



WOLLEGA UNIVERSITY

SCHOOL OF POST GRADUATE STUDIES

**COLLEGE OF NATURAL AND COMPUTATIONAL
SCIENCES**

DEPARTMENT OF PHYSICS

MSc RESEARCH THESIS

Effect of Silver Ion Doped Copper Ferrite Nanoparticles as Magnetic Catalysts to Promote Wastewater Decontamination ($\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$, $x = 0.0, 0.2, 0.4$)

BY

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JANUARY, 2026

NEKEMTE, ETHIOPIA



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MSc Research Thesis

A Research Thesis Submitted to Wollega University School of Graduate
Studies, College of Natural and Computational Science, Department of Physics
for Partial Fulfillment of the Requirements for Master Degree in Condensed
Matter Physics

By: - Desalegn Abeya Fufa

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APPROVAL SHEET FOR SUBMITTING RESEARCH THESIS

As members of the Board of Examining of the Final MSc thesis open defense, we certify that we have read and evaluated the thesis prepared by Desalegn Abeya Fufa under the title “Effect of Silver Ion Doped Copper Ferrite Nanoparticles as Magnetic Catalysts to Promote Wastewater Decontamination ($\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$, $x= 0.0, 0.2, 0.4$)” and recommended that the thesis be accepted as fulfilling the thesis requirement for the **Degree of Master of Science in Condensed Matter Physics**.

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Certification of the Final Thesis

I hereby certify that all the correction and recommendation suggested by the board of examiners are incorporated into the final thesis entitled **“Effect of Silver Ion Doped Copper Ferrite Nanoparticles as Magnetic Catalysts to Promote Wastewater Decontamination”** by **Desalegn Abeya Fufa**.

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Statement of the Author

I hereby declare that this thesis, **“Effect of Silver Ion Doped Copper Ferrite Nanoparticles as Magnetic Catalysts to Promote Wastewater Decontamination” $\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$, $x = 0.0, 0.2, 0.4$** is entirely original with proper citations to all sources of materials. This thesis is being submitted to Wollega University in partial fulfillment of the requirements for a masters degree in Condensed Matter Physics. I hereby certify that I have not submitted this thesis to any other university in order to obtain a degree or diploma. In accordance with Wollega University library policy, the thesis was placed at the university library to be made available to borrowers. Without specific permission, brief quotes from this thesis are permitted as long as the source is properly cited. However, Wollega University, the graduate school, may provide permission for lengthy excerpts from or partial reproductions of this book upon request. Permission from the author is required in all other cases.

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This is to certify that this thesis entitled **“Effect of Silver Ion Doped Copper Ferrite Nanoparticles as Magnetic Catalysts to Promote Wastewater Decontamination”** accepted in partial fulfillment of the requirements for the award of the degree of masters of science in condensed matter physics by the school of graduate studies, Wollega University through the College of Natural and Computational Sciences done by Desalegn Abeya Fufa is genuine work carried out by him under my guidance. The matter embodied in this thesis work has not been submitted earlier for the award of any degree or diploma.

The assistance and help received during the course of this investigation have been acknowledged. Therefore, I recommended that it can be accepted as fulfilling the research thesis requirements.

Advisor

Signature

Date

Acknowledgement

I extend my sincere gratitude to Almighty God for providing the strength necessary to complete this proposal. My deepest appreciation goes to my advisor, Dr. Sanbeto Kena, whose invaluable support, consistent guidance; friendly demeanor, insightful critiques, and encouragement were instrumental throughout my studies. I am also grateful to Efa Lalo Secondary School for the material support essential for conducting this thesis. Finally, I thank my beloved wife, Lelise Mengesha Atakiltu, and my son, Yerosat Desalegn Abeya, for their unwavering tolerance and inspiration during the proposal work.

Acronyms and Abbreviations

Ag (NO ₃)	: Silver anhydrate
AOPs	: Advanced Oxidation Processes
C ₆ H ₈ O ₇	: Anhydrous Citric acid
Cu (NO ₃) ₂ .3H ₂ O	: Copper Nitrate trihydrate
EMI	: Electromagnetic Interference
FCC	: Face Centered Cube
Fe (NO ₃) ₃ .9H ₂ O	: Ferric Nitrate nonahydrate
FWHM	: Full Width at Half Maximum
JCPDS	: Joint Committee on Powder Diffraction Standards
MRI	: Magnetic Resonance Imaging
N _A	: Avogadro number
NH ₃	: Ammonia
NPs	: Nano Particles
OER	: Oxygen Evolution Reactions
SEM	: Scanning Electron Microscope
SSR	: Solid State Reaction
VSM	: Vibrating Sample Magnetometer
UV	: Ultra Violet
XRD	: X-Ray Diffraction
YIG	: Yttrium Iron Garnet

Table of Contents

Content	Page
APPROVAL SHEET FOR SUBMITTING RESEARCH THESIS	ii
Certification of the Final Thesis	ii
Statement Of The Author.....	iv
Declaration.....	v
Acknowledgement	vi
Acronyms and Abbreviations	vii
List of Tables	x
List of Figures	xi
Abstract.....	xii
CHAPTER ONE	1
INTRODUCTION	1
1.1. Background of the Study.....	1
1.2. Statement of the Problem	2
1.3. Objectives of the Study	2
1.3.1. General Objective	2
1.3.2. Specific objectives	3
1.4. Significance of the Research	3
1.5. Limitations the Study (Shortcomings)	4
1.6. Organization of the Study	5
CHAPTER TWO	6
LITERATURE REVIEW	6
2.1. Introduction	6
2.2. Theoretical Concepts.....	6
2.3. Types of Ferrites and Their Applications.....	7
2.3.1. Types of Ferrites.....	7
2.3.2. Uses of Ferrites	10
CHAPTER THREE	12
MATERIALS AND METHOD.....	12
3.1. Introduction (Overview).....	12
3.2. Chemicals to be used (Precursors)	12
3.2.1. Metal Salt Precursors for the Synthesis of Nanoparticles	12
3.2.2. Extra Reagents and Chemicals	12

3.3. Apparatus (Equipments) to be Needed.....	13
3.4. Experimental Method (The Experimental Approach).....	13
3.4.1. The Bottom-Up Method	14
3.4.2. The Top-Down Method	14
3.4.3. Comparing Top-down and Bottom-up Synthesis Methods	15
3.4.4. The Sol-gel method's benefits and drawbacks.....	15
3.5. Experimental Procedures.....	16
3.6. Flow Chart.....	18
3.7. Characterization Techniques	19
3.7.2. Scanning Electron Microscopy (SEM).....	21
3.7.3 Vibrating Sample Magnetometer (VSM)	22
CHAPTER FOUR.....	23
RESULTS AND DISCUSSION	23
4.1. Structural Analysis	23
4.1.1. Introduction	23
4.1.2. X-ray Diffraction (XRD) Analysis	23
4.2. Morphological Studies	25
4.3. Magnetic Studies.....	25
CHAPTER FIVE	27
CONCLUSION AND RECOMMENDATIONS	27
5.1 Conclusion.....	27
5.2 Recommendations	27
References.....	29

List of Tables

Table 4.1.Values of crystallite size (D), lattice parameter (a), d- spacing, volume of unit cell and x-ray density	24
Table 4.2 shows saturation magnetization (M_s), Remnant magnetization (M_r), coercive field and squarness of the given sample $\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$	26

List of Figures

Figure 2.1 Spinel unit cell structure	8
Figure 2.2 Garnet crystal structures	10
Figure 3.1 Equipments needed for the synthesis of samples of $\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$ nanoparticle .	13
Figure 3.2 Top-down versus bottom-up synthesis route.....	15
Figure 3.3 Representation of X-ray diffraction.....	19
Figure 3.4 X-ray diffractometer interfaced with computer.....	21
Figure 3.5 Scanning electron microscope (SEM)	22
Figure 3.6. Vibrating sample magnetometer (VSM)	22
Figure 4.1 XRD pattern of $\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$ ($x= 0.0, 0.2, 0.4$)	24
Figure 4.2 SEM images of $\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$ ($x= 0.0, 0.2, 0.4$)	25
Figure 4.3 Hysteresis loop of sample $\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4$)	26

Abstract

The purpose of this work was to investigate the effect of Silver Ion Doped Copper Ferrite Nanoparticles as Magnetic Catalysts to Promote Wastewater Decontamination prepared using sol-gel method. The structural and surface morphology of the sample was characterized using XRD and SEM, respectively. From the XRD analysis, all the samples are in cubic crystal structure with space group $Fd\bar{3}m$. The XRD confirmed that the crystallite size decreased with increasing the concentration of silver ion from 32.158nm to 18.866nm. The lattice constant also decreased from 0.8359nm to 0.2513nm suggests that silver ions are indeed being incorporated into the crystal lattice, leading to slight structural contraction or distortion. The x-ray density increased with silver ion concentration indicate that the increase in the molecular weight due to the heavier silver ions has a more significant impact on the density than the slight contraction of the lattice parameter; this is a common observation when a heavier element replaces a lighter one, even with slight lattice changes. SEM micrograph showed that the prepared sample was in uniformly shape and less agglomerated form. The VSM measurement showed that the saturation magnetization enhanced from 2.325emu/g to 3.188eu/g but the other parameters, remnant magnetization decreased in the trends. The material's combined properties confirm its potential for promising applications in environmental devices (as magnetic photocatalytic reactors and gas sensors) and biomedical devices (as magnetic hyperthermia agents, targeted drug delivery systems, and antimicrobial coatings).

Keywords: Silver ion (Ag^+) doping, copper ferrite, magnetic catalyst, wastewater decontamination, nanoparticles, characterization, crystal structure.

CHAPTER ONE

INTRODUCTION

1.1. Background of the Study

With the general formula MFe_2O_4 , nanostructured spinel ferrites have become a class of materials that offer notable advantages above their bulk polycrystalline counterparts. Their special blend of dielectric and magnetic characteristics makes them appealing in a variety of contemporary scientific and technological domains. Notably, spinel ferrites display outstanding magnetic behavior, which is especially advantageous for high-frequency applications (Calvo-de la Rosa et al., 2019). These qualities make them invaluable for applications in electronics, sensors, photocatalysis, and air purification systems (Rus et al., 2012).

The successful fabrication of adaptable nanostructured ferrites necessitates the use of a diverse range of synthesis methods, the choice of which is paramount because it fundamentally governs the resulting material attributes, specifically particle size, morphology, and crystallinity. Standard preparation protocols encompass mechanical approaches (e.g., mechanical alloying (Jiang et al., 1999) and mechano-chemical processing (Manova et al., 2011)), solution-phase techniques (including hydrothermal synthesis (Rashad et al., 2012), co-precipitation (Ateia et al., 2017), sol-gel methods (Khanna et al., 2019), and micro-emulsion methods (Rashad et al., 2015)), and high-temperature syntheses (such as thermal treatment (Zakiyah et al., 2015) and combustion techniques (Liu et al., 2008)).

Superparamagnetism, magnetocrystalline anisotropy, and coercivity are important nanoscale-dependent properties of these materials, and their physical characteristics differ greatly from those seen at the micrometric scale. For example, in very small particles, thermal energy can be enough to readily change the orientation of the particle's magnetic moment, resulting in distinctive magnetic behaviors.

Due to its remarkable magnetic and electrical properties, copper ferrite ($CuFe_2O_4$) has garnered significant research interest among the different spinel ferrites. It is highly suitable for a wide range of magnetic applications, including thermal catalysis, magnetic recording media, Li-ion batteries, and various medical applications. It is also a great candidate for power applications due to its high permeability, notable electrical resistivity, and magnetoresistive properties. The ability to tune these properties through doping or synthesis

modification presents exciting opportunities for the development of advanced functional materials.

1.2. Statement of the Problem

One of the biggest threats to the environment and public health worldwide is wastewater poisoning. A complex range of pollutants, such as organic contaminants, heavy metals, and pathogens, are introduced into water bodies by wastewater from home, industrial, and agricultural sources. While somewhat effective, conventional wastewater treatment techniques frequently have drawbacks, including high operating costs, the production of secondary waste, and ineffectiveness in eliminating some stubborn pollutants or newly discovered contaminants. Advanced, reasonably priced, and ecologically friendly methods that effectively cleanse wastewater are desperately needed.

Because they may be easily separated from treated water using an external magnetic field, magnetic catalysts-especially those based on spinel ferrites have shown great promise in wastewater treatment, minimizing post-treatment processing. Because of its superior magnetic and catalytic qualities, copper ferrite (CuFe_2O_4) nanoparticles stand out among the others. Their catalytic efficiency can be further enhanced, though, and little is known about how particular dopants affect their magneto-catalytic performance for wastewater purification.

In particular, not enough research has been done on how copper ferrite nanoparticles are affected by silver ion (Ag^+) doping and, more importantly, how effective they are at catalyzing wastewater decontamination. Although copper ferrites provide magnetic separability and silver is recognized for its antimicrobial and catalytic qualities, further research is necessary to determine the precise mechanism by which silver doping increases the magnetic catalytic activity of copper ferrite nanoparticles in wastewater treatment settings as well as the synergistic advantages. There is a crucial gap in the development of advanced treatment solutions since the full potential of these innovative magnetic nanoparticles for sustainable wastewater decontamination cannot be achieved without such knowledge.

1.3. Objectives of the Study

1.3.1. General Objective

Investigating how silver ion doping affects the structural, magnetic, and catalytic characteristics of copper ferrite nanoparticles for improved wastewater decontamination was the primary goal of this work.

1.3.2. Specific objectives

The specific goals of this work were to:

- Used the sol-gel process to create a series of copper ferrite nanoparticles ($\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$) doped with silver ions at different concentrations.
- Used X-ray diffraction (XRD), describe the structural characteristics of the produced nanoparticles, such as phase purity, crystal structure, and inversion degree.
- Examined the produced nanoparticles' morphological properties with Scanning Electron Microscopy (SEM).
- Utilized Vibrating Sample Magnetometry (VSM), assess the magnetic characteristics of the silver-doped copper ferrite nanoparticles, such as saturation magnetization, coercivity, and remnant magnetization.
- Examined and contrast the doped and undoped copper ferrite nanoparticles' catalytic abilities in facilitating the decontamination of model wastewater contaminants.

1.4. Significance of the Research

This work on the impact of copper ferrite nanoparticles doped with silver ions as magnetic catalysts for wastewater purification has important ramifications for both basic research and real-world applications, advancing material engineering and environmental science.

For the Scientific and Academic Community:

- ❖ This study would help close a significant knowledge gap regarding the specific effects of silver ion doping on the structural, magnetic, and above all magneto catalytic characteristic of copper ferrite nanoparticles. Comprehensive investigations addressing these complex linkages for wastewater treatment are frequently lacking in the literature currently in publication.
- ❖ This work attempts to clarify the fundamental processes by which silver doping improves the catalytic efficiency for pollutant degradation by methodically describing the produced nanoparticles and comparing their characteristics with catalytic performance.
- ❖ The thorough synthesis and characterization of new silver-doped copper ferrite nanoparticles will advance the field of nanomaterials science and provide fresh insights into how to modify material characteristics for particular environmental uses.

- ❖ Other scholars working on advanced oxidation processes, heterogeneous catalysis, and magnetic nanoparticles for environmental remediation will find great value in the discoveries, methods, and characterization data provided in this thesis.

1.5. Limitations the Study (Shortcomings)

In a thesis paper, the term "limitations" refers to possible flaws or constraints that could affect the studies' findings or their generalizability. These may result from a number of things, such as the methodology, research design, or resources that are accessible. Maintaining the research's credibility and directing future investigations depend on acknowledging these limitations. The following are some of the study's problems or limitations:

- ✚ **The sample size:** The findings may not be as broadly applicable to a wider population if the sample is small or non-representative.
- ✚ **Method of Data Collection:** Limitations may be introduced by the data collection method.
- ✚ **Resources and Time Limitations:** Time and budgetary limits might restrict the scope of a study, potentially resulting to insufficient data or a limited focus. The study's scope was restricted to the theoretical analysis, computations, and characterizations of the impact of copper ferrite nanoparticles doped with silver ions acting as magnetic catalysts to aid in wastewater purification due to time constraints. One of the study's limitations was likely a lack of time to analyze the specifics or key findings of the observational study, and websites might not have been accessible enough for the investigation.
- ✚ **Absence of Previous Research:** Because there has been little previous research on the subject, it could be difficult to give the study a thorough context or to compare the results with previous works.
- ✚ **Methodological Decisions:** The researcher's conscious decisions to restrict the study's scope may also be seen as limits.
- ✚ **Data Access:** Research depth and breadth may be limited by restricted access to data sources, such as certain databases or archives. Websites may not be accessible for the study or may be unavailable.

1.6. Organization of the Study

There were five chapters in the thesis. The introduction, which covers a number of subtopics, is covered in the first chapter. These include the study's background, issue statement, aims (both general and specific), significance, and limitations. The research's review of linked literature, which served as its foundation or focal point, is presented in the second chapter. The procedure and necessary supplies are introduced in the third chapter. This chapter introduced the method, experimental procedures, flow chart, apparatus (instruments), chemical to be utilized (precursors), and several characterization approaches. Results and debate were the main topics of chapter four. The conclusion and recommendations are covered in the fifth and final chapter.

CHAPTER TWO

LITERATURE REVIEW

2.1. Introduction

This chapter provides a critical review of the scientific literature across three core research areas essential to the present study: Magnetic Nanomaterials in Catalysis, Copper Ferrite (CuFe_2O_4) Nanoparticles, and the Role of Noble Metal Doping (Specifically Silver Ions) in enhancing both catalytic and antimicrobial performance.

2.2. Theoretical Concepts

Ferrites are an important group of magnetic materials widely used in various applications. They typically form a cubic spinel crystal structure represented as AB_2O_4 , which has two different types of sites for metal ions: tetrahedral (A) and octahedral (B) (Salih and Mahmood, 2023). A particularly interesting type is copper ferrite (CuFe_2O_4) because, unlike the typical ordered spinel structure, it's known to be a random spinel. This means the copper ions (Cu^{2+}) are not confined to just one site but are distributed randomly across both the tetrahedral (A) and octahedral (B) positions. Investigating the unique properties resulting from this random structure is worthwhile (Fakruddin et al., 2024). The appropriate use of ferrites in electronic technology is determined in large part by their physical characteristics, including saturation magnetization, magnetic moment, coercive, Dc resistivity, porosity, and average grain diameter (Dhahri et al., 2020). Permanent magnets, inducting power transformers, channel filters, magnetic recording heads, loading coils, loud speakers, electric motors, and motion guides in the microwave region are only a few examples of the technological devices that can be used because of the physical characteristics listed above. Because ferrites are used in nuclear power engineering computer systems and electrical engineering, they are essential to modern technology.

Nanocrystalline magnetic materials have drawn interest from a variety of disciplines, including physics, chemistry, biology, medicine, materials science, and engineering, because of their exceptional and distinctive qualities.

From a theoretical and practical perspective, spinel ferrites are important and intriguing materials. The thermal and chemical stability of magnetic CoFe_2O_4 , MnFe_2O_4 , CuFe_2O_4 , ZnFe_2O_4 , and NiFe_2O_4 nanoparticles, along with their unique structural, magnetic, optical,

electrical, and dielectrical properties, have drawn a lot of attention. These nanoparticles have a wide range of technological applications, such as photoluminescence, biosensors, humidity sensors, catalysis, magnetic refrigeration, permanent magnets, magnetic drug delivery, and magnetic hyperthermia. Because of their special electrical, magnetic, and catalytic qualities, ferrites have attracted more attention in recent decades. Due to these characteristics, ferrites have a limited range of uses, including catalysis, electronic devices, medical devices, and recording devices (Ding et al., 1998). The copper/iron/oxygen system is one of the most significant ferrite spinel systems and is gaining increased attention in a variety of disciplines, including solid-state physics, ceramics, metallurgy, and geology. Due to their special qualities of electrical conductivity and semiconducting activity, copper ferrites are becoming more and more popular. Copper ferrites shown significant catalytic activity in addition to their heat stability (Stewart et al., 2004). Inverse spinel makes up a significant portion of the copper ferrite structure. At a cubic closed pack structure, copper and iron ions could be arranged at various crystallographic locations encircled by oxygen atoms. The ions may be tetrahedral or octahedral, and they are designated as A and B sites. According to Agourine et al. (2016), the formula for this kind of allocation is $(\text{Cu}_x\text{Fe}_{1-x})_A (\text{Cu}_{1-x}\text{Fe}_{1+x})_B \text{O}_4$, where x is the inversion coefficient that is assigned to be either zero or one, representing the inverse or normal spinel. According to Atia et al. (2016), there are two distinct spinel configurations of copper ferrite: the tetragonal one, which has lattice constants of $a=8.216 \text{ \AA}$, $c=8.709 \text{ \AA}$, and the cubic one, which appears at high temperatures. Eight copper ions are octahedrally positioned in the inverse model pattern (B), while sixteen trivalent iron ions are equally dispersed along the tetrahedral and octahedral positions (Jiang et al., 1999).

2.3. Types of Ferrites and Their Applications

2.3.1. Types of Ferrites

Ferrites are ceramic-like materials comprised of iron oxide (Fe_2O_3) and one or more metallic metals that have been chemically combined. They are examples of ferrimagnetic magnetic oxides, which are widely used in magnetic, electrical, and environmental applications. Ferrites are typically classified into three categories based on their magnetic characteristics and crystal structure (Vedrtnam et al., 2020).

1. Spinel Ferrites (MFe_2O_4)

Structure: Metal cations occupy tetrahedral (A-sites) and octahedral (B-sites) spaces in a cubic, closely packed oxygen lattice. Divalent metal ions, such as Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , etc., are represented by M. Copper ferrite ($CuFe_2O_4$), nickel ferrite ($NiFe_2O_4$), and zinc ferrite ($ZnFe_2O_4$) are a few types of spinel ferrites.

Qualities:

- ✓ High electrical resistivity,
- ✓ Moderate magnetization, and
- ✓ Usefulness in catalytic and
- ✓ Magnetic applications-Pertinence to the research:

The foundation material used in this investigation is copper ferrite, a kind of spinel ferrite. Doping with silver ions (Ag^+) to improve magnetic and catalytic properties is made possible by the structure. Based on their distribution of cat ions, spinel ferrites are divided into three groups.

Normal Spinel Ferrites: When all trivalent iron ions occupy the B-site and the divalent metal ions occupy the A-site, the resulting ferrite is referred to as typical normal spinel ferrites. Zinc ferrite has this kind of cation distribution.

Inverse Spinel Ferrites: These ferrites are characterized by the presence of trivalent iron ions in both the A- and B-sites and all divalent metal ions in the B-site. Both cobalt and nickel ferrites have this kind of cation distribution.

Random Spinel Ferrites: The ferrite that results from the occupation of A- and B-sites by divalent metal ions and trivalent iron ions are referred to as mixed spinel ferrite. If the degree of inversion and its cation distribution are present in cobalt ferrites, then this kind of cation distribution is present.

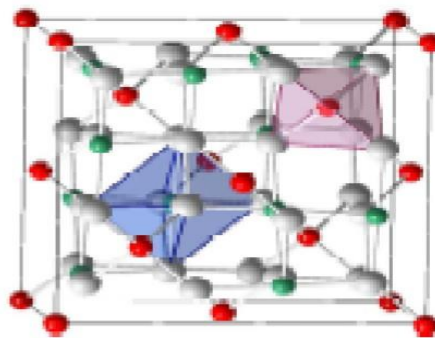


Figure 2.1 Spinel unit cell structure

2. Hexaferrites ($MFe_{12}O_{19}$)

Hex ferrites are hexagonal or rhombohedra ferromagnetic oxides with the general formula $MFe_{12}O_{19}$, where M is an element such as barium, lead, or strontium. A variety of ferrites crystallize in a hexagonal structure, and some of them have gained significant technological significance in the modern era. Barium ferrite possesses a hexagonal crystal with a unit cell made up of two unit formula, while hex ferrites have a minor axis known as the "a" axis and a major preferred axis called the "c" axis. The preferred direction is employed as a permanent magnetic substance. Since the oxygen ions are closely packed in the spinel structure, they can be replaced in the lattice by Ba^{2+} , Sr^{2+} , or Pb^{2+} ions, which are now included in oxygen layers. These ions have ionic radii that are comparable to those of the oxygen ions. Hexaferrite is frequently composed of Ba^{2+} or Sr^{2+} and Fe^{3+} ions and displays a hexagonal crystal structure.

Features include;

- Strong anisotropy
- High coercivity, and
- Magnetic stability and widespread application in microwave and permanent magnet systems.

3. Garnet Ferrites ($Y_3Fe_5O_{12}$ -YIG, for example)

One of the most intricate crystal forms is garnet, and it is challenging to create a two-dimensional illustration that accurately depicts all 160 ions in the unit cell. To keep things simple, figure 2.2 merely displays an octant of a garnet structure that displays the cation locations. Octahedral (trivalent cations surrounded by six oxygen ions), tetrahedral (trivalent cations surrounded by four oxygen ions), and 12-sided polyhedral-dodecahedral (trivalent cations surrounded by eight oxygen atoms) sites are all constituents of the garnet structure (Collomb et al., 1986). According to Valenzuela et al. (2012), garnet's chemical formula is $3Me_2O_3 \cdot 5Fe_2O_3$, where Me stands for trivalent rare earth elements like lanthanum and yttrium.

Thin monocrystalline films of complex garnets have been developed for bubble domain memory devices, and yttrium-based garnets are used in microwave devices. The structure of garnet ferrite is more complex than spinels, with three distinct sites for cation occupancy. For example, Yttrium iron garnet (YIG) has the following characteristics: high magneto-optical

activity, excellent microwave properties, and applications in optical isolators and microwave filters.

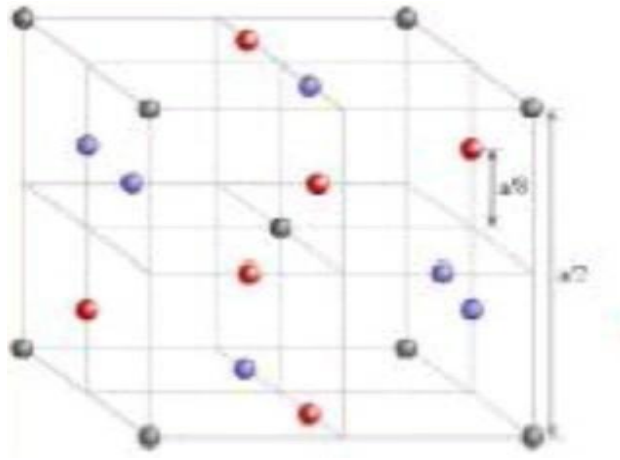


Figure 2.2 Garnet crystal structures

2.3.2. Uses of Ferrites

Because of their special electrical, magnetic, and catalytic qualities, ferrites can be used in a variety of ways.

Magnetic and Electronic Equipment

- Soft ferrites, such as MnZn or NiZn, are utilized in transformers and inductors because of their low eddy current losses and high permeability.
- Ferrites aid in the reduction of electromagnetic interference (EMI) in magnetic cores and antennas.
- Permanent magnets: Motors and loudspeakers use hard ferrites, such as $\text{BaFe}_{12}\text{O}_{19}$.

Uses in Biomedicine

- Drug delivery: Therapeutic drugs are guided by magnetic ferrites that use external magnetic fields.
- Magnetic resonance imaging (MRI) is used as contrast agents.
- Treatment for hyperthermia: Magnetic nanoparticles provide heat to destroy cancer cells.

Applications to the Environment

- In wastewater treatment, ferrites especially spinel ferrites are employed as adsorbents and catalysts because of their redox-active metal ions, high chemical stability, magnetic reparability, and surface reactivity.

- Adsorption of heavy metals and toxic ions, fenton-like catalysis for advanced oxidation processes (AOPs), and photocatalysis for the breakdown of colors and organic pollutants are some examples of specific functions.
- This work examines the dual functions of copper ferrite nanoparticles doped with silver ions: improved catalytic degradation of contaminants and simple magnetic recovery from treated water.

Energy Storage and Catalysis

- Because of their surface activity, ferrites operate as heterogeneous catalysts in organic reactions and are employed in oxygen evolution reactions (OER) in batteries and super-capacitors.

CHAPTER THREE

MATERIALS AND METHOD

3.1. Introduction (Overview)

In order to facilitate wastewater purification, silver ion (Ag^+) doped copper ferrite (CuFe_2O_4) nanoparticles were created and their magnetic and catalytic qualities assessed. Copper ferrite was selected as the foundation material because of its strong magnetic behavior, spinel structure, and thermal stability, all of which make it a viable option for use as a magnetically recoverable catalyst. In order to improve the catalytic breakdown of contaminants, doping with silver ions is meant to increase the material's surface activity, redox potential, and electron transfer ability. The materials and techniques utilized for the nanoparticles' production, characterization, and catalytic testing of the particle. Because of its benefits in controlling stoichiometry, particle size, and homogeneity, the sol-gel method was used to synthesize the Ag^+ doped copper ferrite nanoparticles.

3.2. Chemicals to be used (Precursors)

The analytical-grade compounds utilized in this investigation didn't require any additional purification. Deionized water was used to prepare all of the solutions. The following chemicals were used as precursors to create copper ferrite nanoparticles doped with silver ions and to assess how well they catalyzed wastewater treatment.

3.2.1. Metal Salt Precursors for the Synthesis of Nanoparticles

- ❖ Copper (II) Nitrate Trihydrate $-\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$:- source of Cu^{2+} ions for copper ferrite formation;
- ❖ Iron (III) Nitrate Nonahydrate $-\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$:- source of Fe^{2+} ions needed for spinel ferrite structure;
- ❖ Silver Nitrate or Silver anhydrate $-\text{Ag}(\text{NO}_3)$:-A dopant precursor that provides Ag^+ ions for surface or lattice modification.

3.2.2. Extra Reagents and Chemicals

- ❖ Citric acid anhydrous ($\text{C}_6\text{H}_8\text{O}_7$) (sol-gel method): During combustion synthesis, it serves as both a fuel and a chelating agent.
- ❖ Using ammonia solution (NH_3 25%) to regulate PH: It can be used to regulate the reaction medium's PH to 7.

- ❖ Water that has been deionized or distilled is used as a solvent for washing and solution preparation.
- ❖ Acetone

3.3. Apparatus (Equipments) to be Needed

A 150 ml beaker, spoon, spatula, cotton, electronic balance (mass measurement), magnetic stirrer, magnetic bead, evaporating dish, hot oven, agate mortar with pestle, alumina crucible, temperature-programmed electric furnace, alumina plate, and litmus paper were used to examine the impact of silver ion-doped copper ferrite nanoparticle. The procedures outlined in the paper were followed in the application of the methodologies and techniques.

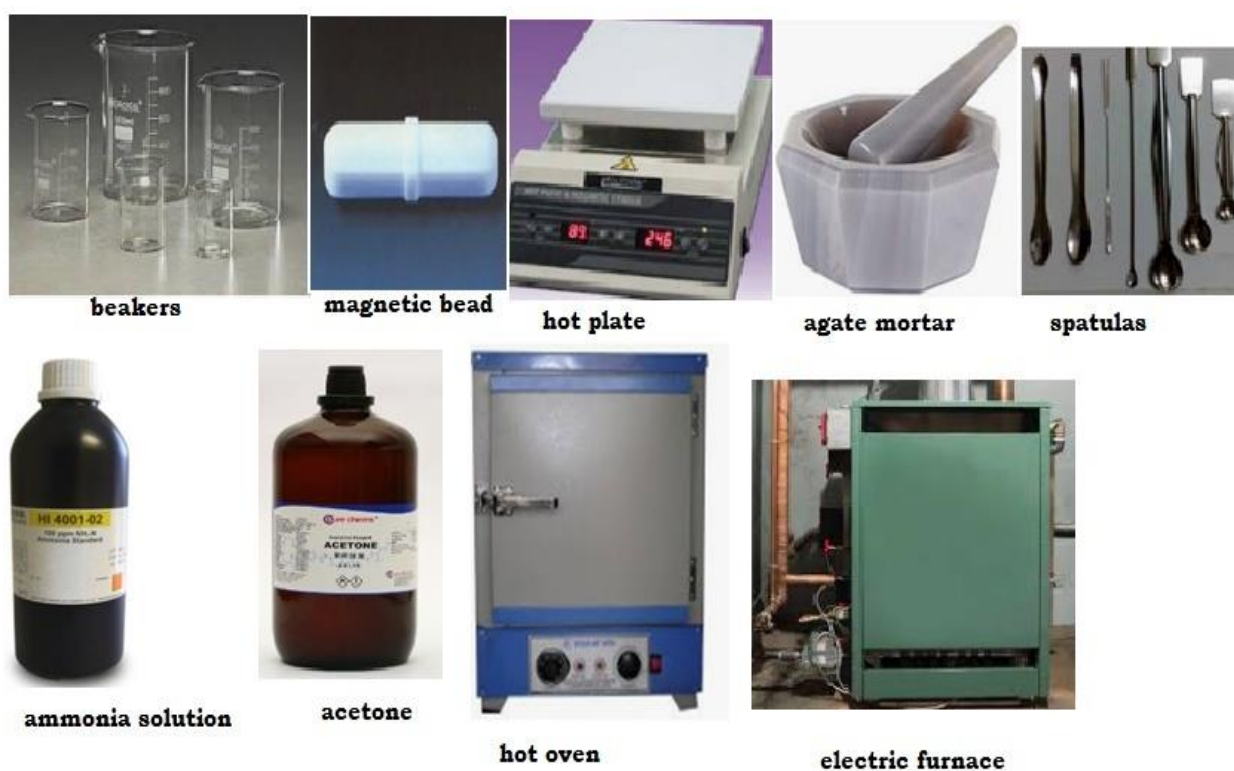


Figure 3.1 Equipments needed for the synthesis of samples of $\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$ nanoparticles

3.4. Experimental Method (The Experimental Approach)

Researchers in materials science are working to create new materials that are more practical, have higher qualities, and are less expensive than the ones that are currently on the market. To increase the performance of nanomaterials with superior characteristics and to better control the size and distribution of the particles, a number of physical and chemical techniques have been developed. There are two methods for creating nanoparticles; both top-

down and bottom-up methods.

Generally speaking, there are two primary methods for creating nanomaterials: top-down and bottom-up. The top-down method reduces the size of bulk materials, whereas the bottom-up method synthesizes materials at the atomic level.

3.4.1. The Bottom-Up Method

Down to the atomic level combined with additional self-assembly processes that result in the creation of nanostructures are examples of bottom-up techniques. Basic units are joined into more substantial, stable structures during self-assembly by means of physical forces acting at the nanoscale. The creation of nanoparticles from colloidal dispersion and quantum dots during epitaxial growth are typical instances.

Building a material from the bottom up; atom by atom, molecule by molecule, or cluster by cluster is known as the "bottom-up approach." The majority of nanoscale materials that can produce a homogeneous size, shape, and distribution are prepared more frequently using this method. Chemical synthesis is covered in detail, and the reaction is carefully regulated to prevent additional particle formation. Despite being nothing new, the bottom-up method is crucial to the creation and processing of nanomaterials and nanostructures.

3.4.2. The Top-Down Method

When treating nanostructures, the top-down method uses bigger (macroscopic) starting structures that are controllable from the outside. Ball milling, etching through the mask, and applying extreme plastic deformation are typical instances. Typical solid-state processing of the materials includes top-down pathways. Using physical operations like crushing, milling, and grinding, this method starts with bulk materials and breaks them up into smaller pieces. Even with significant energy consumption, it is very difficult to achieve very fine particles, and this method is typically not appropriate for creating materials with uniform and consistent shapes, and even with significant energy consumption, it is exceedingly challenging to produce very fine particles.

The surface structure's imperfections are the main issue with the top-down method. The surface chemistry and physical characteristics of nanostructures and nanomaterials would be greatly impacted by such an imperfection. It is commonly known that the traditional top-down method can seriously harm the processed patterns' crystallographic integrity.

3.4.3. Comparing Top-down and Bottom-up Synthesis Methods

Top-down approaches start with a larger-scale pattern and then reduce it to the nanoscale; they are inherently slow and unsuitable for large-scale production; bottom-up approaches begin with atoms or molecules and work their way up to nanostructures; and fabrication is far less expensive.

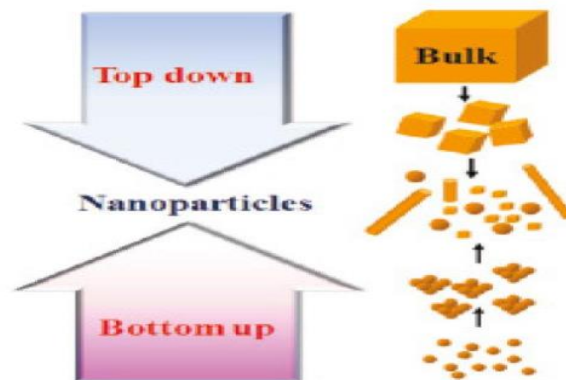


Figure 3.2 Top-down versus bottom-up synthesis route

There are numerous synthetic techniques available for creating polycrystalline ceramic samples. In experimental condensed matter physics research, the creation of superior materials with desired properties is crucial. The synthesis method determines the final phase's quality and physical behavior, as the chosen process and synthesis pathway can impact the sample's ultimate product quality.

The following techniques can be used to create nanoparticles.

- Sol-gel technique,
- Method of solid state reaction (SSR),
- The hydrothermal approach,
- The method of co-precipitation

Since the sol-gel process requires a low synthesis temperature and makes particle size control simple, we were interested in using it in our work.

3.4.4. The Sol-gel method's benefits and drawbacks

3.4.4.1. The Sol-gel method's benefits

The homogeneous nanostructure and high purity that may be achieved at low temperatures are the primary advantages of sol-gel processing.

A few other significant benefits of this method include lower costs, the ability to introduce a high dopant concentration, improved control over reaction parameters like temperature or PH, increased homogeneity, shorter synthesis times, fewer instrument requirements, and the potential to prepare nanoparticles as small as 1 to 100 nm.

- Versatile: it is possible to incorporate organic materials and nanoparticles into sol-gel produced oxides, and it is better to regulate the structure, including porosity and particle size.
- The extended composition ranges enable the creation of new hybrid organic-inorganic compounds that are not found in nature, as well as the manufacturing of any oxide composition and some non-oxides. It has great purity and improved homogeneity as a result of molecular mixing.
- Reduced energy consumption: since the network structure can be formed at very low temperatures, the melting point need not be reached.

3.4.4.2. Sol-gel Technique Drawbacks

- The price of precursors
- When a wet gel dries, it shrinks, which frequently causes fracture because it creates high capillary tensions and makes it challenging to create huge monolithic portions.
- Due to the varying reactivity of the alkoxide precursors, a specific oxide will preferentially precipitate during sol formation (in multi-component glasses).
- Avoiding OH groups and residual porosity is challenging.

3.5. Experimental Procedures

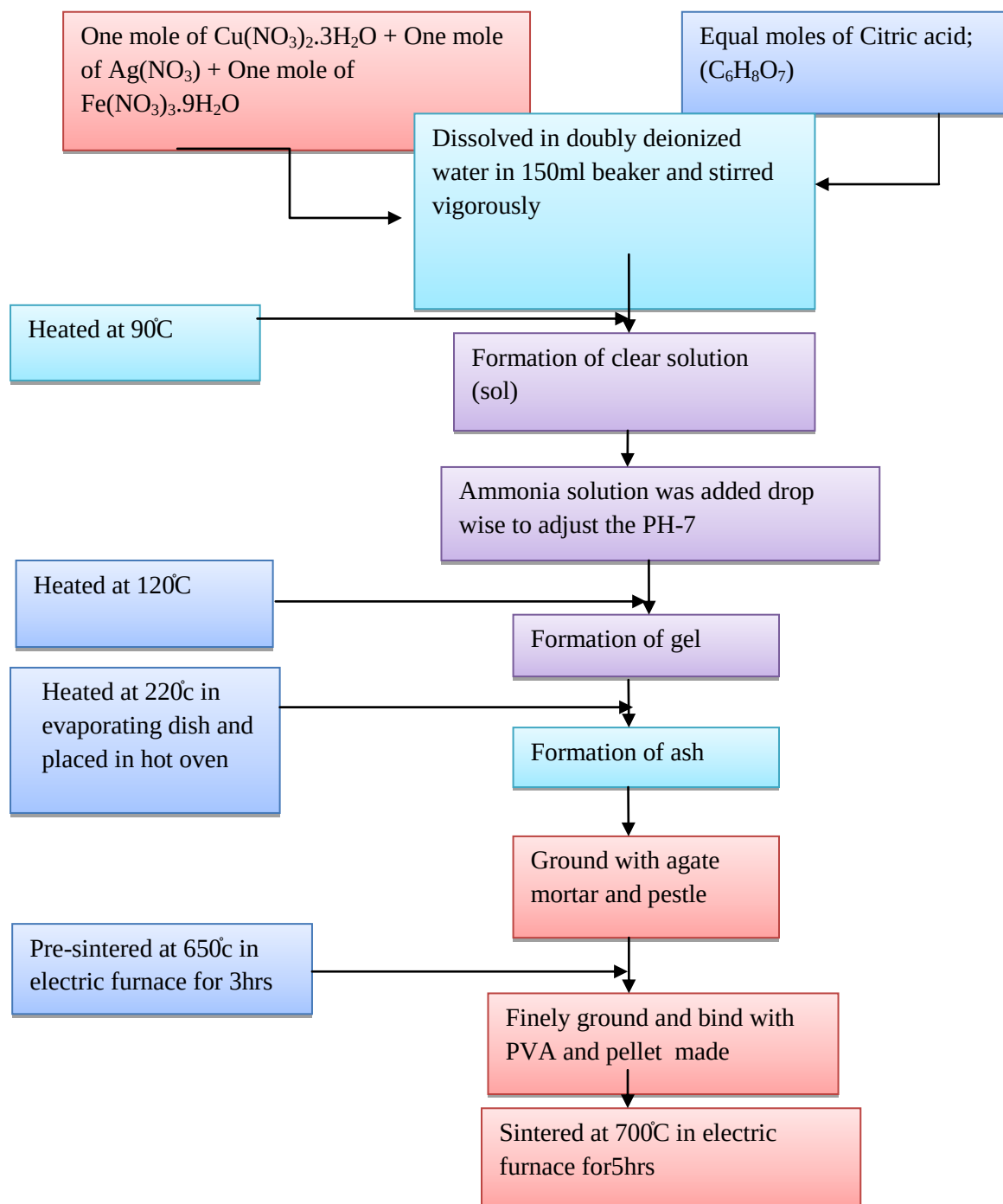
Sol-gel was used to create copper ferrite nanoparticles doped with silver ions. The following steps were part of the process:

- ❖ To create a transparent, uniform metal nitrate solution, stoichiometric volumes of Cu (NO₃)₂·3H₂O, Ag(NO₃) with different silver doping levels, and Fe (NO₃)₃·9H₂O were combined or dissolved in a beaker filled with distilled water and agitated at room temperature.
- ❖ An equal mole of citric acid was added to a solution containing a 1:1 ratio of metal nitrates.
- ❖ To create a transparent suspended solution, or "sol," the mixed solution was agitated with a magnetic stirrer.

- ❖ Ammonia solution was then added drop by drop to bring the PH down to 7.
- ❖ A structural network "gel" developed over time.
- ❖ The gel was then placed onto an evaporating dish and heated to 220 degrees Celsius in a hot oven until ignited ash formed.
- ❖ Agate mortar was used multiple times to finely grind the burning ash.
- ❖ To eliminate contaminants and organic materials (calcinations), the ground powder was stored in an alumina crucible and placed in an electric furnace with a temperature program set at 650 degrees Celsius for three hours.
- ❖ Following its removal, the calcined sample was ground finely multiple times before being placed in an electric furnace set to 700 degree Celsius for five hours in order to further densify it.
- ❖ After being taken out of the furnace, the sintered sample was coarsely powdered and prepared for characterization.

3.6. Flow Chart

Flow chart for the preparation of silver doped copper ferrite by sol-gel method.



3.7. Characterization Techniques

Ceramic characterization is accomplished by a variety of methods. The kind of information we hope to extract from the material will determine which one we use. In the current study, X-ray diffraction was used to investigate the sample's structure and phase purity, and scanning electron microscopy was used to analyze the sample's surface morphology.

The sample must be characterized using various measuring meters once it has been synthesized using the chosen method in order to determine its qualities. Because nanoparticles are so tiny, they cannot be seen with a standard light microscope. More potent tools, such as electron microscopes, which may be SEM or TEM. Therefore, the following characterization procedures would be used to describe the synthesized sample of $(\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4)$.

1. Diffraction of X-rays (XRD)
2. Scanning Electron Microscopy (SEM)
3. The VSM or Vibrating Sample Magnetometer

3.7.1. X-ray Diffraction (XRD)

Using X-ray diffraction (XRD), which is still often the most accurate technique for describing crystal symmetry, Bragg performed the first direct determination of a crystal structure (Cullity et al., 1967). One of the most used methods for describing ceramics is X-ray diffraction (XRD). A practical technique for figuring out the mean or average size of nanocrystallites in nanocrystalline bulk materials is X-ray diffraction. Phase, average crystallite size, and lattice parameter are among the structural and electrical conductivity nanoparticles of Ag^+ doped CuFe_2O_4 ($\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$) that may be obtained using this fundamental characterization approach.

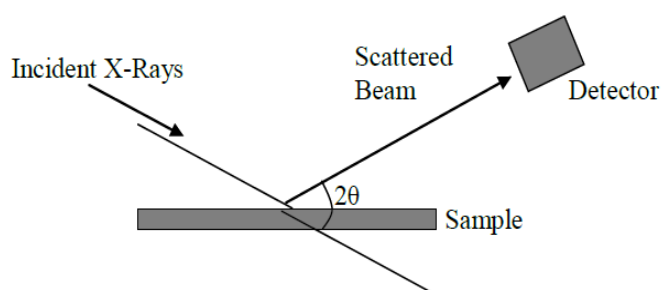


Figure 3.3 Representation of X-ray diffraction

An X-ray diffractometer can provide the following data: (i) the prepared sample's quality and confirmation; (ii) the reflections' interplanar spacing, or "d"; (iii) the intensity of the reflections; and (iv) the unit cell dimensions and lattice type.

The interplanar distance(d-spacing) would be calculated from Bragg's angle and wavelength of x-ray:

$$2d_{hkl}\sin\theta = n\lambda \quad (3.1)$$

The crystal lattice parameter of $\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$ nanoparticles would be calculated by using the following mathematical expression:

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} \quad (3.2)$$

where 'a' is the simple cubic lattice constant, d is the distance between two consecutive planes in (nm) and h, k, l are just notation for miller indices of the crystal plane. The volume of unit cell can be calculated using:

$$V_{\text{cell}} = a^3 \quad (3.3)$$

The average crystallite size of these nanoparticles was also calculated with help of Debye Scherer's formula which is given by

$$D = \frac{k\lambda}{\beta \cos\theta} = \frac{0.89\lambda}{\beta \cos\theta} \quad (3.4)$$

where k is a Scherer constant equal to 0.89 for FWHM of spherical crystals with cubic symmetry, θ is the diffraction angle, β is the full width at half maximum FWHM, and λ is the wavelength notation (0.15406nm). By measuring the full width at half maximum (FWHM) of peaks (β) in radiation at each 2θ in the pattern, the Scherer equation was created to determine the nano crystallite size (D) by XRD radiation of wavelength λ (nm).

The x-ray density would be calculated using;

$$\rho_{x\text{-ray}} = \frac{8M}{N_a V} \quad (3.5)$$

Where M is the molecular weight of the sample, N_a is the Avogadro number, v is the volume of the unit cell.

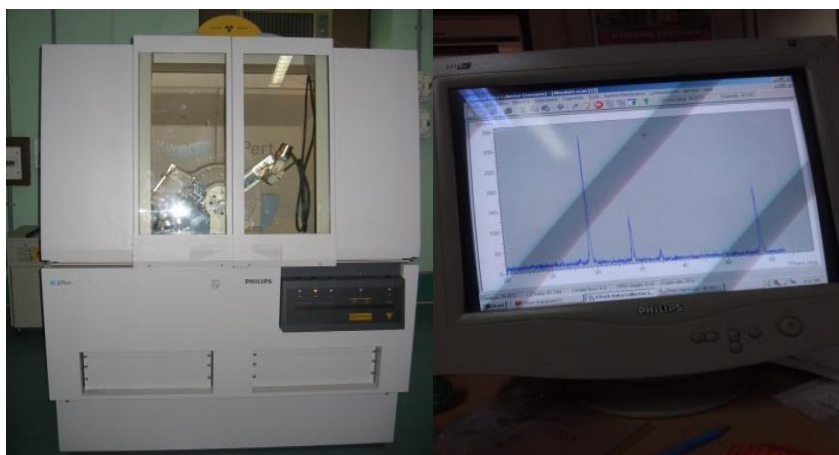


Figure 3.4 X-ray diffractometer interfaced with computer

3.7.2. Scanning Electron Microscopy (SEM)

Particle size and particle size distribution can be obtained using a variety of methods. Particularly for nanoparticles, scanning electron microscopy is a potent method for high resolution surface imaging that provides important details regarding the morphology, grain/particle size, and distribution of the particles (Carter et al., 2007). A concentrated electron beam is used to scan a sample in a scanning electron microscope (SEM), which creates an image of the sample. An electron microscope is a scientific device that examines objects at extremely tiny scales using an intense electron beam. It is used to determine an object's surface characteristics, or how it appears, such as its texture (the topography), the size and shape of the particles that make it up, the size and shape of the grains, the size of the precipitate, the volume fractions, and any defects like cracks or voids (morphology). It also determines the elements and compounds that make up the object and the proportions of each of them (composition). One kind of electron microscope that can create high-resolution images of a sample's surface is the scanning electron microscope (SEM). SEM images have a distinctive three-dimensional appearance due to the manner they are produced, and they are helpful for examining the sample's surface structure.



Figure 3.5 Scanning electron microscope (SEM)

3.7.3 Vibrating Sample Magnetometer (VSM)

S. Foner invented the vibrating sample magnetometer (VSM), a straightforward yet powerful method for describing the characteristics of magnetic materials. The VSM is a perfect laboratory exercise for students in an advanced materials physics course because of its simple design and ongoing use by condensed matter physicists and materials scientists.

A scientific device that uses Faraday's law of induction to assess magnetic characteristics is called a vibrating sample magnetometer (VSM). Faraday's Law of Induction, which states that an electric field will be produced by a changing magnetic field, is the basis for the operation of a vibrating sample magnetometer (VSM). We can monitor this electric field to learn more about the shifting magnetic field. The magnetic behavior of magnetic materials is measured using a VSM. The initial step in using a VSM is to expose the sample under study to a steady magnetic field. The ten components of the VSM are the water-cooled electromagnetic and power supply, vibration exciter and sample holder (with angle indicator), sensor coils, hall probe, amplifier, control chassis, lock-in amplifier, meter, and computer interface. According to Faraday's Law of Induction, the alternating magnetic field will create an electric field in the pick-up coils; the more magnetization, the greater the induced current.



Figure 3.6. Vibrating sample magnetometer (VSM)

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. Structural Analysis

4.1.1. Introduction

The experimental results obtained from the synthesis and characterization of copper ferrite nanoparticles ($\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$) doped with silver ions were presented in this chapter. The results are then discussed in light of the literature and known theoretical frameworks. This section's main objective is to fully explain how the addition of silver ions alters the structural, magnetic, and catalytic characteristics of copper ferrite nanoparticles, thus fulfilling the particular objectives outlined in Chapter 1.

4.1.2. X-ray Diffraction (XRD) Analysis

Figure 4.1 presents the XRD patterns of undoped CuFe_2O_4 and silver-doped $\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$ (where $x = 0.0, 0.2, 0.4$) nanoparticles. All diffraction peaks observed for the undoped sample ($x = 0.0$) precisely matched the standard JCPDS card No. 77-0010 (AA Azab et al., 2019) for cubic spinel copper ferrite, confirming the formation of a single-phase spinel structure without any detectable secondary phases. The characteristic diffraction peaks were observed at approximately 2θ values of 18.3° , 30.2° , 35.6° , 37.1° , 43.3° , 53.7° , 57.2° , and 62.8° , corresponding to the (111), (220), (311), (222), (400), (422), (511), and (440) crystallographic planes, respectively. Upon the incorporation of silver ions ($x = 0.0, 0.2, 0.4$), all samples maintained the characteristic diffraction peaks of the cubic spinel structure, indicating that silver doping did not alter the fundamental crystal structure of copper ferrite within the investigated concentration range. No additional peaks corresponding to silver metal or silver oxide phases were detected, suggesting that the silver ions were successfully incorporated into the copper ferrite lattice or were well-dispersed within the spinel structure without forming separate detectable phases.

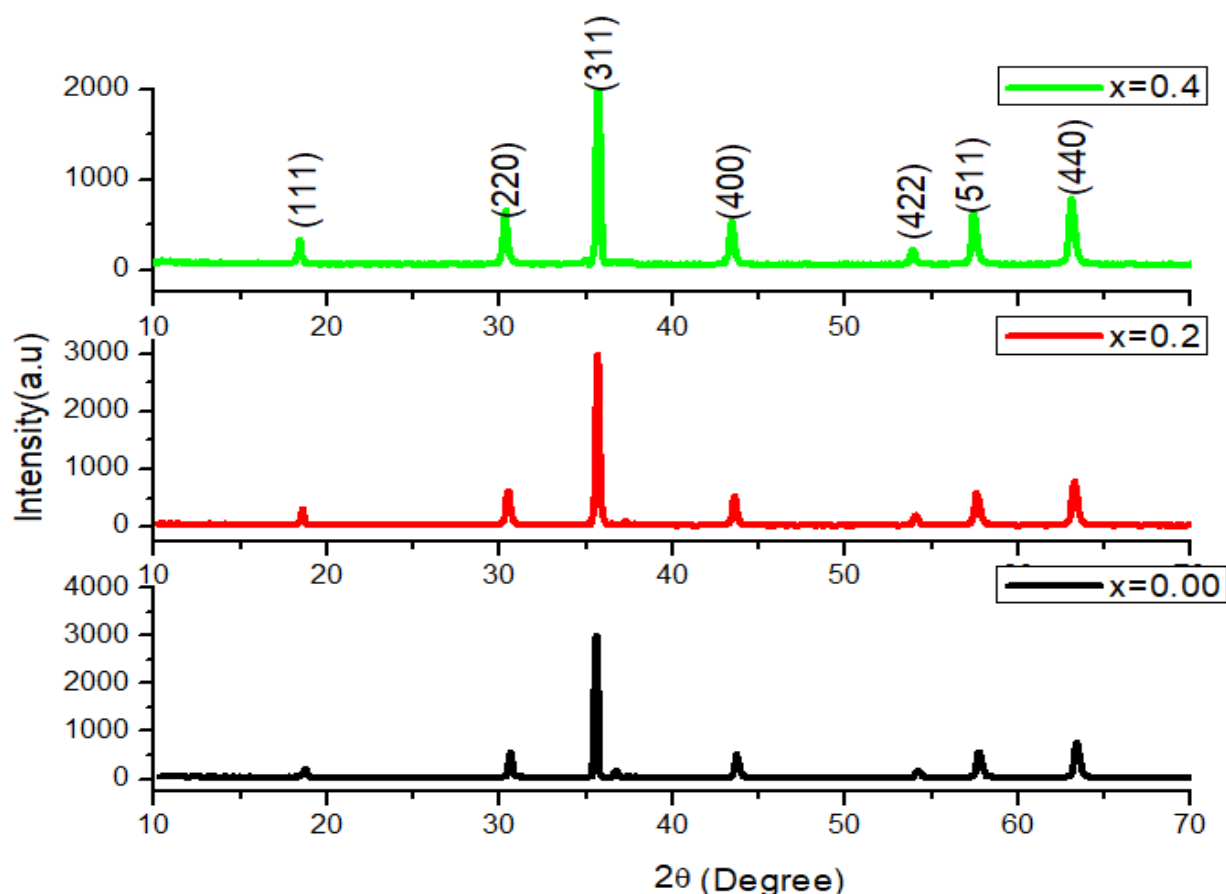


Figure 4.1 XRD pattern of $\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4$)

Table 4.1. Values of crystallite size (D), lattice parameter (a), d- spacing, volume of unit cell and x-ray density

Sample	Crystallite size, D(nm)	d-spacing (nm)	a (nm)	Volume (nm) ³	x-ray density (g/cm ³)
CuFe_2O_4	32.158	0.2520	0.8359	0.5841	5.4410
$\text{Cu}_{0.8}\text{Ag}_{0.2}\text{Fe}_2\text{O}_4$	27.539	0.2517	0.8348	0.5817	5.6660
$\text{Cu}_{0.6}\text{Ag}_{0.4}\text{Fe}_2\text{O}_4$	18.866	0.2513	0.8334	0.5789	5.8969

In Table 4.1, the observed decrease in the lattice constant could be a result of a subtle rearrangement of the lattice due to the limited amount of silver that does substitute, or it may be an artifact of a complex interaction where the very small crystallites have different lattice parameters. However, the most robust explanation is that the expected lattice expansion is not observed because the silver is not fully substituting into the host lattice, but rather is

segregating to the grain boundaries. On the other hand, as the concentration of silver ions increases, the density of these pinning sites on the grain boundaries also increases, leading to a more effective suppression of grain growth and resulting in a smaller final crystallite size.

4.2. Morphological Studies

Figure 4.2 shows the SEM micrograph of silver ion doped copper ferrite ($\text{Ag}^+-\text{CuFe}_2\text{O}_4$) nanoparticles characterized at room temperature. The characterized samples consist of particles with a relatively uniform shape and size. The "homogenous grains" observation indicates that the sol-gel synthesis method was successful in producing a material with a consistent composition throughout the sample. This is particularly important for doped materials, as it confirms that the silver ions were uniformly distributed within the copper ferrite matrix and did not form large-scale clusters or separate phases.

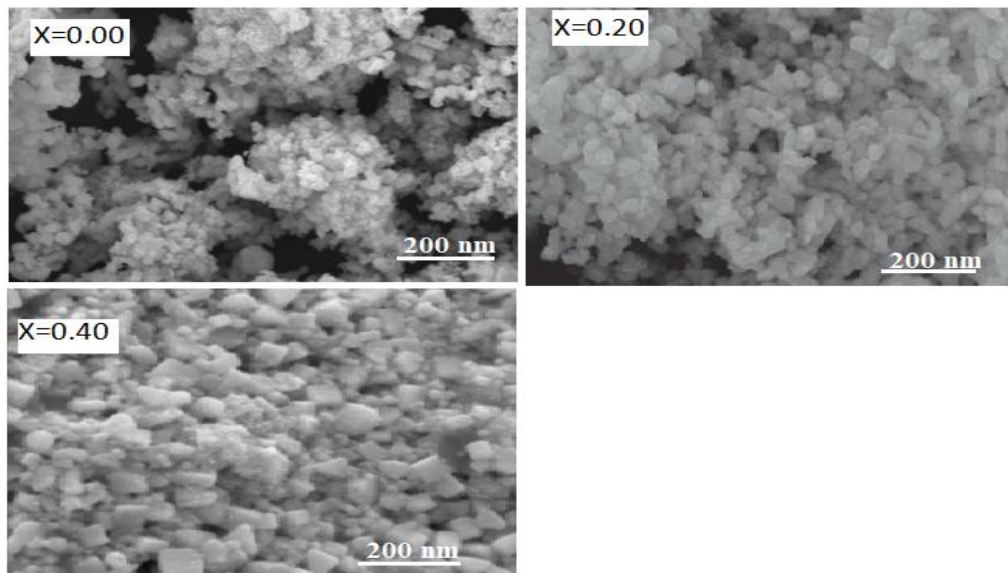


Figure 4.2 SEM images of $\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4$)

4.3. Magnetic Studies

Figure 4.3 shows the M-H hysteresis loop for silver ion doped copper ferrite nanoparticles with maximum applied field of 10,000 G, characterized at room temperature. From the measurement, loop depicts that the saturation magnetization increased with increasing silver ion concentration. This enhancement is not due to a magnetic contribution from silver itself (as the Ag^+ ion has a zero magnetic moment), but rather from its effect on the cation distribution within the material's crystal lattice. This explanation is based on the principles of

ferrimagnetism in spinel ferrite structures, which have two distinct sublattices with opposing magnetic moments: the tetrahedral (A) sites and the octahedral (B) sites.

The decrease in remnant magnetization (M_r) with increasing silver ion concentration is a direct consequence of the material's crystallite size being reduced and the nanoparticles transitioning into a superparamagnetic state. In similar trends, the coercive field (H_c) of the nanoparticles decreased because the silver ion doping caused a reduction in their crystallite size, pushing the material into a superparamagnetic state.

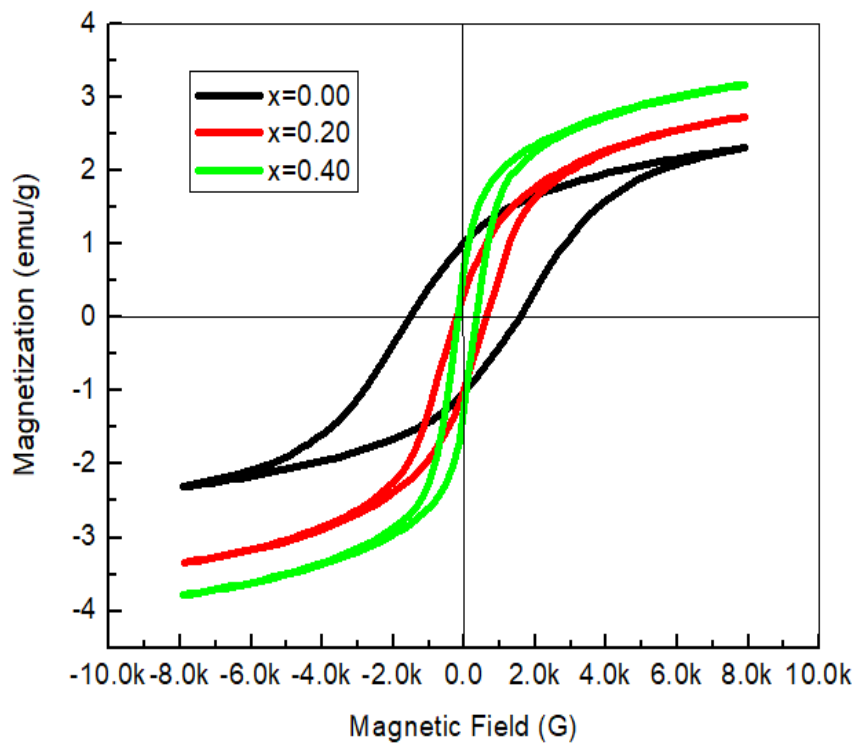


Figure 4.3 Hysteresis loop of sample $\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4$)

Table 4.2 shows saturation magnetization (M_s), Remnant magnetization (M_r), coercive field and squariness of the given sample $\text{Cu}_{1-x}\text{Ag}_x\text{Fe}_2\text{O}_4$

Sample	Magnetization (emu/g), M_s	Remnant magnetization (emu/g) , M_r	Coercive field (G)	Squariness (M_r/M_s)
CuFe_2O_4	2.325	1.039	1518.5525	0.44688
$\text{Cu}_{0.8}\text{Ag}_{0.2}\text{Fe}_2\text{O}_4$	2.747	0.3226	416.8575	0.1174
$\text{Cu}_{0.6}\text{Ag}_{0.4}\text{Fe}_2\text{O}_4$	3.188	0.600	238.204	0.1882

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This study investigated the synthesis, characterization, and catalytic performance of silver ion-doped copper ferrite ($\text{Ag}^+\text{-CuFe}_2\text{O}_4$) nanoparticles for wastewater decontamination.

The sol-gel auto combustion method proved to be an efficient and scalable technique for preparing highly crystalline $\text{Ag}^+\text{-CuFe}_2\text{O}_4$ nanoparticles with the desired spinel ferrite structure. The incorporation of silver ions was confirmed to influence the cation distribution and lattice parameters, which directly impacts the material's surface activity and electronic properties.

XRD and SEM analyses confirmed the successful formation of spinel ferrite structures and homogeneous doping of silver ions. Magnetic property measurements indicated that the doped nanoparticles retained superparamagnetic behavior, which is favorable for magnetic recovery and reuse. Catalytic experiments revealed that $\text{Ag}^+\text{-CuFe}_2\text{O}_4$ nanoparticles exhibited superior efficiency in degrading model organic pollutants under mild conditions, compared to undoped CuFe_2O_4 .

Overall, the silver ion-doped copper ferrite nanoparticles proved to be an effective, stable, and recyclable magnetic catalysts for wastewater treatment applications, offering promising potential for environmental remediation technologies.

5.2 Recommendations

- ❖ To completely comprehend the structural characteristics and morphology of the produced nanoparticles, more thorough characterization investigations are advised. These investigations should include electron microscopy, X-ray diffraction, and surface area analysis.
- ❖ To find the optimal ratio that improves catalytic performance while limiting any possible toxicity associated with silver, future research should investigate the optimization of silver ion doping concentrations.
- ❖ To evaluate the practicality and economic feasibility of the silver ion doped copper ferrite nanoparticles, examine their long-term stability and reusability in actual wastewater settings.

- ❖ To examine the effectiveness of these nanoparticles in actual wastewater treatment scenarios, conduct pilot-scale field studies. Consider aspects like cost-effectiveness, scalability, and integration into current wastewater treatment systems.
- ❖ To guarantee environmental safety and regulatory compliance, conduct thorough toxicity evaluations of the produced nanoparticles as well as the byproducts of their destruction. Prior to widespread use, thorough evaluations of the nanoparticles' possible toxicity and environmental safety are crucial.
- ❖ To further increase pollutant degradation rates, look into possible synergistic effects with other materials or processes. For example, combine these nanoparticles with UV radiation or other cutting-edge oxidation procedures.
- ❖ To enhance overall performance in particular applications, such as addressing specific pollutants, think about creating composite materials that combine copper ferrite nanoparticles doped with silver ions with other materials.
- ❖ To confirm the catalyst's efficacy in complex environments, future research should expand the study to actual industrial or municipal wastewater samples.
- ❖ To comprehend the degradation pathways and reactive species involved, in-depth mechanistic studies employing techniques like radical scavenging or spectroscopy are advised.
- ❖ To assess the practical applicability and economic viability of the synthesized nanocatalysts, long-term reusability tests and pilot-scale demonstrations are required.

References

- Abdel Maksoud, M. I., El-Sayyad, G. S., Abdelkoudous, M., & Awed, A. S. (2020). Controllable synthesis of $\text{Co}_{1-x}\text{MFe}_2\text{O}_4$ nanoparticles (M = Cu and Mn; x = 0.0 and 0.5) by cost-effective sol-gel approach: Analysis of structure, elastic, thermal and magnetic properties. *Journal of Materials Science: Materials in Electronics*, 31(12), 9726–9741. <https://doi.org/10.1007/s10854-020-03518-0>
- Agourine, E., Rabi, B., Essoumhi, A., Razouki, A., Sahlaoui, M., Cost, B., & Sajieddine, M. (2016). Structural and magnetic properties of CuFe_2O_4 ferrite nanoparticles synthesized by co-precipitation. *Journal of Materials and Environmental Science*, 7(11), 4116–4120.
- Andhare, D. D., Patade, S. R., Jadhav, S. A., Somvanshi, S. B., & Jadhav, K. M. (2021). Rietveld refined structural, morphological, Raman and magnetic investigation of superparamagnetic Zn-Co nano spinel ferrites prepared by cost-effective co-precipitation route. *Applied Physics A: Materials Science & Processing*, 127(6), 1–13. <https://doi.org/10.1007/s00339-021-04603-9>
- Anjum, S., Ilayas, T., & Mustafa, Z. (2020). Influence of antimony substitution on structural, magnetic and optical properties of cadmium spinel ferrite. *Applied Physics A: Materials Science & Processing*, 126(3), 1–11. <https://doi.org/10.1007/s00339-020-3407-x>
- Aslam, A., Razzaq, A., Naz, S., Amin, N., Arshad, M. I., Nabi, M. A., Nawaz, A., et al. (2021). Impact of lanthanum-doping on the physical and electrical properties of cobalt ferrites. *Journal of Superconductivity and Novel Magnetism*, 34(7), 1855–1864. <https://doi.org/10.1007/s10948-021-05802-4>
- Ateia, E. E., et al. (2017). Novelty characterization and enhancement of magnetic properties of Co and Cu nanoferrites. *J. Mater. Sci. Mater. Electron.* 28, 241-249 (2017)
- Ateia, E. E., Mohamed, A. T., Maged, M., & Abdelazim, A. (2020). Crystal structures and magnetic properties of polyethylene glycol/poly-acrylamide encapsulated $\text{CoCuFe}_4\text{O}_8$ ferrite nanoparticles. *Applied Physics A: Materials Science & Processing*, 126(9), 1–10. <https://doi.org/10.1007/s00339-020-03841-7>
- Atia, T. A., Altimari, P., Moscardini, E., Pettiti, I., Toro, L., & Pagnanelli, F. (2016). Synthesis and characterization of copper ferrite magnetic nanoparticles by hydrothermal route. *Chemical Engineering Transactions*, 47, 355–360.

- Azab, A. A., El-Khawas, E. H., & Abdellatif, M. H. (2019). Ferrite (CMFO) was indexed with JCDD card No. 77-0010 in which it confirmed the cubic spinel using the crystal planes of orthorhombic structure LBFO using JCPDS card No. 74-2203. *Journal of Electronic Materials*, 48(12), 7471–7483.
- Berastegui, P., Tai, C. W., & Valvo, M. (2018). Electrochemical reactions of AgFeO_2 as negative electrode in Li- and Na-ion batteries. *Journal of Power Sources*, 401, 386–396. <https://doi.org/10.1016/j.jpowsour.2018.09.002>
- Calvo-de la Rosa, J., Segarra, M., (2019). Optimization of the synthesis of copper ferrite nanoparticles by a polymer-assisted sol-gel method. *ACS Omega* 4(19),18289-18298 (2019)
- Carter MR, Edward Gerard Gregorich (2007). Soil sampling and methods of analysis. *CRC press*
- Chativerdi, S., Dave, P. N., & Shah, N. K. (2012). Application of nanocatalyst in new era. *Journal of Saudi Chemical Society*, 16(3), 307–325.
- Collomb A, B Lambert-Andron, JX Boucherle, D Samaras (1986). Crystal Structure and Cobalt Location in the W- type Hexagonal Ferrite $\text{BaCO}_2\text{Fe}_{16}\text{O}_{27}$. *Physica status solidi (a)* 96 (2), 385-395.
- Cullity BD (1976). Some problems in X-ray stress measurements. *Advances in X-ray Analysis* 20, 259-271.
- Dang, H. T., Nguyen, T. M., Nguyen, T. T., Thi, S. Q., Tran, H. T., Tran, H. Q., & Le, T. K. (2016). Magnetic CuFe_2O_4 prepared by polymeric precursor method as a reusable heterogeneous Fenton-like catalyst for the efficient removal of methylene blue. *Chemical Engineering Communications*, 203(9), 1173-1193. <https://doi.org/10.1080/00986445.2016.1174858>
- de Souza, Z. S. B., Silva, M. P., Fraga, T. J. M., Motta, M. A., & Sabrinho. (2021). A comparative study of photo-Fenton process assisted by natural sunlight, UV-A, or visible LED light irradiation for the degradation of real textile wastewater: Factorial designs, kinetics, cost assessment and phytotoxicity studies. *Environmental Science and Pollution Research*, 28(19), 23912–23928.
- Dhahri E, J Massoudi, M Smari, K Nouri, K Khrouni (2020). Magnetic and Spectroscopic properties of Ni-Zn-Al ferrite spinel: from the nanoscale to microscale. *Pups. Rsc. org*
- Ding, J., Miao, W., McCormick, P., & Street, R. (1998). High coercivity ferrite magnets prepared by mechanical alloying. *Journal of Alloys and Compounds*, 281(1), 32–36.

- Dutta, A. K., Maji, S. K., & Adhikary, B. (2014). Fe₂O₃ nanoparticles: An easily recoverable effective photocatalyst for the degradation of rose Bengal and methylene blue dyes in the wastewater treatment plant. *Materials Research Bulletin*, 49, 28–34.
- Fakruddin, A. K. M., Rai, A. K., Tripathi, M. K., and Shukla, A. K. (2024). A comprehensive review on the potential of copper spinel ferrite for gas sensing application. *E3S Web of Conferences*
- Giron-Navarro, R., Linares-Hernandes, I., Teutli-Sequeira, E. A., Martinez-Miranda, V., & Santoyo-Tepole, F. (2021). Evaluation and comparison of advanced oxidation processes for the degradation 2,4-dichlorophenoxyacetic acid (2,4-D): A review. *Environmental Science and Pollution Research*, 28(21), 26325–26358.
- Giria, J., Pradhan, P., Somania, V., & Chelawat, H. (2008). *Journal of Magnetism and Magnetic Materials*, 320, 724.
- Jauhar, S., Singhal, S., & Dhiman, M. (2014). Manganese substituted cobalt ferrites as efficient catalysts for H₂O₂ assisted degradation of cationic and anionic dyes: Their synthesis and characterization. *Applied Catalysis A: General*, 486, 210–218. <https://doi.org/10.1016/j.apcata.2014.08.020>
- Jiang, J., Goya, G. F., & Rechenberg, H. R. (1999). Magnetic properties of nanostructured CuFe₂O₄. *Journal of Physics: Condensed Matter*, 11(20), 4063–4074.
- Kafshgari, L. A., Ghorbani, M., & Azizi, A. (2019). Synthesis and characterization of manganese ferrite nanostructure by co-precipitation, sol-gel, and hydrothermal methods. *Particulate Science and Technology*, 37(7), 900–906. <https://doi.org/10.1080/002726351.2018.1461154>
- Khanna, L., Gupta, G., Tripathi, S.K., (2019). Effect of size and silica coating on structural, magnetic, as well as cytotoxicity properties of copper ferrites nanoparticles. *Mater. Sci. Eng.* 97, 552–566
- Kim, E. S., Yu, Q., & Deng, B. (2011). Plasma surface modification of nanofiltration (NF) thin-film composite (TFC) membranes to improve anti-organic fouling. *Applied Surface Science*, 257, 9863–9871.
- Kumbhar, V. S., Jagdale, A. D., Shinde, N. M., & Lokhande, C. D. (2012). Chemical Synthesis of Spinel Cobalt Ferrite (CoFe₂O₄) Nano-Flakes for Supercapacitor Application. *Applied Surface Science*, 259, 39–43. SCIRP
- Kurian, M., & Nair, D. S. (2015). Heterogeneous Fenton behavior of nano nickel zinc ferrite catalysts in the degradation of 4-chlorophenol from water under neutral conditions. *Journal of Water Process Engineering*, 8, 37–38.

- Ma, H., Wang, H., & Na, C. (2015). Microwave assisted optimization of platinum-nickel nanoalloys for catalytic water treatment. *Applied Catalysis B: Environmental*, 163, 198–204.
- Manova, E., et al. (2011). Nanosized copper ferrite materials: Mechanochemical synthesis and characterization. *J. Solid state Chem.* 184, 1153-1158 (2011)
- Miclea, C., Tanasoiu, C., & Miclea, C. F. (2005). *Journal of Magnetism and Magnetic Materials*, 290, 1258–1261.
- Patila, M. R., Rendale, M. K., Pujar, R. B., & Mathad, C. N. (2015). Structural and IR study of $\text{Ni}_{0.5-x}\text{Cd}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. *International Journal of Self-Propagating High-Temperature Synthesis*, 24(4), 241–245. <https://doi.org/10.3103/S1061386215040081>
- Pieper, M., Morel, A., & Kools, F. (2002). *Journal of Magnetism and Magnetic Materials*, 242, 1408.
- Rashad, M. M., et al. (2015). Investigation of the structural, optical and magnetic properties of $\text{CuO/CuFe}_2\text{O}_4$ nanocomposites synthesized via simple micro emulsion method. *Ceram. Int.* 41, 12237-12245
- Rashad, M. M., et al. (2012). Magnetic and catalytic properties of cubic copper ferrite nanopowders synthesized from secondary resources. *Adv. Powder Technol.* 23, 315-323
- Rus, S., et al. (2012). Synthesis and characterization of CuFe_2O_4 nanoparticles prepared by the hydrothermal ultrasonic assisted method. *J. Optoelectron. Adv. Mater.* 14, 293
- Salih, S. J. and Mahmood, W. M. (2023). Review on magnetic spinel ferrite (MFe_2O_4) nanoparticles: From synthesis to application. *Heliyon*, Vol. 9, Issue 6, e16601. DOI 10.1016/j.heliyon.2023.e16601
- Stewart, S., Tueros, M., Cernicchiaro, G., & Scorzelli, R. (2004). Magnetic size growth in nanocrystalline copper ferrite. *Solid State Communications*, 129(6), 347–351.
- Tanaka, T., Shimazu, R., Nagai, H., Tada, M., Nakagawa, T., Sandhu, A., Handa, H., & Abe, M. (2009). Preparation of spherical and uniform-sized ferrite nanoparticles with diameters between 50 and 150 nm for biomedical applications. *Journal of Magnetism and Magnetic Materials*, 321(10), 1417–1420. ResearchMap
- Thakur, P., & Thakur, A. (2022). Nanomaterials, their types and properties. In *Synthesis and Applications of Nanoparticles* (pp. 19–44). Singapore: Springer Nature Singapore.

- Tsakaloui, V., & Zaspalis, V. T. (2007). *Journal of Magnetism and Magnetic Materials*, 310, 2540.
- Valenzuela R (2012). Nobel Applications of ferrites. *Phys Res International* 2012 (1), 591839.
- Vedrtam, A., Kalauni, K., Dubey, S., and Kumar, A. (2020). A comprehensive study on structure, properties, synthesis and characterization of ferrites. *AIMS Materials Science*, Vol. 7, Issue 6, pp. 800–835
- Wu, Q., & East, B. (2022). Wastewater treatment by enhanced H_2O_2 based advanced oxidation process (AOP) methods: A review. *Journal of Physics: Conference Series*, 2152, 012011. <https://doi.org/10.1088/1742-6596/2152/012011>
- Zakiah, L.B., et al. (2015). up-scalable synthesis of size-controlled copper ferrite nanocrystals by thermal treatment method. *Mater. Sci. Semicond. Process.* 40, 564-569