HAWASSA UNIVERSITY

COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCE

SCHOOL OF POST GRADUATE STUDIES

DEPARTMENT OF CHEMISTRY

MASTER'S THESIS ON

GREEN SYNTHESIS OF COPPER OXIDE NANOPARTICLE US SOLANECIO GIGAS LEAF EXTRACT (YESHKOKO-GOMEN) AND APPLICATION IN CATALYTIC DEGRADATION OF CRYSTAL VIOLATE

BY:

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ID NO chemk/108/09

ADVISOR: ERMIAS HAILE (ASS. PROFESSOR)

MARCH, 2025

HAWASSA, ETHIOPIA

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DECLARATION

I hereby declare that the work in this thesis entitled "**Green Synthesis, Characterization of Copper Oxide Nanoparticle using *Solanecio gigas* leaf extract and their application in Catalytic degradation of Crystal violet"**, is my original work. The information derived from the literature has been acknowledged in a list of references provided. No part of this work has been presented for another university or other institution. I take exclusive responsibility for all errors and oversights in this write-up.

Name: Zeheriya Jatoro

Signature: ________________

This thesis has been submitted for examination with my approval as university

Advisor

Name of advisor: Ermias Haile (Assistant professor of analytical chemistry)

Signature: __________________

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ADVISER APPROVAL SHEET-1

(Submission sheet-1)

This is to certify that the thesis entitled "**Green Synthesis, Characterization of Copper Oxide Nanoparticle using *Solaneio gigas"*** submitted in partial fulfillment of the requirements for the degree of Master of chemistry with specialization in analytical chemistry of the graduate program of the department of chemistry, Hawassa University, and is a record of research conducted by Zeheriya Jatoro (ChemK/108/09), under my supervision, and no part of the thesis has been submitted for any other degree or diploma.

The assistance and help received during the course of this study have been duly acknowledged. Therefore, I recommend that it is accepted as a fulfillment of the thesis requirements.

Ermias Haile (Assistant professor of analytical chemistry)

__________________ __________________ __________________

Advisor Signature Date

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EXAMINERS APPROVAL SHEET-2

(Submission sheet -2)

We, the undersigned, members of the board of examiners of the final defense by Zeheriya Jatoro (ID:-chemK/108/09), we certify that we have read and evaluated this thesis"Green Synthesis and Characterization copper oxide Nanoparticle using Solanecio gigas leaf" examined the candidate. We recommended the thesis to be accepted as fulfilling requirement for the degree of Master of science in chemistry.

Name of Majer Adivor signature Date

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Name of Internal Examiner 1 Signature Date

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Name of External Examiner 2 Signature Date

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Name of External Examiner Signature Date

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Final approval and acceptance of the thesis is contingent upon the submission of the final copy of the thesis to the SGS through the DGC/SGC of the candidate‘s department/School. Thesis approved by:

SGC Signature Date

___________________ _______________________ __________________

ACKNOWLEDGEMENT

First I would like to thank the almighty God who gives me strength and hope in all my life again in achieving this work successfully. Secondly, it gives me great pleasure to express my sincere gratitude to my Mrs. advisor Ermias Haile (assistant professor) for his unlimited and constructive guidance, advice, suggestions, comments and friendly approach during this work. Besides of being an excellent advisor, Mrs. Ermias (assistant professor) was as close as relative and good friend for me. Thank you Ermias again.

thridly, I would like to express my deepest gratitude to Centeral Ethiopia Region for giving me this chance to attend the MSc program and Hawassa University department of chemistry for providing whatever necessary and encouraging in my academic journey.

Finally, I am forever grateful to my beloved family for their unlimited support and initiation throughout my life. They are special to me and last, but not least, I would like to extend my deepest gratitude my friends and classmates who were with me during this study.

Thank you much!

DEDICATION

This work is dedicated to my family and my advisor Mrs. Ermias Haile (Assistant professor)

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LIST OF ABBREVIATIONS AND SYMBOLS

CuO NPs	Copper Oxide Nanoparticle
CV	Crystal violet
FTIR	Fourier Transforms Infrared Spectroscopy
MNPS	Metal Nanoparticles
Nm	Nano Meter
NPs	Nanoparticles
NPS	Nanoparticles
Ppm	Parts per million
SgL	Solanecio gigas Leaf
SPR	Surface Plasmon Resonance
SEM	Scanning Electron Microscope
UV-Vis	Ultraviolet Visible Spectroscopy
XRD	X-ray Diffraction Spectroscopy

ABSTRACT

Metal nanoparticles have enhanced much consideration in the field of organic catalysis and catalytic reactions due to the toxicological problems caused by organic dyes to the environment and human health. In the current study, CuO nanoparticle was synthesized through green method using Solanecio gigas leaf extract and, then evaluated for its catalytic degradation activity. The synthesized CuO nanoparticle was confirmed through visual inspection of colour changes and characterized by using UV-Vis, FT-IR, XRD and SEM techniques. From XRD data, the particle sizes of the synthesized CuO nanoparticle were calculated and found to be 38.91nm and appears to be more crystalline in nature. UV-vis analysis of CuO nanoparticles showed continuous absorption in the visible range. Fourier transform infrared spectroscopy (FT-IR) analysis confirmed the presence of several functional groups, particularly hydroxyl, present in the extracts, which may be responsible for capping of nanoparticles. SEM micrographs showed a combination of different shaped and grain size CuO nanoparticle. From the catalytic degradation study, it is possible to conclude that this green route synthesized CuO nanoparticles have high efficiency to degrade Crystal violet. In the degradation of Crystal violet by CuO nanoparticle, maximum degradation efficiency was 90.57% under optimum condition (catalyst dose 0.08 gram, initial concentration 9 ppm, sodium borohydride 0.10 M, reaction time 20 min and pH of 6) The pseudo kinetic study indicates catalytic degradation of Crystal violate in the surface of CuO nanoparticle follows pseudo- zero-order kinetics. The results from this study illustrate that green synthesized CuO nanoparticles offer a cost-effective, environmentally friendly and efficient means for catalytic degradation of dyes.

Keywords: *Characterization Crystal violate, Degradation efficiency, Green synthesis, $NaBH_4$,*

Nanoparticles, Pseudo kinetics study,

1. INTRODUCTION

1.1. Background

Nanotechnology is one of the most active areas of research in the field of modern materials science. Distinctive and unparalleled features of nanoparticles owing to size shape and particles distribution, and their potential applicability have found its way to various dimensions in biotechnology and biomedical sciences. Nano materials (1–100 nm) offer distinctive structural and physico-chemical properties as compared to bulk counterpart owing to the surface to volume ratio [1]. The most recent advancement in nanotechnology has led to the expansion in the synthesis of NPs by different chemical and physical methods. However Efforts are being made to develop simple, non-toxic, biocompatible and eco-friendly nanomaterials through green chemistry approach [2, 6].

In contrast to the conventional chemical approach that has questioned the safety on human health and environment due to the hazardous by-products released, biological methods are gaining utmost attention for use of non-hazardous stabilizers and reducing agents, its reproducibility and purity. Among the biological methods, the use of microbes has proven to be labor-intensive and elaborate process to purify and maintain aseptic conditions for the culturing purpose. Thus, owing to the simplicity, lack of pathogenicity and eco-friendliness, plants have been preferred as the aptcapping and reducing agents for the synthesis of nanoparticles with well-defined size, morphology and monodispersity.

Plants are a reservoir of organic compounds such as phenolics, terpenoids, alkaloids, steroids, coenzymes and others that act as effective capping and reducing agents during nanoparticle synthesis [2–6]. To date, the biosynthesis of NPs is regarded as environmental friendly approach since no toxic agent is involved in bio-inspired approaches [7–10]. Plants are nature's "chemical factories" and vast repertoires of secondary metabolites [11–14] that can be utilized as redox mediator and stabilizer for the NPs. It is reported that the NPs synthesized using plant products/extracts are more stable and the rate of synthesis is easy as compared to conventional techniques since green approaches are eco-benign, cost effective, simple, and easy to per-form and no toxic agent is involved [15–20]. To date, metal and metal oxide NPs have been prepared successfully using green route and as-prepared NPs have been applied in different field. The size and morphology of nanoparticles can be tuned by varying the concentrations of plant extract and metal salt, pH, temperature and reaction time [21]. There is a growing concern regarding environmental pollution by chemical dyes that are released to water bodies from leather, plastic, textiles, food pharmaceutical and cosmetic industries [22]. Most dyes are resistant to microbial and physico-chemical treatments when in High concentrations. As chemical dyes have been reported to be carcinogenic, there is a need for innovative methods to detoxify organic pollutants without any use of high energy input and bulk organic solvents. Metal nanoparticles have found wide applications in medicine, information storage, optical devices, electronic, magnetic, photonics and catalytic reduction of environmental pollutants [23].

Owing to unique properties and applications, copper oxide nanoparticles have become important in nanotechnology and reduction of dyes. *Solanecio giga* is only found in Ethiopia, where it goes by the names "Yeshkoko-Gomen," "Abezenta," and "Nobe." It is also one of the most widely used plants in Ethiopian traditional medicine. The aboveground whole plant is used to cure colic, diarrhea, gout, otitis media, typhus, wound dressing, anti-abortifacient, and mental faculty improvement (stems, leaves, and flowers). Extracts from the roots are also used to treat typhoid illnesses [24].

Solanecio giga belongs to the Senecioneae family of plants, which includes species including *Cacalia*, *Crassocephalum*, *Emilia*, and *Senecio*, all of which can biosynthesis hepatotoxic pyrrolizidine alkaloids. The plant's widespread use as natural medicine, as well as its taxonomic similarities to the well-studied Senecio species, sparked our interest in conducting scientific research on it [25]. There were few scientific studies on this plant. However, the Solanecio giga has not been reported for the synthesis of copper oxide nanoparticles with catalytic potential so far.

Therefore, the present study was synthesis of copper oxide nanoparticles using the leaf extract of Solanecio giga. The Synthesized copper oxide nanoparticle was characterized by (UV–vis) spectroscopy, X-ray diffraction (XRD) analysis, and Fourier transforms infrared (FTIR) spectroscopy. And synthesized copper oxide nanoparticles was employed as ecofriendly catalysts for the degradation of crystal violate and their reaction kinetics was be reported.

1.2 Statement of the Problem

Organic dyes are the main pollutant discharged to the environment especially, from textiles, leather tanning, paper, pharmaceuticals, and plastic industries. This organic dyes are stable, persistent (can stay with in environment for long time). For instance, the textile industry employs various kinds of dyes and finally emanate large amounts of colour full effluents or wastes into water bodies as a result of the poor, uptake of these dyes from industries. The untreated dye effluents or wastes may have adverse effects on aquatic life, including loss of photosynthetic function in plant, and loss of oxygen [26]. Moreover, they are complex in structure and recalcitrant in nature. The need for effective treatment processes for industrial effluents or wastes before their disposal into surrounding water bodies is vital. Numerous techniques of treatment of waste water like adsorption, flocculation, precipitation, coagulation, electron beam treatment, an oxidation and reductions often transfer pollutants or contaminants from one phase to another or generate secondary pollutants that cause particular health complications.

In addition to this, these traditional techniques require complicated procedures, expensive, ineffective and discharge of massive amount of sludge and toxic intermediates to the environment. Therefore, the development of an effective and eco-friendly protocol for the treatment of industrial effluents is needed. For instance, catalytic reductive degradation of organic dye molecules by metal nano particles in the presence of $NaBH_4$ is a relatively fast process and were recently used extensively because of its several advantageous over the other technology. This advantage includes simple, easy treatment procedure, and no secondary pollutant generation. For the catalytic degradation of these organic dyes, there is a need of preparing different nanomaterial's including metal and metal oxide nanoparticles. Various methods are used for the synthesis of nanoparticles, such as physical, chemical and biological methods. The biological method (green method) is the favored technique as it is cost-effective, eco-friendly, and easy method over the other methods.

1.3. Objectives of the study

1.3.1. General objective

The general objective of this study was to Green synthesis of copper oxide nanoparticle using Solanecio gigas leaf extract and application in catalytic degradation of crystal violate.

1.3.2. Specific objectives

The specific objectives of this study were the following

- To synthesis copper oxide nanoparticles by using Solanecio gigas leaf extract as a reducing and stabilizing agent.
- To characterize the synthesized copper oxide nanoparticles using UV-Vis, FT-IR, XRD and SEM.
- To determine the optimum experimental parameters such as pH, catalyst dosage, exposition time and initial concentration of the dyes in the presence of NaBH4 reducing agent.

1.4. Significance of the Study

This study would be useful to understand a way to treat organic dye polluted water before discharging to environment. It gives a direction to prepare cost effective and environmental friendly catalyst, and thus it can initiate different researchers to use green synthesis method of metal nanoparticles by using different plants that can be simple and easily found at their locality.

1.5. Scope of the Study

Under this study; preparation and characterization of copper oxide nanoparticle and its application for catalytic degradation of selected organic dyes were studied. The pseudo kinetics of the degradation of selected organic dyes on the surface of copper oxide nanoparticle catalysts was also investigated.

2. REVIEW OF RELATED LITERATURE

2.1. Nanoparticle

Nanotechnology has gained huge attention over time. The fundamental component of nanotechnology is the nanoparticles. Nanoparticles are particles between 1 and 100 nanometres in size and are made up of carbon, metal, metal oxides or organic matter [27]. The nanoparticles exhibit a unique physical, chemical and biological properties at nanoscale compared to their respective particles at higher scales. This phenomena is due to a relatively larger surface area to the volume, increased reactivity or stability in a chemical process, enhanced mechanical strength, etc. [28]. These properties of nanoparticles has led to its use various applications. The nanoparticles differs from various dimensions, to shapes and sizes apart from their material [29]. A nanoparticle can be either a zero dimensional where the length, breadth and height is fixed at a single point for example nano dots, one dimensional where it can possess only one parameter for example graphene, two dimensional where it has length and breadth for example carbon nanotubes or three dimensional where it has all the parameters such as length, breadth and height for example gold nanoparticles. The nanoparticles are of different shape, size and structure. It be spherical, cylindrical, tubular, conical, hollow core, spiral, flat, etc. or irregular and differ from 1 nm to 100 nm in size. The surface can be a uniform or irregular with surface variations. Some nanoparticles are crystalline or amorphous with single or multi crystal solids either loose or agglomerated [30].Numerous synthesis methods are either being developed or improved to enhance the properties and reduce the production costs. Some methods are modified to achieve process specific nanoparticles to increase their optical, mechanical, physical and chemical properties. A vast development in the instrumentation has led to an improved nanoparticle characterization and subsequent application [30].

2.2. Classification of Nanoparticles

The nanoparticles are generally classified into the organic, inorganic and carbon based.

2.2.1. Organic nanoparticles

Dendrimers, micelles, liposomes and ferritin, etc. are commonly know as the organic nanoparticles or polymers. These nanoparticles are biodegradable, non-toxic, and some particles such as micelles and liposomes has a hollow core, also known as nanocapsules and are sensitive to thermal and electromagnetic radiation such as heat and light [31]. These unique characteristics makes them an ideal choice for drug delivery. The drug carrying capacity, its stability and delivery systems, either entrapped drug or adsorbed drug system determines their field of applications and their efficiency apart from their normal characteristics such as the size, composition, surface morphology, etc. The organic nanoparticles are most widely used in the biomedical field for example drug delivery system as they are efficient and also can be injected on specific parts of the body that is also known as targeted drug delivery.

2.2.2. Inorganic nanoparticles

Inorganic nanoparticles are particles that are not made up of carbon. Metal and metal oxide based Nanoparticles are generally categorised as inorganic nanoparticles

2.2.2.1. Metal based

Nanoparticles that are synthesised from metals to nanometric sizes either by Destructive or constructive methods are metal based nanoparticles. Almost all the metals can be synthesised into their nanoparticles [32]. The commonly used metals for nanoparticle synthesis are aluminium (Al), cadmium (Cd), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), silver (Ag) and zinc (Zn). The nanoparticles have distinctive properties such sizes as low as 10 to 100nm, surface characteristics like high surface area to volume ratio, pore size, surface charge and surface charge density, crystalline and amorphous structures, shapes like spherical and cylindrical and colour, reactivity and sensitivity to environmental factors such as air, moisture, heat and sunlight etc.

2.2.2.2 Metal oxides based

The metal oxide based nanoparticles are synthesised to modify the Properties of their respective metal based nanoparticles, for example nanoparticles of Copper (Cu) Instantly oxidises to copper oxide (CuO) in the presence of oxygen at room temperature that increases its reactivity compared to Copper nanoparticles. Metal oxide nanoparticles are synthesised mainly due to their increased reactivity and efficiency [33]. The commonly synthesised are Aluminium oxide (Al_2O_3).

2.3. Carbon based

The nanoparticles made completely of carbon are knows as carbon based [34]. They can be classified into fullerenes, graphene, carbon nano tubes (CNT), carbon nanofibers and carbon black and sometimes activated carbon in nano size

2.4. Methods of Synthesis of Nanoparticles

In the past few decades, the synthesis and research of nanoparticles has attracted great attention from Scientists in the field of basic and applied research. Metal nanoparticles (MNP) mainly belong to the engineering type of nanoparticles. Eye-catching attraction have been received by these nanoparticles (MNPs) (such as silver, gold, and iron) due to its electronic, catalytic and unique optical properties, it is very attractive in the field of special sensing, bio conjugation and surface enhanced raman spectroscopy. Recently, a complete set of synthetic methods for the preparation of MNP have been developed such as chemical, photochemical and thermal methods. Amongst various procedures, more and more attention is paid to the use of biological and green technologies to produce various MNPs [35]. In MNP, silver nanoparticles play an important role in the fields of biology and medicine. In addition, silver nanoparticles have recently attracted great interest due to their surface plasmon resonance, optical properties [36], catalytic action [37], excellent antimicrobial activity [38-42], etc. In the past few years, researchers have proved that silver nanoparticles have significant antimicrobial effects against infections and diseases, [43].Although many methods are suitable for synthesizing metal nanoparticles, the most commonly used method is to chemically reduce metal ions into nanoparticles and then stabilize them [44]. Most of these methods are very expensive and involve the use of toxic and hazardous chemicals, which may pose environmental potential and biological risks. Therefore, materials scientists and nanochemists look forward to using ecofriendly substances to obtain metal nanoparticles. Nano biotechnology is dedicated to the synthesis of nanostructures from living organisms. In the biological use of nanoparticle synthesis, plants have found applications especially in the synthesis of metal nanoparticles. Using plants to synthesize nanoparticles may be superior to other biological processes that are not harmful to the environment because it eliminates the complex process of maintaining cell culture. If plants or their extracts are used to produce nanoparticles in an extracellular manner, in a controlled manner according to their size, dispersion, and shape, the biosynthesis process of nanoparticles will be more helpful. Plant use can also be appropriately scaled up to synthesize nanoparticles on a large scale [45-48].

2.4.1. Synthesis of Nanoparticles from Microbes

In material chemistry nanoparticles, have important role. It can be used in the control of microorganisms such as bacteria and fungi. Biosynthetic methods can be chemical or physical. On the bases of location where nanostructures are formed for example stutzeri which is a pseudomonas can be isolated from Copper ores can reduce Cu ions and accumulate silver particles and these nanoparticles are 16 to 40 nm and its diameter is 27 nm. Another example is magneto tactic bacteria, which produce magnetite Fe3o4 or reignite Fe3s4. The antibacterial agent silver can kill around 650 kinds of pathogenic microbes and Copper have electrical, optical and biological properties and can be used in drug delivery, imaging, catalysis and bio sensing [49, 50]. The biosynthetic metal such as silver, gold, copper and zinc can fight against Gram-positive bacteria and Gram-negative bacteria such as Bacillus subtilis, Escherichia coli and Staphylococcus aureus . Copper nanoparticles have received more attention due to green synthesis of plants, bacteria, fungi and yeasts [51]. The green synthesis of CuNps of Streptomyces endophytes was observed to have antimicrobial activity against four plant pathogenic fungi such as Alternaria , Streptomyces , Pythium and Aspergillus niger . Chamomile flower were used to synthesize MgO and MnO2NPs. Green synthetic ZnONPs and TiO2NPs and lemon fruit extract showed antibacterial activity against Dickeya dadantii at room temperature, which is The pathogen of sweet potato stem, and root rot [51-53].

2.4.2. Synthesis of Nanoparticles from Plants

For the synthesis of nanoparticles, plant extracts are used as a reducing agents and it has great advantage over biological processes because of the fact that they eliminate complex cell culture and maintain processes. The plant nanoparticles synthesis is cost effective and environmentally friendly and it is safe for humans. Different size and shapes of Copper, gold, platinum and titanium nanoparticles are synthesized from different parts of plant materials such as extracts from fruits, bark, pericarp and roots [54]. The synthesis of various nanoparticle includes collecting required plant parts and then washing it with distilled water to remove epiphytes and necrotic after than dry and clean plant source in the dark for 10 to 15 days and then use a household mixer to pulverize it then 10 gram of dried powder is boiled with deionized distilled water of 100 ml. Then filter the resulting solution thoroughly until there are no insoluble in broth. Shortly thereafter, collect the filtrate and add CuNO3 solution with a final concentration of 1mM to the filtrate [55, 56]. Then after adding, the mixture will sometimes oscillate in shaking incubator, and the color of the mixture will soon change due to the reduction of pure Copper ions to CuO and it is necessary to regularly monitor the obtained samples in Uv-visible spectrum of the solution to identify the characteristic absorption characteristics of the nanoparticles, which indicates the formation of nanoparticles [57]. Green nanoparticles from different plant species have also identified for example root extract of Morinda citrifolia , Phoenix dactylifera inflorescence extract of Mangifera, aloe vera extract, latex of Jatropha gossypifolia , fruit extract Phyllanthus emblica , Aqueous rosemary extract was used to synthesize the Mg-flowers having antibacterial potentials [58]. The quality, size and shape of these green synthetic NPs depend on many factors, such as plant extract concentration and its composition, metal salt concentration, reaction pH, reaction temperature., titanium dioxide Nps synthesized from fresh lemon fruit extract have antibacterial activity within 8 minutes of reaction time. O. sanctum leaf extract can reduce Copper ions to nano-Copper particles and it has bacterial activity and size range from 4 - 30 nm.

3. MATERIALS AND METHODS

3.1. Chemicals and reagents

The chemicals and reagents used in this work was (Copper Nitrate Trihydrate Cu $(NO_3).3H_2O$ (95 % Sigma-Aldrich), used for synthesis of CuO NPs as metal ion precursor. Crystal violate (Samir Tech-Chem, Ltd) dye was used for the evaluation of catalytic activity of the CuO NPs, Sodium borohydride ($NaBH_4$ (97% extra pure Merck)), ethanol (97% extra pure Sigma-Aldrich), NaOH (Abron Experts-133 001, (India)) and 37% HCl (Sigma-Aldrich) was used for adjusting pH of the sample. Distilled water was used throughout the experiment to prepare plant extract and wash them

3.2. Instrument and Apparatus

The leaf sample and all other chemicals were weighed on a digital electronic balance (Model JA103P,) with 160 gm loading capacity. The extent of the degradation of the dyes was monitored using UV-Vis Spectrophotometer (CRCIL 1021). After degradation, separating the dispersed Copper oxide nanoparticles from the treated solution was done using 80-2 centrifuge with max speed 5000 rpm. Fourier Transform Infrared Spectroscopy (65 FT-IR Perkin Elmer spectrum), Ultraviolet-Visible Spectrophotometer (SM-1600 spectrophotometer), powder X-ray Diffractometer (Shimadzu XRD-7000S) and scanning electron microscopy (JEOL/EO-JCM-6000 plus) was used for characterization of synthesized Copper oxide nanoparticles.

3.4. Preparation of *Solanecio gigas* Extract

Solanecio giga was collected from central Ethiopian region mareko special woreda, washed with tape water first and then with distilled water, and dried at room temperature for 10 days. Subsequently the dried solanecio gigas leaf was grinded by an electric girder to obtain a fine powder. Following this 20 gram of the powdered solanecio giga was mixed with 200 ml of distilled water in an Erlenmeyer flask and heated at 80 ^{0}c while stirring using magnetic stirrer for 30 minutes. Finally the heated solanecio giga solution was allowed to cool for 20 minutes and filtered using whatman No.1 filter paper to obtain a fine solanecio gigas extract solution.

3.5. Green synthesis of copper oxide nanoparticle

The green root synthesis of CuO NPs was done according to the procedure in the literature with slight modification [59]. 20 mL Solanecio gigas aqueous extract was vigorously mixed with a homogeneous solution of copper metal precursor (0.1 M, 80 mL) for 4 h at 80 °C until a black colour was obtained, and then cooled to room temperature. Finally, the formed like product was scratched and calcined in a muffle furnace at 400 °C for 2 h, yielding black-colored nanomaterial.

3.6. Characterization of Copper oxide nanoparticle

The synthesized copper oxide Nanoparticle was characterized using Fourier Transform Infrared Spectroscopy (FT-IR), Ultraviolet-Visible (UV-Vis) Spectroscopy, powder X-ray Diffractometer (XRD) and Scanning electron microscopy. The crystalline phase of the synthesized copper oxide nanoparticles were identified by X-ray diffractometer (Shimadzu XRD-7000S). The patterns will run with Cu-filtered CuKα radiation ($\lambda = 1.54059$ Å) energized at 40 kV and 15 mA. The samples will be measured at room temperature in the range of $2\theta = 10^\circ$ to 60°. From the XRD data obtained, the crystalline size of sample was calculated using Debye-Scherrer"s Equation as shown below:-

$$D = \frac{k\lambda}{\beta cos\theta} \qquad 1$$

Where,

D = Average crystalline size

K = Scherrer constant (usually 0.9)

λ = Wave length of X-ray source, Cu kα radiation (1.5406 Å)

β = Full width at half- maximum (FWHM) of the diffraction in radian

θ = Bragg"s diffraction angle

β obtained from the XRD data was converted to radian unit using the equation shown below:-

$$\beta = \frac{FWHM\ in\ 2\theta \times \pi}{180^\circ} \qquad 2$$

FT-IR analysis of prepared leaf extracts and synthesized nanoparticles will be done using Spectrum 65 FT-IR spectrometer (Perkin Elmer). The FT-IR analysis will be carried out to find out the functional groups present in the nanoparticles. It is also applied to examine the possible significant functional groups present in the leaf extract that are responsible for reducing and capping in the preparation of CuO Nanoparticle with the scanning range of 4000 cm^{-1} to 400 cm^{-1}. For the FT-IR characterization, the sample was mixed with solid KBr uniformly and properly, which was compressed to settle down on a thin transparent film and this thin transparent film was used for FT-IR analysis which was kept in the chamber of the instrument for scanning. Double beam UV-Vis spectrophotometer (SM-1600 spectrophotometer) will be used to obtain the absorption spectrum of the synthesized nanoparticles. The optical absorption was measured in wavelength range of 200-800 nm. 5 mg of synthesized nanoparticles was dispersed in 50 mL of distilled water, and the absorbance data was recorded as a function of wavelength. Distilled water was used as a reference during the measurement.

Scanning electron microscope is one of the most promising techniques for generating particle distribution profiles as well as surface characteristics with the possibility to visually re-evaluate the data by re-assessing the particle. Scanning electron microscopy (JEOL/EO-JCM-6000 Plus) was taken to examine the morphology and dimension of the green route prepared CuO nanoparticle.

3.7 Catalytic degradation performance of Copper oxide Nanoparticles

3.7.1 Catalyst Dose

For the optimization of catalyst dose, catalyst doses from 0.02 gm to 0.12 gm with a gap of 0.020 gm was taken per 25 mL of 9 ppm of crystal violate with constant value of the other parameter and then the catalytic degradation efficiency was calculated.

3.7.2 Initial Concentration of the Dye

To investigate the effect of initial concentration of dyes on catalytic degradation efficiency, different initial concentration 1, 3, 6, 9 and 12 ppm crystal violate was used whereas, other parameter remain constant.

3.7.3. Reaction Time

For the investigation of the total time required for the total degradation of the dyes, a reaction of 5 minute to 35 within 5 minutes gap of six trials was be taken. The other parameters optimized before, catalyst dose and initial concentration of the dyes was applied during the optimization of reaction time.

3.7.4. pH of dye

To study the effects of pH, for the degradation, the other parameters optimized was kept constant and the pH was varied from pH 2 to pH 12 and the optimum pH was investigated.

3.7.5. Concentration of reducing agent NaBH4 catalytic degradation

The effects of concentration of reducing agent ($NaBH_4$) on the degradation of crystal violate was investigated. To determine the optimum concentration of reducing agent for the best catalytic degradation, various concentration of reducing agent was tested from 0.01 to 0.18 M in a fixed concentration of dyes solution, catalyst dose, pH and reaction times.

3.8. Determination of Degradation Percentage

Degradation percent of dye solution was calculated by taking the absorbance values recorded at λmax of 590 nm before and after catalytic degradation. The equation was provided as shown:-

$$Degradation\ percentage = \frac{A0 - At}{A0} * 100 \qquad (3)$$

Where:

Ao = initial absorbance of dyes solution before exposed to sunlight

At = absorbance of dye solution at time t

3.9. Kinetics Study

In this investigation all measurement was done under the optimized experimental conditions. In doing this, calibration curves were constructed for the dye which were aimed at calculating the concentrations of the dye after degradation at different time interval. Then constant concentration (initial concentration with high degradation efficiency) was prepared for both dyes and the extent of the degradation was studied within 5 minute intervals. Then the concentration of dye were calculated by applying Beer-Lambert law

$$A = \in bC \qquad (4)$$

Where A – Absorbance

∈ - Molar absorptivity constant

b – Path length

C – Concentration

This equation is related with $y=mX+b$ and from absorbance versus concentration data slope (m) were calculated and used to calculate the concentration after degradation. Finally pseudo zero order, pseudo first order and pseudo second order kinetics were investigated.

3.10. Instrumental Calibration

The standard stock solutions of dyes were taken for calibration of the instrument for dyes used for experiment. For the instrument calibration, first 1000 ppm of stock solution of each dye was prepared and an intermediate standard solution containing 100 ppm was prepared in 500 mL volumetric flask from the standard stock solution that contained 1000 ppm of interest to be analyzed. Then the intermediate standards were diluted with distilled water to obtain five working standards of each dye of interest for calibration purpose. The objective of calibration of the instrument was to see the linearity of the instrument response and for calculation of the remaining concentration of the dye after degradation in investigating the kinetics of the degradation experiment.

4. RESULTS AND DISCUSSION

4.1 Synthesize of copper oxide nanoparticle

In this study, copper oxide nanoparticle was successfully synthesized by a simple and inexpensive method using aqueous extracts of the Solanecio gigas extract Figure 1. The aqueous extracts of Solanecio gigas initially possessed black brown colour. However, on adding the extracts to the aqueous copper nitrate solution, there was color change with in 1 hour and yielded a deep black solution, indicating the formation of the copper oxide nanoparticle.

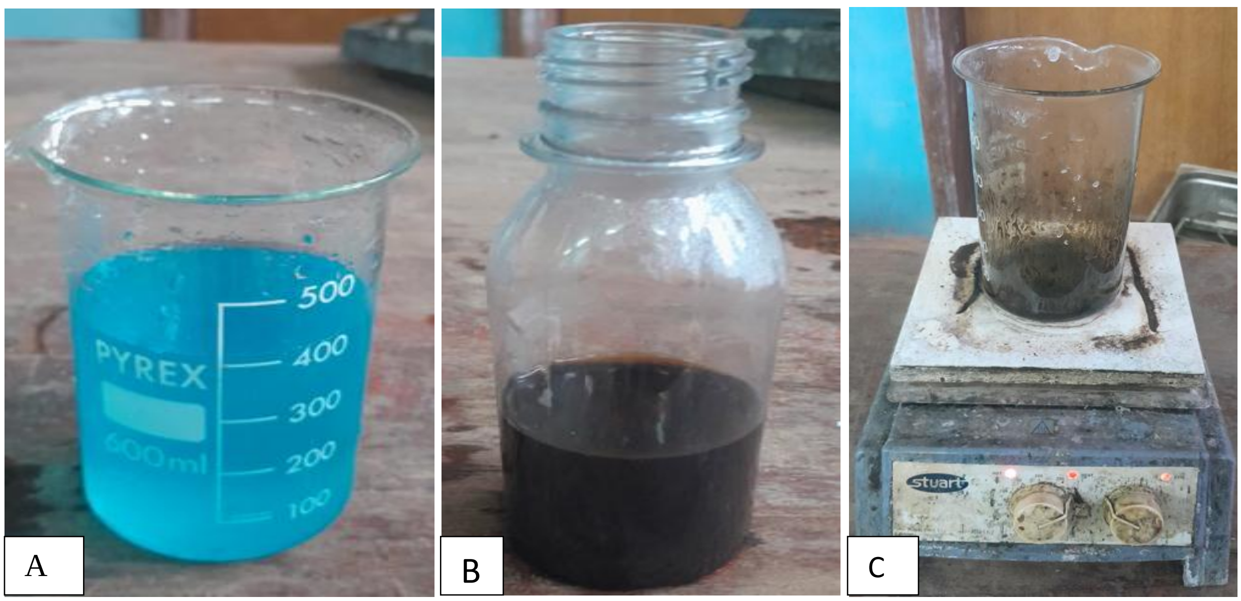


Figure 1: Synthesis of copper oxide nanoparticle (A) aqueous of copper nitrate (B) Solanecio gigas extract (C) copper oxide nanoparticle

4.2 Characterization of Synthesized Copper Oxide Nanoparticles

4.2.1 X-ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) analysis was employed to investigate the surface crystallinity of the green synthesized copper oxide nanoparticle. X- ray diffraction was used to examine the phase purity and crystallinity of green-route synthesized CuO NPs (Figure 2). The XRD analysis of Solanecio gigas leaf extract-mediated greenly synthesized CuO NPs has confirmed the crystalline structure of the nanoparticle. Figure 2 shows typical XRD pattern of green synthesized CuO NPs diffraction peaks at 2 θ of 30.82◦, 35.46◦, 38.66◦, 48.77◦ and 58.32◦, and these diffraction peaks were matched to (1 1 0), (0 0 2), (1 1 1), (2 0 2), and (2 0 2) CuO NPs. These diffraction peaks agree well with JCPDS card 89–2529, confirming that the CuO NPs synthesized are crystalline and monoclinic in structure. The average particle size of the nanoparticle is calculated by the Debye-Scherrer equation, as shown in equation (3) is the average crystalline size, K is the Scherrer constant (usually 0.9), is the X-ray source's wave length, Cu k radiation (1.5406), is the diffraction's full width at half maximum (FWHM) in radians, and is Bragg's diffraction angle, and it was found to be 38.91 nm.

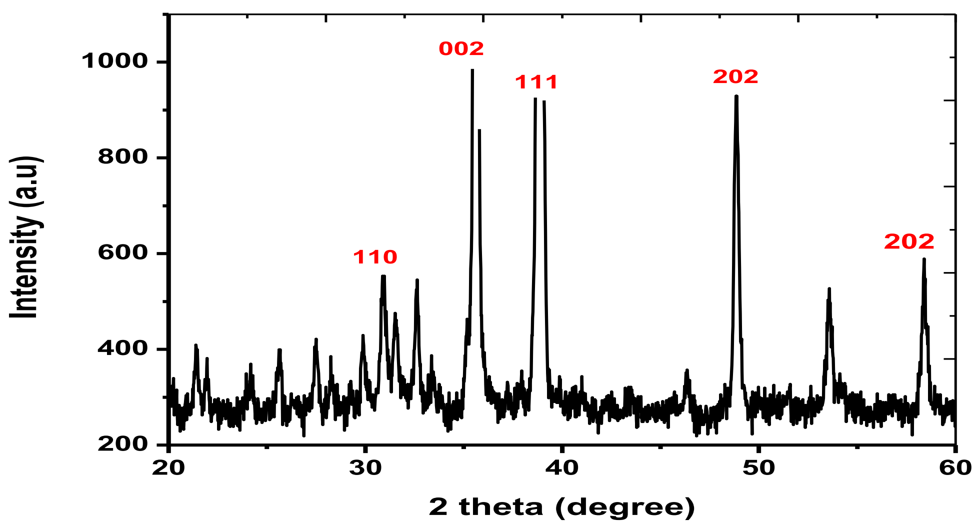


Figure 2 XRD pattern of CuO NPs

4.2.2 Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

Fourier Transform Infrared Spectroscopy, the technique provides information on the interaction between the phytochemicals available in the plant extracts and metal ions responsible for the production and capping of the copper nanoparticles. This was confirmed in terms of the individual band intensities observed in the extracts and their corresponding nanoparticles**.** Figure 3 shows the FT-IR spectrum of the synthesized CuO NPs and Solanecio giga leaves extract. The FT-IR spectrum of the leaf extract indicates intense bands at 3479 cm -1 (O-H stretching vibrations), 1637 cm^{-1} (C=C stretching vibrations), 1357 cm^{-1} (C–O stretching of the ester group), 1046 cm^{-1} (due to C–O bonds). The FT-IR spectrum of CuO NPs displays intense bands at 3455 cm $^{-1}$ (O–H stretching vibrations), 2935 cm^{-1} (C–H and CH2 vibration of aliphatic hydrocarbons), 1750 cm$^{–1}$ (C=C stretching vibrations), and 1046 cm$^{–1}$ (due to C–O bonds stretch of primary alcohol), as well as absorption bands at around 789 cm-1 which corresponds to the Cu-O bond. The nanoparticles possessed similar absorption peaks like that of the extracts, the differences in intensities suggest the importance of functional groups in the reduction and capping processes. From result, it was concluded that the soluble elements present in Solanecio gigas leaves extract could have acted as capping agents preventing the aggregation of CuO NPs.

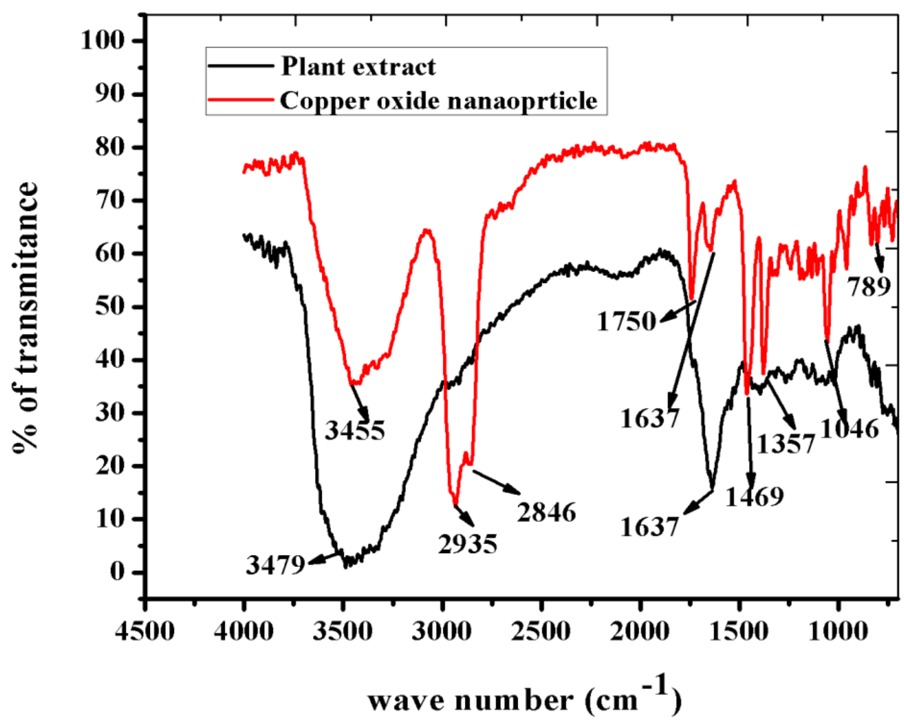


Figure 3: FTIR spectrum of green synthesized Cu NPs (B) and Solanecio giga leaf extract (A).

4.2.3 Ultraviolet-Visible Spectroscopy Analysis

Solanecio giga leaf aqueous extract mediated green synthesized CuO NPs was characterized by Uv-Visible spectroscopy. Optical properties of green synthesized CuO NPs was analyzed by measuring its absorbance from 200 nm to 800 nm wave length range. The brown color leaf extracts were converted to a deep black colored solution after the addition of leaf extract to copper Natrate solution. The UV-vis spectrum of CuO NPs synthesized using aqueous Solanecio giga leaf extract showed continuous absorption in the visible range (Figure 4), this suggests that the synthesized CuO NPs might be polydispersed.

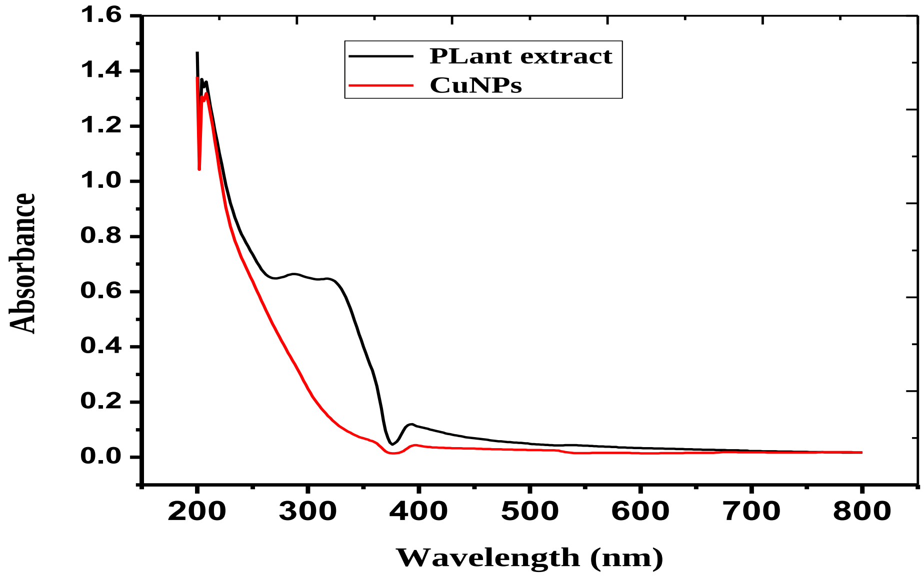


Figure 4: UV-Vis spectrum of green synthesized CuO NPs

4.2.4 Scanning Electron Microscope (SEM) Analysis

The SEM pictures for the synthesized of CuO NPs are shown in Figure 5. The SEM pictures showed that the particles are not uniformly distributed and are various in shapes and size. This may be due to the presence of capping agents present in the plant extract. The analysis was done at two different magnifications, which were aimed at observing the morphology of the synthesized CuO NPs.

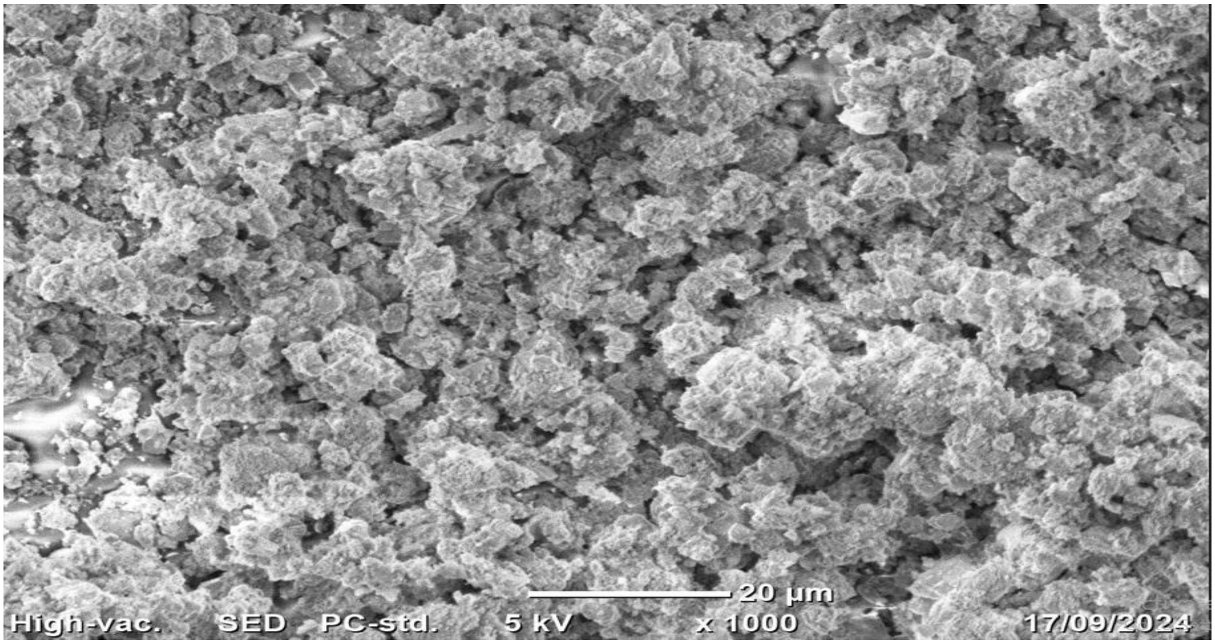


Figure 5: SEM images of green synthesized CuO NPs

4.3 Catalytic Activity of copper oxide nanoparticle

Catalytic activity of the synthesized copper oxide nanoparticle was evaluated by the degradation of Crystal violet. Dyes degradation was visually detected by gradual change in color to colorless solution. The degradation process supported by copper oxide nanoparticle was studied by varying the parameter like initial concentration of dyes, reaction time, pH and dose of nanoparticle. Preliminary screening for the occurrence of degradation was done by observing the color disappearing of dyes aqueous solution and then calculating the present of degradation from the absorbance values measured before and after degradation.

4.3.1. Effect of load of catalyst

The degradation outlines of aqueous Crystal violate (9 ppm) solution over the different copper oxide nanoparticle amounts along with NaBH4 (0.10 M) solution is shown in Figure 6. It was observed that as copper oxide nanoparticle dose increased, the percentage degradation of Crystal violate dye concentration increased. The rate of degradation is very effective with increase in the catalyst amount and this is due to increase in total active sites on catalyst surface. It was seen that the degradation efficiency increases as the copper oxide nanoparticle loading increases from 0.020 to 0.08 gm. This is attributed to the higher availability of surface active sites for the adsorption of BH_4^{-1} ions and the dye molecules with the increase in CuO NPs dose. Therefore, the catalyst loading of 0.08 gm was taken for investigating the other reaction parameter.

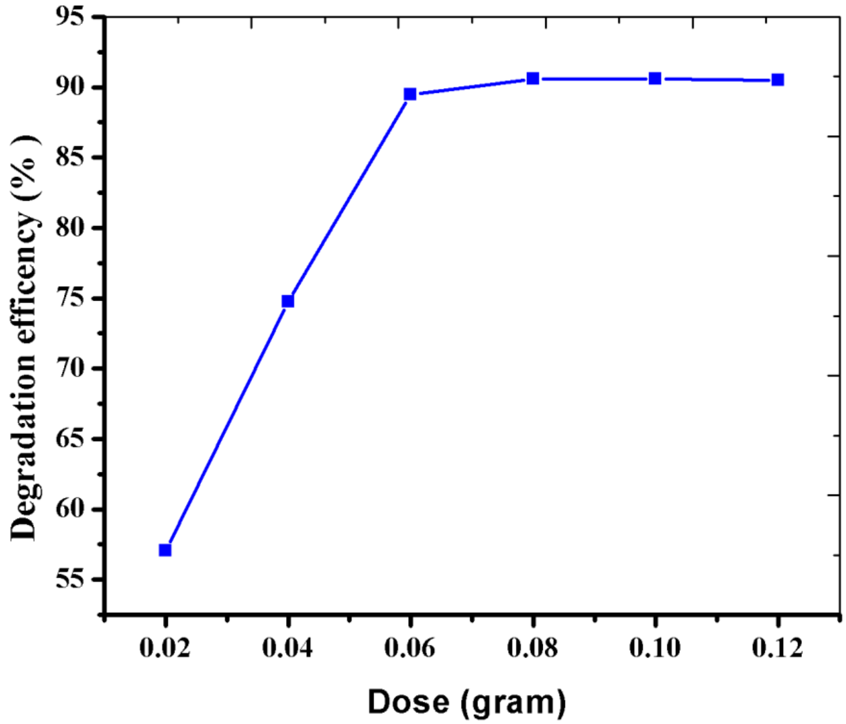


Figure 6 Effect of catalyst dose

4.3.2 Initial concentration of crystal violate

In this study, five aqueous Crystal violate solutions of different concentrations ranging from 1 to 15 ppm were used with fixed concentration of other parameters. As can be seen, from Figure 7 the degradation efficiency increases with increase in concentration from 1 to 9 ppm therefor 9 ppm Crystal violate were taken for other investigation. The rate of degradation decreased with increasing concentration of dye, this decrease in rate is due to the slowing down of the electron transfer process on the nanoparticle surface between $NaBH_4$ and dye.

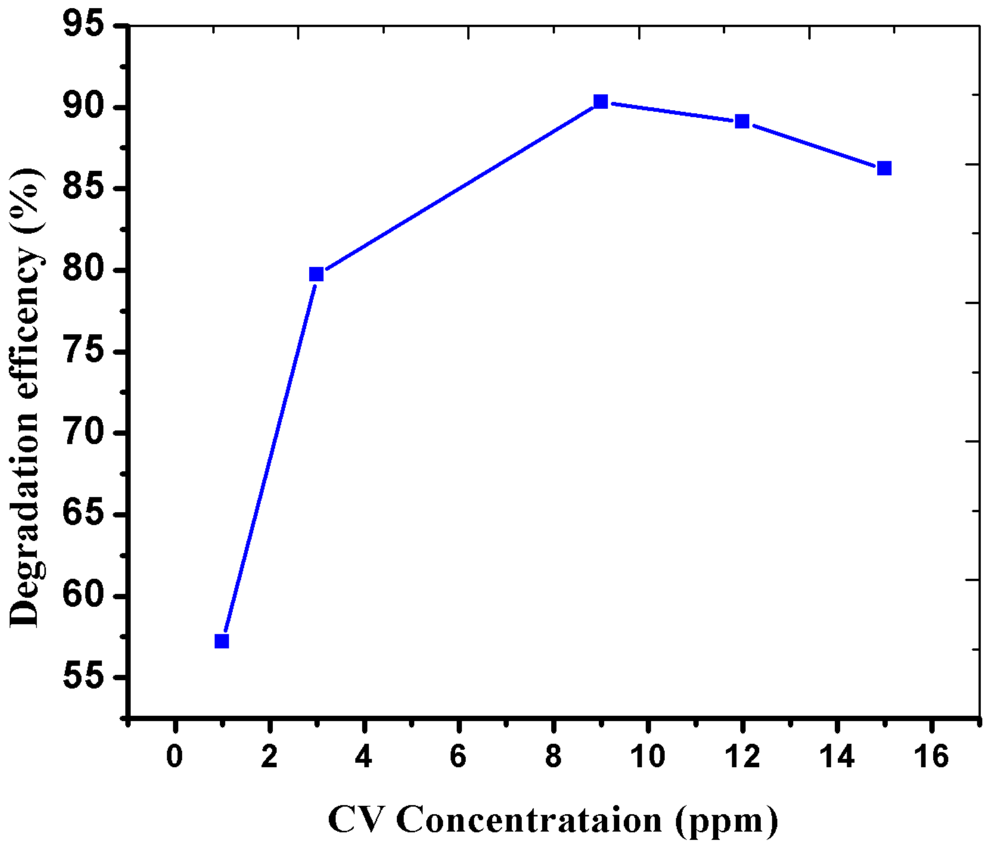


Figure 7 Effect of initial concentration

4.3.3. Effect of NaBH4 concentration

The concentration of $NaBH_4$ was varied to determine the fixed concentration for optimum degradation of Crystal violate. In this case, the nanoparticle dose, Crystal violate concentration was fixed, and $NaBH_4$ concentration was varied from 0.02 to 0.1 M. It was found that the extent of degradation increases upon increasing $NaBH_4$ concentration from 0.01 to 0.10 M Figure 8. The degradation reaches a maximum in the presence of 0.10 M $NaBH_4$ at the prescribed reaction time. Therefore, 0.10 M was chosen as the critical $NaBH_4$ concentration. This observation suggests that an appropriate concentration of $BH_4{}^{-1}$ ions is imperative for achieving the best degradation efficiency of the nanoparticle. In fact, the higher concentration of the $NaBH_4$

enlarged local electron density on the surface of CuO NPs could lead to an increased reaction rate .

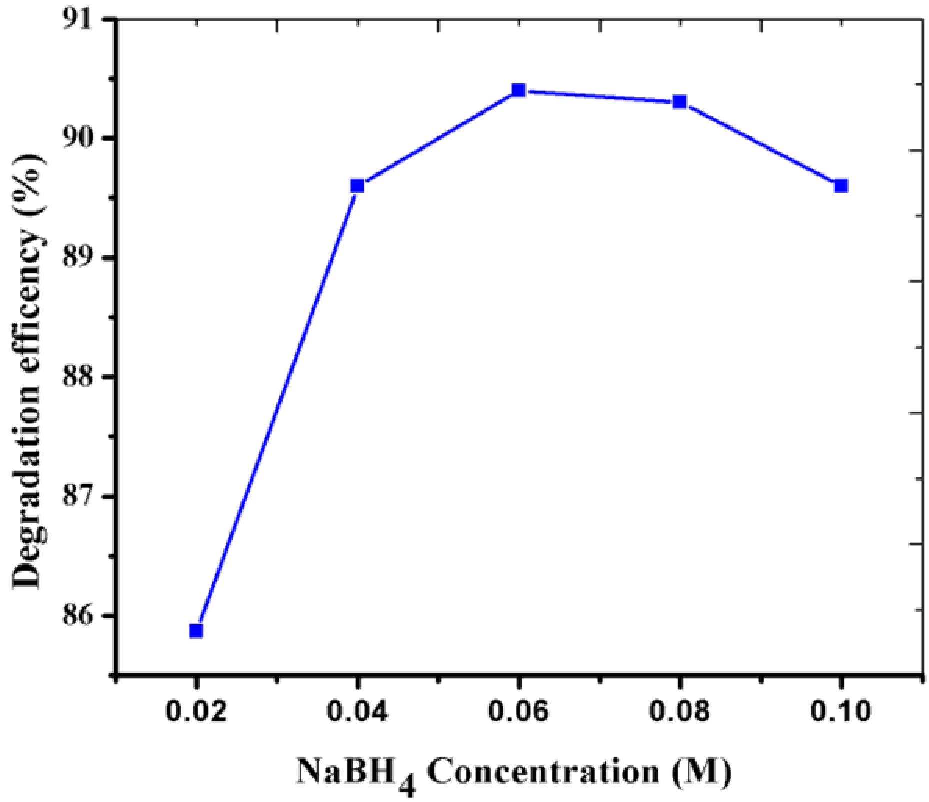


Figure 8 effect of sodium borohydride concentration

4.3.4. Effect of reaction time

The response thus for the reaction time is shown in Figure 9. Degradation efficiency of increased with increase in reaction time and reached a maximum after 20 minute. The maximum Crystal violate degradation was 90.57 % after 20 min of reaction time. In addition, the efficiency seems to have constant above 20 minutes but further reaction time not result in increasing of degradation efficiency.

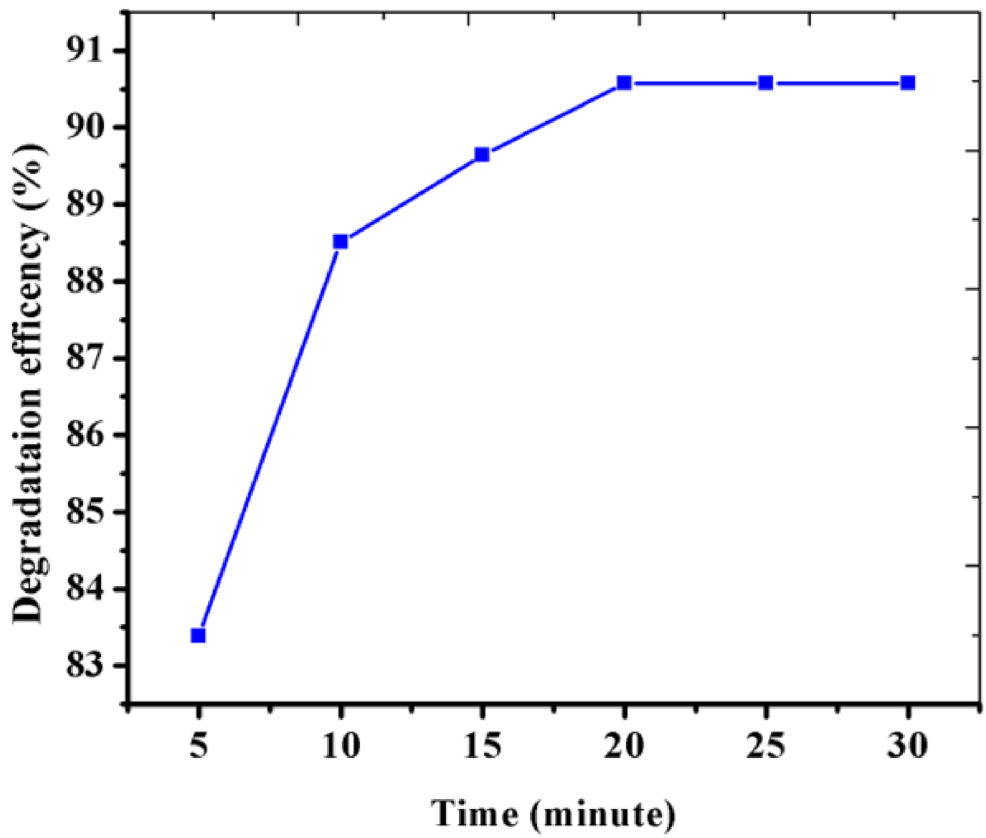


Figure 9 Effect of reaction time

4.3.1.6 Effect of pH

The effect of pH for Crystal violate degradation was studied in the range of 2–10 at 9 ppm initial concentration, 0.08 gram of copper oxide nanoparticle , the response thus obtained is shown in Figure 10. The maximum degradation was achieved at pH 6 (90.52%) dye degradation was achieved and then, by increasing pH to 10, the percentage degradation decreased gradually to 86.06 %. The decrease in higher pH might be due to the formation of copper hydroxide, the active sites of copper oxide nanoparticle were occupied by hydroxides, hence rendering the reduction capacity of copper hydroxide.

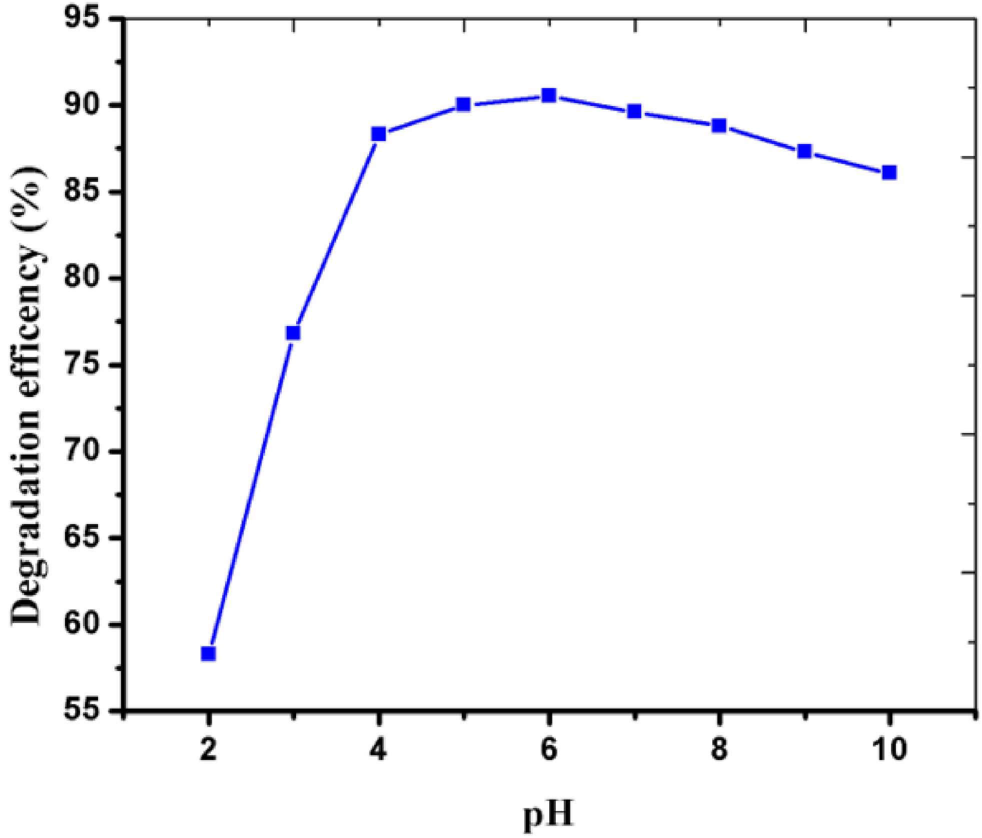


Figure 10 Effect of pH

4.4. Kinetics Studies

4.4.1 Zero order kinetics

The plot of pseudo zero -order kinetics model for the dyes is shown on Figure 11. In zero order-pseudo kinetics study, CuO NPs obtained a high correlation coefficient close to unity (0.7527) for crystal violate degradation, compared to other models, which indicates it, seems to follow pseudo zero - order kinetics. A pseudo zero-order reaction is thus, observed for saturation coverage on the surface of the catalyst and degradation rate is independent of the dye concentration.

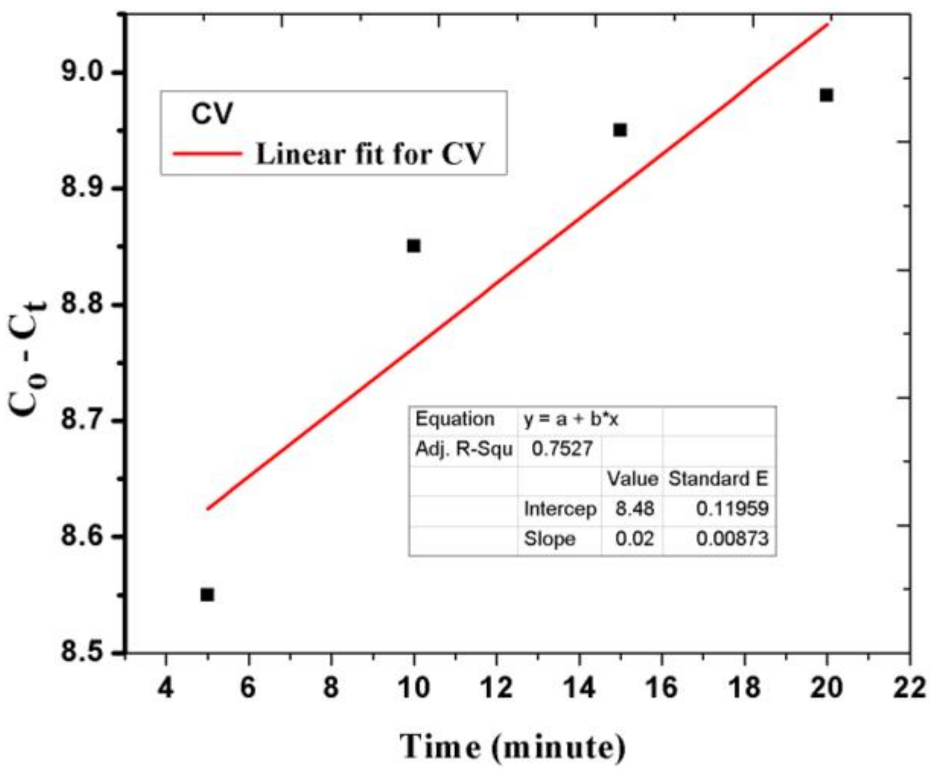
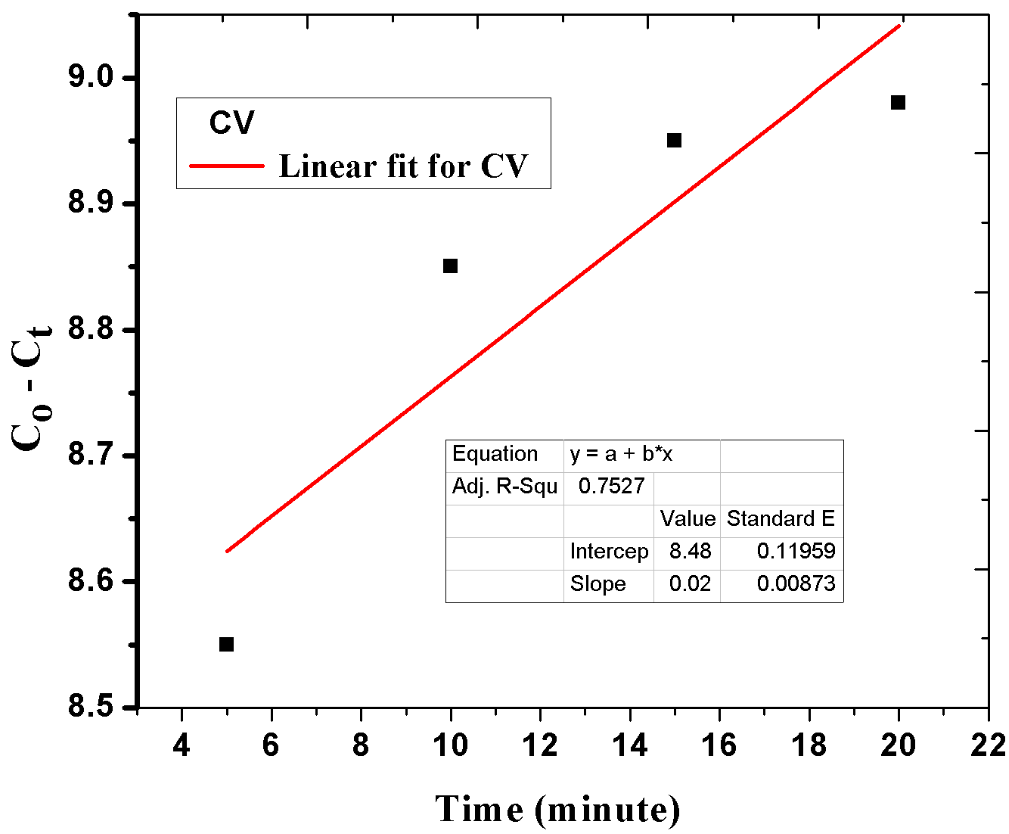


Figure 11 pseudo zero -order kinetics model



4.4.2 Pseudo first-order kinetics

In investigating the pseudo-first order kinetics. The linear graph with correlation coefficient of 0.954 was obtained for crystal violates degradation by CuO NPs. It indicates the catalytic degradation of crystal violate on the surface of CuO NPs catalyst seems to follow pseudo first order kinetics i.e. rate of degradation and concentration of dye are directly proportional.

Figure 12 pseudo first - order kinetics model

4.4.3 Pseudo second-order kinetic

Pseudo second-order kinetics was also investigated for the catalytic degradation of crystal violate. Figure 13 shows graph of pseudo second-order kinetics of both dyes. Relative to the other pseudo kinetics model (pseudo zero order and pseudo first-order) the correlation coefficient of this figure is less which suggest, that the catalytic degradation of dye not fit this model.

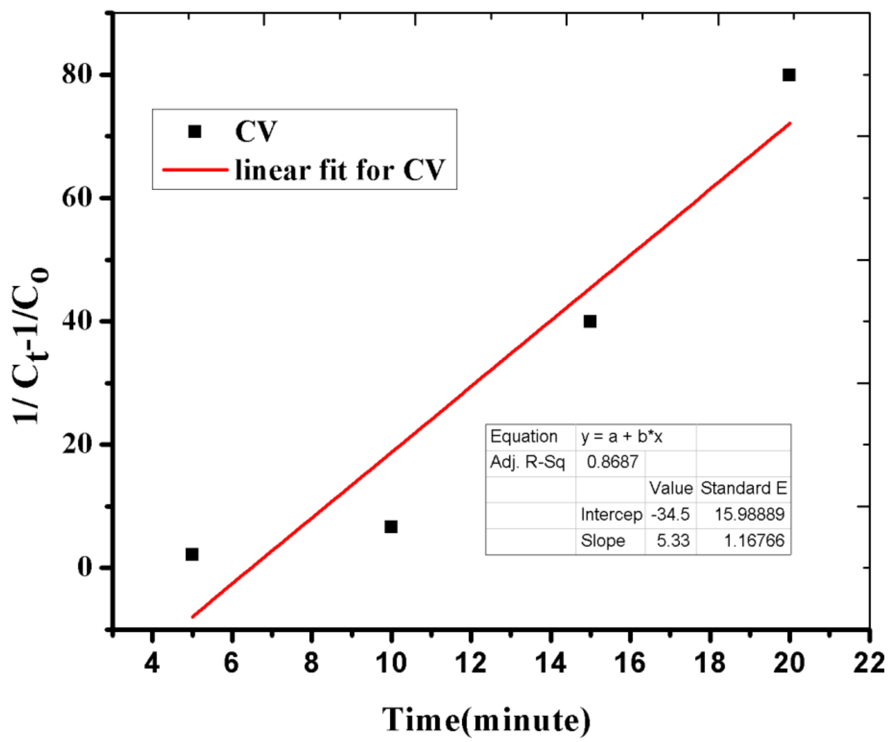


Figure 13 pseudo second - order kinetics model

5. CONCLUSION AND RECOMINDATION

5.1. Conclusions

Under this study, copper oxide nanoparticles were successfully synthesized by green synthetic pathway and applied for catalytic degradation of Crystal violate. The characterization of the Copper nanoparticle was done by different analytical techniques such as UV- visible, FT-IR, XRD and SEM. XRD analysis confirmed the synthesized copper oxide nanoparticle was crystalline in nature. Fourier transform infrared spectroscopy (FTIR) analysis indicated the presence of various functional groups, particularly hydroxyl, present in the extracts, which may be responsible for reducing and capping of the synthesized nanoparticles. The catalytic degradation was found to be strongly dependent on catalyst dose, reaction time, pH and initial concentration of the dyes. In the degradation of organic dye and crystal violate by copper oxide nanoparticle, maximum degradation efficiency was 95.70% under optimum condition (catalyst dose 0.080 gram, initial concentration 9 ppm, sodium borohydride concentration 0.10 M, reaction time 20 min and pH of 6). The pseudo kinetic study indicates catalytic degradation of organic dye in the surface of copper nanoparticle follows pseudo zero-order kinetics. The results from this study demonstrate that green synthesized copper oxide nanoparticle offer a cost-effective environmentally friendly and efficient means for catalytic degradation of dyes.

5.2 Recommendation

There are areas that need more work and not covered by this study. The idea that have to be recommended for further studies are:

- The application of copper oxide nanoparticles as a catalyst in degrading the commercial dye in wastewater treatment has to be included in the future study.

- The determination and characterization of intermediate product formed during the degradation of dyes also need further studies.

- Green Snthesis copper oxide nanoparticles by different plant extract

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