PHOTOCATALYTIC ACTIVITY OF COBALT AND CERIUM DOPED BISMUTH-FERRITE NANOSTRUCTURES SYNTHESIZED BY SOL-GEL AUTO-COMBUSTION METHOD

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Philosophy

Faculty of Science
Universiti Teknologi Malaysia

JANUARY 2020

DEDICATION

Every challenging work needs self effort as well as guidance especially from those who are very close to the heart. My humble effort I dedicate to my precious and loving parents,

Che Mohd Zawawi Bin Awang and Norsalina Binti Mohamed,

Whose affection, love, encouragement and prays of day and night make me able to achieve this success. Thank you for everything.

ACKNOWLEDGEMENT

In the name of Allah S.W.T, the Most Gracious and the Most Merciful,

All praises to Allah, For His Mercy has given me patience and strength to complete this research project.

I would like to express my deepest appreciation to my main supervisor, Dr. Kashif Tufail Chaudhary for his guidance and supports in my research. This thesis would not be a success without his helpful suggestions and constructive comments from the start until final of this research. A special thanks also goes to my co-supervisors, Prof. Dr. Jalil Bin Ali, Dr. Muhammad Safwan Bin Abd. Aziz and Dr. Fairuz Diyana Binti Ismail for their continuous assistance.

I would like to extend my sincere gratitude to all lecturers and staff in Department of Physics and fellow friends that had directly and indirectly helped me throughout my research project. I wish to mention each and every one of them but the list is too long and the space is limited. I am also thankful to Universiti Teknologi Malaysia, UTM for giving me opportunity to complete my research project.

Last but not least, I am forever indebted and grateful to my precious parents, family and my loved ones for their endless motivation, understanding and encouragement. It is such a heart-warming experience I had, and such experience will always be with me. Thank you so much.

ABSTRACT

Large volumes of water and chemicals from textile industry are drained to the environment, which contain different non-biodegradable toxic organic compounds (dyes). These dyes require proper treatment prior to discharge into environment. Rhodamine B (RhB) is a widely used dye in textile industry which is harmful and carcinogenic in nature. Finding the efficient, rapid and cost-effective mechanism for the removal of these harmful dyes from wastewater is the major challenge. This study explores the potential of bismuth ferrite ($BiFeO_3$) nanoparticles as photocatalyst for photocatalytic degradation of RhB dye in solution. The $BiFeO_3$ nanoparticles were prepared by sol-gel auto-combustion method for the photocatalytic degradation of RhB dye. The optical, magnetic and structural properties of the $BiFeO_3$ nanoparticles were tuned by introducing the dopants such as cobalt (Co) and cerium (Ce). The effect of dopants concentrations ($Bi_{1-x}Co_xFeO_3$ and $Bi_{1-y}Ce_yFeO_3$; x and y = 0.1, 0.2, 0.3, 0.4 and 0.5) on the optical, magnetic and structural properties were determined by high-resolution transmission electron microscopy (HRTEM), thermogravimetric analysis (TGA), X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) together with energy dispersive X-ray (EDX), UV-Visible (UV-Vis) and vibrating sample magnetometer (VSM). The degradation of RhB dye was investigated and confirmed through UV-Vis spectroscopy, Fourier transform infrared (FTIR) spectroscopy and high-performance liquid chromatography (HPLC). The XRD analysis of synthesized doped $BiFeO_3$ nanoparticles confirmed the presence of secondary phase (sillenite) along with primary phase in $BiFeO_3$ nanoparticles. The percentage of sillenite phase was significantly increased with the increase in dopant ratios. The microscopic analysis of the $BiFeO_3$ nanoparticles revealed nanosized irregular shape particles in range of 45-50 nm with agglomerated coalescence behaviour. Cobalt- doped $BiFeO_3$ nanoparticles exhibited strong ferromagnetic behaviour. For cerium- doped $BiFeO_3$ nanoparticles, high degradation rate was observed as compared to the cobalt- doped $BiFeO_3$ nanoparticles. However, cerium- doped $BiFeO_3$ nanoparticles possessed soft magnetic nature. The presence of dopant reduced the particle size and the optical band gap. The optical band gap of 2.2 eV was measured for pure $BiFeO_3$ nanoparticles while for cobalt and cerium- doped $BiFeO_3$ nanoparticles optical bandgaps were measured in range of 1.47-1.57 eV and 2.13-2.17 eV respectively. Cobalt and cerium- doped $BiFeO_3$ nanoparticles successfully degraded RhB solution in less than 1 hour compared to pure $BiFeO_3$ nanoparticles. The 0.3 doping concentration of cobalt and cerium was found to be the best for degradation of RhB solution. The $Bi_{0.7}Ce_{0.3}FeO_3$ degraded the RhB solution immediately after the reaction started while $Bi_{0.7}Co_{0.3}FeO_3$ nanoparticles required 25 minutes. The findings show the huge potential of cobalt and cerium- doped $BiFeO_3$ nanoparticles as photocatalyst for effective and rapid degradation of RhB dye.

ABSTRAK

Jumlah air yang besar dan bahan kimia yang mengandungi pelbagai sebatian organik yang tidak terbiodegradasi (pewarna) dari industri tekstil akan mengalir ke persekitaran. Rawatan yang sewajarnya adalah diperlukan sebelum pewarna itu terus mengalir dan mencemarkan persekitaran. Pewarna Rhodamine B (RhB) yang digunakan secara meluas dalam industri tekstil memberi kemudaratan dan mempunyai sifat karsinogenik. Pencarian mekanisma yang cekap, cepat dan menjimatkan kos bagi menyingkirkan pewarna berbahaya dari air buangan masih menjadi cabaran yang besar. Kajian ini meneliti potensi nanozarah bismut ferit ($BiFeO_3$) sebagai fotomangkin untuk degradasi fotomangkin pewarna RhB dalam larutan. Nanozarah $BiFeO_3$ disintesis dengan menggunakan kaedah auto-pembakaran sol-gel untuk mendegradasi pewarna RhB. Sifat optik, magnet dan struktur nanozarah disesuaikan dengan memperkenalkan dopan seperti kobalt (Co) dan serium (Ce). Kesan kepekatan dopan yang berbeza ($Bi_{1-x}Co_xFeO_3$ dan $Bi_{1-y}Ce_xFeO_3$; x dan y = 0.1, 0.2, 0.3, 0.4 dan 0.5) terhadap sifat optik, magnet dan struktur dikaji dengan melakukan analisis mikroskopi electron transmisi peleraian tinggi (HRTEM), termogravimetri (TGA), pembelauan sinar-X (XRD), mikroskopi imbasan elektron pancaran medan (FESEM) bersama-sama dengan analisis sinar-X sebaran tenaga (EDX), cahaya boleh dilihat (UV-Vis) dan magnetometer sampel getar (VSM). Degradasi pewarna RhB diselidik melalui analisis UV-Vis, spektometri inframerah jelmaan Fourier (FTIR) dan kromatografi cecair prestasi tinggi (HPLC). Analisis XRD nanozarah $BiFeO_3$ yang telah disintesis menunjukkan kehadiran fasa sekunder (silenit) disamping fasa utama nanozarah $BiFeO_3$. Peratus fasa silenit dilihat semakin meningkat apabila nisbah dopan meningkat. Analisis mikroskopi nanozarah $BiFeO_3$ menunjukkan bentuk yang tidak teratur, bergumpal dan mempunyai saiz dalam lingkungan 45-50 nm. Nanozarah $BiFeO_3$ didop kobalt menunjukkan tingkah laku feromagnet yang baik. Untuk nanozarah $BiFeO_3$ didop serium, proses degradasi mengambil masa yang sangat singkat berbanding nanozarah $BiFeO_3$ didop kobalt. Walau bagaimanapun, nanozarah $BiFeO_3$ didop serium mempunyai sifat magnet yang lembut. Dengan kehadiran dopan terhadap $BiFeO_3$, saiz zarah dan nilai jurang jalur optik dilihat semakin berkurangan. Didapati nilai jurang jalur optik bagi $BiFeO_3$ adalah sebanyak 2.2 eV. Bagi $BiFeO_3$ didop kobalt, nilai jurang jalur optik adalah dalam julat 1.47-1.57 eV manakala $BiFeO_3$ didop serium pula adalah dalam julat 2.13-2.17 eV. Nanozarah $BiFeO_3$ didop kobalt dan serium kedua-duanya telah berjaya mendegradasi larutan RhB dalm masa kurang daripada 1 jam berbanding nanozarah $BiFeO_3$ tulen. Kepekatan dopan kobalt dan serium sebanyak 0.3 telah menunjukkan keputusan yang baik untuk mendegradasi larutan RhB. $Bi_{0.7}Ce_{0.3}FeO_3$ mendegradasi larutan RhB sejurus eksperimen dimulakan manakala $Bi_{0.7}Co_{0.3}FeO_3$ mengambil masa 25 minit. Keputusan kajian menunjukkan bahawa kehadiran dopan kobalt dan serium kepada nanopartikel $BiFeO_3$ berpotensi tinggi sebagai fotomangkin yang berkesan dan pantas untuk merawat pewarna RhB.

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LIST OF ABBREVIATIONS

·OH	-	Hydroxyl Radical
0D	-	Zero-dimensional
1D	-	One-dimensional
2D	-	Two-dimensional
3D	-	Three-dimensional
Ag	-	Silver
Ag_3PO_4	-	Silver Phosphate
Al	-	Aluminium
AOP	-	Advance Oxidative Process
$BaSO_4$	-	Barium Sulfate
$BaTiO_3$	-	Barium Titanate
Bi	-	Bismuth
$Bi(NO_3)_3.5H_2O$	-	Bismuth (III) Nitrate Pentahydrate
$Bi_{25}FeO_{40}$	-	Sillenite
$Bi_2O_2CO_3$	-	Bismutite
Bi_2WO_6	-	Russelite
$BiFeO_3$	-	Bismuth Ferrite
BiOBr	-	Bimuth Oxide Bromide
$BiPO_4$	-	Bismuth Phosphate
Bi-TNT	-	Bismuth-doped TiO_2 Nanotubes
$BiVO_4$	-	Bimuth Vanadate

$BiVO_4$	-	Bismuth Vanadate
$C_{28}H_{31}ClN_2O_3$	-	Rhodamine B Dye
$C_6H_8O_7$	-	Citric Acid
CB	-	Conduction Band
Ce	-	Cerium
CdS	-	Cadmium Sulfide
Ce_2O_3	-	Cerium Oxide
$CeCl_3.7H_2O$	-	Cerium (III) Chloride Heptahydrate
CH_2	-	Methylene
CH_3	-	Methyl Group
$CH_3CN.H_2O$	-	Acetonitrile
CH_4	-	Methane
CN-	-	Cyanide
Co	-	Cobalt
$Co(NO_3)_2.6H_2O$	-	Cobalt (II) Nitrate Hexahydrate
CO_2	-	Carbon Dioxide
Co_3O_4	-	Cobalt Oxide
COD	-	Chemical Oxygen Demand
COO	-	Carbonate
Cu	-	Copper
CuPp-ZnO	-	Zinc oxide with Copper (II) Porphyrin
D	-	Crystallite Size
DCP	-	Dichlorophenol
e^-	-	Electron

EDX	-	Energy Dispersive X-Ray
E_g	-	Bandgap
$Er\text{-}CeO_2$	-	Erbium Doped Cerium Oxide
Fe	-	Ferrum
$Fe(NO_3)_3.9H_2O$	-	Iron (III) Nitrate Nonahydrate
FESEM	-	Field Emission Scanning Electron Microscope
FNPs	-	Ferrite Nanoparticles
FTIR	-	Fourier Transform Infrared
FWHM	-	Full Width Half Maximum
Gd	-	Gadolinium
H	-	Hydrogen
h	-	Planck's Constant
h^+	-	Hole
H_2	-	Hydrogen
H_2O	-	Water
H_2O_2	-	Hydrogen Peroxide
H_3PO_4	-	Phosphoric Acid
Hc	-	Coercivity Force
HCl	-	Hydrochloric Acid
HNO_3	-	Nitric Acid
HNO_3	-	Nitric Acid
HPLC	-	High-performance Liquid Chromatography
HRTEM	-	High Resolution Transmission Electron Microscope
MCA	-	Multichannel Analysed

Mg	-	Magnesium
MgO	-	Magnesium Oxide
Mn	-	Manganese
MNPs	-	Magnetic Nanoparticles
MO	-	Metal Oxide
MO	-	Methyl Orange
MoO_3	-	Molybdenum Trioxide
MPC	-	Microwave-enhance Photocatalysis
M_r	-	Retentivity/Remanance Magnetisation
MRI	-	Magnetic Resonance Imaging
M_s	-	Saturation Magnetisation
$MWCNT/WO_3$	-	Multi-walled Carbon Nanotube/ Tungsten Oxide
$NaBiO_3$	-	Sodium Bismuthate
$NaBiO_3$	-	Sodium Bismuthate
Ni	-	Nickel
$N\text{-}TiO_2$	-	Nitrogen-Titanium Dioxide
O	-	Oxygen
O_2	-	Oxygen
$P\text{-}g\text{-}C_3N_4$	-	Phosphorus Doped Graphitic Carbon Nitride
$RGO\text{-} TiO_2$	-	Reduced Graphene Oxide-Titanium Dioxide
RhB	-	Rhodamine B
SAED	-	Selected Area Electron Diffraction
SCS	-	Solution Combustion Synthesis
$SrFe_{12}O_{19}$	-	Strontium Ferrite

TEA	-	Triethanol Amine
TGA	-	Thermogravimetric Analysis
TiO_2	-	Titanium Dioxide
TOC	-	Total Organic Carbon
UV-A	-	Ultraviolet-A
UV-LEDs	-	UV-light Emitting Diodes
UV-Vis	-	Ultraviolet-Visible
Uv-Vis NIR	-	Ultraviolet-Visible Near-Infrared
VB	-	Valence Band
VSM	-	Vibrating Sample Magnetometer
XRD	-	X-Ray Diffraction
$ZnFe_2O_4$	-	Zinc Ferrite
Zn	-	Zinc
ZnO	-	Zinc Oxide

LIST OF SYMBOLS

%	-	Percent
°C	-	Degree celcius
μm	-	Micrometre
a	-	Lattice constant
A	-	Proportional Constant
Å	-	Angstrom
cm	-	Centimeter
emu/g	-	Mass Magnetisation
eV	-	Electron Volt
g	-	Gram
g/L	-	Gram per Litre
g/mol	-	Gram per Mole
Hz	-	Hertz
K	-	Kelvin
keV	-	Kiloelectron Volt
kPa	-	Kilopascal
kW	-	Kilowatt
M	-	Molarity
mA	-	Milliampere
mAU	-	Milli-Absorbance Units
mg	-	Milligram
mg/L	-	Milligram per Litre

Min	-	Minute
ml	-	Millilitre
mm Hg	-	Millimetre of mercury
nm	-	Nanometre
Oe	-	Oersted
T_C	-	Curie Temperature
T_N	-	Neel Temperature
v	-	Frequency
β	-	Full-with half maximum
θ	-	Theta
λ	-	Wavelength

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

Industrial wastewater poses a serious threat to the environment worldwide. The textile industry is one of the major wastewater contributors, as the textile manufacturing processes involve the consumption of a considerable amount of water. The principal pollutants in the textile effluent are recalcitrant organics, dyes, toxicants, inhibitory compounds, surfactants, soaps, detergents, chlorinated compounds, and salts. Dye is one of the most difficult constituents of the textile wastewater to treat. The type and amount of dye in the effluent could vary daily, even hourly, depending on the campaign (Nimkar, 2018). Different types of dyes are used in the textile industry, which can be broadly categorised into two groups: natural dyes and synthetic dyes. Natural dyes are dye substances extracted from natural sources, which include haematoxylin, carmine, and orcein. Dyes prepared using organic and inorganic compounds are called synthetic dyes, which are further classified into different groups according to its dyeing mechanism, such as direct, acid, basic, reactive, mordant, metal complex, vat, sulphur, and disperse dyes, among others. These synthetic dyes cost less, impart better properties to the dyed materials, and offer a vast range of new colours (Sharma, 2015).

Different methods have been developed and employed to treat industrial waste, which can be categorised into three types: physical, biological, and chemical methods. For physical method, adsorption and coagulation are the most commonly used techniques for the abatement of organic pollutants. The organic compounds are adsorbed on activated carbons, organo-clays, co-polymers, zeolites, and other resins. For biological method, microbes with diverse metabolic and enzymatic capabilities are used for the detoxification or mineralisation of pollutants. These microbes utilise the carbon contained in the waste for their metabolism and convert them into less toxic intermediates and by-products. For chemical method, chemical coagulation, precipitation, oxidation, ion exchange, and chemical neutralisation and stabilisation are commonly applied to treat wastewater. Low reaction rate, requirement of excessive quantity of chemicals, and production of sludge, all of which require further treatment, are some of the common challenges related to existing wastewater treatment techniques. Recently, advanced oxidative processes (AOPs), such as photocatalytic degradation, microwaves assisted catalytic wet air oxidation, Fenton process, et cetera, have been developed for the degradation of pollutants. Nevertheless, the problems include high maintenance cost and skilled manpower (Singh et al., 2018).

Rhodamine B (RhB) is one of the more commonly used synthetic dyes in the textile industry. It is a water-soluble dye which is bluish-red in colour. Basic Violet 10, Brilliant Pink B, Rheonine B, et cetera, are other names used for RhB. Apart from the textile industry, RhB is also used in paper, plastic, cosmetics, leather, food, and many other industries, resulting in the large discharge of dye effluents. Due to its carcinogenic and neurotoxic behaviours, RhB has been banned in the food processing industry (Yu et al., 2018). However, RhB dye is still widely used in the textile industry and traces of RhB have been reported in wastewater from the textile industry (Cinelli, 2017). The presence of RhB, even at a very low concentration, can cause significant damage to human health and ecological environment if they are not properly disposed or treated (Yu et al., 2018).

To treat RhB from the wastewater, different techniques, such as chemical oxidation (Jafarinejad, 2017), ozonation (Antuch et al., 2019), biological activated sludge, and electrochemical treatment, are employed (Ramteke et al., 2015). However, these techniques result in secondary problems. The biological activated sludge treatment is a low-cost process, but the treatment is not productive for synthetic dyes due to its opposition to aerobic biodegradation. Additionally, the formation of intermediate compounds and intense experimental conditions are harmful to the microorganisms during the degradation of pollutants (Sheng et al., 2017). As for the chemical oxidation process, the process is costly, produces large amounts of waste in the form of sludge, and enhances the mass transfer (desorption) of contaminants in dissolved phases into vapour. This may allow the mobilisation of contaminants outside the monitoring area (Brusseau et al., 2011).

In wastewater treatment, photocatalysts have gained significant attention, as they possess great potential to remove toxic organic compounds via photocatalytic degradation, ideally, to carbon dioxide and water (Umar et al., 2013). Numerous photocatalysts, such as titanium dioxide (TiO_2) nanoparticles (Dong et al., 2015), sodium bismuthate ($NaBiO_3$) nanoparticles (Lu et al., 2013), magnesium doped cobalt ferrite ($Co_{1-x}Mg_xFe_2O_4$) (Sundararajan et al., 2017), and zinc oxide (ZnO) nanopowder (Kaur et al., 2013) have been investigated and applied in the photodegradation of organic contaminants. The photocatalytic process generates hydroxyl (·OH) radicals in aqueous solution once the photocatalytic particles are exposed to radiations, which leads to the mineralisation of organic pollutants. Hydroxyl radicals are considered to be the primary species that leads to degradation process (Casbeer et al., 2012).

Ferrite nanoparticles have also received significant attention from researchers due to its effectiveness as a tool for water purification and in the elimination of organic contaminants in water (Arimi et al., 2018). Ferrites offer the advantage of having a band gap, having the capability to absorb visible light and enhancing the effectiveness due to the availability of extra catalytic sites by virtue of the crystal lattice and nano-size (Casbeer et al., 2012). In addition, the magnetic properties of ferrites allow for its recollection using magnet (Borhan et al., 2014), making it recyclable.

Therefore, this research aims to explore, identify, and determine the optical, structural, and magnetic properties of the bismuth ferrite ($BiFeO_3$) nanoparticles synthesised via sol-gel auto-combustion method for photocatalytic degradation of RhB dye. The properties of $BiFeO_3$ nanoparticles are explored and determined by introducing cobalt and cerium dopants in $BiFeO_3$ host matrix.

1.2 Problem Statement

Chemical methods, such as ozonation (Li et al., 2016), electrochemical process (Du et al., 2012), Fenton process (Gao et al., 2015), and chemical oxidation (Maruthamani et al., 2015) are commonly used for the treatment of RhB in wastewater. The formation of intermediates, and high equipment and maintenance cost are the major challenges associated with these techniques. Among the different techniques, chemical oxidation has the advantage of degrading organic pollutants. The key issues associated to chemical oxidation process are longer treatment time (Sundararajan et al., 2017), formation of intermediate toxic compound (Ferrari et al., 2013), and chemical cost due to poor post-recovery.

Therefore, this research offers a solution to treat RhB solution using bismuth ferrite nanoparticles as photocatalyst (Bhukal et al., 2014). Bismuth ferrite have a band gap in visible range that can significantly enhance degradation due to the availability of extra catalytic sites by virtue of the crystal lattice and nano-size (Casbeer et al., 2012). In addition, due to its magnetic nature, ferrites can easily be recollected using magnet after the treatment/reaction and then recycled for another treatment process (Borhan et al., 2014).

1.3 Research Objectives

The main objective of this research is to synthesise bismuth ferrite ($BiFeO_3$) nanoparticles via sol-gel auto-combustion method for the photocatalytic degradation of Rhodamine B dye. The specific objectives are:

(a) To synthesise cobalt ($Bi_{1-x}Co_xFeO_3$) and cerium ($Bi_{1-y}Ce_yFeO_3$) doped bismuth ferrite nanoparticles with different doping concentrations (x; and y = 0.1, 0.2, 0.3, 0.4, and 0.5);

(b) To determine the optical, structural, and magnetic properties of synthesised doped and undoped bismuth ferrite nanoparticles in order to understand the role of dopants; and

(c) To identify the photocatalytic activity of synthesised doped and undoped bismuth ferrite nanoparticles on Rhodamine B dye in the context of irradiation/reaction time and doping concentrations.

1.4 Scope of Research

This research project can be divided into two parts: the synthesis of $BiFeO_3$ nanoparticles and photocatalytic activity of synthesised $BiFeO_3$ nanoparticles on RhB.

➢ **Synthesis of $BiFeO_3$ nanoparticles**

$BiFeO_3$ nanoparticles were synthesised via sol-gel auto-combustion route. To optimise the optical, structural, and magnetic behaviour of $BiFeO_3$ nanoparticles, the $BiFeO_3$ nanoparticles were doped with cobalt ($Bi_{1-x}Co_xFeO_3$) and cerium ($Bi_{1-y}Ce_yFeO_3$) with different doping concentrations (x; and y= 0.1, 0.2, 0.3, 0.4, and 0.5) and characterised using:

- High-resolution transmission electron microscope (HRTEM): To determine the size of the nanoparticles;
- X-ray diffraction (XRD): To study the structural characteristics and crystallinity;
- Field emission scanning electron microscope (FESEM) and energy dispersive X-ray (EDX) analysis: To study the surface morphology and elemental ratio respectively for grown nanoparticles;
- Thermogravimetric analysis (TGA): To evaluate thermal decomposition profile of $BiFeO_3$ nanoparticles, and determine and optimise the annealing temperature regime;

- Vibrating sample magnetometer (VSM): To study the magnetic properties; and
- Ultraviolet-visible (UV-VIS) spectroscopy: To identify the optical bandgap.

➢ **Photocatalytic Activity**

The photocatalytic activity of synthesised undoped and doped $BiFeO_3$ nanoparticles with different doping concentrations of 0.1, 0.2, 0.3, 0.4, and 0.5 were performed on the RhB solutions. The RhB solutions were characterised before and after the photocatalytic process using the following diagnostic tools:

- Ultraviolet-visible (UV-VIS) spectroscopy: To study the optical behaviour and degradation of dye before and after performing photocatalytic process;
- Fourier-transform infrared (FTIR) spectroscopy: To identify the chemical structure of RhB solution before and after it is subjected to photocatalytic activity; and
- High-performance liquid chromatography (HPLC): To identify the final products after photocatalytic process.

1.5 Significance of Study

This study presents the use of bismuth ferrite as photocatalyst to degrade Rhodamine B dye solution under visible light (sunlight). This research contributes towards understanding the role of cobalt and cerium as dopants towards the optical, structural, and magnetic properties of bismuth ferrite nanoparticles with respect to doping concentration. This study also observes the behaviour of bismuth ferrite nanoparticles towards the photocatalytic degradation of RhB in the context of dopants and doping concentrations used. This study will contribute to developing a cost-effective method for the treatment of RhB-contaminated wastewater in the textile industry.

1.6 Thesis Outline

This thesis describes the preparation, characterisation, and analyses of doped and undoped bismuth ferrite nanoparticles for the photocatalytic degradation of RhB dye solution. The sol-gel auto-combustion method was used to prepare the bismuth ferrite nanoparticles. This thesis is organised in five chapters, the details are as follows:

Chapter 1 provides a brief introduction and background of the current research. The problem statement, objectives, scope of research, and significance of study are also presented in this chapter.

Chapter 2 presents the literature and detailed information, such as the definition and processes that are related to the synthesis and characterisation of ferrites, photocatalysis process, and RhB dye.

Chapter 3 specifies the experimental details and procedures, such as preparation of bismuth ferrite nanoparticles and photocatalytic degradation process of RhB using prepared nanoparticles. Furthermore, detailed information regarding the characterisation of the samples are underscored.

Chapter 4 presents the results of optical, structural, and magnetic properties of the synthesised $BiFeO_3$ nanoparticles along with the photocatalytic degradation of RhB.

Chapter 5 presents the conclusion and important findings of the research along with the future outlook in this area of study.

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