+} 4 at. % (d) TEM image of NiS doped Pr^{3+} 4 at.% € SAED image of NiS doped Pr^{3+} 4 at. % (f) HR-TEM image of NiS doped Pr^{3+} 4 at. %.

9.3.3 FTIR analysis

The FTIR spectra of NiS doped Pr^{3+} (1 at.%, 2 at.%, 3 at.%, and 4 at.%) are shown in Figure 9.3. The peak at 766 cm^{-1} is due to NiS stretching vibration, indicating the presence of nickel sulfide (NiS) in the nanoparticles. The bands between 857 cm^{-1} and 1104 cm^{-1} are attributed to C-S bond vibrations, implying the presence of carbon-sulfur bonds in the nanoparticles. The bands found at 1415 cm^{-1} are attributed to C-H vibrations, indicating the presence of carbon-hydrogen bonds in the nanoparticles. The existence of adsorbed H_2O molecules is indicated by the absorption bands found at 1634 and 3398 cm^{-1} , which correspond to the vibration of O-H bonds (Gahtar *et al.*, 2022), (Karthikeyan *et al.*, 2015a). The existence of NiS, C-S, C-H, and O-H bonds, as well as adsorbed water molecules, can impact the characteristics and potential applications of nanoparticles in various disciplines, including catalysis, sensing, and others.

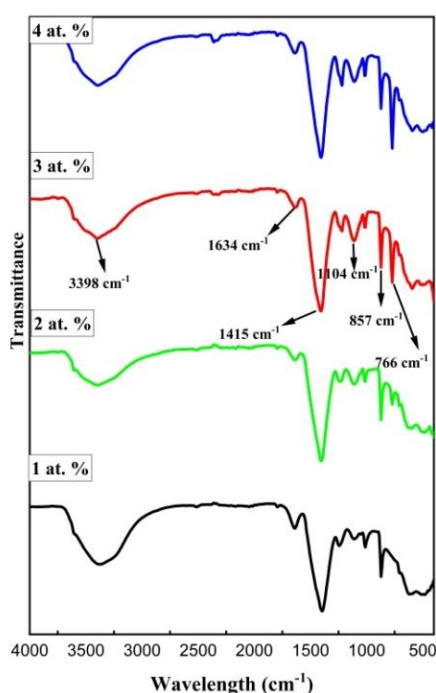


Figure 9.3: FTIR spectra for of NiS doped Pr^{3+} (1 at.%, 2 at.%, 3 at.%, 4 at.%).

9.3.4 Photoluminescence spectroscopy

The emission spectrum of praseodymium involves the emission of light (photons) as electrons within praseodymium atoms shift from higher energy levels to lower energy levels. Figure 9.4 (a) depicts the room temperature emission spectra of NiS doped Pr^{3+} (1 at.%, 2 at.%, 3 at.%, 4 at.%) from 500 to 750 nm when excited at 424 nm. The emission spectrum is composed of six bands, which are assigned to $^3\text{P}_1 \rightarrow ^3\text{H}_5$, $^3\text{P}_0 \rightarrow ^3\text{H}_5$, $^1\text{D}_2 \rightarrow ^3\text{H}_4$, $^3\text{P}_0 \rightarrow ^3\text{F}_2$, $^3\text{P}_0 \rightarrow ^3\text{F}_4$ transitions at 525, 587, 631, 676, and 713 nm, respectively. These transitions are particular to the electronic configuration of praseodymium atoms, and the wavelengths emitted indicate of the energy differences between the involved electronic states (W. Tang *et al.*, 2015), (Cavalli *et al.*, 2015). The luminescence mechanism is that once the Pr^{3+} ion is excited to $^3\text{P}_2$ states, non-radiative de-excitation occurs from $^3\text{P}_2$ to $^3\text{P}_1$, $^3\text{P}_0$, and $^1\text{D}_2$ levels. Finally, photon emission occurs from $^3\text{P}_1$, $^3\text{P}_0$, and $^1\text{D}_2$ to lower-lying states. It has been found that the emission bands at 587 and 631 nm are made up of two spectrally overlapping transitions from the $^1\text{D}_2$ and $^3\text{P}_0$ states (Mitra & Jana, 2015).

The Commission Internationale de l'Eclairage (CIE)

The Commission Internationale de l'Eclairage (CIE) system is a popular way to express colours in terms of colour coordinates. The CIE system is founded on the idea that the human visual system can sense a wide range of colours by stimulating three types of colour receptors, known as the three basic colours: red, green, and blue. Colour is represented in a two-dimensional colour space in the CIE system by chromaticity coordinates, which are generally expressed as (x, y). The tristimulus values, which specify the amounts of the three primary colours required to match a given colour, are used to generate these coordinates. These fundamental colours' respective proportions are represented by the chromaticity coordinates (x, y). We estimated the CIE chromaticity coordinates for Pr^{3+} (1at.%, 2 at.%, 3 at.%, 4 at.%) based on its spectral distribution, as shown in Table 9.3. The chromaticity coordinates of typical white light are (0.33, 0.33) (Access, 2020). The chromaticity coordinates found in this situation are close to the standard value. This implies that

compositions of NiS-doped Pr³⁺ (1 at.%, 2 at.%, 3 at.%, 4 at.%) can yield white light emission and can be employed for solid state lighting, given in Figure 9.4 (b).

Decay lifetime

The decay lifetime of nanoparticles, also known as fluorescence decay or fluorescence lifetime, measures how long a nanoparticle stays excited before reverting to its ground state by emitting a photon. Time-correlated single photon counting (TCSPC) or frequency-domain techniques can be used to empirically calculate the decay lifespan. For many occurrences, the time between the excitation pulse and the detection of emitted photons is recorded in TCSPC. The data is then fitted to a decay curve to determine the decay lifetime. The decay curves were measured by setting the excitation wavelengths for each concentration to 424 nm. Figure 9.4 € depicts the decay curves that were measured. All of the reported decay curves are well fitted by the biexponential equation 9.6 (Premjit Singh *et al.*, 2019):

$$I = I_1 \exp (-t/\tau_1) + I_2 \exp (-t/\tau_2) \quad (9.6)$$

where I_1 and I_2 are the intensities at two distinct periods and τ_1 and τ_2 are the decay times. A nanoparticle's bi-exponential decay behavior is primarily caused by the inhomogeneous distribution of doping ions within the host lattice, energy transfer from the donor atom and defects presents in the host, and impurity. Nanoparticles increased surface effects, quantum confinement, and specific defect states can cause changes in luminous characteristics and decay behavior. Separate time constants may be involved in the energy transfer process for separate paths, resulting in a bi-exponential decay. The average lifetime (* τ) value is then possible to calculate using the following equation 9.7:

$$* \tau = I_1 \tau_1^2 + I_2 \tau_2^2 / I_1 \tau_1 + I_2 \tau_2 \quad (9.7)$$

The average lifespan values for NiS-doped Pr³⁺(1 at.%, 2 at.%, 3 at.%, 4 at.%) derived using the above equation were 1.72, 1.83, 1.94, and 1.92 ms, respectively, and their goodness of fitting (R^2) for the above concentrations is 0.961, 0.972, 0.988, and 0.992. The lifespan values decrease as the concentration of Pr³⁺ ions increases, possibly due to the concentration quenching effect.

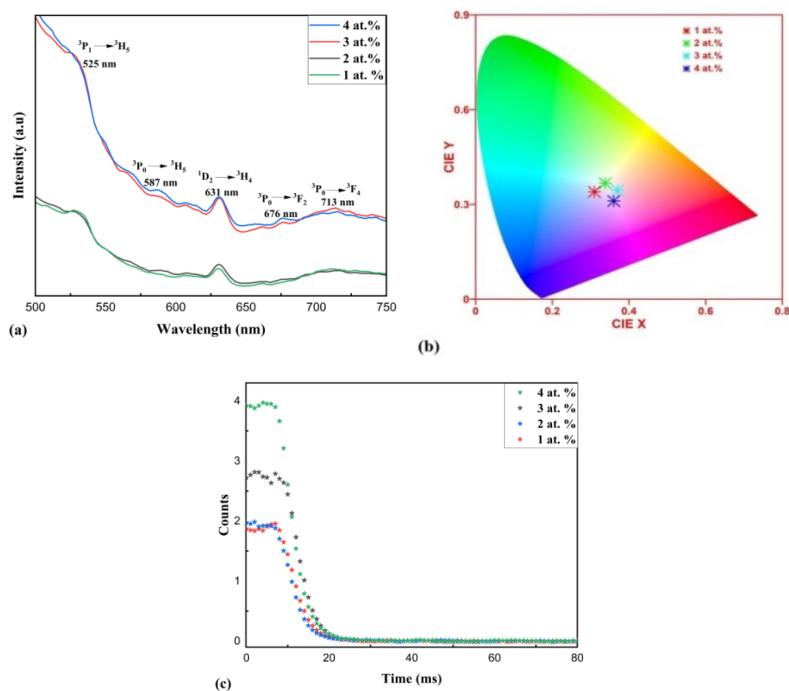


Figure 9.4: (a) Emission spectra of NiS doped Pr^{3+} (1 at.%, 2 at.%, 3 at.%, 4 at.%) (b) CIE image of NiS doped Pr^{3+} (1 at.%, 2 at.%, 3 at.%, 4 at.%) (c) Decay lifetime of NiS doped Pr^{3+} (1 at.%, 2 at.%, 3 at.%, 4 at.%).

Table 9.3: CIE coordinates of NiS doped Pr^{3+} (1 at.%, 2 at.%, 3 at.%, 4 at.%).

Sample	CIE coordinates		CCT
	x	y	
1 at. %	0.310	0.340	6570
2 at. %	0.338	0.367	5294
3 at. %	0.370	0.347	4094
4 at. %	0.360	0.311	4158

9.3.5 BET analysis

The nitrogen adsorption-desorption isotherms surface area of NiS doped Pr^{3+} (1 at.%, 2 at.%, 3 at.%, 4 at.%) were measured and revealed surface area values of 17.43, 21.04, 23.49, and 24.2 m^2/g respectively given in Figure 9.5. The statistics show that the surface area increases as Pr^{3+} concentration increases. The increased surface area of the nanoparticles enhances their catalytic activity. Nanoparticles have a high

surface-to-volume ratio, and as surface area increases, so does the number of active sites available for catalytic reactions. The increased density of active sites allows more reactant molecules to adsorb and participate in catalytic processes. The increased surface area enables improved adsorption of reactants onto the surface of the nanoparticle, enabling catalytic reactions (Mohanta *et al.*, 2021), (Farooq *et al.*, 2019). Furthermore, greater surface area can facilitate product desorption from the catalyst surface, avoiding the accumulation of reaction intermediates and increasing catalytic turnover. Small nanoparticles with large surface areas may have a higher fraction of surface atoms involved in catalysis, resulting in increased reactivity (Azeez *et al.*, 2018). The porosity of materials is also considered in the BET surface area measurement. Nanoparticles with well-defined pore architectures can give more places for reactants to interact with the catalyst, altering catalytic activity.

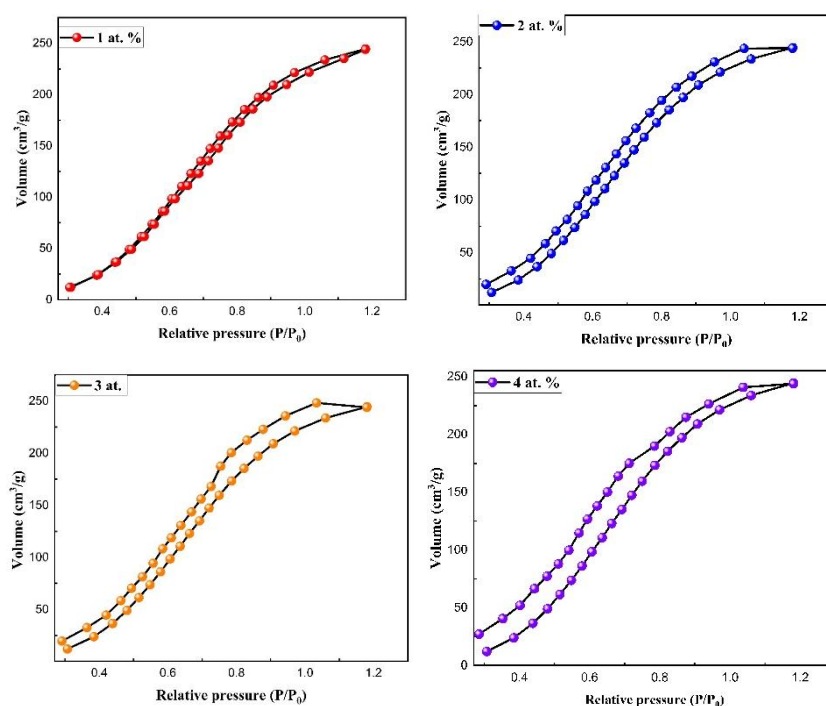


Figure 9.5: BET analysis of NiS doped Pr³⁺ (1 at.%, 2 at.%, 3 at.%, 4 at.%).

9.3.6 UV- Optical studies

UV-visible (UV-Vis) spectroscopy is a frequently employed analytical method that quantifies the amount of ultraviolet and visible light absorption by a material. UV-Vis spectroscopy focuses on electronic transitions. When a molecule absorbs UV or visible light, it moves from a lower energy (ground) to a higher energy (excited) state. A UV-visible spectrum of the sample is taken in the wavelength range of 200 nm to 600 nm, as shown in Figure 9.6(a). The bandgap energy is calculated using Tauc plot equation 9.8 (Kamble *et al.*, 2020):

$$\alpha = k (h\nu - E_g)^n / h\nu \quad (9.8)$$

Where ν is the frequency, h is Plank's constant, k and n are constants. The value of n is 2, where the band gap was found to be 4.32 – 4.62 eV, as shown in Figure 9.6 (b). The primary goal of this research is to utilize catalysts as photocatalysts for the photodegradation of harmful dyes found in wastewater, such as Rhodamine B, Methylene Blue, Methyl Orange, and Congo Red. By adjusting various catalytic parameters (amount of catalyst, optimization of different percentages, and study of different Ph levels), the photocatalytic removal effectiveness of the as-obtained catalyst was investigated.

Optimization of catalyst and the effect of light source on Rhodamine B, Methylene Blue, Methyl Orange, and Congo Red dyes.

The atomic percentages of a catalyst were evaluated to determine their impact on a specific characteristic or performance indicator. The optimization of several atomic percentages was carried out, and based on the results, it was concluded that 4 at.% is the most favourable catalyst for degradation of different dyes shown in Figure 9.6. Three various lighting conditions were used in the research to find the most effective lighting source for the best photo-degradation of dyes: dark, visible light, and UV-irradiation. The catalyst degraded only 12%, 15%, 8%, and 11% of Rhodamine B, Methylene Blue, Methyl Orange, and Congo Red dyes, respectively, under dark conditions. Furthermore, degradation data from visible light and UV-irradiation experiments are compared; the results show that dye removal under UV

light is substantially higher than degradation under visible light. The synthesized catalyst destroys 98.7% of Rhodamine B dye when exposed to UV light, significantly greater than visible light. Similarly, Methylene Blue dye demonstrated 96.12% breakdown activity when exposed to UV light vs visible light. Similarly, UV irradiation degraded 94% of Methyl Orange and 90% of Congo Red. According to the findings, the degradation of dyes in the presence of UV irradiation is greater than that in the presence of visible light, as shown in Figure 9.6(d). UV light's higher energy and specific wavelength ranges make it more effective for photo-degradation of dyes compared to visible light. UV radiation excites electrons in dye molecules to higher energy states, facilitating bond breakage and degradation. This excitation is more pronounced in UV light due to its higher energy.

The effect of catalytic dosage of Rhodamine B, Methylene Blue, Methyl Orange, and Congo Red dyes.

The optimal photocatalyst dosage is a significant factor impacting removal activity. Consequently, the catalyst concentration for dye removal efficiency was examined by raising the catalyst dose from 5 to 30 mg/L using UV-irradiation while keeping other parameters, such as lighting source, dye concentration, and Ph, constant. The results show that the photocatalyst dosage used considerable impact on dye removal efficacy, as shown in Figure 9.6 €. When 5 mg catalyst is used, the results show that only 9.37%, 14.85%, 17.40%, and 19.77% of Rhodamine B, Methylene Blue, Methyl Orange, and Congo Red dye degradation are degraded. As expected, increasing the amount of catalyst to 10 and 15 mg resulted in higher degradation of the dyes, respectively. The highest degradation efficiency for dyes was achieved when 20 mg/L of catalyst was used, achieving 89.90%, 91.34%, 94.12% and 97.44%, respectively. The optimal catalyst dosage was determined to be 20 mg, beyond which degradation percentages declined. When there are more active sites in a reaction, there are more areas where chemical reactions can occur. This, in turn, increases the creation of free radicals. An attainable issue develops when the amount of catalyst exceeds a specific limit. This critical limit is defined as the point in the medium where there is insufficient room for the nanoparticles (probably the catalyst) to disperse efficiently. Due to the excessive amount of catalyst, the nanoparticles have

an inadequate surface area to scatter, and as a result, they tend to clump together and agglomerate. The agglomeration of nanoparticles can be attributed to factors such as particle surface energy, which causes particles to attract and form larger clusters. As a result, the majority of active sites were blocked, and photodegradation performance reduced. At a dosage of 20 mg/L, catalyst-dye mixtures showed the best photodegradation efficacy.

The effect of concentrations of Rhodamine B, Methylene Blue, Methyl Orange, and Congo Red on removal activity

The effect of dye concentrations on dye photodecomposition efficacy was investigated by increasing the dye concentrations from 10 to 50 ppm, using UV irradiation while maintaining a constant catalyst dose of 20 mg/L. The degradation data clearly showed that the best elimination efficiency was observed at the lowest concentration 10 ppm. Rhodamine B elimination activity decreased from 91.17% to 21.25% as the Rhodamine B concentration increased from 10 to 50 ppm. Similarly, as Methylene Blue dye concentration increases from 10 to 50 ppm, its photodecomposition efficacy reduces from 88.33% to 23.67%. Similarly, the maximum degradation occurred at 10 ppm for Methyl Orange and Congo Red, which decreased from 92.22% to 44.4% and 89.81% to 24.55%, respectively. The amount of light absorbed by the catalyst surface influences the efficacy of a photocatalytic reaction. If the catalyst cannot absorb light properly, fewer photo-induced reactions will occur, resulting in a loss in overall efficiency. This decrease in light absorption is directly related to an increase in dye concentration. $\cdot\text{OH}$ ions (hydroxide ions) are essential in the photodegradation process. The reduced light absorption on the catalyst's surface influences the production of $\cdot\text{OH}$ ions. The best removal effectiveness was achieved at concentrations of 10 ppm. Hence, dye concentrations of 10 ppm were chosen for future optimization, as shown in Figure 9.6 (f).

Influence of pH on photodecomposition efficacy of Rhodamine B, Methylene Blue, Methyl Orange, and Congo Red

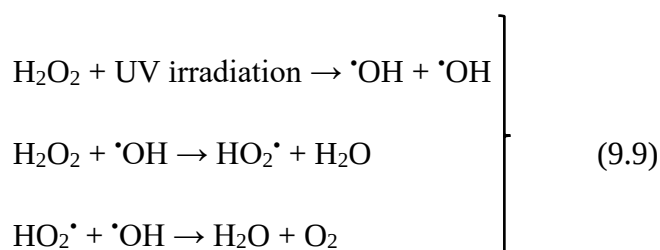
The pH value obviously impacts on the photocatalytic degradation of hazardous dyes, and breakdown effectiveness tends to be related to the amount of hydroxyl radicals ($\cdot\text{OH}$) present in the medium, which greatly enhances photo-degradation efficacy in high pH concentrations. Figure 9.6 (g) displays the impact of pH on the photocatalytic removal of dyes. The effect of solution pH on dye photodecomposition was investigated at three pH levels, ranging from 1 to 10, while maintaining constant other factors (10 ppm dye concentration, 20 mg/L catalyst dosage, and UV irradiation). After 90 minutes, the lowest decomposition performance was obtained at the highest pH value (pH - 10) with degradation percentages of 12.23%, 34.22%, 22.31%, and 12.43% for Rhodamine B, Methylene Blue, Methyl Orange, and Congo Red, respectively. However, by lowering the pH, the catalyst showed greater removal efficacy, degrading 92.33%, 89.78%, 95.55%, and 90.98% of Rhodamine B, Methylene Blue, Methyl Orange, and Congo Red in only 90 minutes at pH 4. At pH 4, the molecular integrity of Rhodamine B, Methylene Blue, Methyl Orange, and Congo Red is compromised due to protonation-induced structural modifications. Rhodamine B undergoes protonation at the xanthene ring nitrogen, resulting in quaternary ammonium ion formation and subsequent degradation. Methylene Blue's dimethylamine groups are protonated, disrupting its electronic structure and facilitating hydrolysis of sulfide bridges between benzene and thiazine rings. Methyl Orange and Congo Red exhibit protonation at their azo linkages ($-\text{N}=\text{N}-$), inducing conformational changes and degradation. The pH 4-induced degradation of Rhodamine B, Methylene Blue, Methyl Orange, and Congo Red is attributed to protonation-mediated structural changes, hydrolysis, and disruption of electron delocalization. Protonation at specific functional groups (xanthene ring nitrogen, dimethylamine, and azo linkages) initiates these degradation pathways.

Effect of H_2O_2

Different amounts of H_2O_2 were used to trigger the degradation dyes with 20 mg/L of the catalyst at room temperature to examine the effect. Adding H_2O_2 is a valuable parameter for enhancing the photocatalytic degradation process, as shown in Figure 9.6 (h). This Figure reveals that increasing the concentration of hydrogen

peroxide to a significant level increases the photocatalytic breakdown rate of the dyes. At 30 ppm H₂O₂ concentration, the maximum deterioration was obtained. Photo-catalysis of H₂O₂ produces hydroxyl radicals, which behave as potent oxidants and electron scavengers. This could be explained by an increase in the amount of ([•]OH) hydroxyl radicals, which increased the photodegradation rate as the catalyst dose increased.

Furthermore, raising the concentration of hydrogen peroxide slowed the rate of photocatalytic degradation, which could be attributed to the scavenging effect. The dye degradation rate increases as the concentration of H₂O₂ increases because more [•]OH is produced (Arshad *et al.*, 2020), (Bisen & Shrivastava, 2015). However, higher H₂O₂ concentration causes dye degradation to be less effective due to a reduced quantity of [•]OH generated. Excess H₂O₂ interacts with [•]OH to produce a hydroperoxyl radical with a lower reduction potential than [•]OH at 1.70 V. The following reactions are largely believed to represent the interaction of H₂O₂ with UV light and free radicals equation 9.9 (Setyaningtyas *et al.*, 2019):



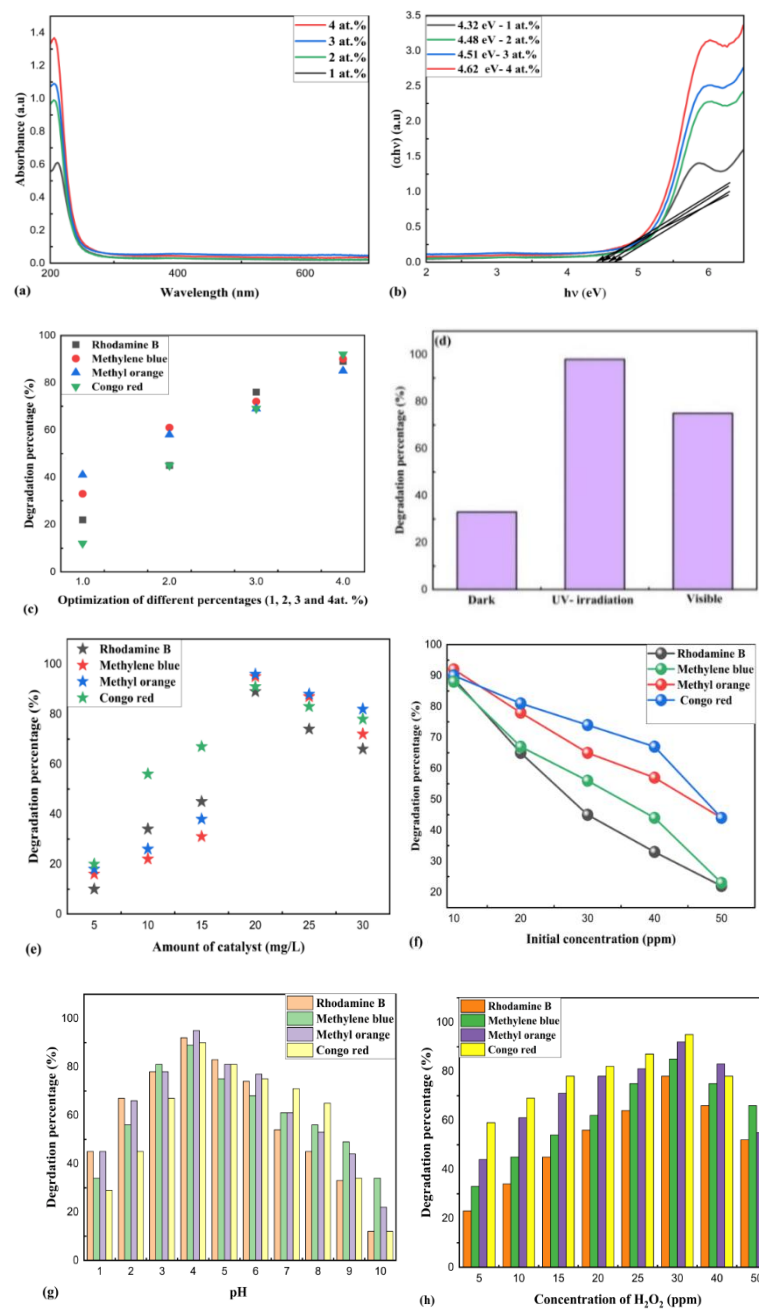


Figure 9.6: (a) UV- absorption spectra of NiS doped Pr^{3+} (1 at.%, 2 at.%, 3 at.%, 4 at.%). (b) Tauc plot of NiS doped Pr^{3+} (1 at.%, 2 at.%, 3 at.%, 4 at.% (c) Optimization of different percentages NiS doped Pr^{3+} (1 at.%, 2 at.%, 3 at.%, 4 at.%). (d) Effect of dark, UV-irradiation and visible light on the degradation of Rbh, MB, MO and CR (e) Amount of catalyst on the degradation of dyes. (f) Initial

concentration of catalyst on the degradation of dyes. (g) Study of pH on the degradation of dyes. (h) Effect of H₂O₂ on the degradation of dyes.

9.3.7 Reusability and degradation of dyes

The reusability of a catalyst is critical for practical and long-term effectiveness in applications such as wastewater treatment and environmental remediation. Catalysts can be deactivated by impurities or byproducts of the reaction. The catalyst is more likely to be reusable if it can be easily regenerated or cleaned to remove these pollutants. The current catalysts are easily separated from the solution and dispersible when stirred (Padikkaparambil *et al.*, 2013), (Sridewi *et al.*, 2011). The catalyst can be easily separated from the cleaned solution via filtration or centrifugation. Following each reaction, the best catalyst was regenerated by centrifugation, washing with water, and 2 hours of further treatment at the catalyst's calcination temperature, 100° C. The activity of several dye pollutants was also evaluated, and it was found to be admirable Figure 9.7 (a). The catalyst was successfully reused for up to five cycles without showing any significant loss of catalytic efficiency.

Figure 9.7 (b,c,d,e) shows the absorption spectra of Rhodamine B, Methylene Blue, Methyl Orange and Congo Red aqueous solutions in the presence of NiS doped Pr³⁺ nanoparticles as a catalyst during different UV-irradiation times. The degradation plots likely illustrate changes in the absorption spectra of these dyes over time or under certain conditions. Each dye initially exhibits absorption bands at specific wavelengths, corresponding to their characteristic electronic transitions. Variations in peak intensities may reflect changes in dye concentration or the efficiency of the degradation process. The absorption peaks at 554 nm in Rhodamine B are related to electron transitions inside the conjugated pi system. The energy required for these transitions corresponds to a visible wavelength. Due to its specific electronic transitions, Methylene Blue exhibits absorption maxima at approximately 280 and 650 nm. These absorption peaks are related to the conjugated system of the molecule and its interactions with light. The absorption peak at 280 nm belongs to the UV spectrum. This peak typically corresponds with the π - π^* transition, which occurs inside the conjugated system of a molecule when an electron transmits from the

highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The 650 nm peak could represent a new electronic transition, such as a charge transfer or a different excited state within the molecule. The absorption peaks of Methyl Orange, located at approximately 250 and 450 nm, are associated with distinct electronic transitions within the molecule. Methyl Orange is an azo dye, and the conjugated system in its chemical structure influences its absorption spectrum. The absorption peak at 250 nm is located in the UV range and is commonly connected with the π - π^* electronic transition. The absorption peak at 450 nm is in the visible, blue section of the spectrum. This apparent absorption peak is frequently linked to other electronic transitions, such as n - π^* transitions. These transitions include electron excitation from non-bonding (n) orbitals to antibonding (π^*) orbitals. The absorption peak of Congo Red at 350 nm is located in the UV range and is commonly connected with the π - π^* electronic transition. The absorption peak at 550 nm is located in the visible section of the spectrum, namely in the orange-red region. This apparent absorption peak is frequently linked to other electronic transitions, such as n - π^* transitions. These transitions involve electrons being excited from non-bonding (n) orbitals to π^* antibonding orbitals. The UV-vis spectrum was used to calculate the beginning dye concentration (C_i) and final dye concentration (C_f) in the photocatalytic process, and the dye degradation efficiency was determined using the following formula equation 9.10.

$$\text{Degradation percentage}(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (9.10)$$

A significant degradation of 96% (Rhodamine B), 92% (Methylene Blue), 95% (Methyl Orange), and 94% (Congo Red) was achieved, highlighting the catalyst's outstanding photocatalytic performance.

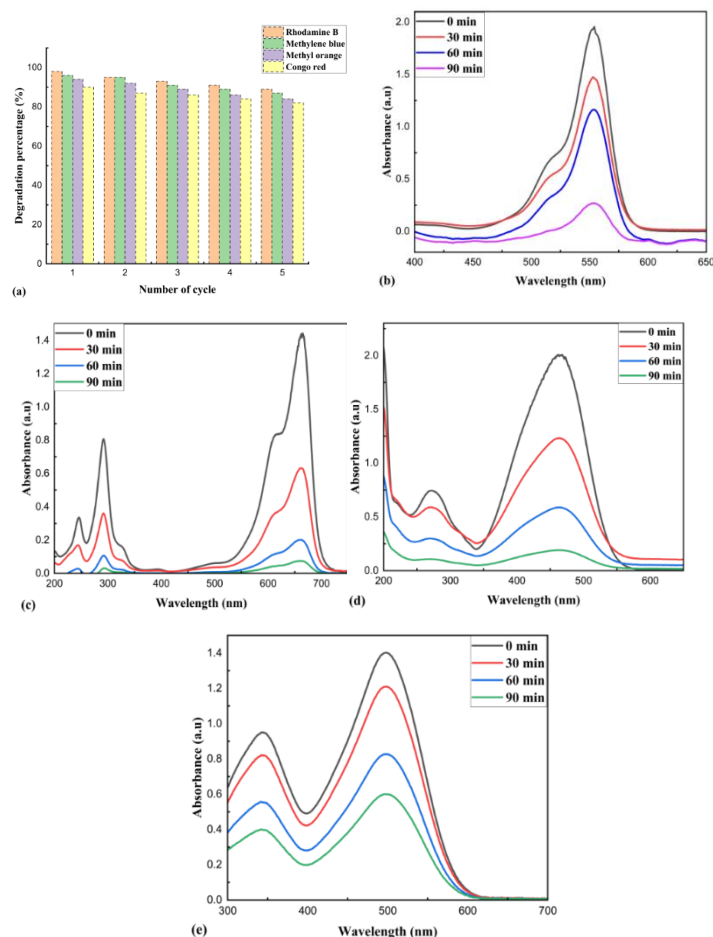


Figure 9.7: (a) Reusability of a catalyst. (b, c, d, e) Degradation of Rhodamine B, Methylene Blue, Methyl Orange and Congo Red within 90 minutes.

9.3.8 Isotherm studies

These models mathematically depict the relationship between the concentration of the solute in the surrounding solution and the amount of solute (adsorbate) adsorbed onto a solid adsorbent. Both models shed light on the interaction between adsorbate molecules and the adsorbent. The Langmuir isotherm presupposes monolayer adsorption, which means that adsorption occurs at specified locations on the adsorbent surface and that no additional adsorption may occur once these locations are occupied. On the adsorbent surface, the Freundlich isotherm allows for multilayer

adsorption. It is an empirical model that can be applied to various adsorption processes. The Sips isotherm model is another mathematical model that describes adsorption processes, particularly in heterogeneous adsorption systems (Naiya *et al.*, 2008). When the assumption of a single monolayer (as in Langmuir) or multilayer (as in Freundlich) adsorption is not appropriate, and interactions between adsorbed molecules exist, the Sips isotherm is frequently used. The Langmuir-Freundlich or Langmuir-to-Freundlich isotherm is another name for the Sips isotherm. The Temkin isotherm model is another empirical equation used to represent the adsorption of solutes onto a solid surface. The Temkin isotherm model is most commonly used when there is considerable electrostatic contact between opposite charges. The UV-Vis data was used to evaluate which of the Langmuir, Freundlich, Sips, or Temkin models best suited the data. Fitting the experimental data to the equations of these isotherm models and evaluating the goodness of fit are involved in this determination.

Each isotherm model has its mathematical equation that connects the amount of adsorbate adsorbed to solution concentration given in equations (9.11-9.14) (Qadeer, 2007), (Ncibi *et al.*, 2007).

Langmuir isotherm

$$\frac{C_e}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} C_e \quad (9.11)$$

C_e indicates the adsorbate equilibrium concentration; q_e represents the quantity of adsorbate adsorbed per unit mass of adsorbent at equilibrium, q_m the maximum adsorption capacity of the adsorbent, and K_L the Langmuir constant.

Freundlich isotherm

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (9.12)$$

Where C_e is the adsorbate's equilibrium concentration and q_e is the amount of adsorbate absorbed per unit mass of adsorbent at equilibrium. K_F is the Freundlich isotherm, and n is the Freundlich exponent equation (Valizadeh *et al.*, 2016).

Sips isotherm

$$q_e = \frac{q_m K_S C_e}{1 + K_S C_e^n} \quad (9.13)$$

Where C_e is the equilibrium concentration of the adsorbate, q_e is the quantity of adsorbate absorbed per unit mass of adsorbent at equilibrium, and q_m is the adsorbent's maximum adsorption capacity. K_s denotes the sips constant, whereas ns denotes the sips exponent given in equation.

Temkin isotherm

$$q_e = B \ln (AC_e) \quad (9.14)$$

C_e is the equilibrium concentration of the adsorbate, q_e is the amount of adsorbate absorbed per unit mass of adsorbent at equilibrium, B is the Temkin constant, and A is the Tenkim constant related to heat adsorption (Yang & Guan, 2018).

Figure 9.8 (a, b, c, d) illustrates the fitting of the Langmuir, Freundlich, Sips, and Temkin isotherm models of adsorbates. The Langmuir isotherm model correlation coefficients R_L^2 values are: 0.9971 for Rhodamine B, 0.9988 for Methylene Blue, 0.9761 for Methyl Orange, and 0.9932 for Congo Red, but for Freundlich isotherm model correlation coefficients R_F values are: 0.9564 for Rhodamine B, 0.9453 for Methylene Blue, 0.9321 for Methyl Orange, and 0.9211 for Congo Red. Sips isotherm model (R_s 2: 0.9213 for Rhodamine B, 0.9452 for Methylene Blue, 0.9331 for Methyl Orange, 0.9398 for Congo Red) and Temkin isotherm model (R_T : 0.9261 for Rhodamine B, 0.9342 for Methylene Blue, 0.9213 for Methyl Orange, 0.9112 for Congo Red) are observed. The R^2 , SSE, and χ^2 tests confirmed that the best-fit model for Rhodamine B and Methyl Orange is the Langmuir isotherm, the Freundlich isotherm for Methylene Blue, and the Temkin isotherm for Congo Red, as shown in Table 9.4.

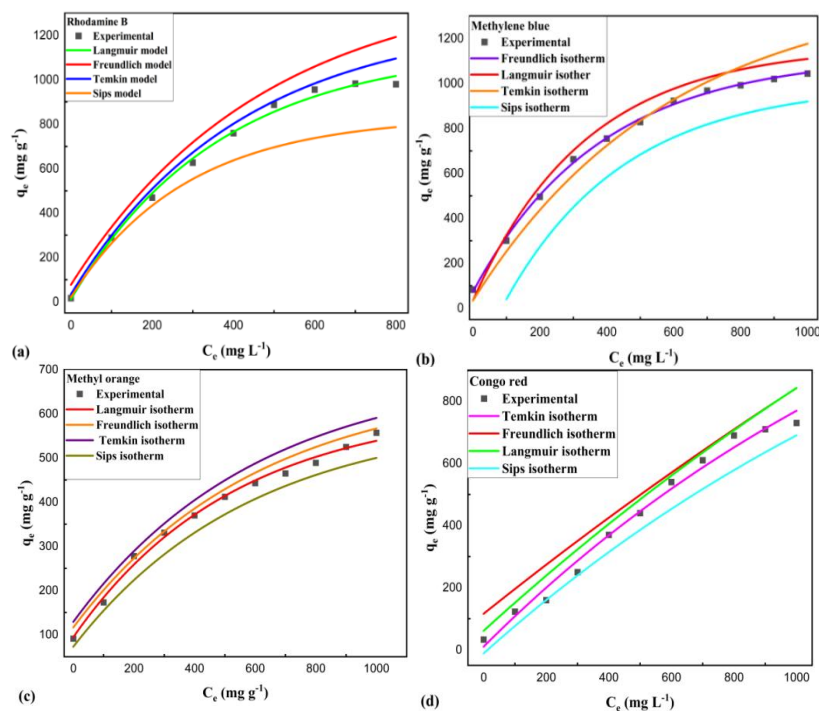


Figure 9.8: (a, b, c, d). Isotherm studies for Rhodamine B, Methylene Blue, Methyl Orange and Congo Red.

Table 9.4: Langmuir, Freundlich, Sips and Temkin isotherm values of dyes.

Model	Parameters	Rhodamine B	Methylene Blue	Methyl Orange	Congo Red
Langmuir model	Q_m (mg g^{-1})	2688.22	2434.90	2791.33	2533.44
	K_L (L mg^{-1})	0.04123	0.00451	0.03124	0.02122
	R_L^2	0.9971	0.9453	0.9761	0.9312
	SSE	1876.90	2711.34	1314.55	2769.08
	χ^2	45.99	123.21	23.99	236.43
Freundlich model	SD (mg g^{-1})	42.90	29.99	28.90	33.44
	K_F (L mg^{-1})	2488.33	2131.33	2654.99	2034.44
	n_F	3.33	4.76	2.22	4.90
	R_F^2	0.9564	0.9988	0.9321	0.9211

	SSE	5675.98	1512.89	7612.88	3423.89
	χ^2	130.99	11.77	90.87	287.98
	SD (mg g ⁻¹)	112.89	56.90	76.88	89.99
Sips model	Q _m (mg g ⁻¹)	1671.90	1893.45	1991.21	1546.67
	Ks (L mg ⁻¹)	0.02349	0.01546	0.07812	0.06342
	ns	2.52	2.97	1.56	3.21

9.3.9 Kinetic studies

Conventional methods for studying adsorption processes include the use of pseudo-first-order and pseudo-second-order kinetic models and the monitoring of adsorption kinetics using UV-vis spectra. The pseudo-first-order kinetic model assumes that the rate of adsorption is proportional to the number of unoccupied sites on the adsorbent surface. Estimating the rate constants k_1 and k_2 provides information about the adsorption process and kinetics. These kinetic models can be used to fit experimental data and estimate rate constants, as well as understand the adsorption mechanism, when analyzing UV-vis spectra taken at different intervals (Kumari *et al.*, 2019), (Chowdhury *et al.*, 2020).

$$\frac{dq}{dt} = k_1 (q_e - q) \quad (9.15)$$

dq/dt is the rate of adsorption at time 't'. The quantity of solute adsorbed at equilibrium is denoted by q_e , the amount of solute adsorbed at time 't' is denoted by q , and the rate constant of the pseudo first order equation is denoted by k_1 .

According to the pseudo-second-order model, adsorption is proportional to the square of the number of vacant sites on the adsorbent surface given in equation 9.16.

$$\frac{dq}{dt} = k_2 (q_e - q)^2 \quad (9.16)$$

The rate of adsorption at time t is denoted as dq/dt , where q_e is the amount of solute adsorbed at equilibrium, q is the quantity of solute adsorbed at time 't,' and k_2 is the rate constant of the pseudo-second order equation.

The kinetics parameters calculated from pseudo-first-order and pseudo-second-order models are shown in Table 9.5. Figure 9.9 (a, b, c, d) shows that the correlation

coefficient (R^2) values for Rhodamine B, Methylene Blue, Methyl Orange, and Congo Red are 0.9956, 0.9823, 0.9981, and 0.9976 for pseudo-first-order models and 0.9612, 0.9544, 0.9521, and 0.9455 for pseudo-second-order models, respectively. The kinetics model R^2 , SSE, and χ^2 values indicate that the best-fitting kinetics model for Rhodamine B, Methylene Blue, Methyl Orange, and Congo Red is the pseudo-first-order model.

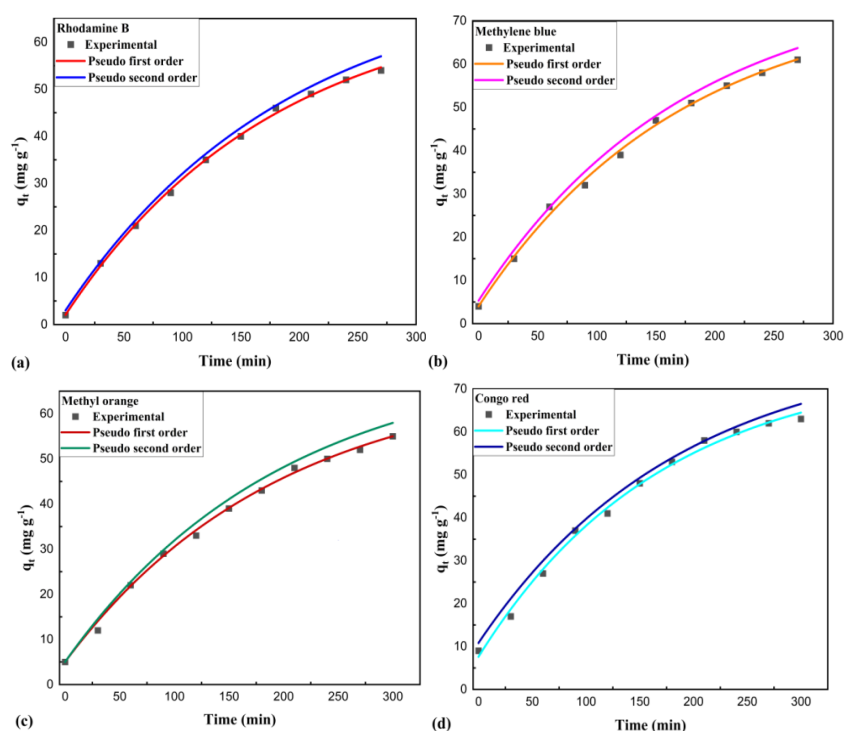


Figure 9.9: (a, b, c, d) Correlation coefficient (R^2) values for Rhodamine B, Methylene Blue, Methyl Orange, and Congo Red.

Table 9.5: Kinetic parameters for the degradation of Rhodamine B, Methylene Blue, Methyl Orange and Congo Red.

Model	Parameters	Rhodamine B	Methylene Blue	Methyl Orange	Congo Red
Pseudo- first	$q_{e,exp}$ (mg g ⁻¹)	61.3	56.88	34.90	21.32

order	¹⁾				
	q _{e,cal} (mg g ⁻¹)	59.90	56.78	45.32	36.78
	k ₁ (min ⁻¹)	0.03214	0.02133	0.03179	0.04415
	R ²	0.9956	0.9823	0.9981	0.9976
	SSE	21.90	14.88	23.56	12.90
	χ ²	0.49	0.22	1.69	2.33
	SD	2.8	5.89	4.66	3.88
Pseudo-second order	q _{e,cal} (mg g ⁻¹)	71.89	23.44	61.60	28.88
	k ₂ (g mg ⁻¹ min ⁻¹)	0.00213	0.05423	0.04531	0.03233
	R ²	0.9612	0.9544	0.9521	0.9455
	SSE	33.89	51.67	52.99	39.89
	χ ²	34.78	22.67	41.66	72.22
	SD	1.67	0.51	2.89	0.88

9.4 Conclusion

This study demonstrates the efficacy of NiS doped Pr³⁺ nanoparticles as a promising photocatalyst for wastewater treatment, specifically in the degradation of recalcitrant dyes such as Rhodamine B, Methylene Blue, Methyl Orange, and Congo Red. The optimized parameters yielded remarkable degradation efficiencies, underscoring the potential of these nanoparticles to mitigate environmental pollution. Optimization studies revealed that NiS doped Pr³⁺ nanoparticles with an atomic percentage of 4 at.

% exhibited superior photocatalytic performance, achieving the highest degradation efficiency. The Langmuir model indicates monolayer adsorption for Rhodamine B and Methyl Orange, while the Freundlich model suggests multilayer adsorption for Methylene Blue. The Temkin model indicates a complex adsorption process for Congo Red. The degradation kinetics of dyes onto nanoparticles follows a pseudo-first-order model. This indicates that the degradation rate is directly proportional to the concentration of the dye. The nanoparticles exhibit exceptional reusability and stability, making them a promising catalyst for wastewater treatment and environmental remediation applications. This study makes a significant contribution to the development of efficient photocatalytic materials for environmental remediation, highlighting the potential of NiS doped Pr^{3+} nanoparticles as a viable solution for mitigating environmental pollution.

CHAPTER 10

A Comparative Study on the Photocatalytic Activity of MgNiS:Eu³⁺ and MgNiS:Sm³⁺ Nanoparticles for the Degradation of Eriochrome Black T Dye

10.1 Introduction

The unregulated discharge of industrial effluent into the environment poses a significant threat to ecological sustainability (Pavithra *et al.*, 2019b). The textile dyeing industry, in particular, is a substantial consumer of groundwater and generates considerable effluent throughout various stages of dyeing process. A portion of these dye effluents are released untreated into soil and waterways, leading to potential environmental hazards (Bafana *et al.*, 2011). This pollution can harm aquatic life, disrupt ecosystem balance, and contaminate soil, reducing its quality and fertility, thereby damaging agriculture and plant life (Lianmawii *et al.*, 2024). The harmful effects of these contaminants on aquatic animals, plants, and other species may result in a loss of biodiversity. Industrial wastewater, including that from paper and pulp, chemical, petrochemical, and dyeing industries, contains hazardous organic and inorganic contaminants that can harm the natural environment (Chan *et al.*, 2009). Some of these colour dyes are extremely toxic and endanger the surrounding ecosystem. Water contamination occurs as a result of industrial wastewater discharge, which includes organic and inorganic pollutants (Ajaz *et al.*, 2020). Industrial contaminants can persist and accumulate in soil, leading to soil pollution, which can impact plant life and agricultural productivity. Volatile components from industrial processes may contribute to air pollution, altering air quality in the vicinity of these industries (Karthikeyan *et al.*, 2015a). Toxic compounds in industrial effluents can bioaccumulate in organisms over time, leading to bioaccumulation in the food chain and disrupting the natural equilibrium of ecosystems (Darezereshki *et al.*, 2021). The proliferation of organic compounds in various industrial and agricultural sectors poses a significant threat to environmental sustainability, potentially leading to the extinction of sensitive species and compromising biodiversity and ecosystem services. The scientific community recognizes the importance of environmental safety, particularly regarding the detrimental effects of

organic pollutants, such as dyes, on aquatic ecosystems (Božič & Kokol, 2008). Dyes are carcinogenic, toxic, and harmful to human health, the environment, and aquatic ecosystems (A. Malik & Grohmann, 2012b). Water contamination is primarily caused by industrial effluents containing organic compounds with aromatic rings, such as nitro, sulfo, and chloro groups. With over 10,000 dyes available and an annual production of over 700,000 tonnes, the impact of these pollutants on the environment is a significant concern (Shanker *et al.*, 2017). The large-scale production of dyes is driven by the demand for colouring and enhancing materials in industries such as textiles, where dyes are essential for achieving desired colours and patterns (Pouretedal *et al.*, 2009). However, this extensive production poses environmental concerns due to the potential release of untreated or improperly treated dye-containing effluent into the environment. Proper handling and disposal of dye effluents are crucial to prevent ecosystem pollution (K. Singh & Arora, 2011). Dyes can be categorized into various types based on their structural bases, including anthraquinone, basic, azo, acidic, dispersion, and metal complex dyes, with the textile industry being the primary consumer of these dyes (Benkhaya, M' rabet, *et al.*, 2020). A significant amount of dye is lost during the colouration process in the paint and textile industries, with approximately 15% of globally produced dyes being wasted during textile dyeing processes (Gregory, 1990). The discharge of coloured effluents from textile and dye industries into water bodies not only leads to aesthetic pollution but also has harmful biological consequences, including the reduction or complete blockage of light transmission and water re-oxygenation, thereby disrupting the delicate balance of aquatic ecosystems and potentially threatening the survival of aquatic life forms (J. A. Khan *et al.*, 2020). Colour effluents can restrict or entirely obstruct light penetration in water bodies, disrupting photosynthesis in aquatic plants and impacting their growth and ecology. The presence of dyes can also impede water re-oxygenation, which is essential for aquatic life (X. Li *et al.*, 2016). Colour effluents can disturb aquatic life by interfering with light penetration and water re-oxygenation, affecting the survival of aquatic organisms such as fish and other wildlife that rely on a well-balanced and oxygen-rich environment (Ebert *et al.*, 2011). Changes in water quality and oxygen levels can reduce biodiversity and, in extreme cases, lead to the death of aquatic organisms. The environmental problem of

wastewater and its toxicity is a significant research topic, with organic dyes being a substantial source of industrial wastewater (Nazri & Sapawe, 2020). Azo dyes, which contain nitrogen π -bonds, are responsible for approximately 50% of the colours found in textiles (Aljamali, 2015).

Antibiotics, such as fluoroquinolone antibiotics (FQs), are widely used in human and veterinary medicine, with ciprofloxacin being a fluorinated quinolone antibiotic with broad efficacy against both gram-positive and gram-negative pathogens (Morones *et al.*, 2005), (Alexandrino *et al.*, 2017). The complexity of textile effluents often surpasses the capabilities of traditional wastewater treatment systems, resulting in treated effluent quality that fails to meet national standards (Lianmawii & Singh, 2023). Therefore, a more effective wastewater treatment system is necessary to address the current challenges. Various therapeutic technologies have been proposed, evaluated, and implemented to meet current and future treatment requirements (Tolia *et al.*, 2012). To meet national effluent quality standards, treatment techniques must ensure the mineralization or removal of pollutants. Over the last 30 years, numerous studies have investigated the efficacy of Advanced Oxidation Processes (AOP's) in treating resistant wastewaters containing refractory and harmful contaminants (Koe *et al.*, 2020). AOPs operate by generating hydroxyl free radicals, which possess a high electrochemical oxidant potential, enabling them to rapidly attack or degrade recalcitrant organic molecules to CO₂, H₂O, and inorganic ions through hydroxylation or dehydrogenation (Oturán, 2000). AOPs are commonly employed in wastewater treatment to reduce total organic content, particularly for pollutant destruction, sludge treatment, and colour and odor removal (Kurian, 2021). AOPs often exhibit high degradation efficiency, breaking down complex dye molecules into simpler and less hazardous by-products, which is crucial when treating wastewater containing persistent and difficult-to-degrade colours (Andreozzi *et al.*, 1999).

MgNiS:Eu³⁺ and MgNiS:Sm³⁺ nanoparticles were successfully synthesized via the reflux method, a widely employed approach for nanoparticle fabrication. This method entails the heating of a reaction mixture to its boiling point under reflux conditions, employing a condenser to prevent the evaporation of volatile compounds,

for a specified duration. This technique enables the containment of the reaction mixture at a constant temperature, allowing for the efficient completion of the reaction without the loss of reactants or products. This approach is often employed to enhance reaction kinetics and nanoparticle yield. The synthesized catalyst was subsequently utilized for the degradation of Eriochrome Black T (EBT) dye.

10.2 Experimental details

10.2.1 Sample preparation

Magnesium nitrate hexahydrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%, Nickel(II) nitrate hexahydrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%, Sodium sulfide, Na_2S , anhydrous, Samarium(III) nitrate hexahydrate, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9%, and Europium(III) nitrate hexahydrate, $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9%, were procured from Alfa Aesar. A solution containing magnesium nitrate hexahydrate and either Samarium(III) nitrate hexahydrate or Europium(III) nitrate hexahydrate was prepared in a beaker, and the mixture was subjected to magnetic stirring for 1 hour at room temperature ($25 \pm 2^\circ\text{C}$) to facilitate complete solvation and homogenization of the components. Sodium sulfide was gradually introduced to the solution in a dropwise manner, ensuring a controlled addition. The resulting mixture was then subjected to reflux conditions at a temperature of 170°C for duration of 48 hours, during which time constant stirring was maintained to ensure uniformity. Refluxing is a widely used technique in organic synthesis, where a reaction mixture is heated to its boiling point under continuous condensation, utilizing a condenser to return the condensed solvent back to the reaction vessel. This process maintains a constant temperature, ensuring efficient completion of the reaction while preventing solvent evaporation and associated reactant loss. This approach enhances reaction rates by creating favourable conditions for high-temperature reactions and ensures uniform heating, preventing volatile solvent loss. The obtained nanoparticles were centrifuged at 8500 rpm, washed with acetone and alcohol, and dried before characterization.

10.2.2 Sample characterization

XRD data were collected using a state-of-the-art D8 Advance Bruker diffractometer, featuring a versatile combination of X-ray sources, sample stages, and detectors. This

allowed for a thorough investigation of the material's crystal structure and lattice parameters. FTIR spectroscopy data were acquired utilizing a Shimadzu spectrometer, operating in the mid-infrared region, with a scan range of 500-4000 cm^{-1} . Scanning Electron Microscopy (SEM) analysis was conducted utilizing a Supra 55 Zeiss instrument, which enabled high-resolution imaging and characterization of the sample's surface morphology. Transmission Electron Microscopy (TEM) analysis was conducted using a JEOL Model: 2100F, capable of high-resolution imaging, enables the visualization of minute features and structures at the atomic level. The decay times and emission spectra of the samples were measured using a Hitachi F-7000 spectrophotometer. The photocatalytic activity of the samples was evaluated using a Thermo Scientific Evolution 220 UV-visible spectrophotometer.

Photocatalytic activity and removal

The photocatalytic activity of the synthesized catalysts was assessed using Eriochrome Black T (EBT) as a target pollutant, which is a harmful dye known to permeate physiological organ barriers and cause organ poisoning. In this study, a 10 ppm EBT solution was prepared by dissolving dye in distilled water. Catalyst dose of 50 mg/L was introduced into 20 mL of dye solution, yielding a uniform dispersion of the catalyst particles in the solution, and the mixture was shaken and left in the dark to achieve adsorption-desorption equilibrium. The absorption spectra were recorded every 30 minutes using a UV-Vis spectrophotometer.

The adsorption performance of the synthesized composites was evaluated by calculating two key parameters: equilibrium adsorption capacity (Q_e) and adsorption efficiency. These parameters were determined using equations 10.1 and 10.2 (Kumari *et al.*, 2019), (Chowdhury *et al.*, 2020):

$$Q_e(\text{mg g}^{-1}) = \frac{(C_0 - C_e)V}{M} \quad (10.1)$$

$$\text{Adsorption efficiency (\%)} = \frac{(C_0 - C_e) \times 100}{C_0} \quad (10.2)$$

The mass (M) of the adsorbent is expressed in units of grams (g), while the volume (V) of the adsorbate solution is expressed in units of liters (L). The initial and equilibrium concentrations of the adsorbates are denoted by C_0 and C_e , respectively.

Statistical error analysis

A statistical error analysis was conducted to identify the most suitable kinetic and isotherm models for the adsorption process. The evaluation of the model's performance involved the computation of several statistical parameters, namely the sum of squared errors (SSE), the Chi-squared test statistic (χ^2), and the standard deviation of the residuals (SD), which provided a comprehensive assessment of the model's fit and precision. The better fitted kinetic and isotherm models were described by the significantly greatest R^2 value and the lowest values of SSE, χ^2 , and SD. Thus, using the following mathematical formulas to evaluate SSE, χ^2 , and SD, respectively, statistical error analysis was carried out using equations 10.3-10.5 (Kumari *et al.*, 2019), (Leite *et al.*, 2017), (Bao *et al.*, 2020):

$$SSE = \sum_{i=1}^n (Q_{e,exp} - Q_{e,m})^2 \quad (10.3)$$

$$\chi^2 = \sum_{i=1}^n \frac{(Q_{e,exp} - Q_{e,m})^2}{Q_{e,m}} \quad (10.4)$$

$$SD = \sqrt{\left(\frac{1}{n-p}\right) \cdot \sum_{i=1}^n (q_{i,exp} - q_{i,model})^2} \quad (10.5)$$

The predicted equilibrium adsorption capacity is denoted by $Q_{e,m}$, while the experimentally determined equilibrium adsorption capacity is represented by $Q_{e,exp}$. The symbols ' n ' and ' p ' represent the total number of experiments and the number of model parameters, respectively

Calculation of thermodynamic parameters

Elucidating the thermodynamic properties of a system is essential for assessing the viability and optimal conditions of the adsorption process at a specific temperature. By examining the thermodynamic characteristics, researchers can gain valuable insights into the energy changes associated with the adsorption process, such as

Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS). The state function temperature is a thermodynamic parameter that is path-independent, meaning its value depends solely on the current state of the system and not on the sequence of events or processes that led to that state. This feature highlights the importance of temperature as a crucial parameter in determining the thermodynamic state of a system, allowing for the characterization of its thermal properties and behavior. The thermodynamic variables, namely Gibbs free energy change (ΔG) (kJ mol^{-1}), entropy change (ΔS) ($\text{kJ mol}^{-1} \text{K}^{-1}$), and enthalpy changes (ΔH) (kJ mol^{-1}), can be determined using the following equations 10.6-10.8 (Bedin *et al.*, 2016), (Shah *et al.*, 2014):

$$K_d = Q_e / C_e \quad (10.6)$$

$$\Delta G = -RT \ln K_d \quad (10.7)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (10.8)$$

The distribution constant, K_d , is a crucial parameter that describes the equilibrium distribution of the adsorbate between the solid and liquid phases. It is calculated as the ratio of the equilibrium adsorption capacity, Q_e (mg/g), to the equilibrium concentration of the adsorbate in the liquid phase, C_e (mg/L). Additionally, the temperature dependence of the adsorption process is described by the Van't Hoff equation, which involves the universal gas constant, R and the absolute temperature, T (K), thereby enabling the evaluation of the thermodynamic driving forces behind the adsorption process.

10.3 Results and discussions

10.3.1 X-ray diffraction (XRD)

Figure 10.1 presents the XRD patterns of MgNiS:Eu^{3+} and MgNiS:Sm^{3+} nanoparticles, which were analyzed to determine their crystal structure and phase composition. The XRD pattern of MgNiS:Eu^{3+} exhibits diffraction peaks at (101), (110), (003), (113), and (104) planes, which are consistent with the rhombo-centered structure of MgNiS (JCPDS No. 44-1418). The lattice parameters were calculated from the (110) peak and found to be $a = 5.21 \text{ \AA}$ and $c = 7.77 \text{ \AA}$, with a space group of

R32 (Deng *et al.*, 2019). Similarly, the XRD pattern of MgNiS:Sm³⁺ shows Bragg peaks at (110), (101), (300), (021), (220), (211), and (410) planes, which are characteristic of the rhomb-centered NiS phase (JCPDS No. 12-0041). The calculated lattice parameters from the (101) peak are $a = 9.781\text{\AA}$ and $c = 3.454\text{\AA}$, with a space group of R3m (Ma *et al.*, 2015), (Shen *et al.*, 2010). According to the ICDD data catalogue, the powder composition of MgNiS:Eu³⁺ and MgNiS:Sm³⁺ consists of Mg(NO₃)₂·6H₂O with a monoclinic lattice (P121/c1 space group). The lattice structure of this combination is monoclinic, with three unequal axes and two axes that intersect at an angle other than 90 degrees (Sirota *et al.*, 2016), (Mahalakshmi *et al.*, 2020). The addition of lanthanide dopants is typically small (less than a few percent by weight or atomic percentage), making it challenging to detect their presence using XRD. However, the lanthanide dopants can substitute into the host lattice positions without significantly altering the crystal structure, resulting in a minimal change in the overall diffraction pattern. The particle size was determined using Debye Scherrer's equation (Lianmawii & Singh, 2023): $D = \frac{0.9\lambda}{\beta \cos\theta}$, and the average particle size calculated was 34 nm for MgNiS:Eu³⁺ and 31 nm for MgNiS:Sm³⁺ respectively.

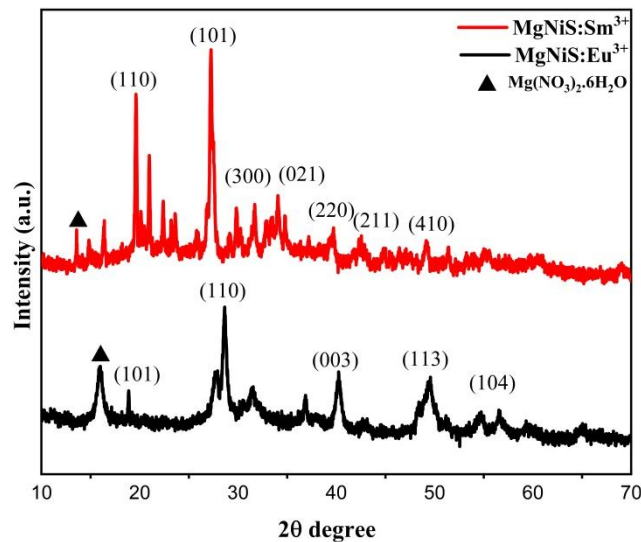


Figure 10.1: XRD pattern of MgNiS:Eu³⁺ and MgNiS:Sm³⁺ nanoparticles.

10.3.2 Scanning Electron Microscopy (SEM)

SEM micrographs presented in Figures 10.2 (a) and (b) reveal the surface morphology of MgNiS:Eu^{3+} and MgNiS:Sm^{3+} nanoparticles, respectively, showing a quasi-spherical shape with a high degree of spherical symmetry. This observation suggests a narrow size distribution and a high level of crystallinity. The term "quasi-spherical" describes particles that approximate a spherical shape but may deviate from perfect sphericity. This morphology suggests that nanoparticles have an approximately spherical form but may exhibit variations in size, surface roughness, and overall shape, making their description more complex than a strictly spherical classification (Stoian *et al.*, 2020), (Jia *et al.*, 2012). The elemental composition of the synthesized nanomaterials was examined using energy-dispersive X-ray (EDX) analysis, which confirmed the presence of all the expected elements, thereby validating the successful formation of the target nanostructures. The EDX spectra, presented in Figures 10.2 (c) and (d), specifically illustrate the incorporation of the desired elements in the MgNiS:Eu^{3+} and MgNiS:Sm^{3+} nanoparticles, further confirming the successful synthesis of these doped materials. The average particle sizes were determined from the corresponding images using J imaging software, yielding values of 29 nm for MgNiS:Eu^{3+} and 34 nm for MgNiS:Sm^{3+} , as shown in the insets of Figures 10.2 (c) and (d). Overall, the EDX results not only verify the elemental composition but also provide insight into the chemical constitution and high purity of the synthesized nanoparticles, supporting their suitability for subsequent applications.

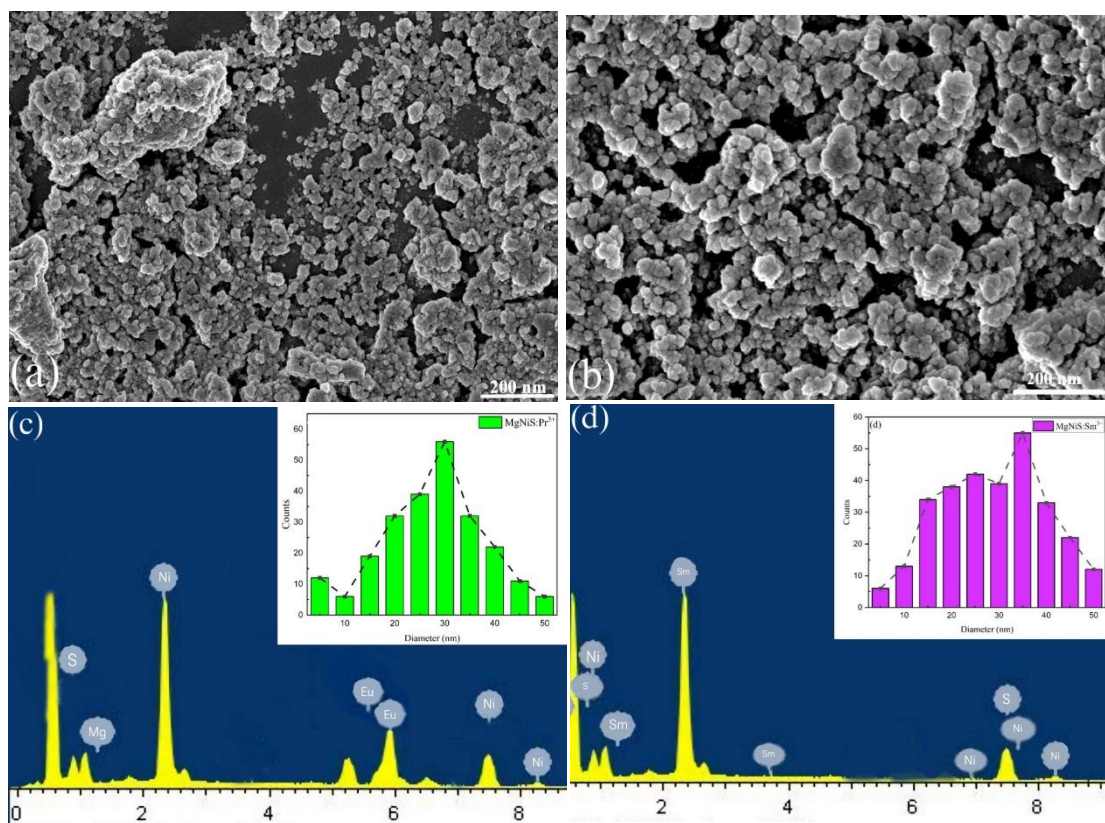


Figure 10.2: (a) and (b) SEM image of MgNiS:Eu³⁺ and MgNiS:Sm³⁺ nanoparticles. (c) and (d) EDX image of MgNiS:Eu³⁺ (inset average particle size), and EDX image of MgNiS:Sm³⁺ nanoparticles (inset average particle size).

10.3.3 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) analysis revealed that nanoparticles exhibit high agglomeration. The TEM images, presented in Figures 10.3 (a) and (b), show that nanoparticles have approximately spherical shapes with sizes ranging from 25 to 35 nm. HR-TEM images, shown in Figures 10.3 (c) and (d), offer a higher magnification view of the MgNiS:Eu³⁺ nanoparticles, displaying lattice fringes with spacing's of 2.69 Å, 2.88 Å, and 2.43 Å. These values are consistent with the interplanar spacing of the (101), (110), and (003) crystallographic planes, respectively, confirming the single-crystalline nature of nanoparticles and providing

valuable information on their crystal structure. Similarly, lattice planes with spacing's of 1.89Å, 1.44Å, and 1.56Å were observed for MgNiS:Sm³⁺ nanoparticles, corresponding to the (110), (101), and (300) planes, respectively. The selected area electron diffraction (SAED) patterns presented in the inset of Figures 10.3 (c) and (d) provide further evidence of the crystalline nature of the MgNiS:Eu³⁺ and MgNiS:Sm³⁺ nanoparticles, respectively. The distinct diffraction rings and spots in the SAED patterns confirm the long-range order and crystal structure of nanoparticles, indicating a high degree of crystallinity and structural integrity

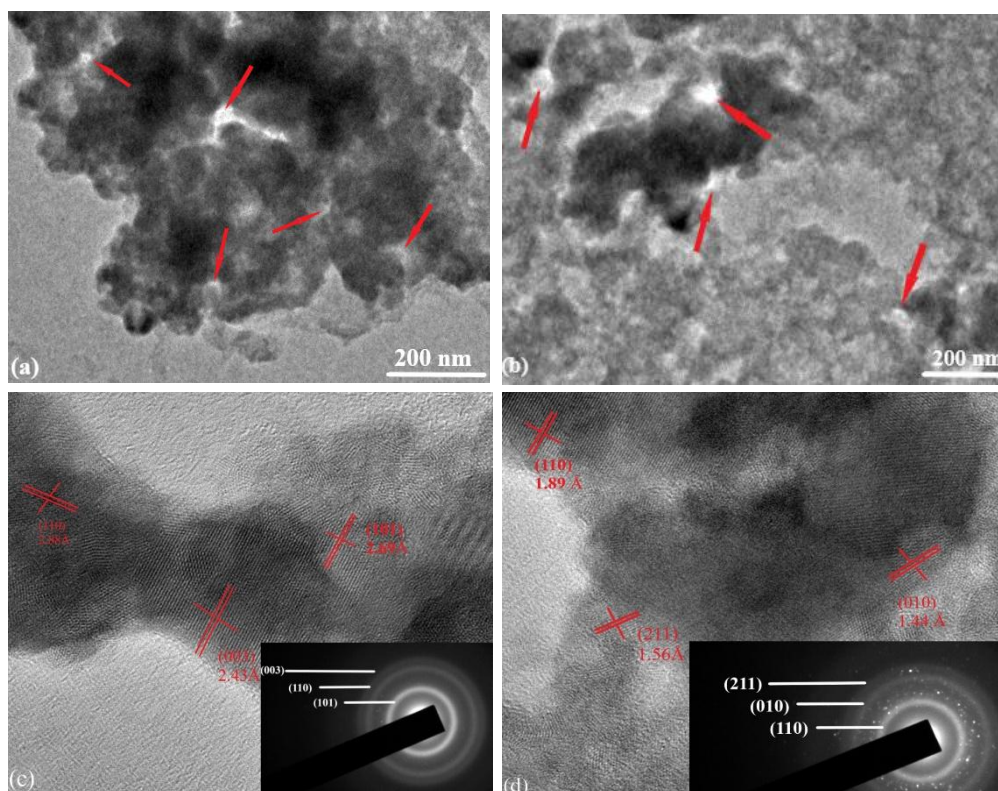


Figure 10.3: (a), (b) TEM images of MgNiS:Eu³⁺ and MgNiS:Sm³⁺ nanoparticles. (c), (d) HR-TEM of MgNiS:Eu³⁺ (inset SAED) and MgNiS:Sm³⁺ nanoparticles (inset SAED).

10.3.4 Fourier Transform Infrared (FTIR)

Figure 10.4 displays the Fourier Transform Infrared (FTIR) spectra of MgNiS:Eu³⁺ and MgNiS:Sm³⁺ nanoparticles, revealing various absorption peaks corresponding to

different functional groups. The spectra exhibit peaks at 2372 cm^{-1} and 2314 cm^{-1} , attributed to C-H stretching modes. A broad peak at 3539 cm^{-1} is associated with N-H stretching of free amines, while the peak at 1520 cm^{-1} corresponds to N-H bending vibrations (Karthikeyan *et al.*, 2015b). Additionally, a peak at 1218 cm^{-1} is assigned to N-O stretching modes, characteristic of magnesium (Gupta *et al.*, 2019). The Ni-S band in NiS particles is represented by symmetrical and asymmetrical stretch modes, observed at 435 cm^{-1} and 598 cm^{-1} , respectively. The bending vibration of the sulfonated group is detected at 1054 cm^{-1} .

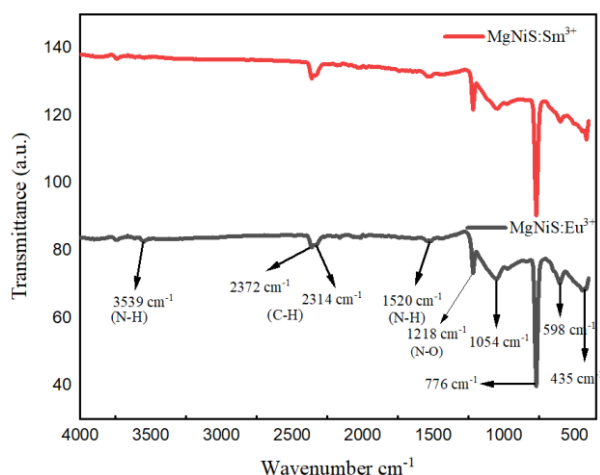


Figure 10.4: FTIR spectra of MgNiS:Eu^{3+} and MgNiS:Sm^{3+} nanoparticles.

10.3.5 Raman spectra

Figures 10.5 (a) and (b) present the room temperature raman spectra of the synthesized catalysts of MgNiS:Eu^{3+} and MgNiS:Sm^{3+} . The spectra exhibit distinct vibrational modes, with six modes observed at 144 , 206 , 432 , 464 , 534 , and 655 cm^{-1} for MgNiS:Eu^{3+} , consistent with previous studies (Salavati-Niasari *et al.*, 2010), (Z. Cheng *et al.*, 2007). In contrast, only three vibrational modes are detected for MgNiS:Sm^{3+} . The prominent peak at 464 cm^{-1} is attributed to the rotation of physically adsorbed hydrogen. However, several vibrational modes remain undetectable, potentially due to the small size effect of the nanomaterials. The crystal lattice vibrations, which heavily influence Raman vibrational modes, may be altered when the crystal size is reduced to the nanoregime, resulting in differences in atom

arrangement within the crystal lattice compared to bulk materials. The Raman spectra provide evidence that the active sites on the Ni metal surface undergo adsorption of H₂S upon exposure to a sulfur-containing fuel, followed by a reaction that yields the formation of NiS₂ (Dong *et al.*, 2006).

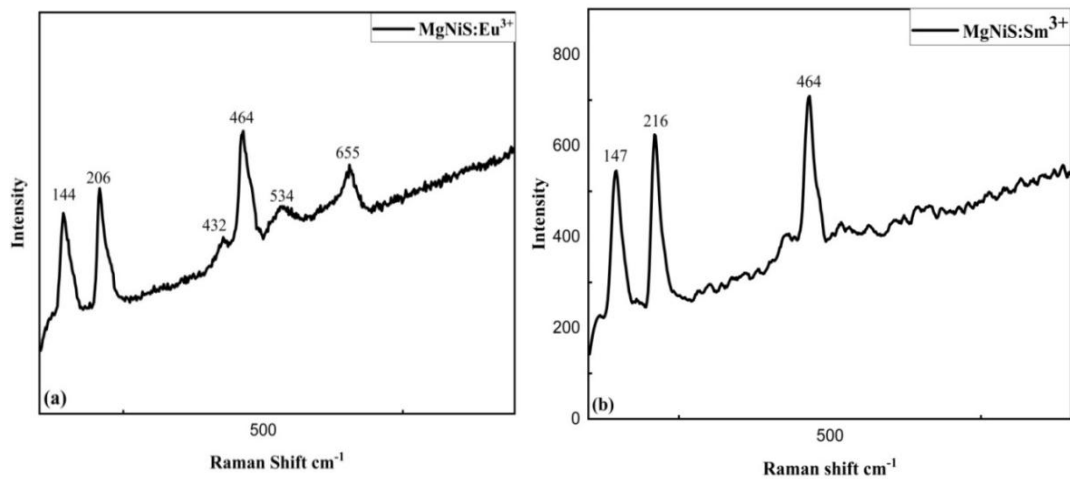


Figure 10.5: (a) Raman spectra of MgNiS:Eu³⁺ and (b) MgNiS:Sm³⁺ nanoparticles.

10.3.6 Photoluminescence studies

The photoluminescence characteristics of the synthesized glass samples were examined at ambient temperature, and the corresponding emission spectra are presented in Figures 10.6 (a-d). These spectra reveal the optical properties of the glass samples, providing valuable insights into their luminescent behavior and potential applications in photonic devices. These Figures illustrate the emission characteristics of the glass samples under optical excitation, providing valuable insights into their electronic transitions and energy levels. Figure 10.6 (a) shows the emission spectrum of MgNiS:Eu³⁺ in the 500-700 nm range, comprising distinct Europium(III) absorption bands centered at 554 nm (⁵D₀→⁷F₀), 594 nm (⁵D₀→⁷F₁), 614 nm (⁵D₀→⁷F₂), 621 nm (⁵D₀→⁷F₃), and 687 nm (⁵D₀→⁷F₄). The ⁵D₀→⁷F₀ transition of Europium(III) ions yields a single emission peak at 554 nm, while the most intense transition occurs at 594 nm, corresponding to the electric-dipole (⁵D₀→⁷F₁) transition, which is hypersensitive to the local environment surrounding the Europium (III) ions. The intensity ratio of the (⁵D₀→⁷F₁) and (⁵D₀→⁷F₂)

transitions serves as an indirect indicator of the disorder around Europium (III) ions. The weaker emissions at 621 and 687 nm are attributed to the ($^5D_0 \rightarrow ^7F_3$) and ($^5D_0 \rightarrow ^7F_4$) transitions, respectively (Irfanullah *et al.*, 2015), (Papan *et al.*, 2016). Upon excitation at 355 nm, the samarium ions exhibit three emission peaks in the 500-650 nm range, situated at 559 nm, 596 nm, and 642 nm. These peaks correspond to the transitions from the $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{7/2}$ and $^4G_{5/2} \rightarrow ^6H_{9/2}$ levels. This observation is consistent with previous reports on Sm^{3+} complexes, as illustrated in Figure 10.6 (b) (Wei *et al.*, 2016), (D. Singh *et al.*, 2021). Figure 10.6 (c) depicts the excitation spectra of europium measured between 360 and 440 nm, with transition peaks at 361 nm ($^7F_0 \rightarrow ^5D_4$), 379 nm ($^7F_0 \rightarrow ^5G_2$), 395 nm ($^7F_0 \rightarrow ^5L_6$) and 416 nm ($^7F_1 \rightarrow ^5L_6$) respectively. Figure 10.6 (d) depicts samarium excitation spectra measured between 350 and 500 nm, with transitions at 367 nm ($^6H_{5/2} \rightarrow ^4L_{17/2}$), 400 nm ($^6H_{5/2} \rightarrow ^6P_{3/2}$), 439 nm ($^6H_{5/2} \rightarrow ^4G_{9/2}$), 474 nm ($^6H_{5/2} \rightarrow ^4I_{11/2}$) and 504 nm ($^6H_{5/2} \rightarrow ^4G_{7/2}$)

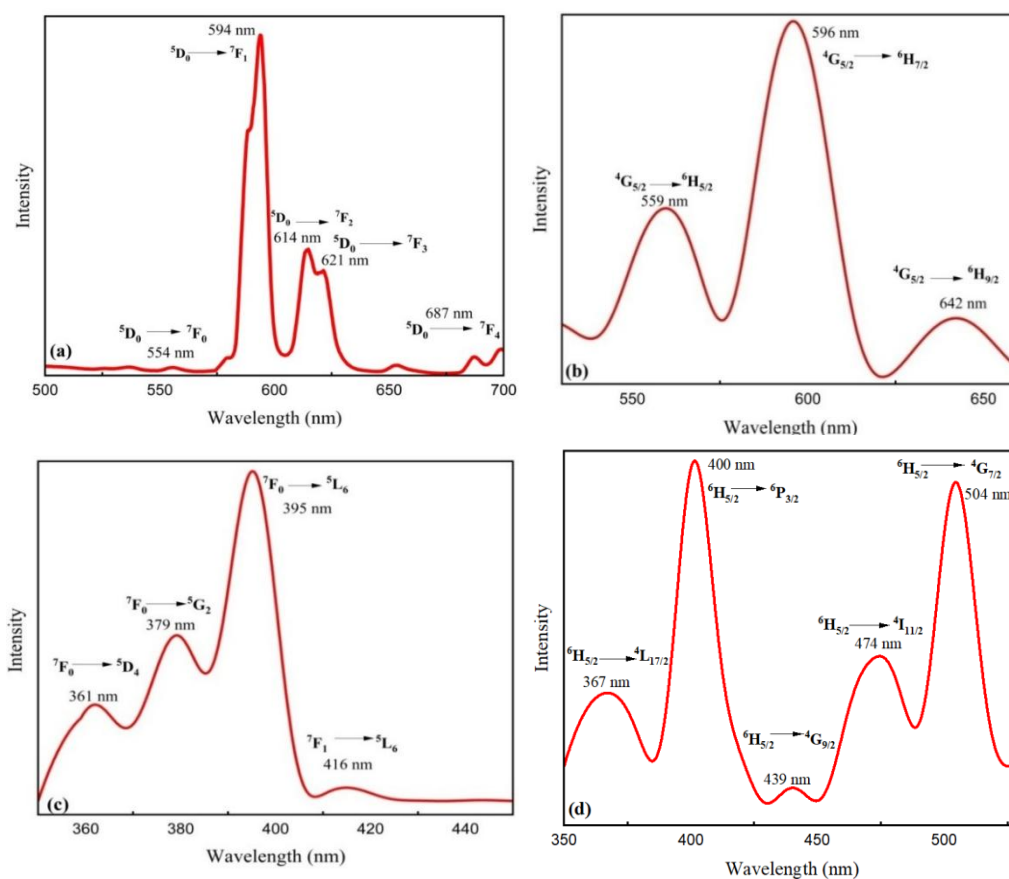


Figure 10.6: (a), (b) Emission spectra of MgNiS:Eu³⁺ and MgNiS:Sm³⁺ nanoparticles. (c), (d) Excitation spectra of MgNiS:Eu³⁺ and MgNiS:Sm³⁺ nanoparticles.

10.3.7 CIE and Lifetime analysis

The Commission International de L'Eclairage (CIE), or International Commission on Illumination, is a global organization that sets standards and recommendations for light and lighting. The CIE's primary objective is to facilitate international collaboration and knowledge sharing in the field of light and lighting. To achieve this, the CIE develops and disseminates standards, recommendations, and guidelines for various aspects of light and colour, ensuring global consistency and comparability in lighting practices. In this study, McCamy's equation was employed to calculate the colour coordinates from the emission spectra, and the corresponding colour temperature (CCT) was determined using equation 10.9 (Lianmawii & Singh, 2023), (N. P. Singh *et al.*, 2017):

$$\text{CCT} = -437n^3 + 3601n^2 - 6861n + 5514.31 \text{ and}$$

$$n = (x - x_e) / (y - y_e) \quad (10.9)$$

The resulting colour coordinates, denoted by x and y , are plotted in the CIE 1931 colour space diagram, as shown in Figure 10.7 (a). This plot reveals that the synthesized catalyst emits a colour that is close to white. Furthermore, the luminescence decay curves of the catalyst were investigated, and the bi-exponential equation 10.10 was used to fit the two observed decay curves:

$$I = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2) \quad (10.10)$$

I_1 and I_2 denote the intensities at two separate time intervals, while τ_1, τ_2 represents the decay times. The average decay time can be calculated using the following equation 10.11:

$$\tau_{ave} = (I_1\tau_1^2 + I_2\tau_2^2) / (I_1\tau_1 + I_2\tau_2) \quad (10.11)$$

The luminescence decay curves of MgNiS:Eu^{3+} and MgNiS:Sm^{3+} were fitted using a bi-exponential equation, yielding average lifetimes of 1.77 ms and 1.81 ms, respectively given in Figure 10.7 (b). The goodness of fit (R^2) for both samples was high, at 0.979 and 0.981, respectively. The parameters obtained from the lifetime study are summarized in Table 10.1.

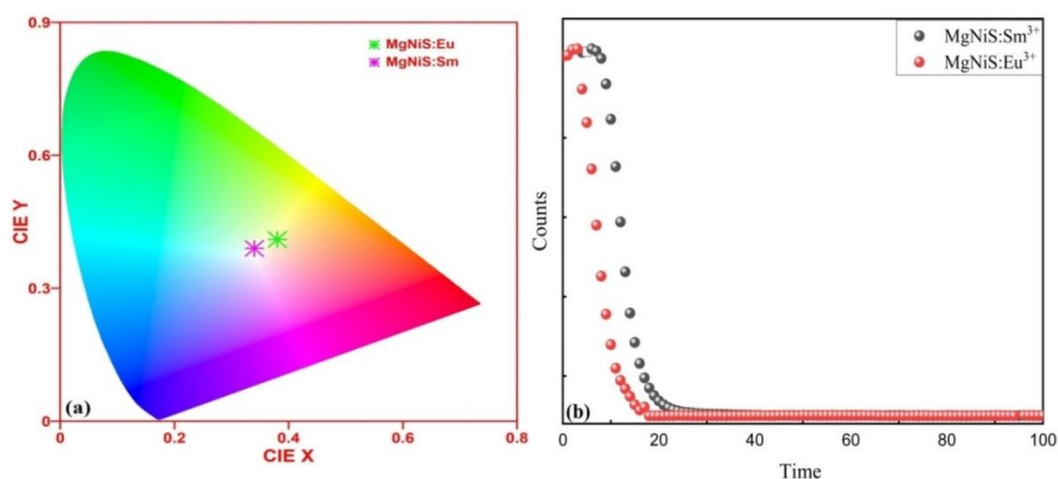


Figure 10.7: (a). CIE analysis of MgNiS:Eu^{3+} and MgNiS:Sm^{3+} (b) Decay lifetime of MgNiS:Eu^{3+} and MgNiS:Sm^{3+} .

Table 10.1: Parameters involved in the lifetime study of MgNiS:Eu^{3+} and MgNiS:Sm^{3+} .

Sample	γ_0	I_1	τ_1	I_2	τ_2
MgNiS:Eu^{3+}	4523.981	213,324.768	1.41233	260,768.009	0.29871
MgNiS:Sm^{3+}	5093.812	112,675.901	0.21445	298,789.132	0.95412

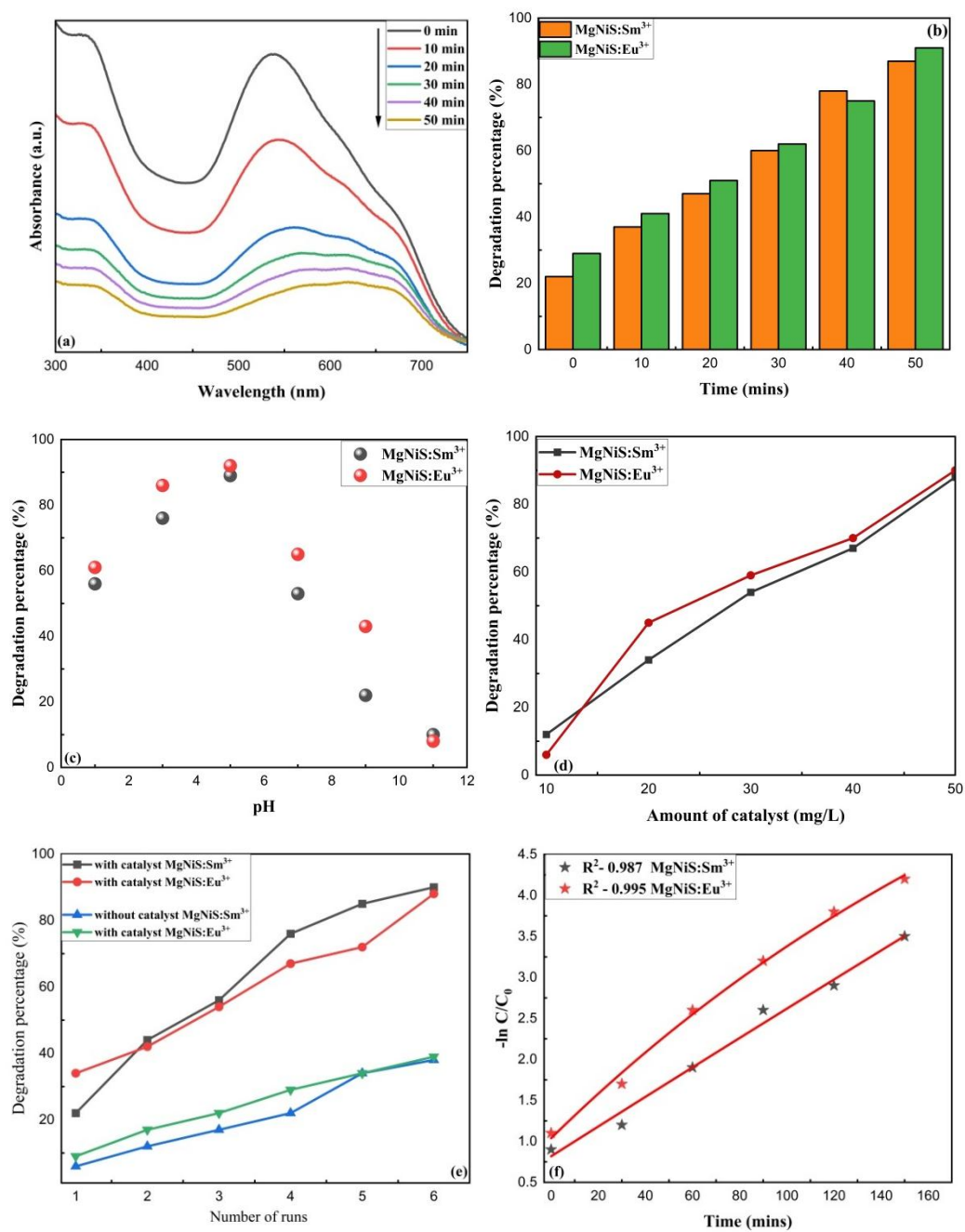
10.3.8 Photocatalytic studies

Figure 10.8 (a) shows the degradation profile of Eriochrome Black T dye over 150 minutes, catalyzed by either MgNiS:Eu^{3+} or MgNiS:Sm^{3+} . As shown in Figure 10.8 (b), MgNiS:Eu^{3+} achieved a higher degradation efficiency of 89.34% within 50 minutes, compared to MgNiS:Sm^{3+} with 83.96% efficiency. The effect of catalyst

concentration was also investigated, and the optimal concentration was found to be 50 mg/L for both catalysts. The optimal pH for degradation was found to be pH 5 for both catalysts, resulting in the highest degradation percentage, indicating that an acidic environment enhances the catalytic activity. This suggests that the catalysts are most effective in acidic conditions, achieving maximum degradation efficiency at pH 5. This is attributed to the sensitivity of Eriochrome Black T to photocatalytic degradation at pH 5, where dye molecule undergoes a visible colour shift from blue to red upon complexation with metal ions. The transition range of Eriochrome Black T is between pH 5-10, with the most noticeable colour shift occurring at pH 5, suggesting increased susceptibility to photocatalytic degradation (Najjar *et al.*, 2021). The production of reactive oxygen species (ROS) such as hydroxyl radicals plays a crucial role in the breakdown of organic compounds, and Eriochrome Black T's sensitivity to ROS may vary with pH, with increased susceptibility to oxidative destruction at pH 5 (Kansal *et al.*, 2013). As a metal complex-forming dye, Eriochrome Black T's behavior is impacted by metal ions, leading to the formation of a metal-dye complex that may be more prone to photocatalytic degradation at pH 5 due to specific interactions with the catalyst or reactive species, as illustrated in Figure 10.8 (c).

The optimal catalyst concentration was determined to be 50 mg/L, at which the highest degradation percentage was achieved for both catalysts, indicating that this concentration maximizes the catalytic activity and efficiency. This concentration likely offers the best balance between preventing catalyst particle agglomeration and providing a sufficient surface area for catalytic processes. The presence of the catalyst at 50 mg/L may also enhance light absorption and utilization, promoting effective photocatalysis. However, excess catalyst could lead to self-shading or increased light scattering, reducing efficiency. The degradation process relies on the interaction between the photocatalyst and Eriochrome Black T molecules, and a concentration of 50 mg/L may facilitate the most effective interactions, leading to enhanced degradation. Higher catalyst concentrations may saturate active sites or have inhibitory effects on the interaction, as shown in Figure 10.8 (d). The catalyst's presence significantly enhanced the degradation of Eriochrome Black T dye, as

shown in Figure 10.8 (e), demonstrating the catalyst's stability and ability to facilitate efficient degradation. This indicates that the synthesized catalyst was effective in breaking down dye molecules, leading to a higher degree of deterioration in the presence of the catalyst. The photocatalytic degradation of dye using MgNiS:Eu^{3+} and MgNiS:Sm^{3+} catalysts follows pseudo-first-order kinetics, as shown in Figure 10.8 (f). The high R^2 values of 0.987 and 0.995 and rate constant ' k ' 0.02347 min^{-1} and 0.03122 min^{-1} , indicate a good fit to the pseudo-first-order kinetic model, suggesting that the degradation process follows a consistent and predictable pattern. Figure 10.8 (g) illustrates a proposed degradation mechanism for Eriochrome Black T dye, providing insight into the possible steps involved in the photocatalytic degradation process. The proposed mechanism involves a surface-mediated process, where dye molecules interact with the catalyst surface, leading to the formation of reactive oxygen species (ROS). These ROS then play a crucial role in the degradation of dye molecule, ultimately resulting in its breakdown. This suggests a catalytic pathway involving surface adsorption, ROS generation, and oxidative degradation, facilitating the efficient breakdown of dye molecule. The specific steps and intermediates involved in the degradation process are depicted in the Figure, offering a clearer understanding of the mechanism.



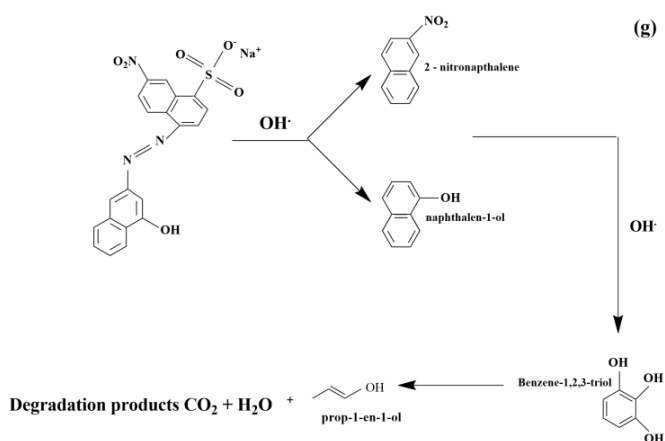


Figure 10.8: (a) Degradation of Eriochrome Black T dyes within 150 minutes. (b) Effect of catalyst dosage. (c) Effect of pH on the degradation of dyes. (d) Effect of catalyst dosage. (e) Effect of the degradation with or without catalyst. (f) Kinetic studies on the degradation of dyes. (g) Degradation mechanism for Eriochrome Black T dye.

10.3.9 Thermodynamic parameters

The thermodynamic parameters for the adsorption of Eriochrome Black T onto the adsorbent were calculated using a dosage of 5 mg/L and a concentration of 5000 mg/L. The results, presented in Table 10.2, indicate the negative values of ΔG (Gibbs free energy) at all temperatures suggest spontaneous and favorable adsorption. The linear correlation between $\ln K_d$ and $1/T$, as illustrated in Figure 10.9, facilitates the calculation of crucial thermodynamic parameters, specifically the enthalpy (ΔH) and entropy (ΔS) values. The negative values of ΔH and ΔS at lower temperatures indicate an exothermic, spontaneous, and favorable adsorption process. These findings suggest that the adsorption process is thermodynamically favorable and occurs spontaneously, with a preference for lower temperatures (Bedin *et al.*, 2016).

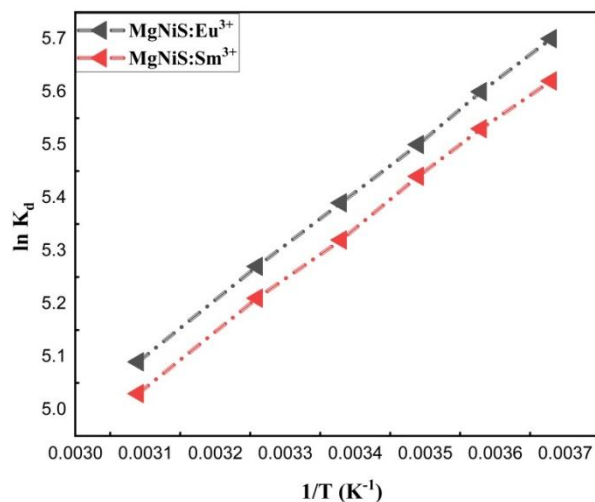


Figure 10.9: Van't Hof plot of $\ln(K_d)$ vs $1/T$.

Table 10.2: Thermodynamic parameters for the adsorption of Eriochrome Black T by MgNiS:Eu³⁺ and MgNiS:Sm³⁺.

MgNiS:Eu ³⁺ Temperature (K)	q _e (mg/g)	C _e (mg/L)	K _d = Q _e /C _e	ΔG = - R _T lnK _d (kJ/mol)	ΔH (kJmol ⁻¹)	ΔS (Jmol ⁻¹ k ⁻¹)
100	1956.22	360.90	7.44	-4.99	-27.9	-24.6
200	1876.66	345.45	7.23	-4.67	-27.4	-24.2
300	1839.90	328.90	6.99	-4.89	-26.7	-23.5
400	1811.78	361.22	6.54	-4.54	-26.1	-23.2
500	1798.67	344.44	6.33	-4.33	-25.7	-23.1
MgNiS:Sm ³⁺ Temperature (K)	q _e (mg/g)	C _e (mg/L)	K _d = Q _e /C _e	ΔG = - R _T lnK _d (kJ/mol)	ΔH (kJmol ⁻¹)	ΔS (Jmol ⁻¹ k ⁻¹)
100	2011.23	342.77	6.89	-4.45	-25.9	-26.6
200	1998.67	312.22	6.54	-4.89	-25.2	-26.2
300	1867.66	354.44	6.34	-4.43	-24.7	-25.8
400	1762.22	334.11	5.56	-4.79	-24.5	-25.4

500	1754.99	313.99	5.21	-4.77	-23.9	-25.1

10.3.10 Adsorption Kinetics

The adsorption kinetics of Eriochrome Black T (EBT) onto MgNiS:Eu³⁺ were investigated by monitoring the UV-vis spectra of dye solutions at various time intervals. The adsorption capacity was evaluated as a function of contact time, using an initial dye concentration of 40ppm and an adsorbent dose of 20 mg/L. The adsorption kinetics was examined using two kinetic models: the pseudo-first-order model Equation 10.12 and the pseudo-second-order model (Equation 10.13). These models enable the determination of the adsorption rate and capacity, providing insights into the mechanisms and efficiency of the adsorption process. To identify the most suitable model, linearized forms of these equations were used, allowing for the determination of the best fit. This analysis helped to understand the adsorption mechanism and rate-determining steps involved in the process (Kumari *et al.*, 2019), (David Kowanga *et al.*, 2016), (Revellame *et al.*, 2020a).

$$q_t = q_e (1 - e^{-k_1 t}) \quad (10.12)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (10.13)$$

The rate constant in pseudo-second-order kinetics is k_2 , (g mg⁻¹ min⁻¹), whereas in pseudo-first-order kinetics it is k_1 (min⁻¹). In terms of adsorbate equilibrium, q_e (mg g⁻¹) is the capacity, and in terms of time ‘ t ’ (min), q_t (mg) is the equilibrium adsorption capacity. The kinetics parameters for the adsorption of Eriochrome Black T dye onto MgNiS:Eu³⁺ were determined using pseudo-first-order and pseudo-second-order models. The values of k_1 , k_2 , and q_e were obtained from the linear plot of q_t vs. t , and the results are presented in Table 10.3. The correlation coefficient (R^2) values indicate that the pseudo-first-order model ($R^2 = 0.9788$) fits the data better than the pseudo-second-order model ($R^2 = 0.9544$), as shown in Figure 10.10. Additionally, the pseudo-first-order model has lower values of SSE, SD, and χ^2 , further confirming that it is the better-fitting kinetics model for the current dye adsorption system (Revellame *et al.*, 2020b).

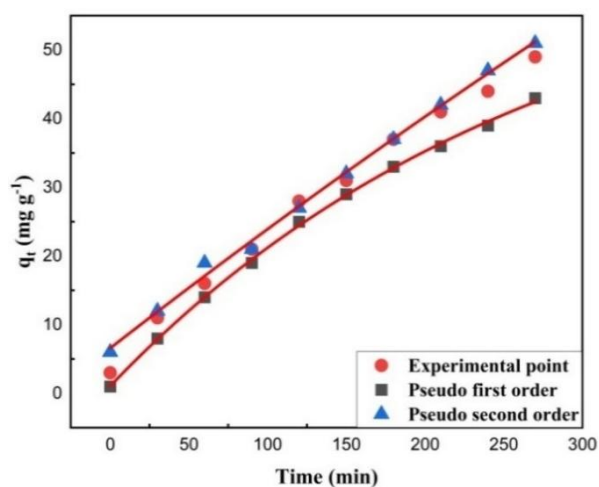


Figure 10.10: Pseudo first and second order kinetic study of MgNiS:Eu³⁺.

Table 10.3: Kinetic parameters for the adsorption of Eriochrome Black T dye using MgNiS:Eu³⁺.

Model	Parameters	Eriochrome Black T dye
Pseudo first order	$q_{e,exp}$ (mg g ⁻¹)	72.56
	$q_{e,cal}$ (mg g ⁻¹)	54.34
	k_1 min ⁻¹	0.032451
	SD	2.23
	χ^2	0.51
	SSE	24.33
	R ²	0.9788
Pseudo second order	$q_{e,cal}$ (mg g ⁻¹)	43.22
	k_2 (g mg ⁻¹ min ⁻¹)	0.0021034
	SD	12.34

	χ^2	0.99
	SSE	54.67
	R^2	0.9544

10.3.11 Adsorption Isotherms

The adsorption behavior of Eriochrome Black T dye onto MgNiS:Eu³⁺ was investigated using various isotherm models, including Langmuir, Freundlich, Sips, and Temkin models (Equations 10.14-10.17). The experiments were conducted by mixing 40 ppm of dye solution with 20 mg/L of catalyst, stirring at room temperature until equilibrium was reached. UV-Vis spectroscopy was used to analyze the solutions before and after adsorption, and the data were fitted to different isotherm models to determine the best-fit model. The study successfully determined the adsorption capacity and affinity of MgNiS:Eu³⁺ for dye, shedding light on the underlying adsorption behavior. By elucidating the adsorbent-adsorbate interaction, this research contributed to the understanding of the adsorption process, enabling the optimization of MgNiS:Eu³⁺ for efficient dye removal (Wang *et al.*, 2016), (Kumar *et al.*, 2016), (Hu *et al.*, 2021).

$$Q_e = \frac{Q_m K_L C_e}{1 + C_e K_L} \quad (10.14)$$

$$Q_e = K_F C_e^{1/n_F} \quad (10.15)$$

$$Q_e = \frac{Q_{max} K_S C_e^{1/n_S}}{1 + K_S C_e^{1/n_S}} \quad (10.16)$$

$$Q_e = B \ln(K_T C_e) \quad (10.17)$$

In this case, the equilibrium concentration is represented by C_e (mg L⁻¹) and the equilibrium adsorption capacity of the adsorbates after adsorption is indicated by Q_e (mg g⁻¹). The term Langmuir constant, or K_L (L mg⁻¹), reflects the binding energy in adsorption, while Q_m (mg g⁻¹) stands for maximum adsorption capacity. Adsorption intensity is indicated by n , and K_F indicates adsorption capacity from the Freundlich

isotherm. The exponent of the Sips isotherm is $1/n_s$, and the Sips constant is K_s . The maximum adsorption capacity of the Sips isotherm is expressed as Q_{max} (mg g^{-1}). The Temkin and equilibrium binding constants, B (J mol^{-1}) and K_T (L mg^{-1}), are associated with the maximal binding energy and the heat of adsorption, respectively. The gas constant is R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and the absolute temperature is T (K). The Freundlich isotherm indicates a multilayer, non-ideal, non-uniform distribution of sorption sites with varying affinities, while the Langmuir isotherm assumes an ideal monolayer and uniform distribution with equal energy sites. The Sips isotherm is a combination of the Langmuir and Freundlich models, and the Temkin isotherm is useful for systems with significant electrostatic interactions. Figure 10.11 provides a visual representation of the different isotherm. The correlation coefficients in Table 10.4 show that the Freundlich isotherm ($R^2 = 0.9877$) is the best fit model for Eriochrome Black T dye adsorption, followed by the Langmuir ($R^2 = 0.9612$), Sips ($R^2 = 0.9231$), and Temkin ($R^2 = 0.9121$) isotherms. This suggests that the adsorption behavior is more accurately described by the Freundlich model, which accounts for the non-ideal and non-uniform distribution of sorption sites based on the R^2 , SSE, SD, and χ^2 tests (Y. Yang & Guan, 2018), (Alkaim *et al.*, 2015), (Rovani *et al.*, 2019).

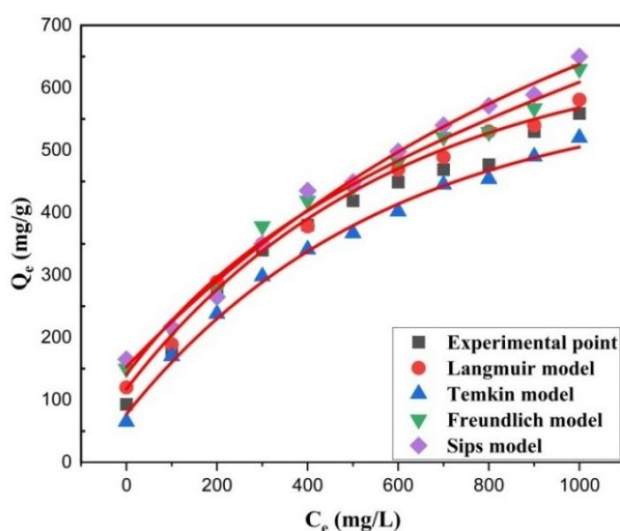


Figure 10.11: Different isotherm model plots for the adsorption of dye of MgNiS:Eu^{3+} .

Table 10.4: Langmuir, Sips, Temkin and Freundlich model isotherm parameter of MgNiS:Eu³⁺.

Model	Parameter	Eriochrome Black T
Langmuir model	Q _m (mg g ⁻¹)	2245.76
	K _L (L mg ⁻¹)	0.01221
	RL ²	0.9612
	SSE	1767.90
	SD (mg g ⁻¹)	130.90
	χ ²	75.67
Freundlich model	K _F (L mg ⁻¹)	422.43
	n _F	2.45
	RF ²	0.9877
	SSE	1233.55
	χ ²	12.34
	SD (mg g ⁻¹)	54.22
Sips model	Q _m (mg g ⁻¹)	2132.70
	K _s (L mg ⁻¹)	0.0319
	N _s	1.34
	RS ²	0.9231
	SSE	1679.90
	χ ²	65.90
Temkin model	SD (mg g ⁻¹)	120.90
	B (J mol ⁻¹)	4131.99
	KT (L mg ⁻¹)	0.4797
	RT ²	0.9121
	SSE	1899.89
	χ ²	120.99
	SD (mg g ⁻¹)	60.90

10.4 Conclusion

This investigation has successfully devised a methodology for synthesizing of MgNiS:Eu^{3+} and MgNiS:Sm^{3+} nanoparticles, which have demonstrated exceptional adsorption proficiency for Eriochrome black T dye. The comprehensive characterization of these nanoparticles revealed their unique physical and chemical properties, including average particle sizes of 29 nm and 34 nm, respectively, as well as a quasi-spherical morphology. The kinetic and thermodynamic analyzes demonstrated the excellent adsorption performance of these nanoparticles, as predicted by a pseudo-first-order model and Freundlich isotherm, with optimal adsorption occurring at lower temperatures. Notably, the photocatalytic degradation efficiency of these catalysts was found to be remarkably high, with 89.34% and 83.96% degradation of Eriochrome black T dye within a short duration of 50 minutes for MgNiS:Eu^{3+} and MgNiS:Sm^{3+} , respectively. These outstanding results demonstrate the potential of these catalysts for effective dye removal from contaminated water, outperforming existing adsorbents in terms of adsorption capacity and recyclability. This study highlights the potential of MgNiS:Eu^{3+} and MgNiS:Sm^{3+} nanoparticles as promising candidates for wastewater treatment applications, offering a cost-effective and efficient solution for removing hazardous dyes from contaminated water. The findings of this research have significant implications for the development of sustainable and environmentally friendly wastewater treatment technologies.

SUMMARY

This research presents an in-depth investigation into the synthesis, characterization, and photocatalytic efficacy of a series of lanthanide-doped metal sulfide nanoparticles, namely Zinc Sulfide (ZnS), Cadmium Sulfide (CdS), Nickel Sulfide (NiS), and Cobalt Sulfide (CoS). These nanoparticles were synthesized through diverse chemical routes, including reflux, hydrothermal, and co-precipitation methods, each chosen for its capacity to yield nanomaterials with desirable morphological and structural properties. To further enhance their functional performance, nanoparticles were doped with selected trivalent lanthanide ions (Eu^{3+} , Sm^{3+} , Pr^{3+} , Tb^{3+} , and Ce^{3+}), which are known to introduce beneficial modifications to the electronic structure and surface properties of semiconductor materials. The incorporation of lanthanide dopants was found to influence the crystallographic, optical, and catalytic characteristics of the host sulfides. The morphological and optical properties of the synthesized lanthanide-doped and undoped metal sulfide nanoparticles were comprehensively characterized using a suite of advanced analytical techniques. These included X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Ultraviolet–Visible (UV–Vis) Spectroscopy, Photoluminescence (PL) Spectroscopy, and Fourier Transform Infrared (FTIR) Spectroscopy. Each technique provided critical insights into the structural, morphological, electronic, and surface chemical attributes of the nanomaterials, which collectively govern their photocatalytic performance.

XRD analysis confirmed the successful formation of highly crystalline phases, with diffraction patterns indicative of both cubic zinc blende structures and rhombohedral symmetries, depending on the metal sulfide composition and the nature of lanthanide doping. The sharp and well-defined diffraction peaks across all samples signify excellent crystallinity and structural order. Moreover, the absence of secondary phases or extraneous impurity peaks indicates the high phase purity of the synthesized nanoparticles, underscoring the effectiveness of the adopted synthetic protocols. SEM micrographs revealed that nanoparticles exhibited relatively uniform

surface morphologies, with consistent particle shapes and size distributions. The materials appeared well-dispersed and free from notable agglomeration, suggesting the presence of adequate steric or electrostatic stabilization mechanisms during synthesis. TEM analyses provided precise measurements of particle size and shape, as well as detailed observation of lattice fringes in high-resolution mode, confirming the crystalline nature of the materials.

SAED patterns displayed discrete diffraction rings or spots, further corroborating the XRD findings and indicating polycrystalline or single-crystalline domains, respectively. UV–Vis absorption spectroscopy revealed notable shifts in the absorption edge of nanoparticles, which were dependent on dopant type and concentration. These shifts, either toward shorter wavelengths (blue shift) or longer wavelengths (red shift), reflect modifications in the band gap energies a critical parameter for light absorption in the visible region. Reduced band gap energy enhances the photocatalytic efficacy of nanoparticles by enabling more efficient utilization of the solar spectrum under ambient light conditions. PL spectroscopy provided additional insights into the recombination dynamics of photogenerated charge carriers. The doped nanoparticles exhibited moderate to enhanced PL intensities, which suggest alterations in radiative recombination efficiency. Importantly, a moderate PL emission generally implies suppressed electron–hole recombination, which correlates with prolonged charge carrier lifetimes an essential prerequisite for effective photocatalytic activity. FTIR spectroscopy further elucidated the surface chemistry of nanoparticles. The spectra exhibited characteristic metal sulfur (M–S) stretching vibrations, confirming the formation of metal sulfide frameworks. Additionally, absorption bands corresponding to surface hydroxyl groups, adsorbed water, and other surface-bound species were observed. These functional groups are likely to serve as active sites for dye adsorption and subsequent photocatalytic degradation, thereby contributing to the overall efficiency of the system.

Eu³⁺-doped ZnS nanoparticles with varying doping concentrations of 2 at.%, 4 at.%, and 6 at.% were successfully synthesized using a controlled reflux method. The broadening of the diffraction peaks, as predicted by the Scherrer equation, further

supports the nanosized nature of the particles. Photoluminescence (PL) spectroscopy revealed distinct emission peaks at 528 nm ($^5D_0 \rightarrow ^7F_1$), 543 nm ($^5D_0 \rightarrow ^7F_2$), 565 nm ($^5D_0 \rightarrow ^7F_3$), 572 nm ($^5D_0 \rightarrow ^7F_4$), 603 nm ($^5D_0 \rightarrow ^7F_5$), and 636 nm ($^5D_0 \rightarrow ^7F_6$). These emissions are indicative of successful incorporation of Eu^{3+} ions into the ZnS host lattice and effective radiative transitions, which are essential for optoelectronic applications. The chromaticity coordinates, calculated from the CIE diagram, showed that all the Eu^{3+} -doped ZnS samples emitted light in the near-white region. This suggests their potential applicability in white light-emitting diodes (WLED's) and other optical display technologies, highlighting their dual utility as photocatalysts and luminescent materials. The photocatalytic performance of the 6 at.% Eu^{3+} -doped ZnS nanoparticles was evaluated through the degradation of methyl red dye under acidic conditions. Using a catalyst dosage of 6 mg/L, an initial dye concentration of 15 ppm, and pH 3, a degradation efficiency of approximately 90% was achieved. The kinetics of the degradation process were found to follow a pseudo-first-order model, indicating that the concentration of dye molecules likely governs the rate-limiting step.

The effects of praseodymium (Pr^{3+}) doping on the structural, optical, and photocatalytic properties of cadmium sulfide (CdS) nanoparticles were systematically investigated. XRD analysis confirmed that the Pr^{3+} :CdS nanoparticles retained a hexagonal crystalline structure, indicative of successful doping without altering the fundamental lattice of the host CdS material. The diffraction patterns showed well-defined peaks, consistent with high crystallinity and phase purity. Morphological studies via SEM and TEM revealed uniformly distributed nanoparticles with defined shapes and minimal agglomeration. High-resolution TEM images further provided evidence of lattice fringes, corroborating the crystalline nature observed in the XRD results. FTIR spectra showed characteristic peaks corresponding to Cd–S stretching vibrations, along with additional bands associated with surface hydroxyl groups and adsorbed water molecules, suggesting the presence of active sites for photocatalytic reactions. UV–Vis spectroscopy revealed a shift in the absorption edge upon Pr^{3+} doping, indicating a modification in the band gap energy, which plays a vital role in enhancing visible-light absorption and,

consequently, photocatalytic performance. Photoluminescence spectra revealed moderate emission intensities, implying reduced recombination of photogenerated charge carriers an essential factor for improving photocatalytic efficiency. The colour emission behavior of the Pr^{3+} :CdS nanoparticles was further evaluated using the Commission Internationale de l'Éclairage (CIE) chromaticity diagram. The emission profiles suggest that the doped nanoparticles exhibit potential for use in optical and photonic devices due to their tunable luminescent properties. Photocatalytic experiments were conducted to assess the degradation efficiency of two model organic dyes: Methylene Blue (MB) and methyl red (MR). The optimal photocatalyst dose was determined to be 5 mg/L. Under alkaline conditions (pH 9 for MB and pH 11 for MR), the degradation efficiencies reached 89% and 94%, respectively. The degradation kinetics followed both the pseudo-first-order (PFO) and Langmuir–Hinshelwood (L–H) models, indicating a complex interaction between dye molecules and the catalyst surface involving both adsorption and reaction steps.

The synthesis and comprehensive characterization of samarium Sm^{3+} -doped Zinc Sulfide (ZnS) nanoparticles were carried out using a reflux-assisted chemical method. The primary objective was to investigate the influence of Sm^{3+} incorporation on the structural, morphological, chemical, optical, luminescent, kinetic, isothermal, and photocatalytic properties of the resulting nanomaterials. The incorporation of Sm^{3+} was found to significantly enhance both the luminescence and photocatalytic activity of ZnS nanoparticles, indicating the effectiveness of rare-earth doping in tuning the functional behavior of semiconductor materials. Among the various doping concentrations studied, the 9 at.% Sm^{3+} -doped ZnS nanoparticles exhibited the highest photocatalytic activity and were thus selected for further performance optimization. The optimal conditions for maximum dye removal were identified as a catalyst dosage of 15 mg/L, a reaction time of 210 minutes, pH 5, and an initial dye concentration of 10 ppm. These parameters facilitated efficient degradation of the target dye, Indigo Carmine, highlighting the excellent catalytic potential of the synthesized materials under mildly acidic conditions. X-ray Diffraction (XRD) analysis confirmed that all Sm^{3+} -doped ZnS samples crystallized in a cubic zinc blende phase with high purity, as evidenced by the absence of secondary phases.

Scanning Electron Microscopy (SEM) revealed a uniform nanoparticle morphology with an average particle size of approximately 5.15 nm, indicating successful synthesis of nanoscale materials. The nanostructured morphology is known to enhance surface reactivity and light absorption, both of which are beneficial for photocatalytic applications. Photoluminescence (PL) studies conducted under an excitation wavelength of 395 nm exhibited characteristic emissions at 559 nm ($^4G_{5/2} \rightarrow ^6H_{5/2}$), 595 nm ($^4G_{5/2} \rightarrow ^6H_{7/2}$), and 642 nm ($^4G_{5/2} \rightarrow ^6H_{9/2}$). These emissions are attributed to the 4f-4f electronic transitions of Sm^{3+} ions in the $4f^5$ configuration and confirm their successful integration into the ZnS host lattice.

CIE chromaticity diagram revealed that the emission colour lies within the visible spectrum, suggesting that the material holds promise for optoelectronic and photonic device applications. Kinetic studies demonstrated that the degradation of Indigo Carmine followed pseudo-first-order kinetics, indicating that the rate of reaction was dependent on the concentration of dye. Isothermal studies showed that the Langmuir model provided the best fit to the experimental data, suggesting monolayer adsorption of dye molecules onto a homogeneous catalytic surface. Reusability studies further confirmed the stability and durability of the Sm^{3+} -doped ZnS catalyst. The catalyst retained a high level of photocatalytic activity over five successive cycles without significant loss of efficiency, underscoring its potential for long-term environmental applications. The primary objective was to investigate the influence of Sm^{3+} incorporation on the structural, morphological, chemical, optical, luminescent, kinetic, isothermal, and photocatalytic properties of the resulting nanomaterials. The incorporation of Sm^{3+} was found to significantly enhance both the luminescence and photocatalytic activity of ZnS nanoparticles, indicating the effectiveness of rare-earth doping in tuning the functional behavior of semiconductor materials. Among the various doping concentrations studied, the 9 at.% Sm^{3+} -doped ZnS nanoparticles exhibited the highest photocatalytic activity and were thus selected for further performance optimization. The optimal conditions for maximum dye removal were identified as a catalyst dosage of 15 mg/L, a reaction time of 210 minutes, pH 5, and an initial dye concentration of 10 ppm. These parameters facilitated efficient degradation of the target dye, Indigo Carmine, highlighting the excellent catalytic

potential of the synthesized materials under mildly acidic conditions. XRD analysis confirmed that all Sm^{3+} -doped ZnS samples crystallized in a cubic zinc blende phase with high purity, as evidenced by the absence of secondary phases. SEM revealed a uniform nanoparticle morphology with an average particle size of approximately 5.15 nm, indicating successful synthesis of nanoscale materials. The nanostructured morphology is known to enhance surface reactivity and light absorption, both of which are beneficial for photocatalytic applications. PL studies conducted under an excitation wavelength of 395 nm exhibited characteristic emissions at 559 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$), 595 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$), and 642 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$). These emissions are attributed to the 4f–4f electronic transitions of Sm^{3+} ions in the 4f^5 configuration and confirm their successful integration into the ZnS host lattice. CIE chromaticity diagram revealed that the emission colour lies within the visible spectrum, suggesting that the material holds promise for optoelectronic and photonic device applications. Kinetic studies demonstrated that the degradation of Indigo Carmine followed pseudo-first-order kinetics, indicating that the rate of reaction was dependent on the concentration of dye. Isothermal studies showed that the Langmuir model provided the best fit to the experimental data, suggesting monolayer adsorption of dye molecules onto a homogeneous catalytic surface. Reusability studies further confirmed the stability and durability of the Sm^{3+} -doped ZnS catalyst. The catalyst retained a high level of photocatalytic activity over five successive cycles without significant loss of efficiency, underscoring its potential for long-term environmental applications. The enhanced activity is attributed to improved charge carrier separation and suppressed electron–hole recombination due to the presence of Sm^{3+} dopants acting as electron traps within the ZnS matrix.

The photocatalytic degradation of malachite green dye using terbium Tb^{3+} -doped nickel sulfide (NiS) nanoparticles as an active catalyst, with the performance further evaluated in the presence of various additives including inorganic oxidants, transition metal ions, and inorganic anions. The novelty of this research lies in its focus on lanthanide ion doping specifically Tb^{3+} as a strategic approach to enhance photocatalytic activity, while also shedding light on the fundamental role of such doping in tailoring the synthesis, structural properties, and photocatalytic

applications of semiconductor materials used for organic dye degradation. Structural analysis revealed that the synthesized Tb³⁺-doped NiS nanoparticles crystallized in a rhombohedral phase with a space group of *R3m*. The average crystallite sizes were calculated to be approximately 12 nm and 16 nm, indicating nanoscale dimensions suitable for high-surface-area applications. Furthermore, particle size analysis using ImageJ software determined the average particle size to be around 19 nm, corroborating the nanostructured nature of the materials. Photoluminescence studies conducted under an excitation wavelength of 351 nm exhibited four characteristic emission peaks at 488 nm, 543 nm, 584 nm, and 620 nm. These emissions correspond to the well-known 4f–4f transitions of Tb³⁺ ions, specifically ⁵D₄→⁷F₆, ⁵D₄→⁷F₅, ⁵D₄→⁷F₄, and ⁵D₄→⁷F₃ transitions, respectively. The presence of these sharp emission lines confirms the successful incorporation of Tb³⁺ into the NiS host lattice and the stabilization of the trivalent oxidation state within the material. The optical properties of the doped nanoparticles were found to be significantly altered upon Tb³⁺ incorporation. An increase in the optical band gap was observed, which suggests enhanced electron–hole separation. This widening of the band gap is attributed to Tb³⁺-induced changes in the electronic structure, which potentially create localized states that inhibit the rapid recombination of charge carriers. This effect is highly beneficial for photocatalytic applications, as it increases the lifetime of photogenerated electrons and holes, thus enhancing the degradation efficiency of target pollutants. Photocatalytic performance tests were conducted to evaluate the degradation of malachite green dye under visible light irradiation. Tb³⁺-doped NiS catalyst achieved a degradation efficiency of 94% within 90 minutes, demonstrating excellent photocatalytic potential. Further investigations into the role of various additives revealed that the presence of transition metal ions and inorganic oxidants significantly enhanced the degradation rate, likely by generating additional reactive oxygen species. Conversely, the presence of inorganic anions such as Cl[−], SO₄^{2−}, or NO₃[−] was found to hinder the degradation process, possibly due to the competitive adsorption or scavenging of reactive radicals.

This following study presents a comprehensive investigation into the photocatalytic efficiency of PEG@ZnS:Au and PVP@ZnS:Au nanoparticles for the degradation of

Rhodamine B (RhB) dye under UV irradiation. Nanoparticles demonstrated remarkable photocatalytic performance, achieving degradation efficiencies of 94.25% and 91.45%, respectively, thus affirming their potential as efficient nanocatalysts for wastewater treatment applications. Structural and morphological characterizations confirmed that both catalysts possess a cubic zinc blende lattice structure. The analysis further revealed a heterogeneous distribution of particle shapes and surface textures, indicative of a mesoporous nature. The observed pore sizes ranged between 2-50 nm, supporting their capacity for high surface area-mediated adsorption and enhanced photocatalytic interaction with dye molecules. Temperature-dependent studies showed that the photocatalytic degradation efficiency increased consistently with rising temperature, likely due to enhanced diffusion rates and accelerated radical-mediated reaction kinetics at elevated thermal conditions. Catalyst loading optimization identified 15 mg/L as the critical dosage for achieving maximal degradation efficiency, beyond which the rate of improvement plateaued or declined, potentially due to light scattering or catalyst aggregation effects. The addition of hydrogen peroxide (H_2O_2) was found to significantly boost photocatalytic performance by generating an increased number of hydroxyl ($\cdot\text{OH}$) radicals, which are known to play a pivotal role in the oxidative breakdown of dye molecules. In contrast, the presence of inorganic anions such as chloride (Cl^-), phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), and nitrate (NO_3^-) was observed to impede the degradation process to varying degrees. This inhibitory effect is attributed to the scavenging of reactive radicals or the competitive adsorption of anions on active catalyst sites. The adsorption behavior of Rhodamine B on the surface of both PEG@ZnS:Au and PVP@ZnS:Au nanoparticles followed the Langmuir isotherm model, indicating monolayer adsorption onto a homogenous surface with a finite number of active sites. Moreover, the kinetics of the photocatalytic degradation process were best described by the pseudo-first-order model, suggesting that the rate-limiting step was directly proportional to the concentration of dye in the solution.

In the continuation of this research, the photocatalytic activity of cerium-doped cobalt sulfide (CoS:Ce^{3+}) nanoparticles was systematically investigated for the degradation of three representative organic pollutants: Congo Red, Methylene Blue,

and the pharmaceutical compound Cefixime. The CoS:Ce³⁺ nanoparticles exhibited excellent photocatalytic performance, achieving high degradation efficiencies for all three contaminants within a remarkably short reaction time of 25 minutes. Among the various doping concentrations tested, the optimal photocatalytic efficiency was observed at a Ce³⁺ concentration of 0.50 at.%, which was attributed to improved optical absorption, enhanced electron–hole separation, and superior charge transport properties induced by the Ce³⁺ dopant. Structural and surface analysis revealed that the CoS:Ce³⁺ nanostructures possess a highly porous architecture with a complex pore system and large surface area. These factors collectively enhance the availability of active sites for dye molecule adsorption and catalytic interaction. This structural advantage, along with the electronic modifications conferred by Ce³⁺ incorporation, significantly contributed to the observed increase in photocatalytic efficiency. Kinetic studies of dye adsorption on the surface of CoS:Ce³⁺ nanoparticles indicated conformity with the pseudo-first-order model, suggesting that dye concentration directly influences the degradation rate. Additionally, the equilibrium adsorption behavior was found to fit well with the Langmuir isotherm model, indicating monolayer adsorption on a homogeneous catalyst surface with uniform active sites.

The next study demonstrates the potential of praseodymium-doped nickel sulfide (NiS:Pr³⁺) nanoparticles as highly effective photocatalysts for wastewater treatment applications, particularly in the degradation of persistent and hazardous dyes such as Rhodamine B, Methylene Blue, Methyl Orange, and Congo Red. The photocatalytic performance was systematically evaluated under various experimental conditions, with optimization studies revealing that a doping concentration of 4 at.% Pr³⁺ yielded the most effective catalytic activity. At this concentration, nanoparticles achieved exceptional degradation efficiencies across all tested dyes, thereby underscoring their suitability for addressing environmental pollution. Adsorption isotherm modelling provided more profound insights into the interaction between dye molecules and the nanoparticle surface. The Langmuir isotherm model fits well with Rhodamine B and Methyl Orange, indicating monolayer adsorption onto a homogeneous surface with a finite number of identical sites. Freundlich isotherm model was more applicable for

Methylene Blue, suggesting a heterogeneous surface and the occurrence of multilayer adsorption. The adsorption of Congo Red, however, conformed to the Temkin model, implying a complex adsorption mechanism likely influenced by electrostatic interactions and surface heterogeneity. Kinetic studies of the degradation process revealed that dye degradation followed pseudo-first-order kinetics, indicating that the rate of photodegradation is directly proportional to the concentration of dye. This kinetic behavior is characteristic of heterogeneous photocatalytic reactions, where the rate-limiting step is typically the interaction of adsorbed dye molecules with photogenerated reactive species.

In the last investigation, a novel methodology was successfully developed for the synthesis of europium- and samarium-doped magnesium nickel sulfide (MgNiS:Eu^{3+} and MgNiS:Sm^{3+}) nanoparticles, which exhibited outstanding adsorption and photocatalytic capabilities toward the removal of Eriochrome Black T dye from aqueous media. Detailed physicochemical characterization revealed quasi-spherical morphologies with average particle sizes of 29 nm for MgNiS:Eu^{3+} and 34 nm for MgNiS:Sm^{3+} . These morphological and structural attributes contributed significantly to the high surface activity and adsorption potential of the synthesized nanomaterials. Kinetic analysis indicated that the adsorption process followed a pseudo-first-order model, suggesting that physical adsorption was the rate-limiting step. Furthermore, the adsorption behavior conformed well to the Freundlich isotherm model, implying heterogeneous surface adsorption and multilayer dye uptake. Thermodynamic studies revealed that adsorption was more favorable at lower temperatures, indicative of an exothermic adsorption process. The photocatalytic performance of nanoparticles was also found to be highly efficient. Under optimized conditions, MgNiS:Eu^{3+} and MgNiS:Sm^{3+} achieved degradation efficiencies of 89.34% and 83.96%, respectively, for Eriochrome Black T dye within just 50 minutes of irradiation. These results not only underscore the rapid and effective photocatalytic activity of the materials but also position them as superior alternatives to conventional adsorbents and photocatalysts. In addition to their exceptional degradation and adsorption efficiencies, both MgNiS:Eu^{3+} and MgNiS:Sm^{3+} nanoparticles demonstrated robust reusability, maintaining performance across multiple cycles without significant loss

of catalytic activity. This underscores their economic and environmental viability for long-term application in wastewater remediation.

Overall, this research demonstrates that lanthanide-doped metal sulfide nanoparticles are highly effective, reusable, and tunable photocatalysts for the degradation of dyes in wastewater. Their enhanced charge separation, improved light absorption, and surface-active sites make them superior to undoped systems and many conventional photocatalysts. The ability to degrade multiple dye types within short timeframes, along with high reusability and structural stability, positions these materials as promising candidates for real-world environmental remediation. The findings make a substantial contribution to the growing field of photocatalytic nanotechnology, providing insights into how dopant selection, synthesis methods, and environmental conditions impact catalytic efficiency. Future work should focus on scaling up these systems, integrating them into pilot-scale water treatment plants, and exploring visible-light-driven photocatalysis for broader environmental applicability.

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BIO-DATA OF THE CANDIDATE

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6. **Educational Qualifications:**

Qualification	Year of Passing	Board/University	Subjects	Marks %	Division
HSLC	2013	Mizoram Board of School Education	English, Mizo, Mathematics, Science, Social sciences	64.8%	First
HSSLC	2015	Mizoram Board of School Education	English	65%	First
B.Sc (Chemistry)	2018	Mizoram University	Chemistry, Botany, Zoology, General	71.58%	First
M.Sc (Chemistry)	2020	Mizoram University	Chemistry (Project in Organic Chemistry)	72.5%	First

List of Publications

A. Publication from thesis

1. **Lianmawii, L.,** Chuaudingpuia, P. C., Leishangthem, N., Lalrindiki, F., & Singh, N. M. (2025). Photocatalytic degradation of rhodamine B dye using PEG@ ZnS: Au and PVP@ ZnS: Au nanoparticles. *Journal of Industrial and Engineering Chemistry*, 146, 621-640. <https://doi.org/10.1016/j.jiec.2024.11.045>
2. **Lianmawii, L., & Singh, N. M.** (2025). Effect of additives on the photocatalytic degradation of malachite green using NiS: Tb³⁺ nanoparticle and their photoluminescence properties. *Journal of Molecular Structure*, 1320, 139748. <https://doi.org/10.1016/j.molstruc.2024.139748>
3. **Lianmawii, L., & Singh, N. M.** (2023). Luminescence and photocatalytic degradation of indigo carmine in the presence of Sm³⁺ doped ZnS nanoparticles. *Scientific Reports*, 13(1), 22450. <https://doi.org/10.1038/s41598-023-49912-6>
4. **Lianmawii, L.,** Shagolsem, B. S., Singh, N. H., & Singh, N. M. (2025). A comparative study on the photocatalytic activity of MgNiS:Eu³⁺ and MgNiS:Sm³⁺ nanoparticles for the degradation of eriochrome black T dye. *Inorganic Chemistry Communications*, 172, 113694. <https://doi.org/10.1016/j.inoche.2024.113694>
5. **Lianmawii, L., & Singh, N. M.** (2025). Photocatalytic degradation of congo red, methylene blue, and cefixime using CoS:Ce³⁺ nanoparticles: A kinetic and thermodynamic analysis. *Materials Chemistry and Physics*, 344, 131067. <https://doi.org/10.1016/j.matchemphys.2025.131067>
6. **Lianmawii, L., & Singh, N. M.** (2025). Photocatalytic Degradation of Tartrazine Dye using CoS, NiS, and ZnS: A Comprehensive Study on Isotherms, Kinetics, Thermodynamics, and Photoluminescence Analysis. *Materials Chemistry and Physics*, 131354. <https://doi.org/10.1016/j.matchemphys.2025.131354>

7. **Lianmawii, L., & Singh, N. M.** (2025). Enhanced Photocatalytic and Photoluminescence Properties of NiS Doped with Pr^{3+} for Efficient Dye Degradation: Kinetics and Isotherm Studies. *Chemistry Select*, 10(34), e01479. <https://doi.org/10.1002/slct.202501479>
8. **Lianmawii, L., & Singh, N. M.** (2024). Photoluminescence and photocatalytic degradation of methylene blue and methyl red using Pr^{3+} doped CdS nanoparticles. *Russian Journal of Physical Chemistry B*, 18(1), 325-342. <https://doi.org/10.1134/S1990793124010329>
9. **Lallianmawii, & Singh, N. M.** (2023, May). Effect of Eu^{3+} on the Luminescence and Photocatalytic Properties of ZnS Nanoparticles. In *International Conference on Inventive Material Science Applications* (pp. 13-28). Singapore: Springer Nature Singapore. https://doi.org/10.1007/978-981-99-4189-6_2
10. **Lianmawii, L., Singh, K. B., Singh, N. R., & Singh, N. M.** (2025). A review: photocatalytic degradation of dyes by metal sulfide nanoparticles. *Brazilian Journal of Chemical Engineering*, 42(1), 1-30. <https://doi.org/10.1007/s43153-023-00425-9>

B. Publication from other area

Shagolsem, B. S., Lianmawii, L., Chuaudingpuia, P. C., Lalrindiki, F., Moirangthem, R. S., & Singh, N. M. (2025). Synthesis, Structural Analysis, and Photocatalytic Evaluation of $\text{Fe}_3\text{O}_4/\text{SnO}_2:\text{Pr}^{3+}$ Nanocomposite Using *Artocarpus heterophyllus* L., for Dye and Pesticide Degradation. *Chemistry–An Asian Journal*, e202500503. <https://doi.org/10.1002/asia.202500503> ‘

C. Conference/Workshop

1. Presented 'Photocatalytic degradation of dyes using Pr^{3+} ions doped CdS nanoparticles their structural, optical and photoluminescence properties' at *Mizoram Science Congress*, (2022) on 24th to 25th November, 2022 at Mizoram Science Congress 2022 on 24-25 November 2022, Organized by Mizoram Science, Technology, and Innovation Council (MISTIC) in collaboration with Mizo Academy of Sciences (MAS), Mizoram Science Society (MSS), Science Teachers' Association, Mizoram (STAM), Geological Society of Mizoram (GSM), Mizoram Mathematics Society (MMS), Biodiversity and Nature Conservation Network (BIOCON) and Mizoram Information & Technology Society (MITS); Aizawl, Mizoram, India.
2. Presented 'Photoluminescence study of Pr^{3+} doped CdS Nanoparticles and its photocatalytic activity' at the *International Conference on Metallomics, Bio-diversity and Human Health Recent Advances and Synthesis* on 3-4th March, 2023, organized by Department of Life Sciences (Zoology), Manipur University.
3. Presented 'Photoluminescence properties and photocatalytic degradation of organic dyes in the presence of Pr^{3+} doped CdS nanoparticles' at the 3rd *International Conference on Material Science, Smart Structures and Applications ICMSS- 2023* on 27-28th March, 2023 organized by the Department of Electronics and Communication Engineering, Surya Engineering College, Erode, Tamil Nadu, India.
4. Presented 'Luminescence properties and visible light photocatalytic degradation of methylene blue and methyl red with Pr^{3+} doped CdS nanoparticles' at the *International Conference on Emerging Trends in Chemistry* on 16-17th March, 2023 organized by the Department of Chemistry, Pandu College, Assam Don Bosco University, Tapesia Garden, Sonapur, Assam, India.
5. Presented 'Structural, Optical and Photoluminescence properties of Eu^{3+} doped ZnS nanoparticles' at the *International Conference on Recent Advances in Energy Materials and its Applications* on 30-31st May 2023

organized by the Department of Physics, Pachhunga University College, Mizoram University, Aizawl, Mizoram, India.

6. Presented 'Effect of Eu^{3+} on the Luminescence and Photocatalytic Properties of ZnS Nanoparticles' at the 6th *International Conference on Inventive Material Science and Applications (ICIA 2023)* on 11-12th May, 2023 organized by PPG Institute of Technology, Coimbatore, India.
7. Presented 'Effect of Terbium Ion Doping in ZnS on the Luminescence Performance and Photocatalytic Degradation of Norfloxacin at the *International Conference on Current Trends in Green and Sustainable Chemistry (ICCTGSC -2023)* on 11-12th May, 2023 organized by Department of Chemistry, Pachhunga University, College.
8. Presented 'Effect of lanthanides on the luminescence properties and photocatalytic degradation of methylene blue' at the *International Conference on Science and Technology for Innovative and Sustainable Development (STISD-2023)* on 28-30th June, 2023 organized by Department of Chemistry and Department of Industrial Chemistry, Mizoram University, Aizawl, India.
9. Presented 'Effect of Metal Sulfide Nanoparticles on the Photocatalytic Degradation and Photoluminescence properties' at the *International Conference on Recent Advanced in Mathematical, Physical and Chemical Science (ICRAMPC - 2024)* on 21-23rd February, 2024 organized by School of Physical Science, Mizoram University, Aizawl, India.
10. Presented 'Effect of additives on the photocatalytic degradation of Malachite Green using NiS:Tb^{3+} Nanoparticle and their photoluminescence properties' at National Convention of Chemistry Teachers (NCCT-2024) and International Conference on Current Advances in Chemical Science Research and Education (CACSRE-2024) on 6-8th November, 2024 organized by Mizoram University, Association of Chemistry Teachers (ACT), Mizoram, India.



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Photocatalytic degradation of rhodamine B dye using PEG@ZnS:Au and PVP@ZnS:Au nanoparticles

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ABSTRACT

The textile industry significant contribution to water pollution necessitates the development of innovative solutions for efficient wastewater treatment. This study reports the successful synthesis of PEG@ZnS:Au and PVP@ZnS:Au nanoparticles via co-precipitation method, characterized by a suite of analytical techniques including photoluminescence (PL), Brunauer-Emmett-Teller (BET) analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). The photocatalytic activity of the synthesized nanoparticles was evaluated, revealing that PEG@ZnS:Au and PVP@ZnS:Au nanoparticles degraded 94.25 % and 91.45 % of rhodamine B dye, respectively, within a 30-minute timeframe, showcasing their exceptional catalytic performance. Kinetic studies revealed pseudo-first-order behavior, conforming to the Langmuir isotherm model, with an endothermic adsorption process. The degradation process is mediated by forming reactive oxygen species (ROS), which are generated by electron-hole pairs upon photoexcitation. This research underscores the potential of nanoscale materials for enhanced photocatalysis. It provides valuable insights into developing efficient wastewater treatment strategies, highlighting a promising approach for mitigating the environmental impact of textile industry effluents.

Introduction

The persistence of organic dyes in water bodies poses a critical environmental and public health issue due to their recalcitrant characteristics and toxicological properties. Consequently, the need for efficacious water treatment solutions has become a pressing priority in the 21st century, underscoring the imperative for innovative and sustainable remediation technologies to mitigate these hazards. The textile industry is a significant sector globally, employing approximately 35 million people and generating annual revenues of around \$1 trillion, accounting for 7 % of global exports [1]. However, this industry also substantially contributes to environmental pollution, relying heavily on fuels and chemicals in its production processes. Heavy metal pollution from wastewater constitutes a significant environmental and health hazard. The release of toxic elements like lead, mercury, cadmium, and arsenic can degrade aquatic ecosystems and contaminate the food chain. Human exposure to these pollutants is associated with severe health outcomes, including organ damage, neurological disorders, developmental impairments, and carcinogenesis. Food dye removal from wastewater is

vital due to health and environmental concerns [2]. A critical aspect of the textile industry's environmental footprint is its water usage, particularly in the washing, bleaching, and dyeing stages [3]. The multifaceted utility of synthetic dyes has led to their pervasive adoption in diverse industries, notably textile, leather, pharmaceutical, and paper production, driven by their ability to impart vibrant colors and functional properties. The textile industry generates significant amounts of solid waste, comprising discarded fabric, broken yarn, and packaging materials, presenting both opportunities for recycling and waste reduction, as well as serious environmental challenges. Unremoved dyes can contaminate waterways, harming aquatic ecosystems and human well-being. Pesticide pollution of water resources constitutes a major environmental and public health concern. The infiltration of pesticides into aquatic systems through non-point sources, such as agricultural runoff, can have far-reaching consequences, including human health impairments and ecological degradation [4]. Furthermore, the complex composition of textile sludge, a byproduct of wastewater treatment in the textile industry, poses a substantial environmental risk, with high concentrations of micronutrients, heavy metal cations, organic

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Effect of additives on the photocatalytic degradation of malachite green using NiS:Tb³⁺ nanoparticle and their photoluminescence properties

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Nanoparticles

ABSTRACT

The contamination of wastewater with synthetic dyes presents a critical challenge, highlighting the need for advanced technologies and approaches to effectively manage, treat, and remediate polluted wastewater and mitigate its adverse environmental and health impacts. This study focuses on the photocatalytic degradation of malachite green dye, a widely used synthetic dye, using nickel sulfide nanoparticles doped with Tb³⁺ ions. The objective is to explore the potential of this approach in breaking down the dye into harmless components, thereby reducing its toxicological impacts on the environment and human health. The catalyst was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), photoluminescence spectroscopy (PL), X-ray photoelectron spectroscopy (XPS), and ultraviolet-visible spectroscopy (UV). The effects of pH levels and various additives, including transition metals, inorganic oxidants, and inorganic anions, on the degradation process were systematically examined. The results demonstrate a high degradation efficiency of 94 % within 90 min, highlighting the efficacy of the photocatalytic process. Notably, adding transition-metal ions and inorganic oxidants enhanced the degradation rate, whereas inorganic anions had an inhibitory effect. Furthermore, an artificial neural network (ANN) model was developed to predict the degradation rate, demonstrating a strong correlation between experimental data and predicted values. This study provides valuable insights into optimizing photocatalytic degradation processes. It showcases the potential of ANN modelling in predicting the photocatalytic activity of nickel sulfide nanoparticles doped with Tb³⁺ in the presence of various additives.

1. Introduction

Water contamination in the biosphere has increased due to rapid urbanization, changing consumption habits, population growth, and rapidly increasing socioeconomic development rates [1]. Heavy metals, dyes, toxic organic compounds, phenols, and so on are all significant pollutants from residential and commercial activities that can alter natural water color [2,3]. This pollution load poses a significant challenge for wastewater management because it raises treatment costs and adds a range of chemical and microbiological contaminants to water sources [4]. Water-dye pollution prevents sunlight from penetrating the surface and causes photosynthesis to proceed more slowly [5]. Also, colorants disrupt gas solubility, impacting the development of aquatic vegetation and animal life. The colors used in textiles are highly toxic and carcinogenic [6]. The wastewater's multicolored discharge also has an adverse visual effect because human eyes can sense color at quantities as low as 1 ppm [7]. Water clarity and gas solubility are impacted by the

colored effluent's ability to absorb and reflect sunlight [8]. The increasing water contamination due to various pollutants has made wastewater management challenging. Textile dye wastewater contains various toxic dyes, including congo red, methylene blue, and malachite green dye (MGD). MGD is a widely used cationic dye in the textile, paper, and leather industries due to its antiseptic and therapeutic properties in treating fish diseases. Therefore, it is essential to develop strategies for safely handling, treating, and disposing of MGD-containing wastewater to mitigate its harmful effects. Recently, semiconductor-mediated photocatalysis has emerged as a viable and eco-friendly strategy for addressing environmental challenges. The development of photocatalysts with enhanced stability, efficiency, and affordability is crucial for harnessing the full potential of this technology [9,10]. The treatment costs have increased significantly, and the presence of chemical and microbiological contaminants in water sources has raised concerns over public health and safety [10]. UV energy and photocatalysis are both crucial for heterogeneous photocatalysis to

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OPEN Luminescence and photocatalytic degradation of indigo carmine in the presence of Sm^{3+} -doped ZnS nanoparticles

Lal Lianmawii^{1,2} & N. Mohondas Singh^{1,2}✉

Industrial wastewater discharge is well acknowledged to constitute a significant environmental and public health risk. In addition, synthetic dyes used in the textile sector are major culprits in water pollution. The amount of water polluted by these dyes is simply staggering. We urgently address this issue to protect our planet and health. The degradation of indigo carmine dye in the presence of Sm^{3+} -doped ZnS nanoparticles is reported in this study and characterized by XRD, FTIR, SEM, EDX, TEM, BET, PL, UV, etc. The particle size calculated from the Scherrer equation was 3–12 nm. When excited at 395 nm, Sm^{3+} undergoes f–f transitions, which are visible as prominent peaks in the photoluminescence spectrum at 559, 595, and 642 nm wavelengths. The catalyst showed vigorous catalytic activity for dye degradation, with a 93% degradation rate when used at 15 mg/L catalyst within 210 min. The reaction was found to have pseudo-first-order kinetics. After applying the Freundlich and Langmuir data, the Langmuir isotherm offered the best fit. The findings indicate that the Sm^{3+} -doped ZnS catalyst might be successfully used in the degradation of dyes present in the environment. Doping with Sm^{3+} ions can significantly change the photocatalytic breakdown of indigo carmine and the luminescence characteristics of ZnS.

Abbreviations

XRD	X-ray diffraction
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
SAED	Selected area electron diffraction
EDX	Energy dispersive X-ray analysis
TEM	Transmission electron microscopy
BET	Brunauer–Emmett–Teller
PL	Photoluminescence
UV	Ultraviolet spectroscopy
AOP	Advanced oxidation process
FWHM	Full width half maximum
ROS	Reactive oxygen species
VB	Valence band
CB	Conduction band

Dyes and dye-related intermediates, surfactants, and minor metal residues are the chemical pollutants concerned with environmental preservation^{1–3}. 10–15% of all dyes are lost to wastewater during dyeing. Therefore, the effluent must be treated before being released into the environment^{4,5}. Dyes may remain in the water for an extended period, lowering the quality of the aquatic ecosystem⁶. Dyes have the potential to pollute the environment due to their chemical makeup, persistence, and negative environmental impacts. These pigments frequently resist both biological and physical processing methods. Industries, including textile, printing, and papermaking, frequently employ dyes. These companies pollute the water by discharging wastewater that contains dyes. Fish, algae, and other aquatic life may become poisoned by certain dyes and byproducts of their decomposition. Persistent and poisonous dyes may build up in the food chain. Animals that consume tainted food or water may collect toxic

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Short communication

A comparative study on the photocatalytic activity of MgNiS:Eu^{3+} and MgNiS:Sm^{3+} nanoparticles for the degradation of eriochrome black T dyeLal Lianmawii, Brojendro Singh Shagolsem, Nongmaithem Herojit Singh, N. Mohondas Singh^{*}

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ABSTRACT

Discharging synthetic dyes into aquatic ecosystems and soil poses significant threats to marine life and soil fertility, necessitating urgent remediation solutions. Developing efficient photocatalysts for dye degradation has recently garnered significant attention as a viable solution. MgNiS:Eu^{3+} and MgNiS:Sm^{3+} nanoparticles were successfully synthesized via the reflux method, exhibiting potential as photocatalytic materials. The synthesized nanoparticles were comprehensively characterized using various analytical techniques such as TEM, SEM, XRD, FTIR, PL, UV and Raman spectroscopy. Their photocatalytic activity was evaluated for degradation of the Eriochrome Black T (EBT) dye, demonstrating potential for environmental remediation. The synthesized nanoparticles exhibited uniform particle sizes, ranging from 31–34 nm, as determined by the Debye-Scherrer equation. Notably, these nanoparticles demonstrated exceptional photocatalytic efficacy in degrading Eriochrome Black T, a notorious textile dye pollutant. MgNiS:Eu^{3+} and MgNiS:Sm^{3+} nanoparticles efficiently degraded EBT by 89.34 % and 83.96 %, respectively, at pH 5, 50 mg/L dosage, and 10 ppm initial concentration, within 50 min. The kinetic analysis revealed that the photocatalytic degradation of Eriochrome Black T dye follows pseudo-first-order reaction kinetics. This indicates that the reaction rate is directly proportional to the dye concentration. The Freundlich isotherm model best describes the adsorption data for Eriochrome Black T dye. The outstanding photocatalytic performance of MgNiS:Eu^{3+} and MgNiS:Sm^{3+} nanoparticles underscores their potential as efficacious catalysts for the remediation of hazardous dye pollutants, thereby contributing to the advancement of sustainable environmental solutions.

1. Introduction

The unregulated discharge of industrial effluent into the environment poses a significant threat to ecological sustainability [1,2]. The textile dyeing industry is a substantial consumer of groundwater and generates considerable effluent throughout various stages of the dyeing process. A portion of these dye effluents are released untreated into soil and waterways, leading to potential environmental hazards [3]. This pollution can harm aquatic life, disrupt ecosystem balance, and contaminate soil, reducing its quality and fertility, thereby damaging agriculture and plant life [4]. The harmful effects of these contaminants on aquatic animals, plants, and other species may result in biodiversity loss [5,6]. Industrial wastewater, including that from paper and pulp, chemical, petrochemical, and dyeing industries contains hazardous organic and inorganic contaminants that can harm the natural environment [7,8]. Some of these dyes are extremely toxic and endanger the surrounding ecosystem. Water contamination occurs as a result of

industrial wastewater discharge, which includes organic and inorganic pollutants [9]. Industrial contaminants can persist and accumulate in soil, leading to soil pollution, which can impact plant life and agricultural productivity [10]. Volatile components from industrial processes may contribute to air pollution, altering air quality in the vicinity of these industries [11]. Toxic compounds in industrial effluents can bioaccumulate in organisms over time, leading to bioaccumulation in the food chain and disrupting the natural equilibrium of ecosystems [12]. The proliferation of organic compounds in various industrial and agricultural sectors poses a significant threat to environmental sustainability, potentially leading to the extinction of sensitive species and compromising biodiversity and ecosystem services. The scientific community acknowledges the imperative of environmental safety, particularly with regard to the detrimental impact of organic pollutants, such as dyes, on aquatic ecosystems [13]. Dyes are carcinogenic, toxic, and harmful to human health, the environment, and aquatic ecosystems [14]. Water contamination is primarily caused by industrial effluents

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Photocatalytic degradation of congo red, methylene blue, and cefixime using CoS:Ce³⁺ nanoparticles: A kinetic and thermodynamic analysis

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ABSTRACT

This investigation demonstrates the efficacy of CoS:Ce³⁺ nanoparticles in degrading industrial dyes achieving exceptional degradation efficiencies of 94 % for congo red, 96 % for methylene blue, and 89 % for cefixime, completed within an impressively short reaction time of 25 min. XRD analysis confirms the successful synthesis, revealing a well-defined cubic spinel structure with crystallite sizes within a range of 25–49 nm. SEM analysis reveals a Ce³⁺ concentration dependent evolution in nanoparticle morphology, yielding hierarchical structures with varied sizes and shapes. Nitrogen adsorption-desorption analysis discloses high surface areas and complex pore structures, with enhanced surface area and pore volume at elevated Ce³⁺ concentrations. The novelty of this work lies in integrating advanced material synthesis techniques, the systematic optimization of nanoparticle properties through Ce³⁺ doping, and a comprehensive analytical approach that offers mechanistic insights into the rapid and efficient degradation of industrial dyes and environmental pollutants.

1. Introduction

The textile industry's persistent organic pollutants and effluents have been a longstanding research focus, with a particular emphasis on the remediation of harmful organic dyes that compromise water quality [1, 2]. Studies indicate that up to 50 % of dyes utilized in textile production remain unfixed to the fiber, contaminating water bodies [3]. Untreated dye pollutants in aquatic ecosystems can harm water quality, leading to aesthetic degradation, reduced photonic transmission, inhibited photosynthetic activity, and depleted dissolved oxygen levels [4–6]. Despite employing conventional treatment methods, including adsorption, coagulation, ion exchange, and enzyme degradation, complete mineralization of dye effluents remains an elusive goal, underscoring the need for novel and sustainable solutions to address this pressing environmental concern [7,8]. Furthermore, conventional methods have been found to have significant limitations, including the generation of toxic byproducts such as gases and sludge, which require additional processing and preclude complete mineralization, necessitating innovative and sustainable remediation strategies [9]. The contamination of water resources by textile dyes has evolved into a paramount global issue, transcending national boundaries and necessitating immediate attention [10]. The proliferation of these dyes in aquatic ecosystems poses a profound threat to aquatic life, culminating in irreversible harm and

far-reaching consequences for other organisms and human populations that depend on these ecosystems [11]. The escalating use of reactive dyes across diverse industrial sectors exacerbates this environmental crisis, necessitating urgent action and sustainable solutions to mitigate the detrimental impacts of dye pollution on the environment and human well-being [12]. Alternative technologies, such as heterogeneous photocatalysis employing nano-semiconductors, have shown promise in mitigating the issue of dye pollutants in wastewater [13]. Industrial effluents and waste contain diverse dyes and pollutants, posing significant global environmental challenges [14]. These dyes are harmful to the environment, exhibit carcinogenic properties, contaminate water bodies and forming a colorful, foam-like layer that impedes oxygen availability for aquatic flora and fauna [15]. Human society faces the dual challenges of reducing energy consumption and environmental pollution, exacerbated by the increasing number of industries generating waste, disrupting the environment [16]. Industrial effluents from diverse sectors, including textile, chemical, poultry, dairy, and pharmaceutical industries, contain toxic, carcinogenic, and non-biodegradable pollutants that are discharged directly into aquatic ecosystems, posing significant threats to human health, aquatic life, and livestock welfare [17,18]. The textile industry, in particular, is a significant contributor to water pollution, utilizing various dye colorants that generate pollutants in water [19]. Heterogeneous photocatalysis, an

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Photocatalytic degradation of tartrazine dye using CoS, NiS, and ZnS: A comprehensive study on isotherms, kinetics, thermodynamics, and photoluminescence analysis

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HIGHLIGHTS

- CoS, NiS, and ZnS used for photocatalytic Tartrazine Yellow degradation.
- ZnS exhibited the highest degradation efficiency of 95 %.
- Kinetic analysis and reusability of catalysts evaluated.
- Co-precipitation method used for synthesizing CoS, NiS, and ZnS catalysts.
- Catalyst preheating at 500 °C enhanced photocatalytic activity.

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ABSTRACT

This study presents a comprehensive and comparative investigation into the photocatalytic degradation of Tartrazine dye using Cobalt sulfide, Nickel sulfide, and Zinc sulfide nanoparticles as photocatalysts. The catalysts were synthesized via co-precipitation method and characterized by XRD, SEM, TEM, PL, Raman, and UV-Vis spectroscopy. From the Scherrer equation, the nanoparticles exhibited average crystalline sizes of 41 nm (CoS), 34 nm (NiS), and 18 nm (ZnS). Their specific surface areas, determined by BET analysis, were 28 m²/g (CoS), 38 m²/g (NiS), and 49 m²/g (ZnS), respectively. Under optimized conditions (15 mg/L catalyst dosage, pH 3, initial dye concentration 25 ppm, and 500 °C), ZnS achieved the highest degradation efficiency of 95 % within 50 min. The study introduces the evaluation of CoS, NiS, and ZnS for Tartrazine dye degradation, providing a comprehensive understanding supported by detailed kinetic, isotherm, and thermodynamic analyses. The Langmuir isotherm model best describes the adsorption behaviour, suggesting monolayer dye adsorption. In contrast, kinetic studies revealed pseudo-second-order degradation dynamics, with ZnS showing the highest rate constant and exhibiting strong linearity ($R^2 > 0.955$). Photoluminescence studies involving samarium doping, have demonstrated enhanced charge separation and reduced recombination, thereby significantly improving photocatalytic performance. The unique integration of samarium doping and comparative analysis of three distinct sulfide catalysts under identical conditions highlights the novelty and practical significance of this work, offering valuable insights for designing efficient photocatalytic systems for wastewater treatment.

1. Introduction

Global industrialization and population expansion have significantly increased the demand for water, despite the relatively constant amount of water availability [1]. Maintaining a sufficient quantity of fresh water thus grown in importance as a worldwide concern. Water conservation is vital for ensuring a sustainable future for humanity and for protecting

the environment. Scientific and technical developments continue to fuel progress, but these advancements also have significant environmental consequences that could impact future generations [2]. The availability of freshwater is severely declining as a result of human activities that have seriously harmed ecosystem health and water quality [3]. A major worldwide crisis has resulted from this circumstance. The development and implementation of economical, effective, and ecologically friendly

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Enhanced Photocatalytic and Photoluminescence Properties of NiS Doped with Pr³⁺ for Efficient Dye Degradation: Kinetics and Isotherm Studies

Lal Lianmawii^[a] and N. Mohondas Singh^{*[a]}

This study presents the successful synthesis of NiS doped with Pr³⁺ nanoparticles via the reflux method, followed by characterization techniques such as XRD, SEM, TEM, FTIR, BET, Raman, PL, and UV-vis spectroscopy. The nanoparticles exhibited particle sizes ranging from 12 to 19 nm using the Scherrer equation. EDX analysis confirmed the presence of Ni, S, and Pr, verifying the successful incorporation of Pr³⁺. When excited at 424 nm, the photoluminescence emission spectrum shows electronic transitions such as $^3P_1 \rightarrow ^3H_6$, $^3P_2 \rightarrow ^3H_6$, $^1D_2 \rightarrow ^3H_4$, $^3P_0 \rightarrow ^3F_2$. Chromaticity (CIE) of the doped samples at varying Pr³⁺ concentrations indicates the potential for white light emission,

highlighting their applicability in solid-state lighting. BET analysis reveals a notable increase in surface area with higher Pr³⁺ doping levels. NiS doped with Pr³⁺ nanoparticles demonstrate excellent photocatalytic degradation efficiencies under UV light, achieving 96% degradation of rhodamine B, 92% of methylene blue, 95% of methyl orange, and 94% of congo red within 90 min, and follow pseudo-first-order kinetics. This study offers a detailed evaluation of the influence of Pr³⁺ doping on the luminescent and photocatalytic performance of NiS nanoparticles, underscoring their potential for environmental remediation and optoelectronic applications.

1. Introduction

The discovery of photocatalytic water splitting on semiconductor nanoparticles in the 1970's marked a significant advancement in photocatalysis, particularly for hydrogen generation.^[1] Since then, researchers have concentrated on understanding the fundamental mechanics of photocatalytic reactions and increasing their efficiency, particularly in environmental applications such as dye degradation. Nanoscale materials typically range between 1 and 100 nm, have gained a lot of interest due to their distinct physical and chemical properties.^[2] Their high surface-to-volume ratio makes them more reactive.^[3] As nanotechnology has rapidly developed into a major scientific and industrial field in the twenty-first century, its use in a variety of applications has increased substantially. Because of their structural flexibility and customizable electronic properties, semiconductor nanostructures, particularly metal sulfide nanostructures (MSNs), have received a lot of attention among photocatalysts.^[2] Metal sulfides and oxides work as effective sensitizers for photo-induced redox reactions in these environments.^[4] When exposed to light, they can form electron-hole pairs because their electrical structure often includes an empty conduction band and a fully occupied valence band. These charge carriers can undergo surface interactions with ambient species or recombine. The holes can oxidize hydroxide or water ions, resulting in reactive oxygen species (ROS) such as superoxide anions or hydroxyl

radicals, which are required for the decomposition of organic contaminants.^[5] In recent decades, heterogeneous photocatalysis employing semiconductor materials has emerged as a feasible and environmentally acceptable method for addressing critical challenges in water purification and energy conversion. Metal sulfide nanoparticles (MSNPs) outperform traditional metal oxide catalysts such as ZnO and TiO₂ in terms of photocatalytic activity^[6] which promote the generation of ROS such as $^{\bullet}\text{OH}$, $\text{O}_2^{\bullet-}$, and photogenerated holes, as well as their narrower band gaps, which allow for visible-light activation.^[7] Furthermore, elemental doping, shape control, and heterojunction formation can be employed to accurately tune the electrical properties of MSNPs. MSNPs are appealing materials for photocatalytic environmental remediation due to their properties as well as their lower cost as compared to noble metal-based photocatalysts such as platinum and gold. They offer distinct photocatalytic properties such as intense light absorption, small band gaps, and tunable electronic structures, there has been a lot of interest in employing them to degrade hazardous dyes in wastewater.^[8] Their low quantum efficiency, which reduces overall degradation efficiency due to rapid electron-hole recombination during photocatalysis, is a major issue.^[9] Furthermore, extended exposure to light can promote photocorrosion in certain metal sulfide nanoparticles, such as CdS, resulting in instability and poor reusability.^[10] While these materials have demonstrated promise activity in controlled lab settings, their effectiveness in wastewater systems, contain complex mixes of dyes, surfactants, and competing organic and inorganic chemicals, has yet to be completely explored. Another significant research gap is an insufficient grasp of the basic degradation mechanisms. The majority of existing research focuses on removal efficiency, with regard to whether degradation occurs

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A review: photocatalytic degradation of dyes by metal sulfide nanoparticles

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Abstract

Over the past few decades, environmental contamination from the wastewater industry has gravely threatened the environment and public health. According to reports, thousands of different dyes and pigments are used in a range of industries around the world each year, producing more than 7×10^5 tonnes of synthetic dyes. Environmental contamination can be prevented by using semiconductor metal sulfide nanostructures (MSNSs) with doping and heterojunction as photocatalysts for the long-term, economical removal of hazardous organic dyes. The current review focuses on the degradability of hazardous dyes in the environment by metal sulfide nanoparticles such as ZnS, CdS, CuS, Ag₂S, CoS, and FeS.

Keywords Environment · Dyes · Industries · Metal sulfide · Nanoparticles · Photocatalyst · Wastewater

Abbreviations

ZnS	Zinc sulfide
CdS	Cadmium sulfide
CuS	Copper sulfide
Ag ₂ S	Silver sulfide
CoS	Cobalt sulfide
FeS	Iron sulfide
MSNSs	Metal sulfide nanostructures
RO	Reverse osmosis
UF	Ultrafiltration
ETAD	The ecological and toxicological association of dyes and organic pigments

AIMCM	A mesoporous aluminosilicate material,
VOC	Volatile organic compounds
COD	Chemical oxygen demand
BOD	Biological oxygen demand
AOP	Advanced oxidation process
PVDF	Polyvinylidene fluoride
GQD'S	Graphene quantum dots
DE	Degradation efficiency
BTB	Bromothymol blue
RB	Rose Bengal
R6G	Rhodamine 6G
Rhb	Rhodamine B
CR	Congo red
MB	Methylene blue
CV	Crystal violet
MO	Methyl orange
MG	Malachite green
IC	Indigo carmine
NB	Nile blue
MV	Methyl violet
ROS	Reactive oxygen species
TOC	Total organic carbon
VB	Valence band
CB	Conduction band
GO	Graphene oxide
PVDF	Polyvinylidene fluoride
PVP	Polyvinylpyrrolidone
PEG	Polyethylene glycol
PDA	Polydopamine

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DEGREE	Doctor of Philosophy (Ph.D.)
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Head

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ABSTRACT

PHOTOCATALYTIC DEGRADATION OF ORGANIC DYES WITH METAL SULFIDE NANOPARTICLES

**AN ABSTRACT SUBMITTED IN PARTIAL FULFILLMENT OF
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**DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICALSCIENCES**

JULY, 2025

**PHOTOCATALYTIC DEGRADATION OF ORGANIC DYES WITH METAL
SULFIDE NANOPARTICLES**

BY
LALLIANMAWII
Department of Chemistry

Under the supervision of
Prof. N. MOHONDAS SINGH

Submitted
In partial fulfillment of the requirement of the Degree of Doctor of Philosophy in
Chemistry of Mizoram University, Aizawl.

Abstract

Nanotechnology has emerged as a promising and rapidly evolving field in wastewater treatment, necessitating deeper research and a more comprehensive understanding. Various types of nanomaterials are employed depending on the specific contaminants present and the level of treatment efficiency required. Nanostructured materials have gained significant interest in recent years due to their exceptional properties that differ markedly from those of bulk materials. Advanced oxidation processes have shown superior effectiveness in wastewater treatment, with numerous strategies being explored and documented. Over the past decade, semiconductor-based photocatalysts have garnered significant attention as a sustainable method for degrading hazardous pollutants and minimizing energy loss through the utilization of solar energy. These materials are not only cost-effective and environmentally benign, but also reusable and capable of facilitating multi-step electron transfer reactions. Recent research has focused on engineered semiconductor materials with tailored size, shape, and enhanced optical, electrical, and catalytic properties, aiming to optimize their performance in applications related to energy generation, environmental protection, and biological systems. II–VI semiconductor nanoparticles have garnered attention for their tunable photoluminescent and electroluminescent properties, which vary with particle size and are highly valuable in optoelectronic applications. Metal sulfides stand out as a leading candidate due to their favourable optical and electronic characteristics. ZnS, NiS, CdS, and CoS are commercially significant II–VI semiconductors that possess a wide band gap, making them particularly suitable for optical technologies, especially in their nanocrystalline form. Lanthanide elements in metal sulfides have proven to be an effective method for enhancing dye degradation, especially in photocatalytic wastewater treatment. Lanthanide ions serve as traps for photogenerated electrons or holes, which helps to suppress the recombination of charge carriers. As a result, more electrons and holes remain available to participate in the active photocatalytic breakdown of dye molecules.

Chapter 1: This chapter provides a comprehensive overview of nanoparticles, with a particular focus on the classification of organic nanoparticles and their applications in the environment. It also addresses the environmental impact of synthetic dyes, highlighting their toxicity and the ecological threats they pose when discharged into natural water bodies without adequate treatment. The chapter introduces advanced oxidation processes (AOPs) as an effective approach for the degradation of dyes, emphasizing their mechanism and advantages over conventional treatment methods. In addition, a detailed literature review is presented, summarizing previous research efforts in this area to establish a foundation for the current study. The scope and objectives of the present research are also clearly defined.

Chapter 2: Characterization of the synthesized materials represents a vital component of the research process, as it allows for the comprehensive evaluation of their physical, chemical, and structural properties using a range of analytical techniques. This chapter presents an in-depth discussion of the various instrumental methods employed in this study, including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray analysis (EDAX), Brunauer-Emmett-Teller (BET) surface area analysis, photoluminescence (PL), and UV-visible spectroscopy. These techniques were crucial for analyzing the fundamental properties of the materials. The morphology and particle size, which play a critical role in determining the behaviour and reactivity of the nanomaterials, were investigated through SEM and TEM imaging. Crystallinity, which directly influences the electronic and catalytic properties of the material, was examined using XRD analysis. Surface area and porosity, critical for applications such as adsorption and catalysis, were assessed using BET analysis. Optical properties and band gap estimations were obtained through UV-Vis and photoluminescence studies. Collectively, these characterization tools provided a thorough understanding of the synthesized materials, enabling informed evaluation of their potential performance in various applications.

Chapter 3: In this study, europium-doped zinc sulfide (Eu^{3+} doped ZnS) nanoparticles were synthesized via the reflux method. A range of physicochemical

characterization techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR), photoluminescence (PL), and UV-visible spectroscopy, were employed to investigate the structural, morphological, and optical features of the synthesized material. Photoluminescence analysis revealed that the strongest emission corresponded to the electric dipole transition $^5D_0 \rightarrow ^7F_2$, which is highly sensitive to the surrounding chemical environment of Eu^{3+} ions, especially under excitation at 350 nm. Chromaticity coordinate evaluations using the CIE diagram demonstrated that all synthesized samples emit within the white light region, indicating promising applicability in areas such as optical devices and outdoor lighting systems. Photocatalytic experiments demonstrated that the catalyst achieved a 90% degradation efficiency for methyl red dye, consistent with first-order reaction kinetics. The incorporation of Eu^{3+} was found to significantly contribute to the formation of reactive oxygen species, thereby enhancing the photocatalytic degradation performance. The doped material exhibited excellent stability and reusability, underscoring its potential for the treatment of dye-contaminated wastewater.

Chapter 4: This chapter presents the synthesis and characterization of praseodymium-doped cadmium sulfide ($\text{Pr}^{3+}:\text{CdS}$) nanoparticles using the reflux method, with doping concentrations of 0, 5, 7, 9, and 11 atomic percent. X-ray diffraction (XRD) analysis confirmed that all prepared samples were crystalline and exhibited a hexagonal crystal structure. Scanning electron microscopy (SEM) images revealed nanoparticle agglomeration, a common feature in nanostructured materials due to high surface energy. Photoluminescence (PL) studies performed under excitation at 423 nm showed distinct electronic transitions corresponding to $^3P_1 \rightarrow ^3H_5$, $^3P_0 \rightarrow ^3H_5$, $^3P_0 \rightarrow ^3H_6$, and $^3P_0 \rightarrow ^3F_2$. With increasing Pr^{3+} doping concentration, the PL emission intensity, peak sharpness, and resolution improved significantly, indicating enhanced luminescence properties. Chromaticity coordinates plotted on the Commission Internationale de l'Éclairage (CIE) diagram revealed that the emission color of the doped samples was close to white light, highlighting their potential suitability for applications in solid-state lighting technologies. The

photocatalytic efficiency of the Pr^{3+} :CdS nanoparticles was evaluated for the degradation of two common organic dyes: methylene blue and methyl red. Optimal degradation performance was achieved at a catalyst dosage of 5 mg/L, with pH values of 9 for methylene blue and 11 for methyl red, yielding degradation efficiencies of 89% and 94%, respectively. The presence of Pr^{3+} ions significantly improved the photocatalytic activity by facilitating efficient charge separation and enhancing the formation of reactive species. Kinetic analysis of the degradation process indicated that the experimental data conformed well to both the Langmuir–Hinshelwood (L–H) and pseudo-first-order (PFO) models. However, the PFO model provided a better fit, especially under optimized experimental conditions. These findings demonstrate that Pr^{3+} -doped CdS nanoparticles have strong potential as efficient and stable photocatalysts for removing toxic dyes from wastewater.

Chapter 5: In this study, the photocatalytic degradation of indigo carmine dye was investigated using samarium-doped zinc sulfide (Sm^{3+} :ZnS) nanoparticles. The synthesized nanomaterials were thoroughly characterized using a range of analytical techniques, including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET) surface area analysis, photoluminescence (PL), and UV-visible spectroscopy. The average crystallite size, estimated using the Scherrer equation, ranged from approximately 3 to 12 nanometres. Photoluminescence analysis under excitation at 395 nm revealed distinct f–f transitions of Sm^{3+} ions, with intense emission peaks observed at 559, 595, and 642 nm. These emissions are indicative of the enhanced luminescence properties introduced by the doping rare-earth ions. The photocatalyst demonstrated exceptional activity in degrading indigo carmine dye, achieving a 93% degradation efficiency at a catalyst dosage of 15 mg/L over a period of 210 minutes. Kinetic modelling confirmed that the degradation followed pseudo-first-order reaction kinetics. Adsorption isotherm analysis further indicated that the Langmuir model provided the best fit for the experimental data, suggesting monolayer adsorption on a homogeneous surface. The results underscore the effectiveness of Sm^{3+} doping in enhancing both the photocatalytic and luminescent

properties of ZnS nanoparticles. Overall, the study suggests that $\text{Sm}^{3+}:\text{ZnS}$ nanomaterials hold considerable promise as efficient and reusable photocatalysts for removing dye pollutants from contaminated water sources.

Chapter 6: This study addresses the pressing issue of wastewater contamination caused by synthetic dyes, which poses serious environmental and public health concerns. To tackle this challenge, the research explores the photocatalytic degradation of malachite green, a commonly used and environmentally persistent dye, using terbium-doped nickel sulfide ($\text{NiS}:\text{Tb}^{3+}$) nanoparticles as the catalyst. The primary objective is to evaluate the effectiveness of these doped nanoparticles in breaking down the dye into less harmful by-products, thereby mitigating its toxicological effects. The synthesized catalyst was thoroughly characterized using several advanced analytical techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), photoluminescence (PL) spectroscopy, X-ray photoelectron spectroscopy (XPS), and UV–visible spectroscopy (UV-Vis), to investigate its structural, morphological, and optical properties. The study systematically examined the influence of different operational parameters on the degradation efficiency, particularly pH and the presence of various additives such as transition metal ions, inorganic oxidants, and anions. Results revealed an impressive degradation efficiency of 94% within 90 minutes under optimal conditions. Enhancement in photocatalytic activity was observed upon the addition of transition-metal ions and inorganic oxidants, whereas the presence of inorganic anions negatively affected the degradation performance.

Chapter 7: The substantial contribution of the textile industry to global water pollution underscores the urgent need for advanced and effective wastewater treatment technologies. In response to this challenge, the present study details the successful synthesis of polymer-stabilized zinc sulfide-gold nanocomposites $\text{PEG}@\text{ZnS}:\text{Au}$ and $\text{PVP}@\text{ZnS}:\text{Au}$, using a co-precipitation method. The structural, morphological, and surface characteristics of the synthesized nanomaterials were comprehensively examined using a range of analytical tools, including photoluminescence (PL) spectroscopy, Brunauer–Emmett–Teller (BET) surface area analysis, scanning electron microscopy (SEM), transmission electron microscopy

(TEM), Fourier-transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). The photocatalytic capabilities of both PEG- and PVP-capped ZnS: Au nanoparticles were evaluated by assessing their ability to degrade rhodamine B dye, a common and persistent pollutant in textile wastewater. Remarkably, PEG@ZnS: Au and PVP@ZnS: Au nanoparticles achieved degradation efficiencies of 94.25% and 91.45%, respectively, within just 30 minutes of exposure under photoirradiation, indicating outstanding catalytic performance. Kinetic analysis revealed that the dye degradation followed pseudo-first-order kinetics and conformed well to the Langmuir adsorption isotherm, suggesting monolayer adsorption with an endothermic nature. The photocatalytic process was primarily driven by the generation of reactive oxygen species (ROS), which are produced through the separation of photoexcited electron-hole pairs within the nanocomposite structure. These findings highlight the significant potential of polymer-modified ZnS: Au nanomaterials for use in photocatalytic wastewater treatment applications. This study not only emphasises the effectiveness of nanoscale photocatalysts in removing toxic dyes from effluents but also provides a promising strategy for mitigating the environmental impact of textile industry discharges.

Chapter 8: This chapter presents a comprehensive investigation into the photocatalytic performance of cerium-doped cobalt sulfide (CoS: Ce³⁺) nanoparticles for the degradation of industrial dyes and pharmaceutical pollutants. The synthesized nanoparticles demonstrated outstanding degradation efficiencies 94% for Congo red, 96% for methylene blue, and 89% for cefixime within a notably short reaction time of just 25 minutes, underscoring their rapid and effective catalytic capabilities. X-ray diffraction (XRD) analysis confirmed the successful formation of the nanoparticles, revealing a distinct cubic spinel crystalline structure with crystallite sizes ranging from 25 to 49 nm. Scanning electron microscopy (SEM) provided further insights, showing a clear dependence of nanoparticle morphology on Ce³⁺ doping concentration, which led to the development of hierarchical nanostructures exhibiting diverse shapes and dimensions. Additionally, nitrogen adsorption–desorption measurements revealed high surface areas and complex porous architectures. A significant enhancement in surface area and pore volume was observed with

increasing Ce^{3+} content, which is believed to contribute to the superior photocatalytic efficiency by providing more active sites for dye adsorption and degradation. The novelty of this study lies in the integration of advanced synthesis techniques with systematic doping strategies to fine-tune the properties of nanoparticle. Coupled with an in-depth characterization approach, this work provides valuable mechanistic insights into how Ce^{3+} incorporation influences both structural and catalytic behaviour. Overall, the findings highlight the potential of $\text{CoS}:\text{Ce}^{3+}$ nanoparticles as highly efficient catalysts for the rapid breakdown of hazardous industrial dyes and pollutants, contributing to the development of next-generation materials for environmental remediation.

Chapter 9: This study presents the successful synthesis of praseodymium-doped nickel sulfide ($\text{NiS}:\text{Pr}^{3+}$) nanoparticles using a reflux method. The synthesized materials were thoroughly characterized through a suite of analytical techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR), photoluminescence (PL), Brunauer–Emmett–Teller (BET) surface area analysis, and UV-visible spectroscopy. Crystallite size analysis using the Scherrer equation revealed particle sizes ranging from 12 to 19 nm. The results revealed that Pr^{3+} doping had a pronounced effect on the structural and optical characteristics of the NiS nanoparticles, enhancing their luminescence and photocatalytic behavior. The doped nanoparticles exhibited outstanding photocatalytic efficiency, achieving degradation rates of 96% for Rhodamine B, 92% for Methylene Blue, 95% for Methyl Orange, and 94% for Congo Red within 90 minutes. The degradation processes were found to follow pseudo-first-order kinetics, indicating a consistent and reliable catalytic mechanism. This research provides a comprehensive evaluation of how Pr^{3+} doping affects the physicochemical and catalytic properties of NiS nanoparticles. The findings highlight the potential of $\text{NiS}:\text{Pr}^{3+}$ as an effective photocatalyst for treating dye-contaminated wastewater, demonstrating high efficiency under both controlled laboratory conditions and environmentally relevant scenarios.

Chapter 10: In this investigation, europium- and samarium-doped magnesium nickel sulfide nanoparticles (MgNiS:Eu^{3+} and MgNiS:Sm^{3+}) were successfully synthesized via the reflux method, demonstrating significant potential as photocatalysts for environmental applications. A comprehensive suite of analytical techniques including transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), photoluminescence (PL), UV-visible spectroscopy, and Raman spectroscopy was employed to characterize the structural, morphological, and optical properties of the synthesized nanomaterials. The nanoparticles exhibited a uniform particle size distribution, with crystallite sizes ranging from 31 to 34 nm as calculated using the Debye–Scherrer equation. Their photocatalytic performance was assessed through the degradation of Eriochrome Black T (EBT), a commonly used but environmentally persistent textile dye. The MgNiS:Eu^{3+} and MgNiS:Sm^{3+} nanoparticles achieved remarkable degradation efficiencies of 89.34% and 83.96%, respectively, under optimized conditions (pH 5, catalyst dosage of 50 mg/L, and an initial dye concentration of 10 ppm) within just 50 minutes. Kinetic studies indicated that the degradation process adheres to pseudo-first-order kinetics, implying a direct dependence of the reaction rate on the concentration of the dye.

Furthermore, the adsorption behavior of EBT onto the catalyst surfaces was best described by the Freundlich isotherm model, suggesting multilayer adsorption on heterogeneous surfaces. Overall, the excellent photocatalytic efficiency and favorable kinetic and adsorption profiles of MgNiS:Eu^{3+} and MgNiS:Sm^{3+} nanoparticles highlight their promise as effective materials for the degradation of hazardous dye pollutants. These findings contribute to a meaningful contribution to the development of sustainable and efficient technologies for wastewater treatment and environmental remediation.