

**Green Synthesis of Various Metal Oxides  
Nanoparticles and their Application to Photo-  
catalytic Degradation of Azo Dyes**



By

*Naveed Ul Ihsan*

*Under the supervision of*

*Prof. Dr. Zareen Akhtar*

Department of Chemistry

Quaid-i-Azam University

Islamabad

**February 2017**

**Green Synthesis of Various Metal Oxides  
Nanoparticles and their Application to Photo-  
catalytic Degradation of Azo Dyes**



**A dissertation submitted to the Department of Chemistry,  
Quaid-i-Azam University, Islamabad, in partial fulfillments of the  
requirements for the degree of**

**Master of philosophy  
in  
Inorganic / Analytical Chemistry**

**By  
Naveed-Ul-Ihsan  
Department of Chemistry  
Quaid-i-Azam University  
Islamabad  
(Feb 2017)**



*In the name of Allah  
The Most Gracious  
and Most Merciful*



*Dedicated to,*

*My Beloved Parents*

*and Teachers.*

*Specially my father for his*

*guidance, support, love and care*

## DECLARATION

This is to certify that this dissertation entitled “*Green Synthesis of Various metal Oxides nanoparticles and their applications to Photo-catalytic degradation of Azo Dyes*” by *Mr. Naveed Ul Ihsan* is accepted in its present form by the Department of Chemistry, Quaid-I-Azam University, Islamabad, Pakistan as satisfying the dissertation requirements for the degree of *Master of Philosophy in Analytical/Inorganic Chemistry*.

Supervisor:

---

**Prof. Dr. Zareen Akhter**  
Analytical/Inorganic Section  
Department of Chemistry  
Quaid-I-Azam University,  
Islamabad

Head of Section:

---

**Prof. Dr. Amin Badshah**  
Analytical/Inorganic Section  
Department of Chemistry  
Quaid-I-Azam University,  
Islamabad

Chairman:

---

**Prof. Dr. Muhammad Sadiq**  
Department of Chemistry  
Quaid-I-Azam University,  
Islamabad

External Examiner:

---

## ACKNOWLEDGEMENTS

---

Praise is to Allah, the Cherisher and Sustainer of the worlds, who showed His countless blessings upon us. **Almighty Allah** enabled me to compile my humble endeavours in the shape of this thesis. All respect goes to the Holy Prophet **Hazrat Muhammad (PBUH)** whose teachings strengthened our faith in Allah, who is the source of knowledge and wisdom for entire humanity.

It's a matter of immense pleasure for me to express my heart felt sincere gratitude to my honourable supervisor, **Prof.Dr. Zareen Akhtar**, who provided me an opportunity to work under his able guidance. His scholarly advice, friendly discussion, constant encouragement and moral support enabled me to accomplish this task successfully. I would like to acknowledge **Dr. Muhammad Siddiq** (Chairman of department of chemistry QAU) and **Prof.Dr. Amin Badshah** (Head of Analytical/Inorganic section). I am really Thankful all other teachers, for their valuable time to make me proficient in using their lab facilities by myself. I am also thankful to **Usman Liaqat** (Quaid i Azam university Islamabad) **Adeela Rehman**, **Javeria Malik**, **Muhammad Adeel Asghar** and **Muhammad Adeel Addi** for their guidance throughout my research work.

I would like to thank my all lab members. They helped me in different aspects and I spent wonderful time with them, during M.Phil. Study.

I am highly thankful to my grandfathers, grandmothers, sweet uncles, my loving brothers, cousins, and caring sisters. In short this work would not have been possible without the support of many individuals who have helped me in different ways to grow up as an individual, as a student and as a researcher.

# CONTENTS

<b>CHAPTER 1 INTRODUCTION.....</b>	<b>1</b>
1.1 Nanoparticles.....	1
1.1.1 Background: .....	1
1.1.2 Uniformity:.....	1
1.1.3 Properties:.....	4
1.1.4 Applications of Nanoparticles .....	5
1.1.5 Green Synthesis:.....	8
1.2 Dyes Compounds: .....	10
1.2.1 Azo Dyes:.....	11
1.2.2 Classification of Azo Dyes.....	13
1.2.3 Applications of Azo Dyes .....	14
<b>2 CHAPTER 2 MATERIAL AND METHODS.....</b>	<b>16</b>
2.1 Preparation of Plant Leaves: .....	17
2.2 Synthesis of Various Metal Oxides Nanoparticles:.....	17
2.2.1 Zinc Oxides Nanoparticles Synthesis:.....	17
2.2.2 CuO nanoparticles synthesis: .....	19
2.2.3 CoO nanoparticles synthesis: .....	20
2.2.4 SrO nanoparticles Synthesis:.....	21
2.3 Characterization of Nanoparticles:.....	22
2.3.1 Fourier Transform Infrared Spectroscopy Analysis:.....	22
2.3.2 X-Ray Diffraction Analysis: .....	22
2.3.3 Scanning Electron Microscope: .....	22
2.3.4 Energy Dispersive Spectroscopy (EDS): .....	23
2.4 Photo-catalytic Degradation Experiments.....	23
2.4.1 Procedure:.....	23
2.4.2 Characterizations:.....	24

2.4.3	Effect of nanomaterial dose on degradation:.....	24
2.4.4	Effect of pH on degradation:.....	24
<b>3</b>	<b>CHAPTER 3 RESULTS AND DISCUSION .....</b>	<b>25</b>
3.1	Results of Zinc Oxide NPs:.....	25
3.1.1	FTIR Spectra of ZnO NPs:.....	25
3.1.2	EDS Spectra of ZnO NPs:.....	26
3.1.3	X-Ray Diffraction (XRD) Analysis .....	27
3.1.4	Scanning Electron Microscope (SEM) Analysis:.....	28
3.2	Results of CuO Nanoparticles .....	29
3.2.1	Fourier Transform Infrared Spectrum (FTIR).....	29
3.2.2	Energy Dispersive X-ray Spectrum (EDS) OF CuO:.....	30
3.2.3	X-Ray Diffraction Pattern (XRD) of CuO NPs: .....	31
3.2.4	Scanning Electron Microscopy images (SEM) of CuO NPs: .....	32
3.3	Results of SrO NPs:.....	33
3.3.2	Energy Dispersive X-Ray Spectrum (EDS) of SrO NPs: .....	34
3.3.3	X-Ray Diffraction Pattern (XRD) of SrO NPs: .....	35
3.3.4	Scanning Electron Microscopy images (SEM) of SrO NPs:.....	36
3.4	Results of Cobalt Oxide NPs:.....	37
3.4.1	FTIR Spectra of CoO NPs:.....	37
3.4.2	Energy Dispersive X-ray Spectrum (EDS) OF CoO:.....	38
3.4.3	X-Ray Diffraction Pattern (XRD) of CoO NPs: .....	39
3.4.4	Scanning Electron Microscopy images (SEM) of CoO NPs: .....	40
3.5	Results of degradation Experiment: .....	41
3.5.1	UV-Vis Spectra: .....	41
3.5.2	Cyclic Voltammogram of degradation Experiment: .....	42
3.5.3	Results of Dose Effect on photo-catalytic degradation:.....	43
3.5.4	Results of pH Effect on Photo-catalytic Degradation Experiment: ..	44



<b>4</b>	<b>CHAPTER 4 CONCLUSIONS .....</b>	<b>45</b>
<b>5</b>	<b>REFERENCES .....</b>	<b>46</b>

## List of Figures

Fig 2.1 Schematic diagram for ZnO NPs.....	18
Fig 2.2 Schematic diagram for CuO NPs.....	19
Fig 2.3 Schematic diagram for CoO NPs.....	20
Fig 2.4 Schematic diagram for SrO NPs.....	21
Fig 3.1 FTIR Spectrum of ZnO NPs.....	25
Fig 3.2 EDS Spectrum of ZnO NPs.....	26
Fig 3.3 XRD Spectrum of ZnO NPs.....	27
Fig 3.4 SEM Image of ZnO NPs.....	28
Fig 3.5 FTIR Spectrum of CuO NPs.....	29
Fig 3.6 EDS Spectrum of CuO NPs.....	30
Fig 3.7 XRD Spectrum of CuO NPs.....	31
Fig 3.8 SEM Image of CuO NPs.....	32
Fig 3.9 FTIR Spectrum of SrO NPs.....	33
Fig 3.10 EDS Spectrum of SrO NPs.....	34
Fig 3.11 XRD Spectrum of SrO NPs.....	35
Fig 3.12 SEM Image of SrO NPs.....	36
Fig 3.13 FTIR Spectrum of CoO NPs.....	37
Fig 3.14 EDS Spectrum of CoO NPs.....	38
Fig 3.15 XRD Spectrum of CoO NPs.....	39
Fig 3.16 SEM Image of CoO NPs.....	40
Fig 3.17 UV Spectra of before and after Degradation.....	41
Fig 3.18 Cyclic Voltammograms of before and after Degradation.....	42
Fig 3.19 Effect of dose of ZnO NPs on degradation.....	43
Fig 3.20 Photocatalytical activity of ZnO NPs.....	44

## ABSTRACT

---

Nanoparticles are very fine particles ranging from 10-100nm in diameter. They got attention due to their unique properties from bulk material to its fine particles. Nanomaterials have enormous applications in various fields which includes medicine, material and processes, energy and electronic etc. Various methodologies are adopted for the synthesis of nanomaterial but biosynthesis procedure is less toxic, environmentally benign and cost effective. In the present research work CuO, CoO, SrO and ZnO nanoparticles were synthesized by using *Calotropis gagintea* leaves plant extract. The prepared nanomaterials have been characterized by using various techniques like EDS, SEM, XRD and FTIR. The photo-catalytic degradation efficiency of prepared nanoparticles have been tested on Amaranth red azo dyes. It is concluded that Znic oxide show maximum efficiency towards photo-catalytic degradation. The effect of Znic oxide nanomaterial dose and pH effect on degradation was also tested. It is observed that maximum degradation efficiency have been taken place at acidic pH by using 0.6g of Znic oxid nanomaterial dose.

**1.1 Nanoparticles**

The particles ranging from 1 and 100 nm in diameter are known as nanoparticles. any small thing acting as a whole unit is called a particle. Advance grouping of particles is based on their diameter.Ultrafine particles have diameter between 1 to 100 nm and are same as nanoparticles, the range of the fine particles is from 100 to 2500 nm whereas coarse particles are in between 2,500 to 10,000nm in size. Research on nanoparticles is focused as they have numerous significant applications in optics, physics,<sup>[1]</sup> medicines and electronics.<sup>[2]</sup>

Ultrafine and nanoparticles have identical definition and the reason for that is, throughout the period of 1970s to 1980s, while the initial comprehensive studies with nanoparticles were started in Japan and USA(by Buhrman and Granqvist)<sup>[3,4]</sup>. The name was given to it is ultrafine particles. But, in 1990s before the National Nanotechnology Initiative (NNI) USA was propelled the name, nanoparticle had come to be common<sup>[5]</sup>. Nanoparticles can display properties related to their sizes considerably different from those of either bulk materials or fine particles<sup>[6]</sup>.

The size distribution of nanoclusters are narrow with dimension between 1-10nm. The aggregates of nanoclusters, nanoparticles or ultrafine particles form nano powder. The term nanocrystals are used for nanometer-sized single crystals or Single-domain ultrafine particles.<sup>[7]</sup>

**1.1.1 Background:**

Nanoparticles are linked with modern science but they have very long history. In the fourth century, Artisans were used the NPs in the Lycurgus cup which was made up of dichroic glass. They were also used for the generation of a sparkling effect on the surface of pots which were used in the ninth century Mesopotamia.

The evidence of nanotechnology is easily available in the many old churches. In the middle ages the ruby red color of nanotechnology was used for stained glass windows. The glass windows in various Gothic European cathedrals, among which one of the exceptional masterpieces present in Le ó n Cathedral (Spain) is the best example of application of nanoparticles. These 2000m two colored windows give a sole view that indeed deserves a visit. No doubt, the medieval artisans were using

nanotechnology without any awareness. They only knew a specific procedure that formed attractive effects. For instance, at the world heritage Cathédrale Notre-Dame de Chartres which is present in France one can see the wonderful rose made up of stained glass.

**Table 1.1: Background history of nanoparticles**

Year	Remarks	Country/people
1100 – 1200BC	Soluble form of Gold	Chinese and Egyptian
289 – 330AD	Lycurgus cup	Romnian Alexandria
1619	Gold in colloidal form (1 <sup>st</sup> book)	Antoni F
1675	Drinkable form of Gold (Book is published)	VonLowenstern – Kunckel. J
1718	Gold publications on colloidal	Hatcher H. H
1860	Colloidal Gold Preparation	M. Faraday. RIGB
1903	Surface Plasmon, resonance. (SPR)	Wood R. W, USA J. H University
1910	Electro-magnetic Field scattering and absorption of Nano sphere	Mie. G Göttingen University, Germany
1930	Transmission electron microscopy, TEM	Ruska. E, Knoll. M Berlin Technical University, Germany
1937	Scanning electron microscope	Ardennes Von. M. Germany
1958	Feynman's lecture on bottom plenty of rooms	Feynman P. R. California institute of Technology, USA
1960	Micro electro-mechanical system	Igarashi. I, R& D Toyota centre Japan

## CHAPTER 1

1961	LASER Successful oscillation	Maiman T. H. HRL, USA
1961	Effect of Kubo	Kubo R. Tokyo university
1966	Law of Moore	Moore. G Fairchild Semiconductor Inc USA
1968	Honda effect	Hon K. and Fujishima Tokyo university, Japan
1971	Preparation of photodiode with amorphous hetero-structure by Bottom Up Method	Maruyama. Hitachi Company, Japan
1975	Concept of Nano-Technology	Taniguchi. N TUS Japan
1977	Nano-fibers of Carbon	Endo. M Japan
1977	Use of amorphous silicon in Solar cell	C. R. and Carlson D. E. USA
1981	Quantum Hall Effect	K. von Klitzing Wurzburg university, Germany
1982	Scanning Tunnelling Microscopy	Binnig G. and Rohrer. H IBM Switzerland
1985	Atomic Force Microscopy	Binnig. G IBM. Switzerland
1988	Use of Gold Nanoparticles in Catalysis.	Haruta. M Osaka, Japan
1991	Atoms Controlled with Scanning Tunnelling Microscopy	D. M. Eigler IBM. USA
1992	Carbon nanotubes Discovery	Iijima S. Japan
1993	Atoms and Molecules Manipulation	N.P. Japan

1994	Imprinting of Nano sized materials	Chou S. Y. MU. USA
1998	Nano-sheet Synthesis	Sasaki. T Japan
2001	NatiOnal Nan0techn0l0gy initiative	USA
2004	Development of Nano-technology research	USA
2006	Nano-techn0l0gies and Nan0-science	Action Plan of Europe

### 1.1.2 Uniformity:

The synthesis of and chemical processing, areas requires the practice of high-purity polymers, and ceramics. The irregular shapes and particle sizes in a usual powder often form non-uniform morphologies in compressed bodies formed from powder that causes variations in packing density in the powder compact.

Van der Waals forces cause uncontrolled aggregation of powders which increase heterogeneity of the particles. If the packing density changed during compaction like for kiln preparation are frequently enlarge at the time of sintering, gives heterogeneous densification. The density variations and some pores causes structural defects which reveal to perform a damaging role.

It is highly favorable that a material should be utilized with uniformity with which is necessary for distribution of components and greater porosity, instead of using particle size distributions.

### 1.1.3 Properties:

Nanoparticles are interconnected with bulk materials and structure of the atoms or molecules. Physical properties of the nanoparticles are size-dependent whereas bulk material, regardless of its size, have constant physical properties. That's why, properties of materials can be modify by tuning their size to the nanoscale.

Nanoparticles usually have unpredictable optical properties because they restrict their electrons due to smaller size which cause quantum effects. For instance, grey silicon nanoparticles show red color while yellow gold nanoparticles show red to blackish color and melting the point of gold nanoparticles is much lower (~300 °C for

2.5 nm size) than the gold which is 1064°C. Nanoparticles of a material absorb higher amount solar radiation as compare to its thin films of that material. In both solar thermal and solar PV applications, solar absorption can be controlled by controlling the shape, material and size of the particles.

The quantum confinement is also size-dependent property in case of semiconductor materials. The supra para magnetism and Surface Plasmon resonance are also dependent upon sizes of particles. The surface of the particles also interact strongly with the solvents to overcome differences in density and hence form suspensions of nanoparticles.

The diffusion of nanoparticles have high due to marvelous driving force provided by the surface area to volume ratio, particularly at high temperatures. Moreover, nanoparticles also impart some additional properties to different products. For example, the self-cleaning effect is imparted owing to titanium dioxide nanoparticles. Small size particles themselves are not visible. Zinc oxide particles have greater UV blocking properties than in its bulk form. Therefore it is used in sunscreen lotions preparation.

### **1.1.4 Applications of Nanoparticles**

Nanoparticles have wide range of applications. For example, just silver nanoparticles are being use in clothing, food-industry, sunscreens, paints, electronics, bio-sensing, medical devices and cosmetics. These applications increase exposure to humans and thus the potential danger related to their long- and short-term toxicity. In vitro studies on these particles indicate that silver nanoparticles are dangerous to the cells of mammals which are derived from brain, liver, skin, lung, reproductive organs and vascular system. Some studies have also depict that at non-cytotoxic doses, these nanoparticles induce genes associated with DNA damage, apoptosis in human cells and cell cycle progression.<sup>8</sup>

#### **1.1.4.1 Medical Field:**

Nanoparticles are going to be use for the treatment of various diseases so it has become a prevalent in research fields to explore the wide range application of nanoparticles in medical science in current years. The function of these particles are to carry drugs, peptides, vaccines, and oligonucleotides to successfully send them into several targets like cancer effected cells and other disease effected tissues. They have potential applications towards gene therapy therefore used to cure genetic defects *in*



*vivo* and *in vitro*.<sup>9</sup> In the recent years therapeutic materials are transported to targeted tissues with the help of nanoparticles as carriers because they have potentials to cure of a bulk variety of diseases.

Nanomaterials, such as semiconductor nanoparticles, nanorods, nanowires, nanoflowers and metals, display similar dimensions to those of biomolecules, such as DNA and proteins (antigens, enzymes and antibodies). The combination of nanoparticles, which exhibits unique photonic, catalytic and electronic properties, with biomaterials, which have unique catalytic, inhibition and recognition properties, yields new hybrid nanobiomaterials of synergetic functions and properties. The chronic bacterial infections are treated by iron oxide nanoparticles coated on a polymer because they can break bacterial clusters.

#### **1.1.4.2 Manufacturing and Materials:**

The lightweight strong materials are prepared, when ceramic silicon carbide nanoparticles are spread over magnesium.

When nickel nanoparticles are embedded with a polymer a composite material is formed, which is used in synthetic skin. This synthetic skin has self-healing and pressure sensing property. If any material which seals again after cutting, have same properties as original one keeps before cutting, shows the phenomenon of self-healing. The electrical properties of this composite material changes with pressure, make it capable for sense ability i.e. touch. Nanoparticles of Silicate are being utilize to as a barrier for moistures or gasses in the formation of plastic film which is used during packaging and it has the ability to slow down the process of drying out and spoiling of food. The nanomaterial of Zinc oxide are used in industries for coating of plastics, wood to protect from UV rays and textile. The gaps between carbon fibers can be filled by using Silicon dioxide nanoparticles, hence tennis racquets can be strengthen by this way. The bacteria in fabric are killed by using Silver nanoparticles to make them odor-resistant.

#### **1.1.4.3 Nanoparticle and the Environment:**

The oil can be break down into biodegradable compounds by using photocatalytic copper tungsten oxide nanoparticles. Which provides a high surface area for reaction by forming the network, therefore nanomaterials are useful to clean oil spills. The presence of carbon tetra chloride in ground water can be removed by

using iron oxide nano particles while Iron oxide NPs are going to be use to remove arsenic from water wells.

#### **1.1.4.4 Energy and Electronics:**

A well-known transistor named as NPs Organic Memory Field-Effect Transistor (NOMFET) is formed by mixing gold nanoparticles with organic compounds. NOMFET has very interesting applications and works just like a synapses present in nervous system. The platinum-cobalt nanoparticles catalyst used in the fuel cells has twelve times enhanced catalytic activity than platinum in pure form. The coating of Silicon nanoparticles on anodes of the Li-ion batteries can reduce recharge time and enhance the battery power.

#### **1.1.4.5 Micro-wiring applications of NPs:**

Metallic Nanoparticles paste are used for colour circuits in different appliances. The boiling points of metallic particles are low as compare to metals in the bulk form, the construction of conventional circuits by using biopolymer in past decades was impossible task .Similarly the size of wires in wiring essentially in Nano particles range. In Mon phenomenon ink-jet method is used for surface polarisation, rather than costly methods like vacuum evaporation, in past Gold was used for the preparation of Nano wire. However, it is costly so Cu is suggested to use with any anti-oxidant due to its higher oxidation rate.

Nano particles also have medical applications like in surface Plasmon. In which the scattering of light is due to the higher concentration of Nano particles. By taking this advantage the presence of various molecules in our body can be detected. In this way cancerous cell can be distinguished from healthy cells in a body by using Gold nanoparticles. This is due to the gold nanoparticles gives good combinations with antibodies so they have effects on healthy cells and God Nano NPs surface is heavy with the antibodies of cancer cells. Which has significant effects on the shape of nanoparticle. The images of normal cells and cancerous cells can be obtained by the joining of nanoparticles with protein. The display of Plasmon resonance in the infra-

red region is due to the use of IR laser where cancerous cell are cured by the accumulations of Gold on boundary of Nanorods.

### **1.1.5 Synthetic Techniques:**

There are large number of methods for the synthesis of nanoparticles, including hydrothermal, pyrolysis, and attrition synthesis. Radiation chemistry can also be used to synthesize them.

#### **1.1.5.1 Sol-Gel Methods:**

It is a wet-chemical process. Which is extensively utilized in various fields like ceramic engineering and material science. Such techniques are chiefly used for the synthesis of functional materials (e.g. metal oxides) begins from a sol which is short term of chemical solution. That acts a precursor for gel which is a assimilated network of isolated particles or network polymers.

### **1.1.6 Green Synthesis:**

Green chemistry, also called sustainable chemistry, is a field of chemical engineering and chemistry which is focused on the planning of processes and products that decrease the generation and use of hazardous substances. Although environmental chemistry emphasizes on the effects of polluting chemicals found in nature, green chemistry centers on practical approaches to prevent pollution and minimize consumption of nonrenewable resources.

#### **1.1.6.1 Advantages of Green synthesis:**

1. It is better to circumvent waste than to clean up waste after its creation.
2. Synthetic processes should be planned to exploit the integration of all materials being use in the process for the final products.
3. Products which are chemical in nature should be planned to reserve worth of function while decreasing toxicity.

4. Energy necessities should be recognized for their economic and environmental influences and should be reduced. Synthetic methods should be directed at ambient pressure and temperature.
5. A feedstock or raw material should be renewable.
6. Needless derivatization (protection/deprotection, blocking groups and temporary modification) should be avoided whenever possible.
7. Chemical products should be deliberate so that at the end of their function they do not persist in the environment.
8. Analytical practices must to be advance recognized to allow for real-time, in-process monitoring and control before the materialization of dangerous substances.
9. Substances used in chemical processes should be designated to diminish potential for chemical accidents, including explosions, releases and fires.
10. Wherever feasible, synthetic procedures should be planned to make and practice substances that have little or no toxicity to human health and the environment.
11. The use of supplementary substances should be made preventable wherever possible.
12. Catalytic reagents are superior to stoichiometric substances

#### **1.1.6.2 Use of Plant Extract:**

The rising requirement of environmental benign nanoparticles, scientists are using green approaches for the synthesis of different metal nanoparticles for medicinal applications <sup>[10]</sup>. Commonly used chemical synthesis methods like hydrothermal method, sol-gel process, precipitation chemical, chemical vapour deposition, pyrolysis, micelle, etc. produce toxic chemical products that adsorbed on the surface of the nanoparticles that could have confrontational effects in medicinal applications. Some reactions need high temperature or high pressure for initiating the reaction, though some reactions need inert atmosphere shelter, and some reaction need using toxic substances such as H<sub>2</sub>S, poisonous stabilizer and template, and metallic precursors <sup>[11]</sup>. Chemicals used for the synthesis of nanoparticles and their stabilization are toxic and direct to non-ecofriendly byproducts <sup>[12]</sup>. The Biological methodologies using plants, plant extracts and microorganisms for metal or metal oxides nanoparticles synthesis have been proposed as valuable substitutes to chemical methods. Numerous biological systems containing fungi, yeast and bacteria have been

used in the synthesis of metal nanoparticles [13]. Synthesis of metals/ metal oxides nanoparticles by using microorganisms includes intricate process of conserving cell cultures, intracellular synthesis and numerous purification steps. In this respect applying green synthesis methods in for metal oxide nanoparticles has progressively becoming a topic of interests as common methods are costly and need to use of chemical compounds as reducing agents<sup>[14]</sup>.

The plant *Calotropis gigantea* belong to the family *Asclepiadaceae*, also called as Aak, Shwetarka, Vasuka; is distributed throughout Pakistan<sup>[15]</sup>. *Calotropis gigantea* is species of *Calotropis* and present to China, India, Indonesia, Cambodia, Malaysia, Thailand, Philippines, Pakistan and Sri Lanka<sup>[16,17,18]</sup>. This plant is also used in traditional medicine for the cure of dysentery, fever, rheumatism, painful muscular spasm, asthma<sup>[19]</sup> According to my knowledge it is first time that the use of *Calotropis gigantea* leaf extract for the reduction and for surface stabilizing agent for the synthesis of spherical-shaped metal oxides NPs. The morphology, phase and structure, of synthesized metal oxides nanoparticles were examined by the using various characterization techniques.

### 1.2 Dyes Compounds:

Dye is a natural or synthetic coloured substance which shows an affinity towards the substrate to which it is being applied. Usually they are applied in the form of aqueous solution. Mordant is require to improve the fastness of the dye on the substrate. The substrate consist of anything like plastic, fiber, paper, food or wood etc.

Dye stuff was prepared and used in china around 2600 BC but revolution in its history came after 1856. When William Perkin made a first synthetic dye "Mauve" (a basic dye) from the natural dyes during the synthesis of quinine. "Mauve" was the derivative of coal tar and first commercially available dye. From the synthesis of this dye, idea was originated that natural dyes can be prepare in industry and revolution in the field of dyes occurred. Now a days there is hardly an industry which does not use dye.

Dyes are generally aromatic and ionizing organic compound and they have at least one chromophore (light absorbing group). They possess colour for the following reasons

- Have functional group known as chromophore
- Contain conjugated system

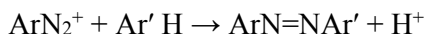
- Show resonance of electrons
- Absorb light in the visible region <sup>[20]</sup>

### 1.2.1 Azo Dyes:

All those compounds which have -N=N- as a functional group are known as azo compounds. Azo compounds are called diazene derivatives by IUPAC system. Eilhard Mitscherlich introduced the simplest aromatic azo compound, azobenzene, in 1834 <sup>[21]</sup>. It was prepared from nitrobenzene using zinc as a reducing agent in the presence of a suitable base <sup>[22, 23]</sup>.

Owing to presence of delocalization of electrons, aryl azo compounds give wide spectrum of colors and widely used as dyes and indicators. Due to bright, high intensity color, good fastness properties and cost effectiveness, currently azo dyes account for 66% of the worldwide commercial dye market. These dyes offer a wide spectrum of colors and are widely used in textile, printing, cosmetic, drug and food-processing industries. They are also used extensively in laboratories as either biological stains or pH indicators <sup>[24]</sup>.

These are generally synthesized by a well-known azo coupling reaction that proceeds by the attack of aryl ring on aryl diazonium cation.



Aromatic amines are generally used for the preparation of aromatic azo compounds through the formation of corresponding diazonium salt as an intermediate by reacting with nitrous acid <sup>[25]</sup>.

Several azo compounds are found to be mutagenic and carcinogenic. The hyperactivity effects in children increase by use of food colors <sup>[26]</sup>. Many azo dyes present genotoxic, mutagenic and carcinogenic activity in tests with microorganisms and mammalian cells. Strongest hyperactivity effects were observed in children receiving azo dyes and benzoic acid combinations <sup>[26]</sup>. Some azo dyes increase allergic reactions towards other substances and affect liver and kidney <sup>[27]</sup>. Azo dyes cause dysfunction in the reproductive organs of rodents. The cell anomalies and chromosome aberrations are also have been reported due to azo compounds. On interaction with hemoglobin azo compounds cause methemoglobinemia <sup>[28]</sup>.

Azo dyes cover a complete rainbow of colors but generally on large scale these are used to supply yellow, red and orange colors. On commercial scale azo dyes are mostly used as acid base indicators, as a colorant in plastic, cosmetic, food stuff

and cloths. Methyl orange, Methyl red and Congo red are generally used as indicator due to exhibition of different colour in different pH mediums.

Color change in azo dyes mainly depends on the extent of delocalization of electrons and geometrical isomerism of the azo group. Extent of delocalization of electrons depends on the nature of the substituents attach on the aromatic ring and position of the attachment of the substituents.

Azo dyes have many advantages over other dyes including

- Ability of light absorption
- Wide range of color spectrum
- Cheap and readily availability of starting material
- Mostly synthetic methods require room temperature
- Water is mostly used as a solvent during synthesis and application <sup>[29]</sup>

#### 1.2.1.1 Preparation Methods

A variety of reactions are used for the preparation of azo dyes. Mostly these reactions are performed in solution form by the involvement of diazonium compound. Now a day, certain combinations are also used in which stable reactant form azo dyes by oxidative coupling reaction. This method is free from mediums and fumes or vapors formation <sup>[30]</sup>.

Azo dyes having catechol are prepared by a coupling reaction between diazonium salt and catechol in alkaline medium. In this process oxidation of catechol into unstable o-quinone took place. The increase in alkaline pH of the medium increase the oxidation and reactivity of the catechol <sup>[31]</sup>.

A green method for the preparation of azo dyes has been reported in which reagents are supported by the polymers. Generally, in this method amines are reacted with bidentate ligand containing compound in the presence of quaternary amine having nitro group as an anion <sup>[32]</sup>.

Azo dyes can be synthesized by diazotization coupling in the presence of suitable conditions as mention below.

Azo compounds can also be synthesized by the oxidation of amine by nitrous acid in the presence of sulfuric acid or hydrochloric acid <sup>[33]</sup>.

### 1.2.1.1.1 Substituents Effect

Substituents on the aromatic ring have great effect on the colour of dye and it is reflected by absorption spectrum<sup>[34]</sup>.

- Electron donating groups like OH and NH have bathochromic effect
- Electron withdrawing group in conjugation with electron donating group has bathochromic effect
- Presence of alkyl group on nitrogen atom increase the electron donating ability of amine group. The absorption maxima of azobenzene in benzene is 319 nm<sup>[35]</sup>.

Substituents effect on dye's colour and absorption spectrum with  $\lambda_{\max}$  values.

Purpose of using colour additives

Colour additives are generally used for

- Precise natural differences in colour
- Improvement of colours that occur naturally
- Providing colour to colourless and "fun" foods
- Making food more appetizing, attractive and informative
- Permitting consumers to recognize products on sight, like medicine dosages or candy flavors
- Counterpoising colour loss due to exposure to light, temperature extremes, air, moisture and storage conditions<sup>[36]</sup>

### 1.2.2 Classification of Azo Dyes

Azo dyes can be classify by the variety of ways. Generally these are classified

On the basis of number of azo groups

- Monoazo dyes
- Disazo dyes
- Trisazo dyes
- Poly azo groups

On the basis of Application Method

- Reactive azo dyes
- Disperse azo dyes
- Direct azo dyes
- Cationic azo dyes
- Anionic azo dyes



- Metallized azo dyes

### 1.2.3 Applications of Azo Dyes

Azo dyes have wide range of applications <sup>[37]</sup>. Currently azo dyes contribute 66% in the commercial dye markets. Some major applications of azo compounds are given below <sup>[38, 39]</sup>

1. As a catalyst
2. As printing material
3. As supramolecules
4. In DVD discs as a recording layer
5. In antifungal and antibacterial activities
6. As a drug delivery in pharmaceutical industry
7. In food and textile industries as colouring agents
8. In photoelectronics, especially as information storage devices
9. Azo metal complexes are widely used as a pigments in vinyl polymers and synthetic leather
10. In biological reactions for protein synthesis, as an inhibitor in RNA and DNA, and carcinogenesis etc <sup>[40, 41]</sup>

Most organic compounds like dyes possess color for the reason that they

- 1) They absorb light in the region of 400–700 nm.
- 2) They have at least one color bearing group called chromophore.
- 3) Possessing conjugated system like structure in which alternative single and double bonds is present.
- 4) They have resonance, which is a force to stabilize the organic compounds.

When any one of these properties is missing from the molecular structure the color will be lost. In combination with chromophores, dyes also contain groups known as *auxochromes* (color helpers), e.g. sulfonic acid, carboxylic acid, hydroxyl, amino groups. Whereas these are not responsible for colour, their occurrence can shift the color of a colorant and they are most frequently used to effect dye solubility.

**Table: 1.1 Wavelength of light absorption versus colour in organic dyes**

Wavelength (nm)	Absorbed Colours	Colours Detected
400–435	Violet	Yellowish Green

## CHAPTER 1

435–480	Blue	Yellow
480–490	Green-Blue	Orange
490–500	Blue Green	Red
500–560	Green	Purple
560–580	Yellowish Green	Violet
580–595	Yellow	Blue
595–605	Orange	Greenish Blue
605–700	Red	Blue Green

The reagents, instruments and apparatus used during my research work are given below.

**Reagents:**

<b>Chemicals</b>	<b>Chemical formula</b>	<b>Company Name</b>
Zinc (II) Nitrate hexahydrate	$Zn(NO_3)_2 \cdot 6H_2O$	Sigma Aldrich
Strontium (II) Chloride hexahydrate	$SrCl_2 \cdot 6H_2O$	Sigma Aldrich
Cobalt (II) Chloride hexahydrate	$CoCl_2 \cdot 6H_2O$	Merck
Copper (II) Chloride dihydrate	$uCl_2 \cdot 2H_2O$	Merck
Sodium hydroxide	NaOH	Sigma Aldrich

All the chemicals were purchased sigma Aldrich and Merck and used as such during my research work.

<b>Instruments</b>	<b>Model</b>
UV-Lamp High Pressure Mercury	(500w)
Sonicator	DSA 100-SK2.8L
UV-Visible Spectrophotometer	T90+Spectrometer
Thermometer	KEHANGE(KH130)
Electronic Balance	Sartorius TE214S
Shaker	Vortex
pH meter	Crison, GLP-21
Muffle furnace	Nabertherm
Hot plate	Electrothermal9100
Magnetic stirrer	Digitek
Fourier Transform Infrared Spectroscopy	Bruker (M:6500S)
Scanning Electron Microscopy	TESCAN VEGA 3
X-ray Diffraction	M: 3040/60 X'Pert
Energy Dispersive Spectroscopy	TESCAN VEGA 3

**Apparatus:**

Erlenmeyer flask (250mL)  
 Measuring Cylinder (100mL, 500mL, 1000mL)  
 Pipette (10mL)  
 Burette (25mL)

Beakers (1000 mL, 500 mL, 250 mL, 100 mL)

The glass wares used during my research work were of Pyrex England. All the Glass wares were thoroughly washed with distilled water and rinse with acetone before used.

### **2.1 Preparation of Plant Leaves:**

Fresh leaves of *Calotropis gigantea* were obtained from botanical garden. These leaves were thoroughly washed with deionized water to remove filth and other materials may present on the leaves. Then the leaves were placed in oven at 50°C after 24 hours the dried leaves of *Calotropis gigantea* were collected from oven and grind with the help of grinder.

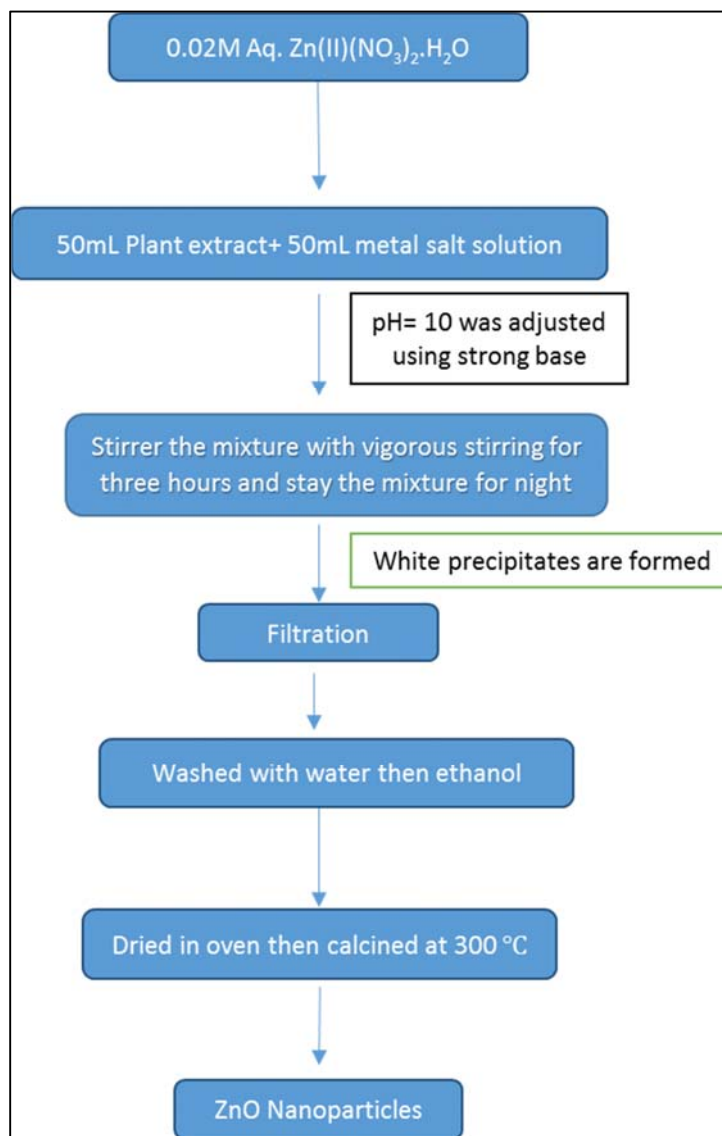
The grinded leaves were placed in a fractioning flask and filled with 500 mL deionized water then the mixture was heated with the help of burner. The extract was collected in a beaker, and then the collected extract was filtered to remove suspended particles. The filtrate (plant extract) was preserved in a beaker. The procedure was repeated for further preparation of Plant extract.

### **2.2 Synthesis of Various Metal Oxides Nanoparticles:**

#### **2.2.1 Zinc Oxides Nanoparticles Synthesis:**

0.01M Zinc (II) Nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) were poured in 100mL distilled water. Then 50mL plant extract were added into the aqueous solution of Zinc Nitrate. The pH of the mixture was maintained at 12 by adding 2M sodium hydroxide (NaOH) drop by drop with the help of burette and pH was monitored by using pH meter. Then the mixture was stirred with help of magnetic stirrer on hot plate at room temperature for three hours and stay for a night.

The white precipitates were formed which were filtered and wash with water then ethanol to remove inorganic and organic impurities. After this these nanoparticles were dried in oven and then calcined at 300°C for two hours for the complete formation of ZnO NPs. These were preserved for characterizations and for further use. The schematic diagram for the synthesis ZnO NPs is shown in fig.2.1



**Fig 2.1 Schematic diagram for ZnO NPs**

### 2.2.2 CuO nanoparticles synthesis:

1.7g of Copper (II) Chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) was dissolved into 1000mL distilled water to prepare 0.01M solution of Copper salt. The aqueous solution of metal salt (50 mL) was mixed with 50mL of plant extract. The pH of the mixture was maintained at 10 by using 2M NaOH aqueous solution with the help of pH meter. Then the solution was stirred for three hours at room temperature using magnetic stirrer and stayed for night. The dark brown precipitates were formed.

Then the mixture was filtered and the residue was washed with distilled water followed by ethanol to remove inorganic and organic impurities. This residue was CuO nanoparticles which was then dried at  $50^\circ\text{C}$  and then calcined at  $300^\circ\text{C}$  for two hours. These nanoparticles were preserved in a sample vial. The whole procedure for

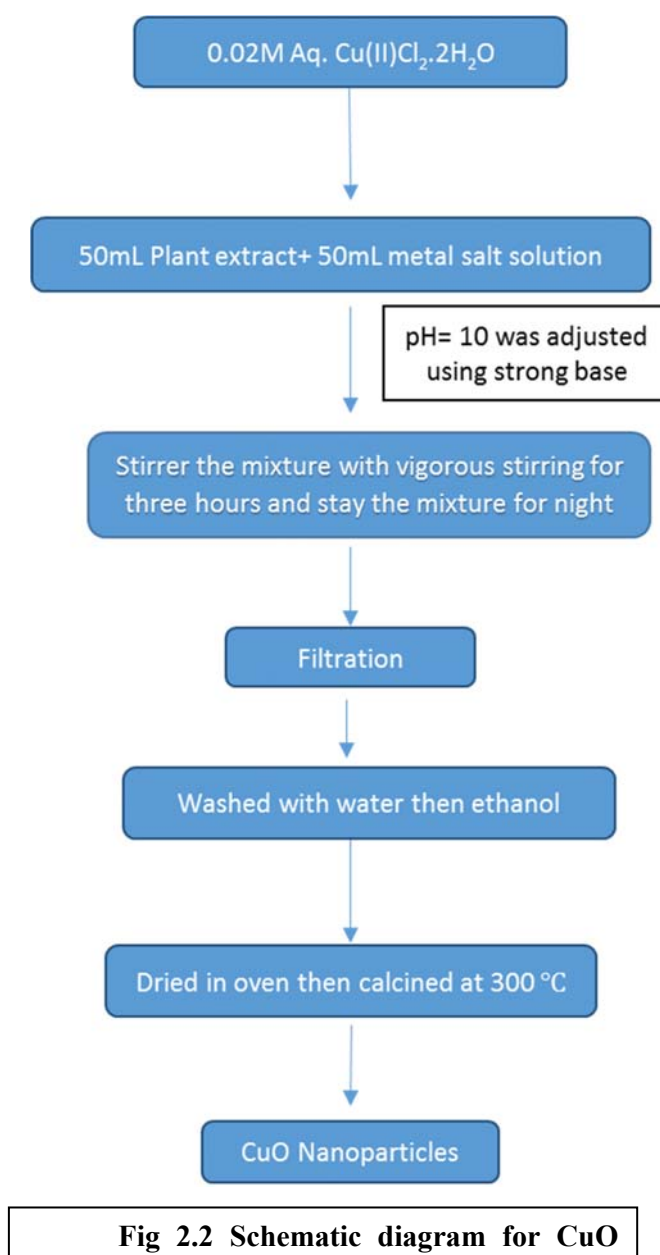


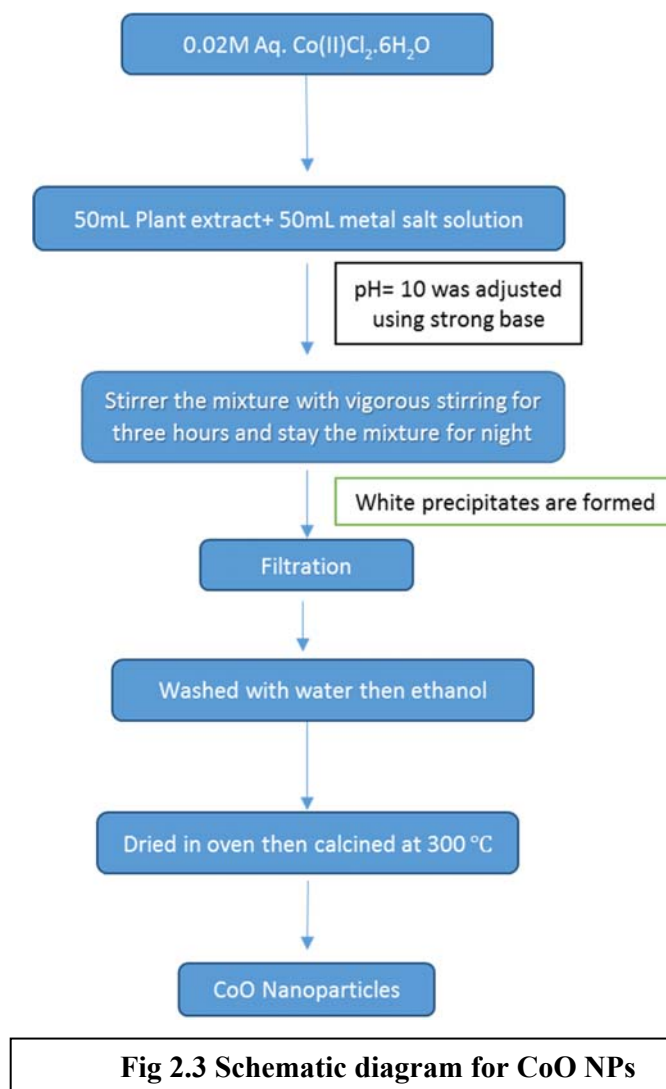
Fig 2.2 Schematic diagram for CuO

the synthesis of CuO NPs is shown in Fig 2.2

### 2.2.3 CoO nanoparticles synthesis:

0.01M solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was prepared in 1000mL distilled water. This aqueous solution of metal salt was mixed with plant extract in 1:1 ratio by taking 50mL of each. The pH of the obtained mixture was adjusted at 10 by adding 2M NaOH drop by drop and monitored with the help of pH meter.

This mixture was stirred for 3 hours at room temperature and then stayed for a night. Black precipitates were formed which were filtered and residue was washed with distilled water then with ethanol. The obtained blackish particles were CoO NPs which were heated and then calcined at  $300^\circ\text{C}$  for two hours. The steps involved

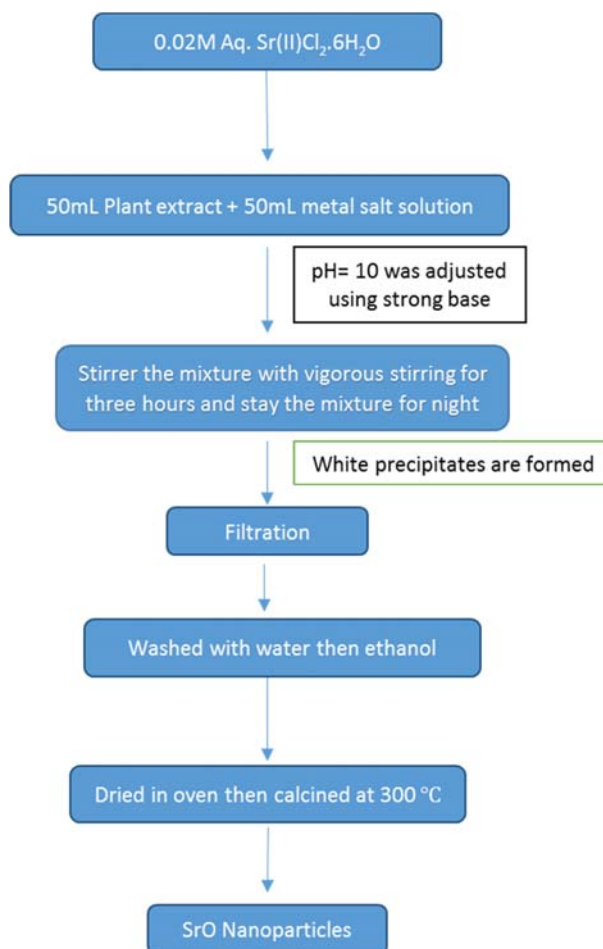


during the synthesis of CoO NPs is shown in Fig 2.3.

#### 2.2.4 SrO nanoparticles Synthesis:

0.01M aqueous solution of  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  was prepared in 1000mL distilled water. Then 50mL of metal salt solution was mixed with the same volume of the plant extract. The pH of the mixture was adjusted at 10 by adding drop by drop 2M NaOH and monitored with pH meter. After this mixture was stirred for three hours and kept for a night. A white precipitates was formed which were filtered and washed with distilled water followed by Ethanol.

This white precipitates were of SrO nanoparticles. These nanoparticles were dried in oven and then calcined at  $300^\circ\text{C}$  for two hours. The steps involved during the synthesis of SrO NPs are given in the Fig 2.4.



**Fig 2.4 Schematic diagram for SrO NPs**



### 2.3 Characterization of Nanoparticles:

Many Characterization techniques were used for newly synthesized nanoparticles. Which includes X-Ray crystallographic analysis, Scanning Electron Microscope (SEM) analysis, EDX Spectroscopic analysis and FTIR Spectroscopic analysis.

#### 2.3.1 FTIR Spectroscopic Analysis:

For the functional group and structural information FTIR studies was performed by using Bruker FTIR (Model 6500 Smart). The range from 400-4000  $\text{Cm}^{-1}$  was taken in account to check absorption of the nanoparticles in IR region. A very small amount of sample in the solid form was used for FTIR analysis.

#### 2.3.2 X-Ray crystallographic Analysis:

XRD analysis was performed to conform the formation of metal oxide nanoparticles and for structural information. The analysis was performed from 20-80° range of angle  $2^{\theta}$ . The instrument was used during analysis X-Ray diffractometer (Model: 3040/60 X'Pert PRO). The sample was used in solid state form.

#### 2.3.3 Scanning Electron Microscope:

Scanning Electron Microscopy is a powerful tool to examine the solid materials. It is used widely in Physics, Chemistry, metallurgy, geology and biology. It is applied to obtain high magnification images, with a efficient depth of field. It can also be used to analyze other features like individual crystals. SEM with high-resolution can show images down to 500 nm in detail.

In my research work SEM were used to check the particle size and morphology of the metal oxides nanoparticles. During sample preparation the metal particles were dispersed in ethanol then sprayed on the sample cubit. Before the SEM analysis gold vapors were deposited on the samples.

##### 2.3.3.1 Methodology:

Before the SEM analysis the samples were dried by using tiny air blower and fine brush for the removal of external particles. The samples were cut 3mm × 3mm in cross sectional area stick on Aluminium stubs with conductive carbon tape. Then the samples were directly sputtered with gold palladium in Sputter Coater (SC7620) and examined using a scanning electron microscope, TESCAN VEGA 3 (Manufactured

byte SCAN, Czech Republic). Images were taken by using the SE detectors i.e., Secondary Electron Detector in different magnifications (200 X to 1,000 X) with pressure upto  $10^{-2}$  torr.

#### **2.3.4 Energy Dispersive Spectroscopy (EDS):**

In EDS the X-ray spectrum emitted from a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. The elements from atomic number 4 (Be) to 92 (U) can be detected, lighter elements can also be detected but not all instruments are equipped for lighter elements ( $Z < 10$ ).

For Qualitative analysis the lines in the spectrum and to the simplicity of X-ray spectra was observed. For Quantitative analysis the intensities of lines was measured for each element in the sample and for the same elements in calibration Standards of known composition.

#### **2.4 Photo-catalytic Degradation Experiments**

Photo-catalytic degradation experiment was performed by using amaranth red azo dye for degradation.

First of all, 15ppm solution of amaranth red was prepared by dissolving 0.015g of azo dye in 1000mL of distilled water. After that 0.2g/L solution of each ZnO, CuO, SrO, and CoO nanoparticles was prepared by dispersing the nanoparticles in water with the help of sonicator.

The high pressure mercury lamp (500W) was used for the purpose of Photo-catalyst.

##### **2.4.1 Procedure:**

50mL of amaranth red solution was taken and 50mL of metal Oxide nanoparticle was added into it. The mixture was stirred vigorously for 2 hours. Then it is placed in high pressure mercury lamp with constant stirring for four hours. The resulting mixture characterized by using UV-VIS Spectrophotometer.

This procedure was repeated to observe degradation efficiency of each metal oxide nanoparticles.

**2.4.2 Characterizations:****2.4.2.1 UV-Visible Spectrophotometer:**

The absorbance of dye solution before and after degradation was measured by using UV-VIS Spectrophotometer (Model: T90+ Spectrometer). The range from 250-800nm was used to monitor the absorbance of mixture and pure solution.

**2.4.2.2 Cyclic Voltammetry:**

The electrochemical behavior of the pure solution of amaranth red and the mixture after degradation was monitored by using cyclic voltammetry. This experiment was performed in the range from 0- -1.2 mV.

**2.4.3 Effect of nanomaterial dose on degradation:**

To observe the effect of nanomaterial dose five different concentrations solutions of ZnO NPs was prepared. The amount 0.2, 0.4, 0.6, 0.8 and 1g of ZnO nanomaterial was for these five systems, while the solutions of azo dyes were kept constant during all the experiments.

**2.4.4 Effect of pH on degradation:**

The pH effect on the photo-catalytic degradation efficiency was also observed by using three solutions different pH systems. These three systems were prepared at pH 3,6 and 9 respectively. The amount of nanomaterial dose and the concentration of dye solution was kept constant.

### 3.1 Results of Zinc Oxide NPs:

#### 3.1.1 FTIR Spectrum of Zinc Oxide NPs:

The FTIR spectrum of ZnO nanoparticles is displayed in the figure 3.1. The peak observed at  $3502\text{cm}^{-1}$  validate the existence of OH. The peaks shown at 1088, 1396 and  $1431\text{ cm}^{-1}$  have allocated to alcohol and phenol, aromatic amines and aliphatic groups respectively. The two peaks observed at  $702$  and  $839\text{ cm}^{-1}$  were confirm the presence of Zn=O.

The mechanism for nanomaterials fabrication by green synthesis route is unfamiliar so far. The investigation ascertains the existence of some alkaloids, terpenoids and proteins that are attached with the metal oxide nanoparticles surface remain entangled although washing repeatedly. The free carboxylic groups and amines that schmoozed with the Zn metal surface prove to attain stability of metal oxide nanoparticles. The heterocyclic compounds present in the leaf extract furnish functionality such as -C-OC-, -O-C- and -C=C- bond and are the capping ligands of the nanoparticle.

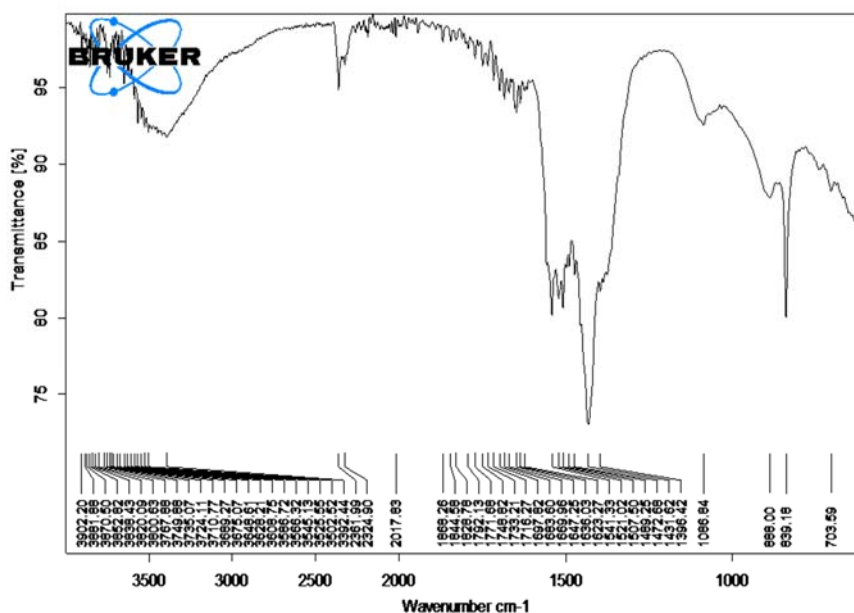
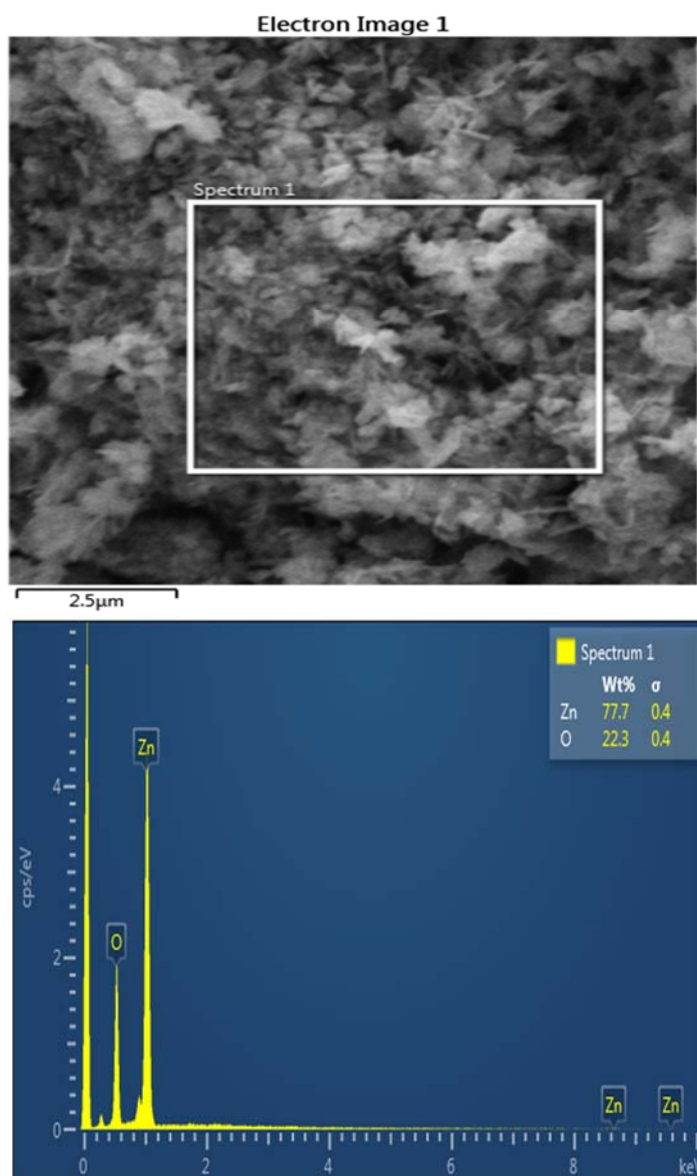


Fig 3.1 FTIR Spectrum of ZnO NPs

### 3.1.2 EDS Spectrum of Zinc Oxide NPs:

The chemical and elemental investigation of Zinc Oxide nanomaterials was verified by energy dispersive X-ray (EDX) spectrometric analysis. The EDX spectrum of zinc oxide is shown in Fig 3.2. The spectrum revealed the existence of zinc and oxygen atoms. The spectrum also confirmed the absence of any impurity present in the sample. The peak next to 0.51 keV was because of oxygen and the peaks at 9.61, 8.6 and 1 keV were verifying the existence of Zinc. The percentage of Zinc and oxygen in the sample was observed 77.3% and 22.3% respectively.



**Fig 3.2 EDS Spectrum of ZnO NPs**

### 3.1.3 XRD Pattern of Zinc Oxide NPs:

The solid samples in powder form were employed in powder X-Ray Diffractometer to observe the presence of Zinc Oxide nanoparticles and examining their structure. The graph of the XRD pattern of Zinc Oxide particles is shown in fig 3.3. The most intense peaks reliable with  $2\theta$  value were observed at  $36.23^\circ$ ,  $34.41^\circ$  and  $31.74^\circ$ . These observed peaks were compared with a reference file (JCPDS File no.5-0664) and found the best agreement with the reference file no. which was confirmed the presence of Zinc Oxide NPs. By Peaks broadening the smaller size of nanomaterials was also confirmed.

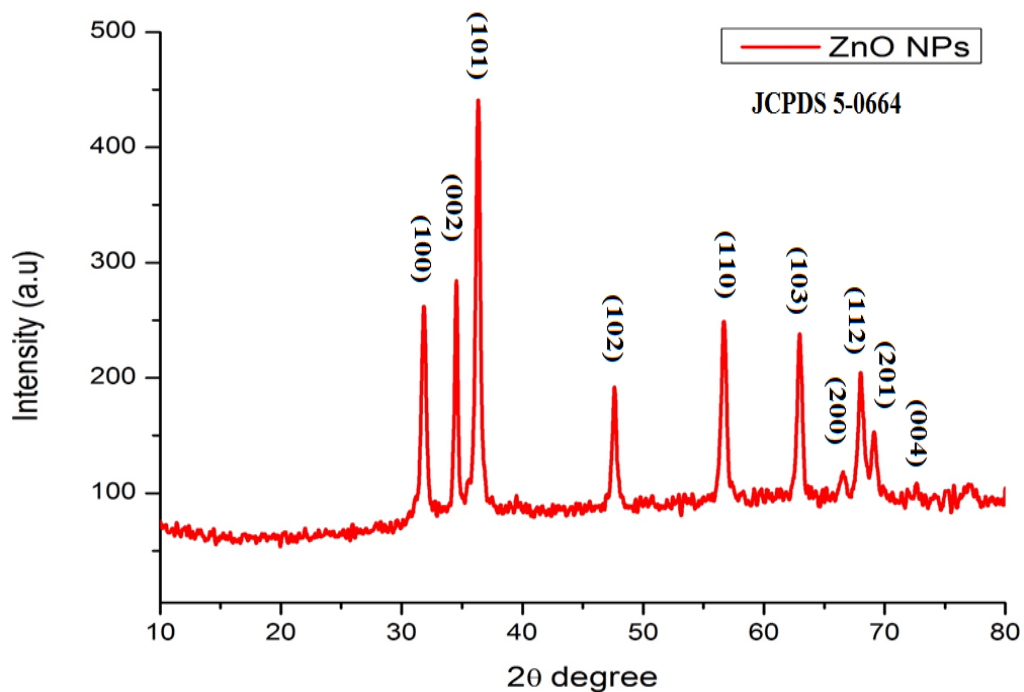
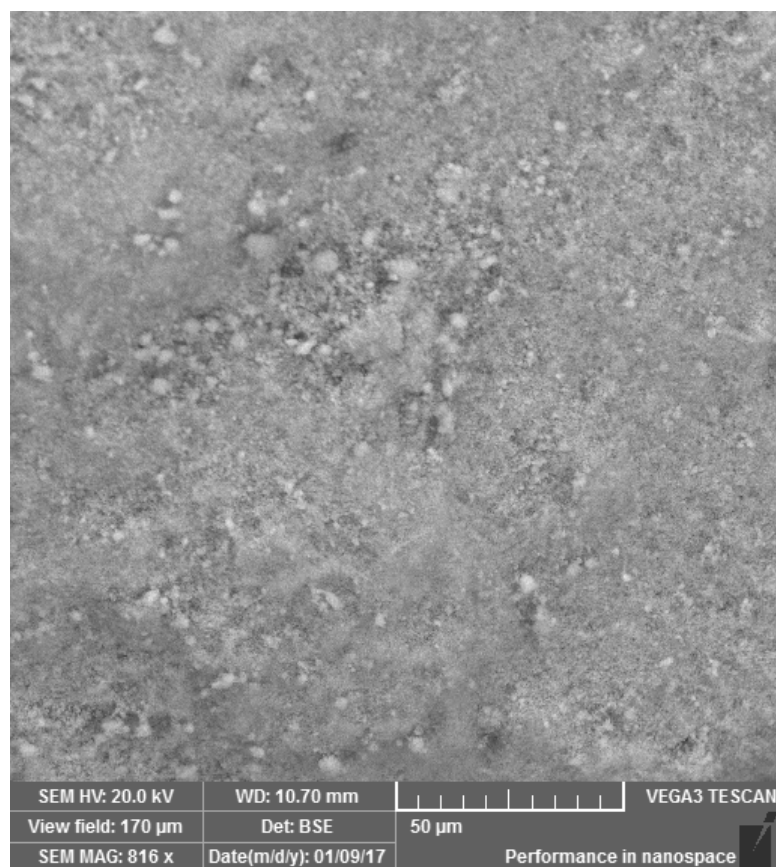


Fig 3.3 XRD Spectrum of ZnO NPs

### 3.1.4 SEM Images of Zinc Oxide NPs:

The scanning electron microscope (SEM) analysis was performed to elaborate the size and shape of the synthesized NPs. The SEM image has shown separate zinc oxide nanoparticles and their aggregates. The SEM images are displayed in the figure 3.4. Comparatively spherical shaped nanoparticles were revealed by the SEM. The aggregates formed have diameter in the ranges of 2-5 micrometer.



**Fig 3.4 SEM Image of ZnO NPs**

## 3.2 Results of CuO Nanoparticles

### 3.2.1 FTIR Spectrum of Copper Oxide NPs:

By using Bruker spectrometer, the FTIR spectrum of CuO nanoparticles was carried out. The small peak at  $1045\text{ cm}^{-1}$  confirmed the development of CuO nanoparticles. The broad peak at  $3235\text{ cm}^{-1}$  showed the presence of OH group. The peak broadening may be due to moisture present in the sample. The peak at  $1636\text{ cm}^{-1}$  showed the presence of C=C bond, which might be due to the impurities, such as proteins, terpenoids or phenolic compounds that stuck to the surface of CuO nanoparticles even after recurring washing. The free amino and carboxylic groups that have attached with the metal surface are responsible for the stability of CuO nanoparticles. The figure 3.5 outlines the clear picture of FTIR spectrum of CuO NPs.

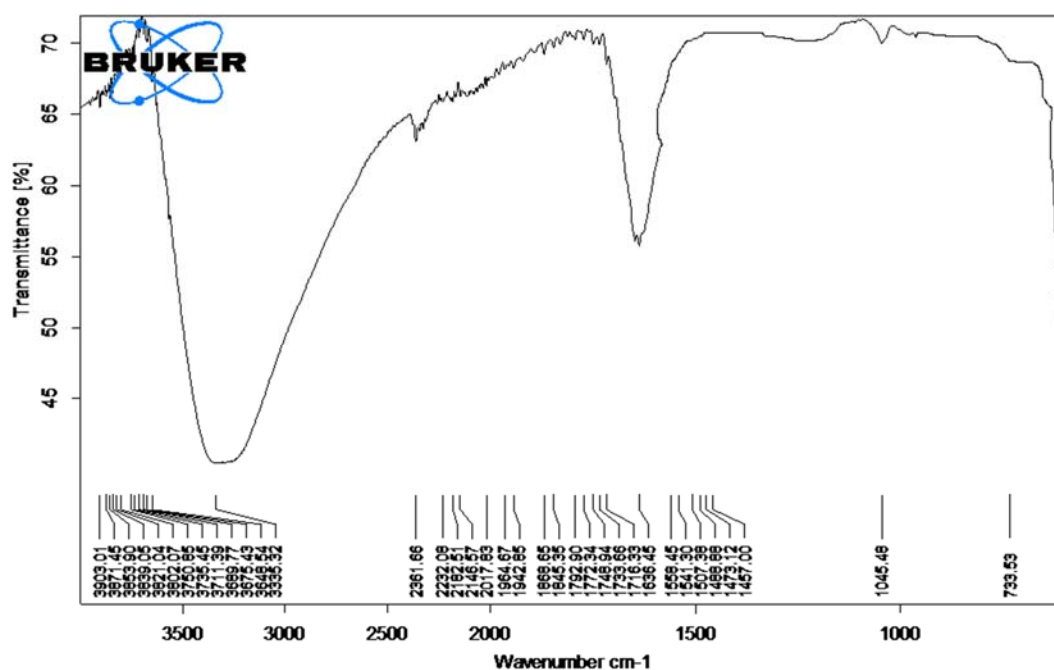
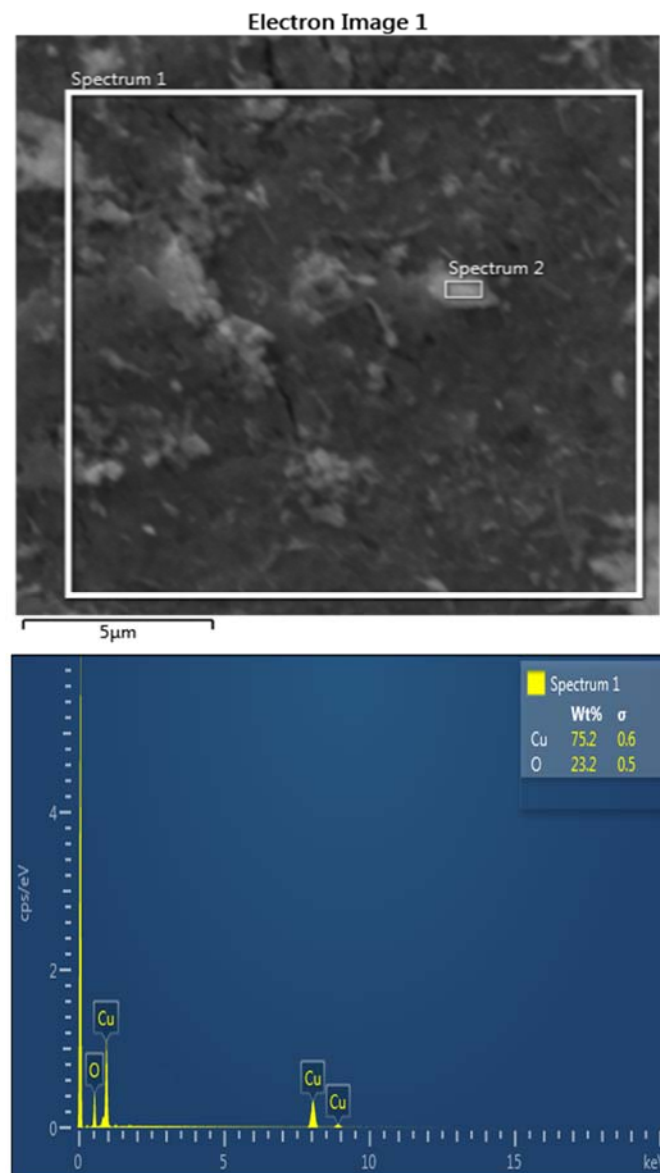


Fig 3.5 FTIR Spectrum of CuO



### 3.2.2 EDX Spectrum of Copper Oxide:

Energy dispersive X-ray spectrometry (EDS) analysis was used to confirm the elemental and chemical analysis of CuO nanoparticles. The EDS spectrum of the CuO nanoparticles revealed the existence of Cu and O elements. The peak at 0.5Kev confirmed the presence of oxygen and the peaks near 0.9, 8 and 8.9Kev respectively confirmed the presence of Cu. The data in the spectrum showed that Cu was 75.2% and O was 23.2%. The EDS analysis has also verified the purity of CuO nanoparticles and is shown in the Fig 3.6.



**Fig 3.6 EDS Spectrum of CuO NPs**

### 3.2.3 XRD Pattern of Copper Oxide NPs:

The sample in powder form was used by a  $\text{CuK}\alpha$ -X Ray Diffractometer for verifying the existence of CuO NPs and for their structure determination. The spectrum showed main peaks consistent to  $2\theta$  values at  $37.7^\circ$ ,  $40.4^\circ$  and  $49.23^\circ$  which is given in Fig 3.7. These spectral peaks clearly matched with the reference report (JCPDS File no 80-1268). Hence, existence of copper oxide nanoparticles confirmed. Crystalline nature of the synthesized nanostructures was confirmed by the sharpness of peaks. The peak broadening showed smaller particle size.

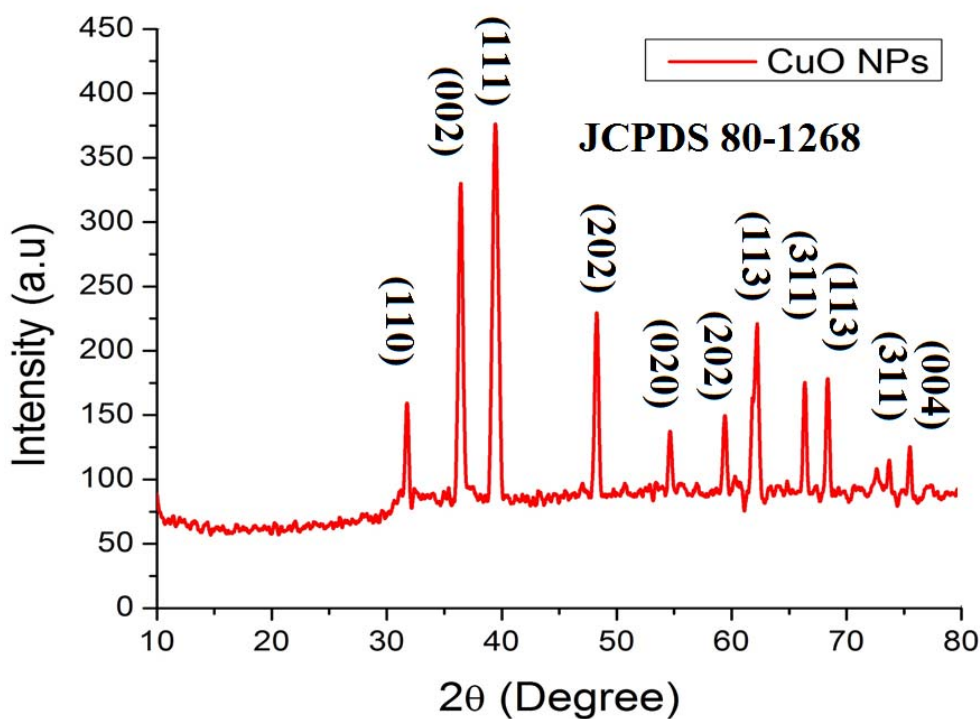
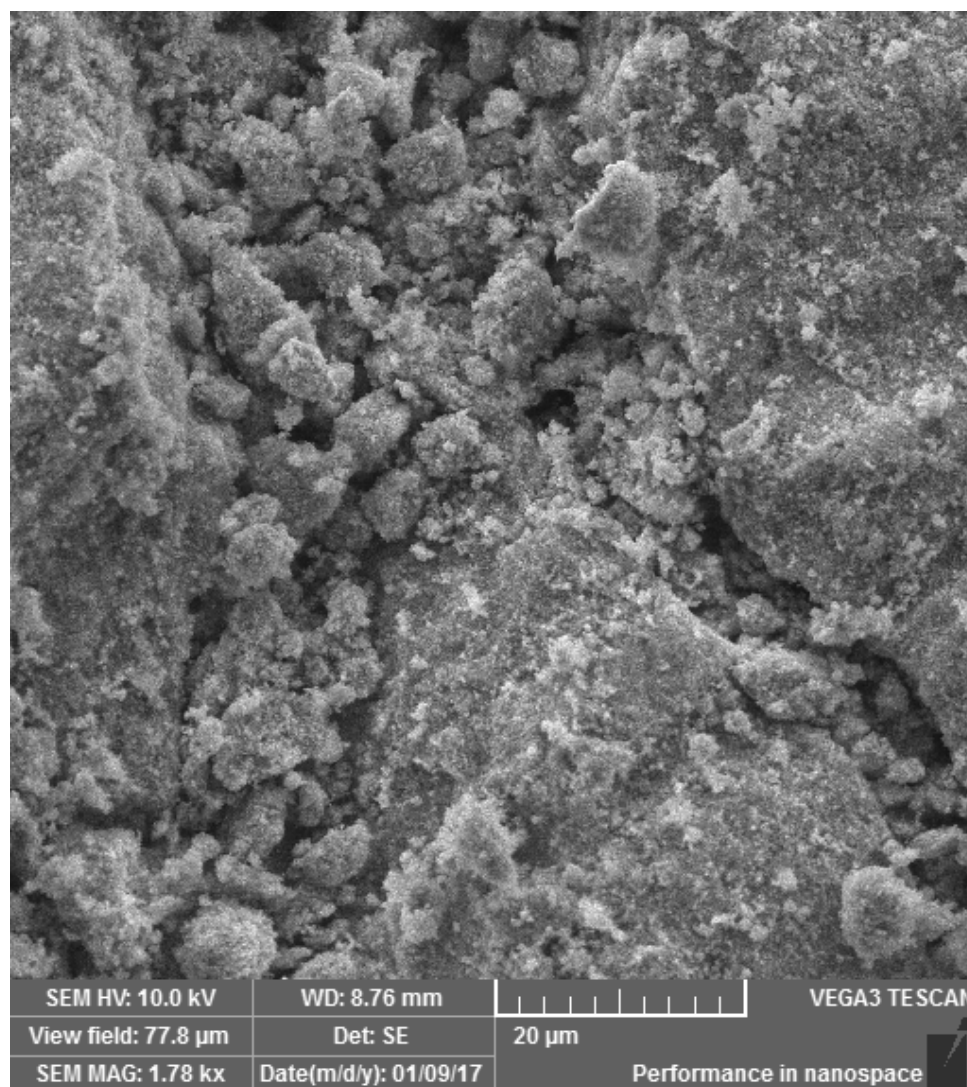


Fig 3.7 XRD Spectrum of CuO NPs

### 3.2.4 SEM Images of Copper Oxide NPs:

The structure and size of the Copper Oxide NPs was defined using the scanning electron microscope (SEM) examination and is shown in Fig 3.8. The SEM images have showed separate copper particles as well as an aggregate. Comparatively rod shaped CuO nanoparticles were confirmed by the SEM images. Aggregated molecules formed in the range of 2  $\mu\text{m}$ .



**Fig 3.8 SEM Image of CuO NPs**

### 3.3 Results of SrO NPs:

#### 3.3.1.1 FTIR Spectrum of Strontium Oxide NPs:

To verify the development of SrO nanoparticles, the FTIR analysis of synthesized SrO nanoparticles was carried out. Fig 3.9 gives the clear picture of the entitled spectrum. The stretching vibrations of Sr-O-Sr bonds gave rise to the strong absorption peak at about  $1436\text{ cm}^{-1}$ , the sharp absorption bands at  $866\text{ cm}^{-1}$  and  $701\text{ cm}^{-1}$  might be due to stretching vibration of Sr=O. The small absorption peaks at  $3446\text{ cm}^{-1}$  assured the presence of OH. The OH is due to the formation of Sr-OH which was present even after calcinations.

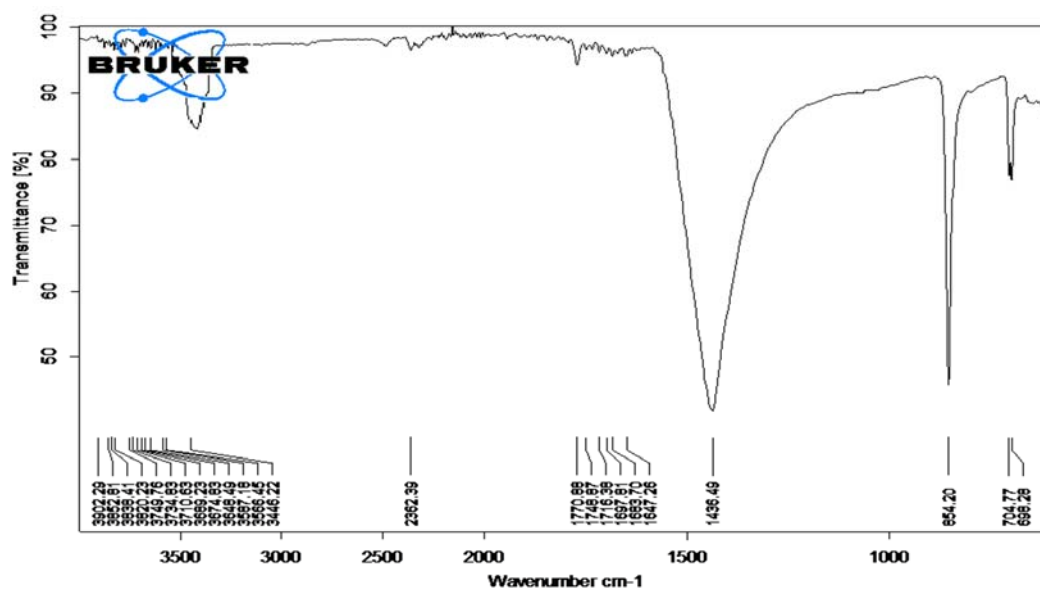
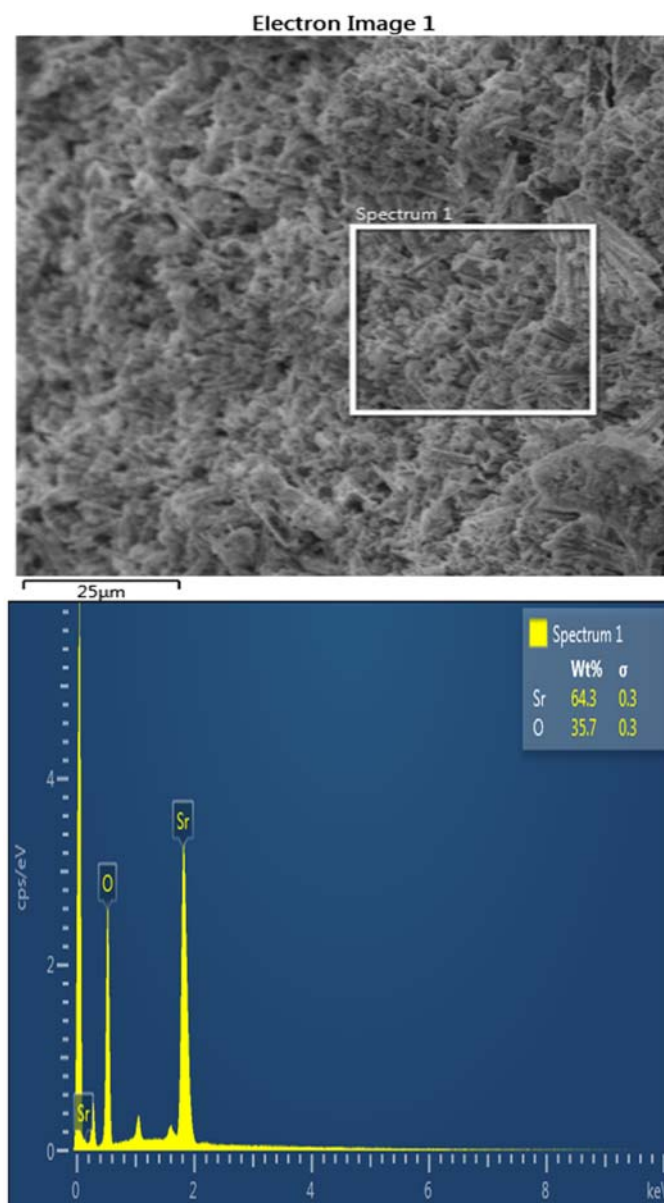


Fig 3.9 FTIR Spectrum of SrO NPs

### 3.3.2 EDX Spectrum of Strontium Oxide NPs:

The chemical and elemental exploration of synthesized NPs of Strontium Oxide was verified by the EDX spectrometric analysis. The EDX spectrum exposed the existence of Oxygen and Strontium element. The sharp peak at 0.45Kev was confirm the existence of Oxygen however the peaks at 1.9 and 0.2Kev were confirmed the existence of Sr. It is shown from the figure 3.10 that the percentage of Sr was 64.3% and O has 35.7%. The purity of the nanoparticles was also verified by this analysis.



**Fig 3.10 EDS Spectrum of SrO NPs**

### 3.3.3 XRD Pattern of Strontium Oxide NPs:

The powdered sample was subjected to CuK $\alpha$ -X Ray Diffractometer to confirm the formation of SrO NPs. The spectrum gave main peaks on  $2\theta$  values at  $26.2^\circ$ ,  $32.4^\circ$  and  $42.23^\circ$  as shown in Fig 3.11. The peaks of the spectrum were compared with reference report (JCPDS File no 001-1113). A comparison of the position of peaks with reference values confirmed the existence of SrO nanoparticles. The sharpness of the peaks showed crystalline nature of the particles and peak broadening confirmed smaller particle size.

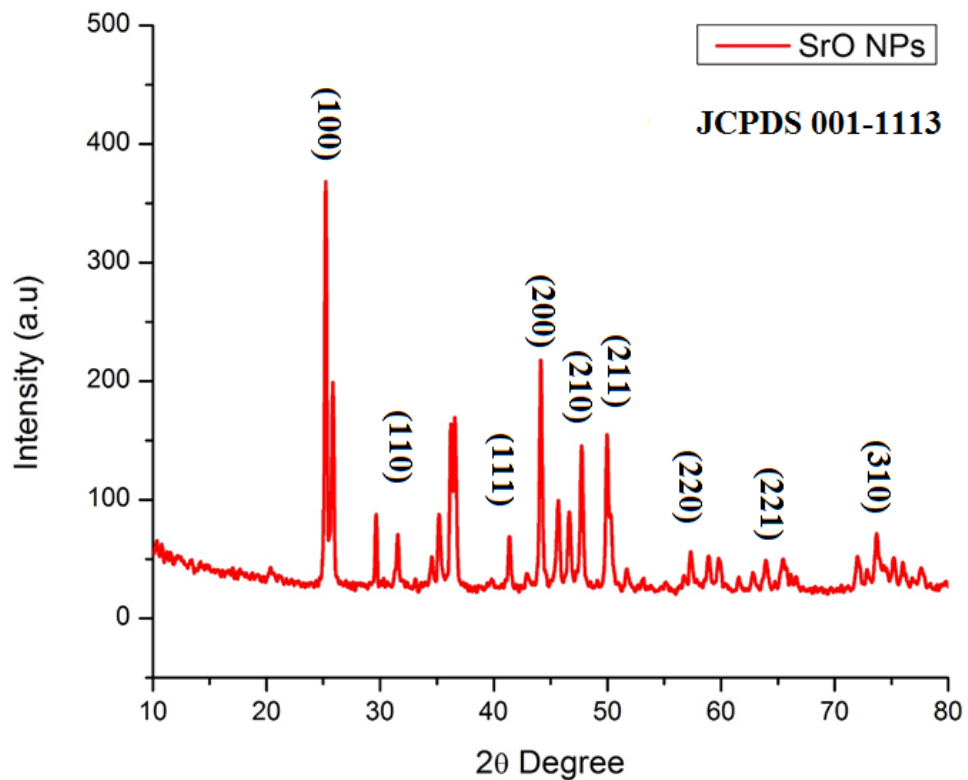
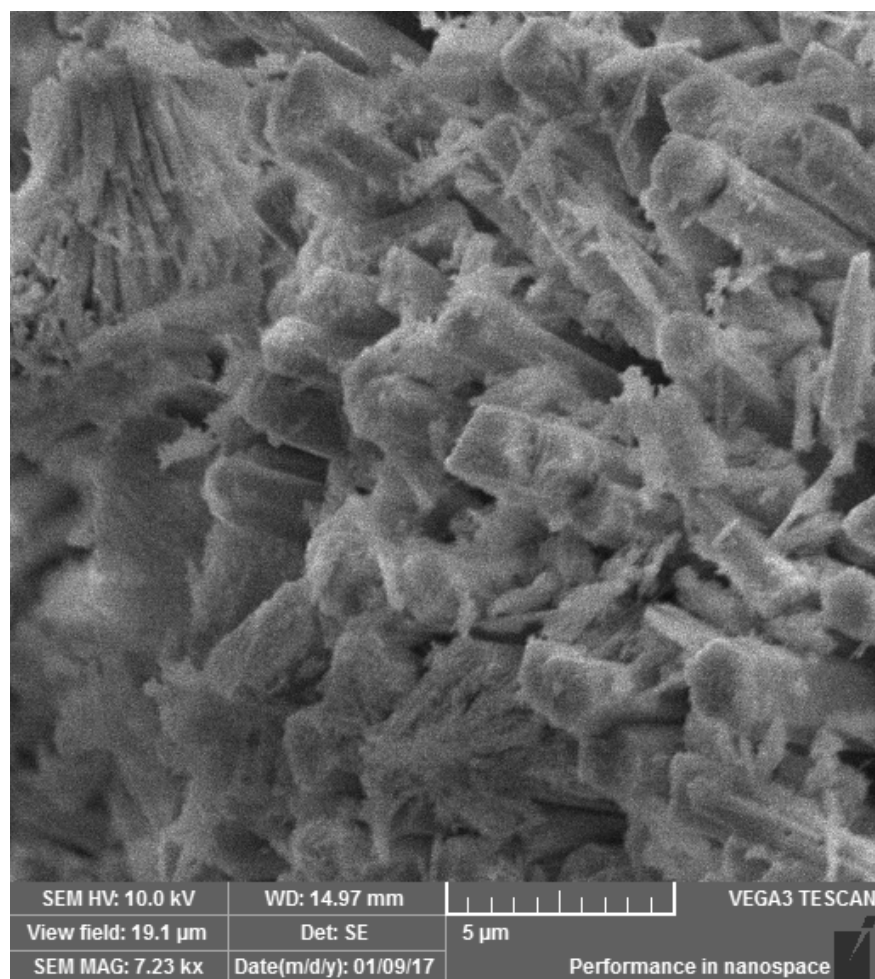


Fig 3.11 XRD Spectrum of SrO NPs

### 3.3.4 SEM Images of Strontium Oxide NPs:

To ascertain the structure and particle size of the prepared SrO NPs, the scanning electron microscope (SEM) analysis was performed. Separate strontium particles as well as an aggregate were confirmed via SEM images. The SEM image confirmed comparatively rod shaped nanoparticles. The aggregated molecules of approximately 5  $\mu\text{m}$  diameters were formed as it was clear from SEM analysis. One of the representative SEM images of SrO NPs is shown in Fig 3.12.



**Fig 3.12 SEM Image of SrO NPs**

### 3.4 Results of Cobalt Oxide NPs:

#### 3.4.1 FTIR Spectrum of Cobalt Oxide NPs:

The formation of Cobalt Oxide nanoparticles were revealed by FTIR. The FTIR spectrum of cobalt oxide is presented in the Figure 3.13. The OH group gave rise to peak at  $3379\text{ cm}^{-1}$ . The peaks shown at  $1457\text{ cm}^{-1}$ ,  $1374\text{ cm}^{-1}$  and  $1087\text{ cm}^{-1}$  were allotted to various Phenolic Groups alcohol and, protein molecules existing in the plant. The peak observe at  $859\text{ cm}^{-1}$  were due to Cobalt Oxide.

The mechanism for the fabrication of nanostructures is still unknown. Some sort of proteins, terpenoids or phenolic compounds present in plant extracts are attached to the surface of CoO nanoparticles.

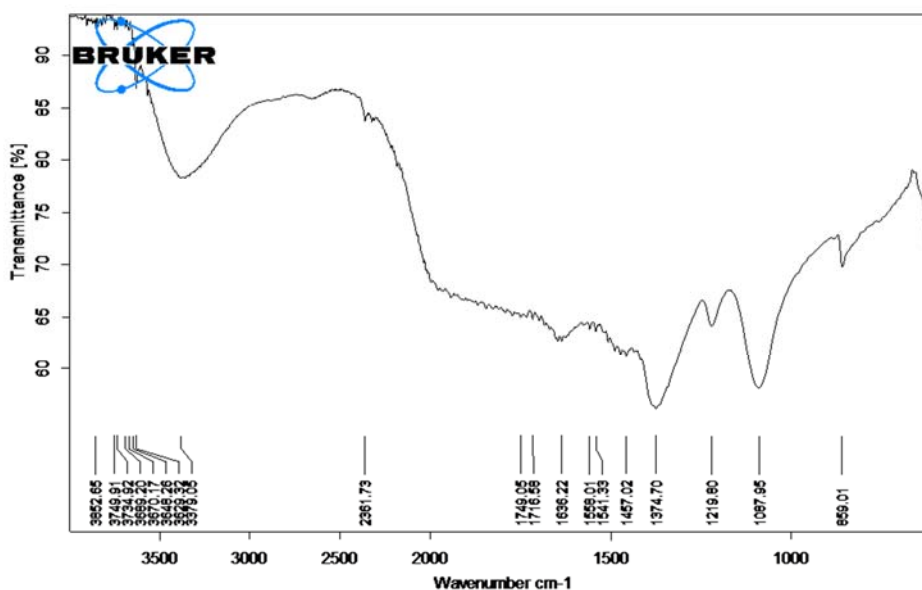


Fig 3.13 FTIR Spectrum of CoO NPs



### 3.4.2 EDS Spectrum of CoO NPs:

Energy dispersive X-ray spectrometry (EDS) revealed the detailed description of elemental and chemical analysis of the Cobalt Oxide NPs. The existence of Oxygen and Cobalt elements in the CoO nanoparticles was confirmed via EDS spectrum, the intense peak at 0.51Kev verify the presence of Oxygen element and the sharp peaks at 7.6, 6.9 and 0.8Kev were assigned to the existence of Cobalt. It is shown from the Fig 3.14 that the percentage of Co was 75.2% and that of O was 23.2%. Through EDS analysis, purity of CoO nanoparticles was also verified.

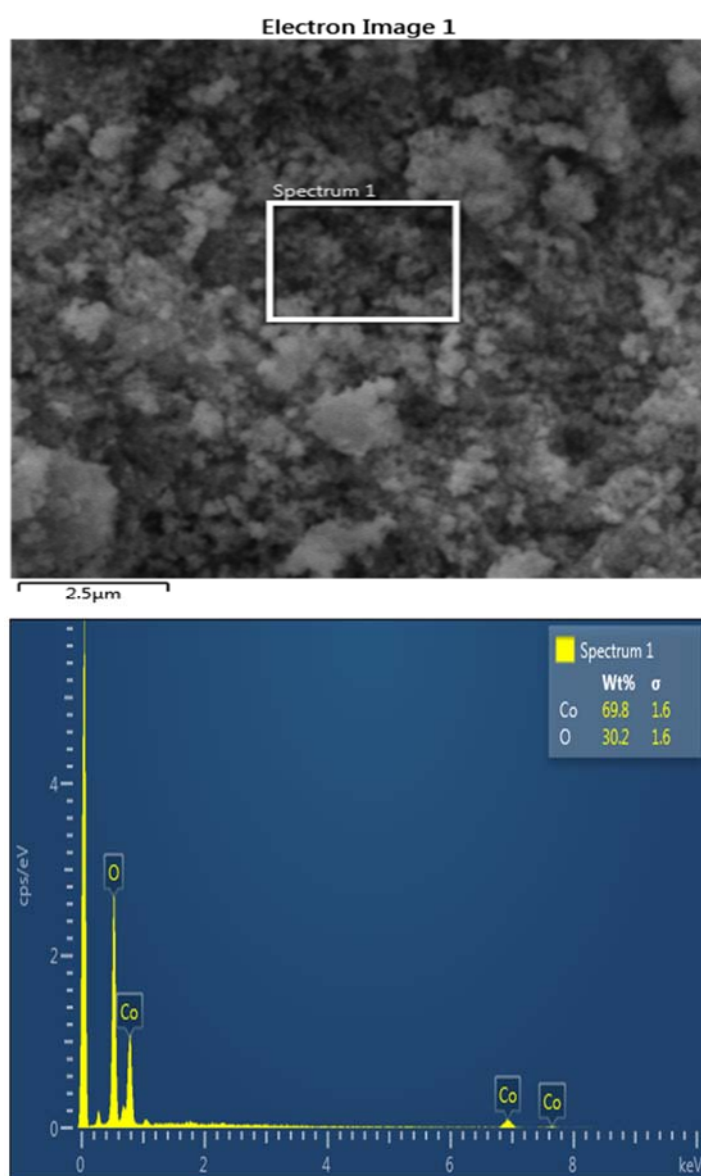


Fig 3.14 EDS Spectrum of CoO NPs

### 3.4.3 XRD Pattern of Cobalt Oxide NPs:

The X-Ray Diffraction was utilized to validate the actuality of Cobalt Oxide nanoparticles with its crystallinity and particles size. The figure 2.15 shows intense peaks in  $2\theta$  region at  $64^\circ$ ,  $38.1^\circ$  and  $43^\circ$ . These intense peaks were compared with reference paper. A comparison of peaks position with the reference data confirmed the formation of CoO NPs. The sharpness of the peaks showed crystalline nature of the particles and peak broadening confirmed smaller particle size.

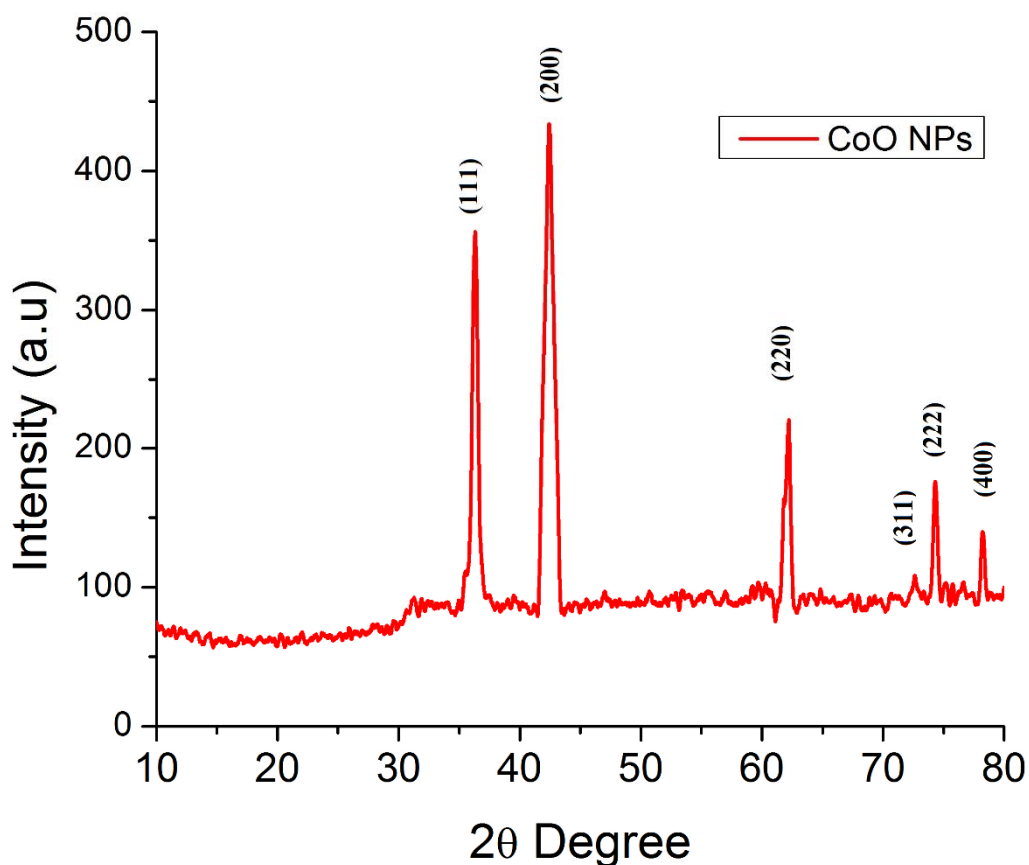
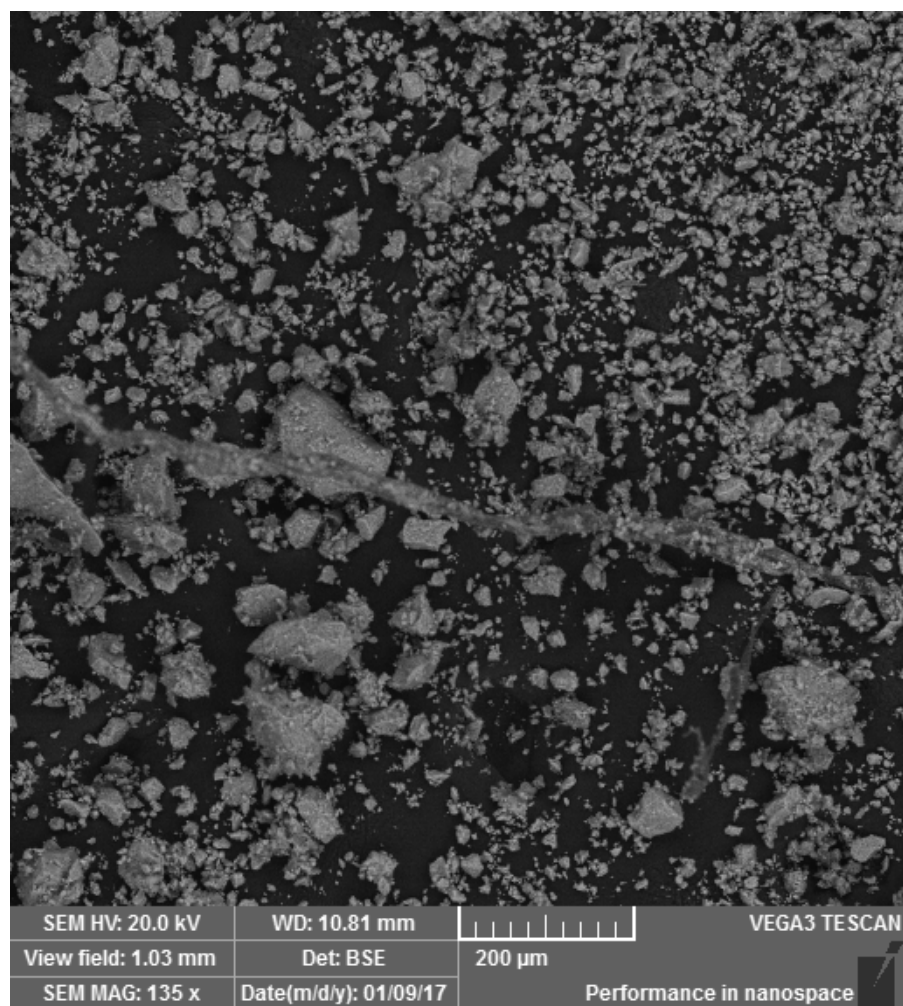


Fig 3.15 XRD Spectrum of CoO NPs

### 3.4.4 SEM Images of Cobalt Oxide NPs:

The Scanning Electron Microscope (SEM) analysis was utilized to explore the structure and size of the synthesized particles. The SEM image of CoO is shown in the Fig 3.16. It is clear from the images that separate CoO nanoparticles and aggregates are formed. Comparatively rod shaped nanoparticles were formed as it was clear through the SEM image. The size of the aggregated molecules formed are in the range of 5 $\mu$ m.



**Fig 3.16 SEM Image of CoO NPs**

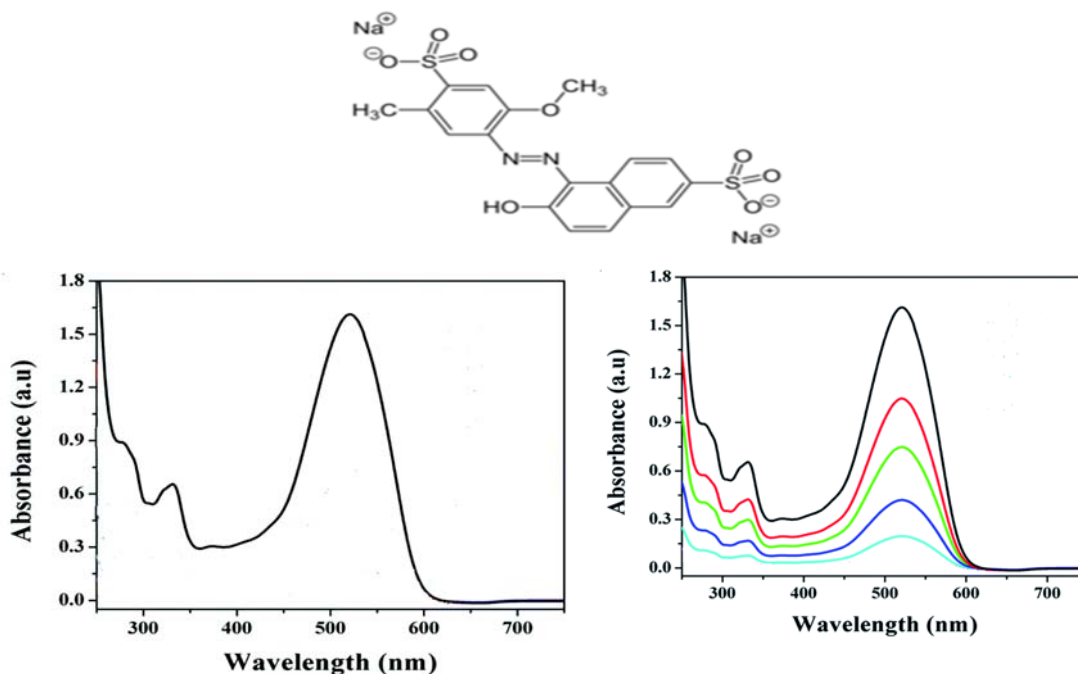
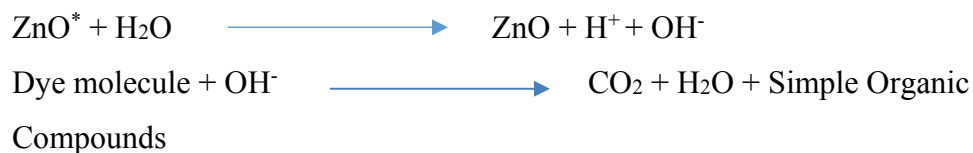
### 3.5 Results of degradation Experiment:

#### 3.5.1 UV-Vis Spectrum of degradation:

The dye solution exhibited maximum absorbance at 510 nm as it was clear from the UV-Vis spectrum of amaranth red. In degradation testing, three various types of experimentations were made under diverse conditions in addition to measure their decolorization percentage with respect to time.

In the first step 0.5g/L of nanomaterial of each metal oxide was mixed with 15ppm azo dye (amaranth red) solution and decolorization percentage was tested once it was placed in a HPM-500W lamp (high pressure mercury lamp). The photo-catalytic degradation for ZnO, CuO, CoO and SrO nanoparticles were observed at 88, 75, 57 and 37% respectively. The remarkable degradation efficiency was observed for ZnO nanoparticles as shown in the fig 3.17.

The suggested mechanism during the whole process of degradation of azo dye is shown as.

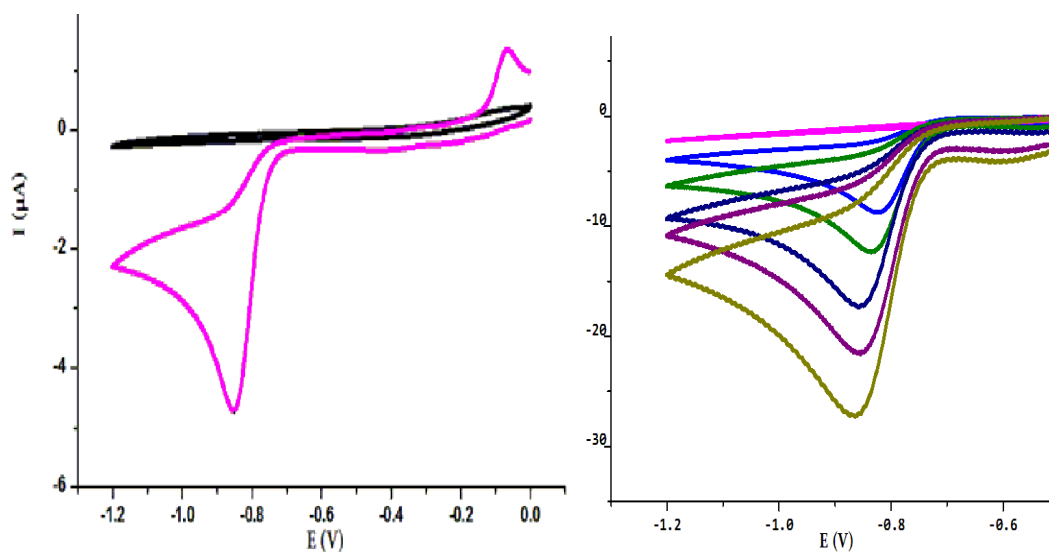


**Fig 3.17 UV Spectra of before and after Degradation**

### 3.5.2 Cyclic Voltammogram of degradation Experiment:

The reduction peak of amaranth red was observed at -0.9V. The photo-catalytic degradation was also verified by using CV and the same results were obtained which confirmed the UV results.

The maximum efficiency was observed with ZnO nanoparticles as shown in cyclic voltammogram below.



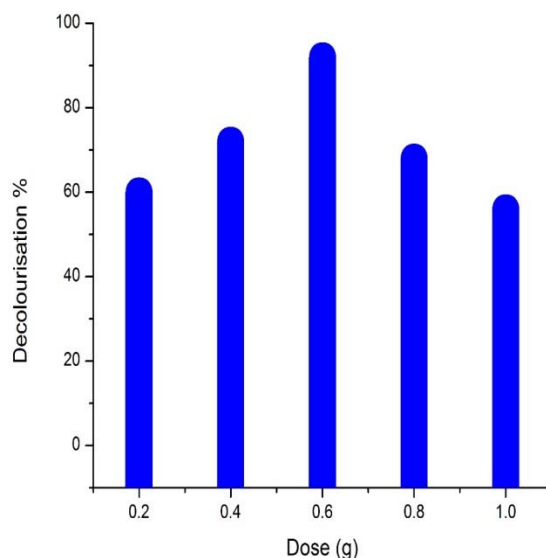
**Fig 3.18 Cyclic Voltammograms of before and after Degradation**

### 3.5.3 Results of Dose Effect on degradation:

The ZnO nanomaterials dose effect was determined on Photo-catalytic degradation of azo dye.

First the percentage of decolorization was increased by increasing the amount of NPs from 0.2-0.6 g as it is evident from the graph 3.19. After that, the decolorization percentage was decreased with further increasing the dose of nanomaterial. The supreme rate of degradation was detected with 0.6 g of nanoparticles.

The percentage of decolorization was decreased after a certain amount of dose of nanoparticles in the assay under examination. The decrease in decolorization was because of the fact that the photo light enhance aggregation of additional amount of the nanoparticles. Furthermore, the UV radiation could not penetrated by using concentrated mixture of a solution.



**Fig 3.19 Effect of dose of ZnO NPs on degradation**

### 3.5.4 Results of pH Effect on Photo-catalytic Degradation Experiment:

In photo-catalytic degradation experiment the effect of pH on degradation is very important factor. The pH effect was explored on ZnO nanoparticles because of their remarkable efficiency for degradation. The percentage of decolorization was tested with time. It is cleared from the graph that the maximum percentage of decolorization was 98.5 which was attained at pH = 3 then two other systems. The percentage of decolorization at pH 6 and 9 was 81 and 41% respectively. The graphical representation of pH effect is shown in figure 3.20. Which confirm that acidic media was best for amaranth red azo dye degradation.

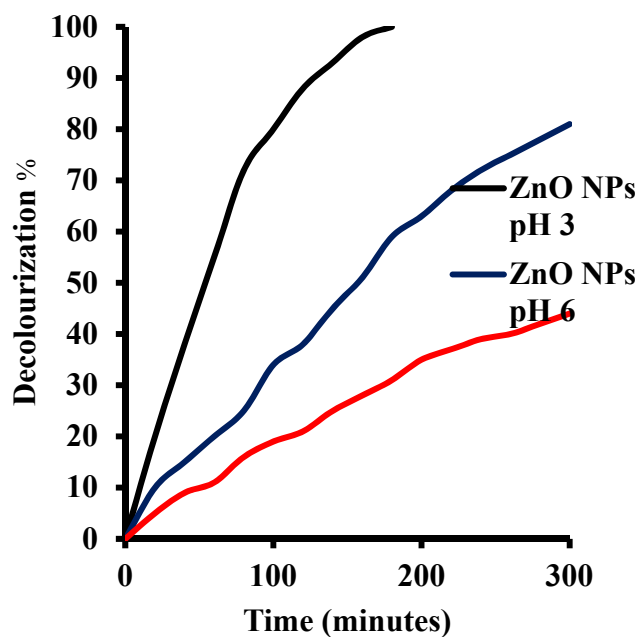


Fig 3.20 Photocatalytic activity of ZnO NPs

The biogenic route was adopted to synthesize nanoparticles of strontium oxide, copper oxide, zinc oxide and cobalt oxide. These various metal oxides NPs were synthesized by using *Calotropis gigantea* plant leaf extract. Then variety of characterization techniques were used to confirm and characterize these nanomaterials. The formation of metal oxides NPs was confirmed with the help of Fourier transform infrared spectroscopy (FTIR). Then XRD was employed to verify the results and to test the purity and crystallinity of the synthesized particles. The chemical and elemental analysis was performed with the help of energy dispersive x-ray spectroscopy (EDX) which verified the appropriate percentages and purity of prepared metal oxide nanoparticles. Scanning Electron Microscopy (SEM) was used to confirm the size of nanomaterials which revealed that the nanoparticles were formed in the range of 1-5 micro meter this was because of aggregation. Which proves that it is difficult to control the size of NPs by using biogenic route.

Then their comparative photo-catalytic degradation efficiency was tested by using Amaranth red as a reference dye. In this experiment HPM-500W (high pressure mercury lamp) was employed for photo-catalyst. The whole process was observed by using UV-VIS spectrophotometer and the degradation efficiency was observed by the percentage at which dye was decolorized in a unit time. The results showed that the maximum degradation efficiency gave zinc oxide nanoparticles than the rest of the three metal oxides NPs. The pH effect and the effect of dose on degradation was also tested by using zinc oxide NPs. It was observed that the maximum degradation was took place at 0.6g of nanoparticles dose at pH=3. Which conform that acidic medium is favourable for dyes degradation.



## REFERENCES

---

1. (a) Hübler, A. W.; Osuagwu, O., Digital quantum batteries: Energy and information storage in nanovacuum tube arrays. *Complexity* **2010**,*15* (5), 48-55; (b) Stephenson, C.; Hubler, A., Stability and conductivity of self assembled wires in a transverse electric field. *Scientific reports* **2015**,*5*, 15044.
2. Taylor, R.; Coulombe, S.; Otanicar, T.; Phelan, P.; Gunawan, A.; Lv, W.; Rosengarten, G.; Prasher, R.; Tyagi, H., Small particles, big impacts: a review of the diverse applications of nanofluids. *Journal of Applied Physics* **2013**,*113* (1), 1.
3. Granqvist, C.; Buhrman, R.; Wyns, J.; Sievers, A., Far-infrared absorption in ultrafine Al particles. *Physical Review Letters* **1976**,*37* (10), 625.
4. Uyeda, T.; Hayashi, C.; Tasaki, A., *Ultra-Fine Particles: Exploratory Science and Technology*. Elsevier: 1995.
5. Kiss, L.; Söderlund, J.; Niklasson, G.; Granqvist, C., New approach to the origin of lognormal size distributions of nanoparticles. *Nanotechnology* **1999**,*10* (1), 25.
6. (a) Buzea, C.; Pacheco, I. I.; Robbie, K., Nanomaterials and nanoparticles: Sources and toxicity. *Biointerphases* **2007**,*2* (4), MR17-MR71; (b) ASTM, E., 2456-06: Standard Terminology related to Nanotechnology. ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959 USA (2006).
7. Gültekin, A.; Ersöz, A.; Sarıözlü, N. Y.; Denizli, A.; Say, R., Nanosensors having dipicolinic acid imprinted nanoshell for *Bacillus cereus* spores detection. *Journal of Nanoparticle Research* **2010**,*12* (6), 2069-2079.
8. Ahamed, M.; AlSalhi, M. S.; Siddiqui, M., Silver nanoparticle applications and human health. *Clinica chimica acta* **2010**,*411* (23), 1841-1848.
9. Cai, X.; Conley, S.; Naash, M., Nanoparticle applications in ocular gene therapy. *Vision research* **2008**,*48* (3), 319-324.
10. Sivakumar, J.; Premkumar, C.; Santhanam, P.; Saraswathi, N., Biosynthesis of Silver Nanoparticles Using *Calotropis gigantea* Leaf. *Afr J. of Basic & App Sci* **2011**,*6* (3), 265-270

11. Ponarulselvam,; Panneerselvam,; Murugan,; Aarthi,; Kalimuthu,; Thangamani, Synthesis of silver nanoparticles using leaves of *Catharanthus roseus* Linn. G. Don and their antiplasmodial activities, *A. Paci J. of Tro Bio***2012**, 574-58.
12. Singhal, G,; Bhavesh, R,; Kasariya, K,; Ranjan A,; Rajendra S, Biosynthesis of silver nanoparticles using *Ocimum sanctum* (Tulsi) leaf extract and screening its antimicrobial activity, *Journal of Nanoparticle Research* **2011**, 13, 2981–2988
13. Ravindra P,; Vineet K,; Raghvendra, S,; Prashant K,; Avinash C, Biological approach of zinc oxide nanoparticles formation and its characterization, *Adv. Material Letters***2011**, 2 (4), 313-317.
14. Akl M,; Nidà M,; Amany O,; Biosynthesis of Silver Nanoparticles using *Olea europaea* Leaves Extract and its Antibacterial Activity *Nanoscience and Nanotechnology*,**2011**, 2 (6), 164-170.
15. Hudlikar, M,; Joglekar, S,; Dhaygude, M,; Kodam, K,; Latex-mediated synthesis of ZnS nanoparticles, *Journal of Nanoparticle Research*,**2012**,14, 865
16. Mason, C,; Vivekanandhan, S,; Misra, M,; Kumar, A, Switchgrass (*Panicum virgatum*) Extract Mediated Green Synthesis of Silver Nanoparticles, *World J. of Nano Sci and Engg***2012**, 2, 47-52
17. Sharma P,; Yelne M,; Dennis T, Data base on medicinal plants used in ayurveda. **2008**, 1, 70-71. Ahmad N,; Sharma S, Green Synthesis of Silver Nanoparticles Using Extracts of *Ananas comosus*, *Green and Sustainable Chemistry*.**2012**, 2, 141-147
18. Alagumuthu, G,; Kirubha, R, Green synthesis of silver nanoparticles using *Cissus quadrangularis* plant extract and their antibacterial activity University, *Int J. of Nanomaterials and Biostructure*,**2012**, 2,(3), 30-33
19. Sangeethaa G,; Rajeshwaria S,; Venckatesh, R, Green synthesis of zinc oxide nanoparticles by aloe *barbadensis* miller leaf extract: Structure and optical properties, *Materials Research Bulletin* **2011**,12 (46), 2560–2566
20. Gregory, P., High-technology applications of organic colorants. *Springer Science & Business Media* **2012**.
21. Gold, V,; Loening, K,; McNaught, A,; Shemi, P,IUPAC Compendium of Chemical Terminology. Blackwell Science, Oxford **1997**.

22. Merino, E.; Ribagorda, M., Control over molecular motion using the cis–trans photoisomerization of the azo group. *Beilstein journal of organic chemistry***2012**, 8 (1), 1071-1090.
23. Kind, L.; Klaus, A. J.; Rys, P.; Gramlich, V., Cyclopalladation of 1, 1'-Azonaphthalene (= Di (naphthalen-1-yl) diazene): Isolation and characterization of two isomeric complexes. *Helvetica chimica acta***1998**, 81 (2), 307-316.
24. Pinheiro, H.; Touraud, E.; Thomas, O., Aromatic amines from azo dye reduction: status review with emphasis on direct UV spectrophotometric detection in textile industry wastewaters. *Dyes and pigments***2004**, 61 (2), 121-139.
25. Clarence, O. K., Essence of Photoelectric Colorimetric Assays of Alcoholic Methyl Red Dye Solution in the Purification of Azo Dye-Contaminated Waste-Water. *African Journal of Chemistry***2013**, 1 (3), 071-076.
26. Lappe, P.; Hofmann, T., Pentanols. Ullmann's Encyclopedia of Industrial Chemistry**2005**.
27. Shihad, A. A. A. Preparation and Spectrophotometric Study of 2 [2-(5-bromo thiazolyl) azo]-4-methoxy phenol. *Eastern Mediterranean University (EMU)-Doğu Akdeniz Üniversitesi (DAÜ)*,**2013**.
28. Bateman, B.; Warner, J. O.; Hutchinson, E.; Dean, T.; Rowlandson, P.; Gant, C.; Grundy, J.; Fitzgerald, C.; Stevenson, J., The effects of a double blind, placebo controlled, artificial food colourings and benzoate preservative challenge on hyperactivity in a general population sample of preschool children. *Archives of Disease in Childhood***2004**, 89 (6), 506-511.
29. de Campos Ventura-Camargo, B.; Marin-Morales, M. A., Azo dyes: characterization and toxicity—a review. *Textiles and Light Industrial Science and Technology***2013**.
30. Haghbeen, K.; Tan, E. W., Facile synthesis of catechol azo dyes. *The Journal of Organic Chemistry***1998**, 63 (13), 4503-4505.
31. Balon, W., One-step process of preparing azo dyes by simultaneous diazotization. *Google Patents*:**1974**.

32. Caldarelli, M.; Baxendale, I. R.; Ley, S. V., Clean and efficient synthesis of azo dyes using polymer-supported reagents. *Green Chem.***2000**, 2 (2), 43-46.
  33. Wang, M.; Funabiki, K.; Matsui, M., Synthesis and properties of bis (hetaryl) azo dyes. *Dyes and Pigments***2003**, 57 (1), 77-86.
  34. Wagner, S.; Leyssner, F.; Kördel, C.; Zarwell, S.; Schmidt, R.; Weinelt, M.; Rück-Braun, K.; Wolf, M.; Tegeder, P., Reversible photoisomerization of an azobenzene-functionalized self-assembled monolayer probed by sum-frequency generation vibrational spectroscopy. *Physical Chemistry Chemical Physics* **2009**, 11 (29), 6242-6248.
  35. Meena, C. R.; Mehra, N.; Adivarekar, R., Electrolyte-Free Dyeing of Textiles with Cationic Reactive Dyes.
  36. Breithaupt, D. E., Simultaneous HPLC determination of carotenoids used as food coloring additives: applicability of accelerated solvent extraction. *Food chemistry***2004**, 86 (3), 449-456.
  37. Stolz, A., Basic and applied aspects in the microbial degradation of azo dyes. *Applied microbiology and biotechnology***2001**, 56 (1-2), 69-80.
  38. Badea, M.; Olar, R.; Cristurean, E.; Marinescu, D.; Emandi, A.; Budrugaec, P.; Segal, E., Thermal stability study of some azo-derivatives and their complexes, Part 2. New azo-derivative pigments and their Cu (II) complexes. *Journal of thermal analysis and calorimetry***2004**, 77 (3), 815-824.
  39. Geng, Y.; Gu, D.; Gan, F., Application of novel azo metal thin film in optical recording. *Optical Materials***2004**, 27 (2), 193-197.
  40. Anitha, C.; Sheela, C.; Tharmaraj, P.; Shanmugakala, R., Studies on Synthesis and Spectral Characterization of Some Transition Metal Complexes of Azo-Azomethine Derivative of Diaminomaleonitrile. *International Journal of Inorganic Chemistry***2013**.
  41. Wang, J., Analytical electrochemistry. *John Wiley & Sons: 2006*.
-