

**GREEN SYNTHESIS OF COPPER DOPED TIN OXIDE
GRAPHITE CARBON NITRIDE NANOCOMPOSITE FOR
VISIBLE-LIGHT PHOTOCATALYTIC DEGRADATION OF
METHYLENE BLUE DYE**



Endeshaw Beko Legesse

A Thesis Submitted to The department of Chemistry

College of Natural Science

Presented in Partial Fulfillment of the Requirement for

The Degree of Master's in Chemistry(Inorganic)

SALALE UNIVERSITY

May 2024

Fitche, Ethiopia

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Name of main Advisor: Gezehagn Faye(Asso. Professor)

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Approval of Board of Examiners

We, the undersigned, members of the Board of Examiners of the final open defense by Endeshaw Beko Legesse have read and evaluate his/her thesis entitled “Green synthesis of Copper doped tin oxide graphite carbon nitride nano composite for visible- light photocatalytic degradation of methylene blue dye” and examined the candidate. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirement of the Degree of Master in Chemistry (Inorganic)

Gezahegn Faye (Asso. professor) _____

Name of Advisor

Signature

Date

Chairperson

Signature

Date

Internal Examiner

Signature

Date

External Examiner

Signature

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DECLARATION

I hereby declare that this MSc Thesis is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis have been duly acknowledged

Name: Endeshaw Beko Legesse

Signature: _____

This MSc dissertation has been submitted for examination with my approval as thesis advisor/ dissertation Supervisor.

Name: Gezahegn Faye (Asso. Professor)

Signature: _____

Date of submission: _____

Advisor's approval sheet

To Chemistry department Subject: Thesis Submission This is to certify that the thesis entitled green synthesis of copper doped Tin Oxide graphite carbon nitride nano Composite for visible-light photo catalytic degradation of methylene blue dye submitted in partial fulfillment of the requirements for the degree of Master's degree in inorganic chemistry, the Graduate program of the department of chemistry, and has been carried out by Endeshaw Beko Id. No –RM0079/14, under my/our supervision. Therefore, I/we recommend that the student has fulfilled the requirements and hence hereby he/she can submit the thesis to the department.

Gezehagn Faye (Asso. Professor)

Name of major Advisor

Signature

Date

ACKNOWLEDGEMENT

I would like to express my deepest gratitude to my thesis advisor Gezehagn Faye (Asso. Professor) for his guidance, support and expertise throughout the research process. His valuable feedback and encouragement have been instrumental in shaping this thesis.

I am grateful to Salale University for providing the resources and facilities needed to conduct this research.

I would like to acknowledge the support of my family and friends who have stood by me and offered their encouragement during this challenging journey.

Lastly, I would like to thank all the participants who took part in this study, whom this research would not have been possible. Thank you to everyone who has played a part in the completion of this thesis.

List of Acronyms and Abbreviations

CB-Conduction band

DPPH-2,2-diphenayl-1-picryl hydrazyl

ECB-Edge potential conduction band

EVB-Edge potential valance band

EV-electro volt

FTIR-Fourier transforms infrared

MB-Methylene blue

NHE-Normal hydrogen electrode

NP-Nano particle

ROS-Reaction oxygen species

RSA- Radical Scavenging Activity

SEM-Scanning electron microscopy

VB-Valance band

XRD-X-ray diffraction

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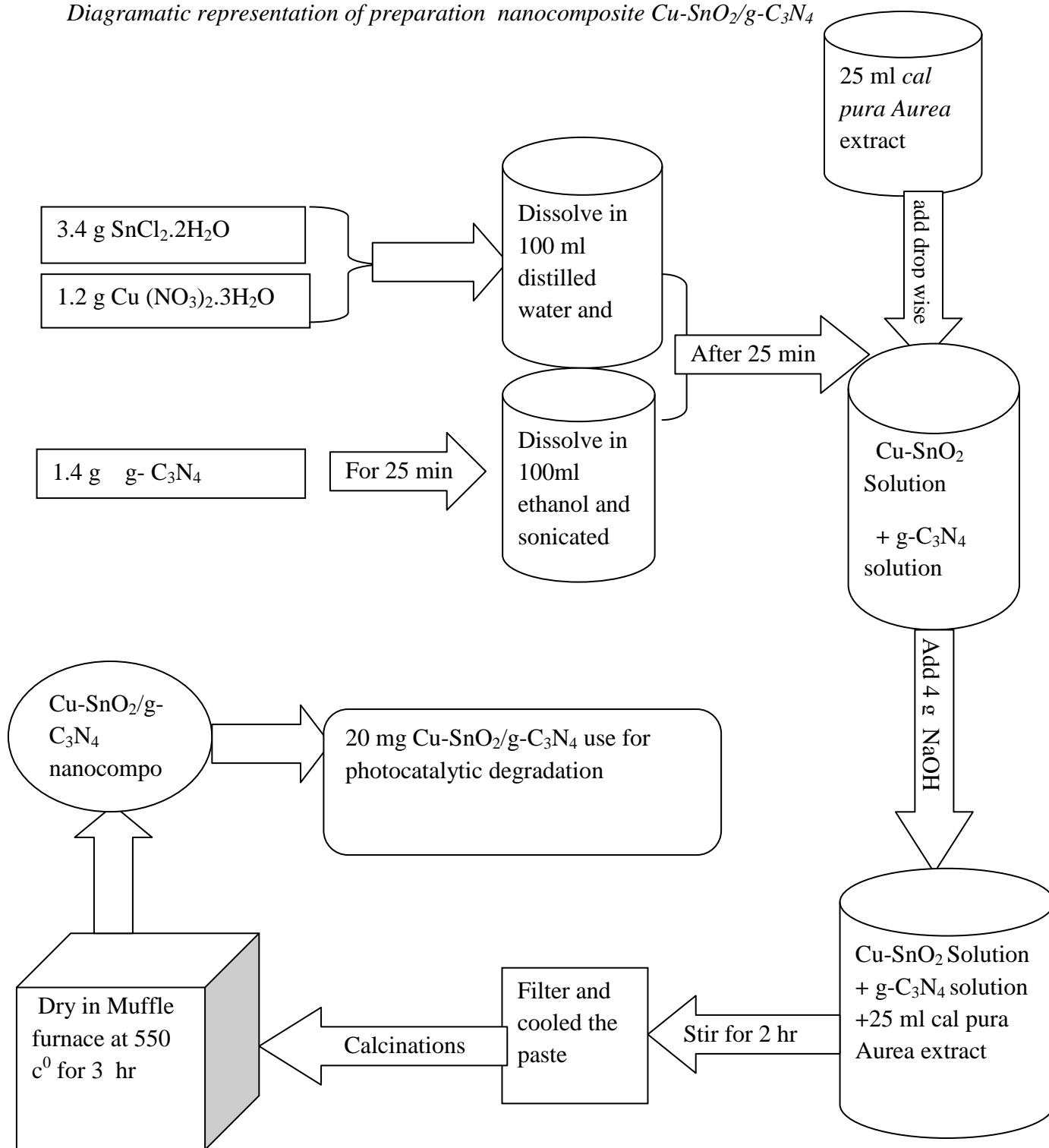
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ABSTRACT

Green synthesis approach was utilized to prepare copper-doped tin oxide (Cu-SnO₂)/graphite carbon nitride (g-C₃N₄) nano composite for the visible-light photocatalytic degradation of methylene blue (MB) dye. The composite material was prepared using environmentally friendly methods by using plant extract. Maximum methylene blue (MB) photocatalytic degradation was observed with the copper doped tin oxide (5% Cu-SnO₂) NPs compared to other (1, 2, 3, and 4%) Cu-SnO₂ nano particles. The 5% Cu-SnO₂ NPs were then homogenized with g-C₃N₄ to develop nanocomposite of Cu-SnO₂/g-C₃N₄ with the most significant degree of MB degradation. The synthesized samples were identified by modern characterization methods such as FT-IR, SEM, UV-visible, and XRD. The Cu-SnO₂/g-C₃N₄ composites showed a significant increase in MB degradation and degraded 97.6% of MB after 60 minute of simulated sun light irradiation. Cu-SnO₂/g-C₃N₄ nano composite catalyst has been found to exhibit a free radical scavenging activity of 79.9% in a DPPH solution, which is comparable with the free radical scavenging activity of ascorbic acid, the standard free radical scavenger. The results showed that Cu-SnO₂/g-C₃N₄ nanocomposite has the potential to be used in wastewater treatment applications, addressing environmental concerns related to MB dye contamination in water bodies.

Keywords: Cu-SnO₂/g-C₃N₄, Nano composite, Green synthesis, Photocatalytic degradation, Methylene blue, Radical scavenging activity

Diagrammatic representation of preparation nanocomposite $\text{Cu-SnO}_2/\text{g-C}_3\text{N}_4$



1. INTRODUCTION

Human activities such as industrialization and urbanization are increasing day to day with the increase of urbanization(Qamar, M.A. *et al.*, 2022).Organic pollutants such as industrial dyes and agricultural wastes are the major causes of aquatic pollution, due to which human health and its ecosystem are affected badly. Dyes are applied to the substrates to give them permanent color, which can resist fading upon exposure to water, light, oxidizing agents, sweat, and microbial attack (Khan, I *et al.*,2020).Due to these advantages, various dyes are used in different industries such as textiles, food, rubber, printing, cosmetics, medicine, plastic, concrete, and the paper industry for multiple purposes (Ahmad, M,*et al.*,2021).These industries generate a tremendous amount of wastewater containing carcinogenic and toxic dyes that pollute water, which becomes unfit for human consumption (Pandey*et al.*,2020.)

Among these industries, the textile industry is the most dye-consuming industry utilizing textile dyes, which are highly complex compounds with different structural groups(Fong, W.M., Affam, A.Chung, W, 2020). One of the highest-consuming materials in the dye industry is methylene blue (MB), which is commonly used for colorings silk, wool, cotton, and paper. Pharmaceutical, chemical, and textile industries dispose of organic pollutants and dyes directly into the environment and produce colored wastewater (Mulushewa Dinbore, 2021).Textile industries are releasing about 10–50 mg/L of dye during the dying process which is a high enough concentration to pollute water along with colors. In developing countries, 1.6 million deaths per year occur just because of drinking contaminated, untreated water.

Textile industries usually release a large amount of methylene Blue dyes in water sources, which becomes a health threat to human beings and microbes(Pang, *et al.*, 2018). Methylene Blue dye is harmful to human health above a certain concentration due to its substantial toxicity MB is toxic, carcinogenic, and non-biodegradable and can cause a serious threat to human health and destructive effects on the environment(Sun, L.*et al.*,2019).Methylene Blue causes several risks to human health such as respiratory distress, abdominal disorders, blindness, and digestive and mental disorders(Contreras, M.*et al.*,2019).It also causes nausea, diarrhea, vomiting, cyanosis, shock, gastritis, jaundice, tissue necrosis, and increased

heart rate causing the death of premature cells in tissues and skin, eye irritations (Abdelrahman E.A.Hegazey., R.Mand El-Azabawy. R.E, 2019).Methylene Blue contact with the skin may result in skin redness and itching. Methylene Blue dye discharge into the environment is a significant threat for aesthetical and toxicological reasons. It also reduces light penetration and is a toxic supply to food chains for organisms (Jawad, A.H.Abdulhameed, A.S.andMastuli, M.S, 2020).Methylene Blue presence in water bodies, even at a very low concentration, makes highly colored sub-products. Which reduces sunlight transmittance; it decreases oxygen solubility, affects the photosynthetic activity of aquatic life, and decreases the diversity and aesthetics of the biological community (Jawad, A.H.Abdulhameed, A.S.andMastuli, M.S, 2020).

Improvement of water quality standards, the complexity of water pollution is becoming more and more serious. Photocatalytic technology can remove pollutants from water at room temperature and atmospheric pressure by using cheap solar energy without secondary pollution (Guiying L.*et al.*, 2016).In recent years, photocatalytic technology has developed into an ideal environmental treatment technology (HuiZ, *et al.*, 2016).The main factors affecting photocatalytic efficiency are semiconductor band gap, morphology, carrier separation, and migration efficiency (Chuyong Z and Bo Yang Yannan Y, 2014). Due to g-C₃N₄ is a polymer with low crystalline and high exciton binding energy, it is unfavorable to the separation and migration of photo-generated carriers, which leads to the lower quantum efficiency of photo catalysis. By combining metal-doped SnO₂ /g-C₃N₄ the photo-generated carriers can be separated from each other in space, which can inhibit the recombination of carriers and improve the photo-catalytic performance.

Metal-doped SnO₂/g-C₃N₄ have been the promising choice of researchers for elementary research and practical applications due to their chemical inertness, high activity, non-toxicity, and low cost (Joshi,N.C.Gururani, andP.Gairola, S.P,2021).Among various metal-oxide-semiconductor that have been employed as a photo catalyst, stannic oxide (SnO₂) nanoparticles, a natural n-type semiconductor with a band gap of 3.6eV, have been projected to be a strong photo catalyst for the degradation of organic pollutants owing to its unique properties, for instance, high transparency, cost-effectiveness, high photo sensitivity, and environmental friendliness (Awoke,N.*et al.*,2021).

SnO₂ NPs synthesized by either chemical reduction or bio reduction plant extracts exhibit distinctive photocatalytic properties for the degradation of many organic pollutants (Mohanta and Ahmaruzzaman, 2016). However, In addition, the green synthesis of metal-doped SnO₂ NPs utilizing plant extracts highlighted that different plant extracts govern the different morphologies and particle sizes that are significantly correlated with various chemical properties (Gebreslassie and Gebretnsae, 2021). The low-cost and high-content secondary metabolites in its plant extracts are a good candidate for development as a bio-reductor source (Selvam *et al.*, 2017).

The influences of plant extract concentration on the morphology and physical properties of the nanoparticles. The green synthesis of environmentally friendly and sustainable photo catalysts for the degradation of organic pollutants in water systems has garnered significant attention in recent years. Among these, metal-doped tin oxide/graphitic carbon nitride nano composites have emerged as promising candidates due to their enhanced photocatalytic properties. Incorporating metal dopants into tin oxide and graphitic carbon nitride structures can significantly improve the efficiency of dye degradation processes under visible light irradiation.

In a recent study by (Zhang *et al.*, 2020) the authors investigated the green synthesis of metal-doped tin oxide/graphitic carbon nitride nanoparticles for enhanced photo-catalytic degradation of dyes. The research focused on developing a cost-effective and sustainable approach to fabricate a highly efficient photo catalyst for the treatment of dye pollutants in water systems. By utilizing a green synthesis method, the study aimed to minimize the environmental impact of the synthesis process while maximizing the catalytic performance of the resulting nano composites. Generally green synthesis metal doped SnO₂/g-C₃N₄ Photocatalytic degradation of dye technology can remove pollutants from water and have high efficiency.

1.1 Statement of the problem

The severity of the persistent increase of organic pollutants that emanates from households and industrial effluents poses a great threat to both aquatic and human life (Chakhtouna, H. *et al.*, 2021). Methylene blue (MB) dye is majorly employed in different industrial applications with core applications in textile industries. MB is mostly used for coloring silk, wood, sticks,

paper, and cotton (Perumal,V.*et al.*, 2022).It has also been used in coloring drugs and cosmeticsin aqueous drug solutions. The discharge of these dyes causes effluents to water which is harmful to both domestic and aquatic life (Sujatmiko,F.*et al.*, 2021).Over the last decades, different methods have been established and used to degrade such pollutants from different sources. Most methods employed to purify wastewater are precipitation, adsorption, ion exchange, and membrane processing (Ahmed, M.K.*et al.*, 2021).However, numerous progress has been recorded in this field. The majority of these approaches are usually impossible for large-scale applications. Most of these methods are costly and do not degrade the toxic materials completely, hence generating a lesser toxic product (Qin,Q.*et al.*, 2021).

The efficiency of the photo-induced electrons (e^-) migration determines the photocatalytic performance; hence, it is necessary to appraise the relevant band positions. The composite photo catalyst was excited by visible light, the electrons absorbed abundant energy and leap from the valance bands (VB) of SnO_2 and $\text{g-C}_3\text{N}_4$ to the conduction bands (CB) of SnO_2 and $\text{g-C}_3\text{N}_4$.Photo induced electrons were concentrated in the CB and photo-generated holes (h^+) were distributed in the VB. SnO_2 has a large energy band gap of around 3.6 eV and cannot generate electron-hole pairs under visible light irradiation. Photo-induced electrons and a hole (h^+) were concentrated in the CB and VB of $\text{g-C}_3\text{N}_4$, respectively. Then, the CB of $\text{g-C}_3\text{N}_4$ and the VB of SnO_2 were adjacent and the VB of SnO_2 was slightly lower, and they photo generated. Aphoto-generated carrier it was short-lived, it has low photocatalytic efficiency under visible light and other flaws restraining its degradation efficiency(Darvishi-Farash, *Set al.*, 2020).

Many approaches have been proposed to solve these problems, such as element doping, morphological control and so on (Kadam, S.*Ret al.*,2020).Modifying the photo catalyst to be a hetero junction was found to be an efficient means to enhance the visible light utilization of $\text{g-C}_3\text{N}_4$ and control its cost. Heterojunction-based $\text{g-C}_3\text{N}_4$ was fabricated, such as metal-doped $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4$, $\text{ZnO}/\text{g-C}_3\text{N}_4$, and $\text{MnO}_2/\text{g-C}_3\text{N}_4$ and so on. So if Cu-doping followed by green synthesis of Nanocomposites was applied the photocatalytic activity and light absorption capacity of the Nanocomposites increased which also increased the photocatalytic degradation of dyes. Therefore Cu- doping of carbon nitride with plant extract increases the photo catalytic degradation of dyes. Biological methods using plant extract and

microorganisms have been proposed as alternatives for the synthesis of nanoparticles as chemicals because chemically formulated drugs cause side effects.

1.2. Objective

1.2.1. General Objective

To synthesis Cu-SnO₂/g-C₃N₄ nanocomposite by using plant extract for visible light photocatalytic degradation of methylene blue and free radical scavenging study.

1.2.2. Specific Objectives

- To synthesize Cu-SnO₂/g-C₃N₄ nanocomposite by using calpura aurea leaf extraction method as a sustainable and eco-friendly approach.
- To study the structural, morphology and optical properties of Cu-SnO₂/g-C₃N₄ nanocomposite using XRD, SEM and UV-visible techniques.
- To investigate the photocatalytic degradation efficiency of Cu-SnO₂/g-C₃N₄ nanocomposite for the degradation under visible-light irradiation.
- To optimize the synthesis parameters for enhanced visible light photocatalytic degradation of methylene blue by using Cu-SnO₂/g-C₃N₄ nanocomposite by using *Cal Pura Aurea* plant leaf extract

1.3. Significance of the Study

Cu-SnO₂/g-C₃N₄ has become an exciting area in nanoscience and technology due to its many applications in versatile fields and even proven promise in human life aspects. Synthesis of nanoparticles through eco-friendly routes attracted much awareness in recent years because of its environment-friendly nature, that is, non-toxic to the environment, reaction process, short time, low temperature, and safe, mild reaction conditions.

The finding of this study is expected to fill the knowledge gap concerning Cu-SnO₂/g-C₃N₄ nanocomposite for photocatalytic degradation of methylene blue and antioxidant activity. To provide necessary information about Cu-SnO₂/g-C₃N₄ nanocomposite for photocatalytic degradation of methylene blue towards the environment.

1.4 Delimitation of the study

The delimitation of the study focuses on the green synthesis of Cu-SnO₂/g-C₃N₄ nano composite for the photocatalytic degradation of methylene blue. The study specifically excludes other types of catalysts or synthesis methods, and does not investigate the degradation of other pollutants or dyes. The research is limited to the characterization and evaluation of the photocatalytic activity of the nano composite in degrading methylene blue and anti oxidant activity under specific experimental conditions, without exploring other potential applications or environmental factors that may affect the degradation process

2. LITERATURE REVIEW

2.1 Graphitic Carbon Nitride (g-C₃N₄)

Graphitic carbon nitride (g-C₃N₄) is assumed to have a tri-s-triazine nucleus with a 2D structure of nitrogen hetero atom substituted graphite frame work. Bulky carbon nitride can be synthesized through thermal condensation of nitrogen-rich (without a direct C-C bound) precursors such as cyan amide, dicyandiamide, thiourea, urea, and melamine. Also, it can be synthesized through the polymerization of nitrogen-rich and oxygen-free precursors by physical vapor deposition, chemical vapor deposition, and solid-state reactions.

In chemistry photo catalysis is the acceleration of a photoreaction in the presence of a catalyst. Therefore, to achieve an ideal photo catalyst, semiconductor photo catalysts need to have a suitable band gap to utilize sufficient solar energy. Having the band gap of 2.7 eV and the conduction and valence band position at -1.4 eV and 1.3 eV, respectively, versus NHE (normal hydrogen electrode), g-C₃N₄ have shown great ability to carry photo catalytic activity in the visible light irradiation without the addition of any noble-metal co-catalyst (GuoW, *et al.*, 2019).

The g-C₃N₄ is known as a metal-free polymer and a conjugative π structure material. This material has many ideal properties, such as unique electric, optical, structural, and physicochemical properties, these properties already make g-C₃N₄-based materials become the ideal substance for catalytic and energy applications (Y.Tachibana, L. Vayssieres, and J. R. Durrant, 2019). This is a promising nonmetallic photo catalyst in the decomposition of pollutant organic matter in visible light and the analysis of water into hydrogen and oxygen. However, the using of these photocatalysts are still faced with some drawbacks, for example, the absorption of visible light is ineffective, and the quick recombination of electron-hole (J. Wen, J. Xie, X. Chen, and X. Li, 2017). To improve the photocatalytic performance of g-C₃N₄, various studies were conducted, including non-metallic g-C₃N₄ doping. The doping of g-C₃N₄ by various elements such as B, C, P, and S (M. Seredychet *al.*, 2016) has been successfully conducted, resulting in the photocatalytic activity of the materials is greatly improved.

The doping of g-C₃N₄ by non-metallic elements has become a topic of research, opening up a new field of research, preparing materials that have good photocatalytic effects under visible light that meet the practical requirements. In addition to enhancing the photocatalytic activity by doping a nonmetal in the lattice, the addition of a metal or metal oxide on the surface of g-C₃N₄ has also been of interest recently. Among the metals, Ag is most concerned with the acceptable price and the ability to increase the activity of Ag nanoparticles. In this case, Ag acts both as a photosensitive agent to increase the ability to absorb visible light and to exhibit a surface Plasmon effect (Y. Chen *et al.*, 2018)

2.2 Metal Oxide Nanoparticles Photo catalytic degradation of dye

Metal oxide nanoparticles having wide-band gaps are irradiated with light energy, and the positive hole-electron pairs are formed; substrates may adsorb on the surface of the photocatalyst and react directly or indirectly with the generated holes and electrons. Metal oxide nanoparticles degrade the organic pollutants and toxic inorganic substrates into readily degradable compounds even mineralize them into less harmful carbon dioxide and water.(Cao,D.*et al.*,2019).Nanoparticles used in the photo degradation of dyes are ZnO,TiO₂, ZrO₂,CeO₂, MnO₂, CuO and SnO₂.

Tin oxide nanoparticles (SnO₂ NPs) are widely used in several fields such as photocatalytic activity, energy storage application, and organic transformation used as catalysts in various fields(Suthakaran, *et al.*, 2019).Tin oxide is an n-type semiconductor with a band gap of 3.6 eV at ordinary temperature. SnO₂ nanoparticles show good optical and electrical properties at room temperature, photocatalytic activity, and low resistivity. SnO₂ NPs are also used in the coating, photo-voltaic, photo-sensors, gas sensors, etc.(Viet P.V.,Thic.M.andHieu L.V., 2016).(Elango, G.and Roopan, S.M., 2016) reported the utilization of biologically synthesized SnO₂ NPs (using methanolic extract of Cyphomandrabetacea) in the photo degradation of methylene blue present in aqueous effluent.

The rod-shaped SnO₂ NPs with particle size 21 nm were found excellent photo catalysts to degrade methylene blue in the effluent.(Tammina, S.K., Mandal, B.K.and Kadiyala, N.K,2018) utilized the SnO₂ NPs to degrade methylene blue under ultra-violet radiation. The smaller-sized SnO₂ NPs exhibited a higher rate of degradation within 30 min. (Li, Y.*et al.*,2018) considered the photocatalytic applications of SnO₂ NPs in the degradation of

methylene blue and Rhoda mine B present in the aqueous effluent. More than 90% methylene blue and Rhoda mine B were degraded under UV light irradiation within 50 min and 270 min, respectively. (Viet P.V., Thic.M.andHieu L.V., 2016) used the SnO₂ NPs to degrade methylene blue under sunlight. The smaller-sized SnO₂ NPs degraded 87% methylene blue within 120 min. (Titus, D. and Samuel, E.J.J, 2019) applied the green synthesized SnO₂ NPs (using methanolic extract of rachishypogea) to degrade Congo red under ultra-violet light 84 % degradation was recorded after 50 min.

2.3. Metal doped tin oxidenanoparticles photo catalytic degradation of dye

Metal-doped tin oxide (M-SnO₂) nanoparticles have emerged as promising photo catalysts for the degradation of organic dyes due to their enhanced photocatalytic activity. The incorporation of metal ions into the SnO₂ matrix can alter the electronic band structure, improve charge separation efficiency, and enhance the photocatalytic performance of the nanocomposite material. Various metals such as copper, silver, and iron have been investigated as dopants in SnO₂ nanoparticles to enhance their catalytic properties for dye degradation applications.

In a study by (Wang *et al.*, 2020) copper-doped SnO₂ nanoparticles were synthesized via a sol-gel method and exhibited superior photocatalytic activity for the degradation of methylene blue under visible light irradiation. The presence of copper ions in the SnO₂ matrix promoted the generation of reactive oxygen species, leading to efficient dye degradation. Similarly, silver-doped SnO₂ nanoparticles prepared by (Li *et al.*, 2019) demonstrated enhanced photocatalytic performance for the degradation of Rhoda mine B due to the synergistic effect between silver and SnO₂.

Overall, metal-doped SnO₂ nanoparticles hold great potential for environmental remediation applications, particularly in the degradation of organic dyes. By tailoring the composition and structure of M-SnO₂ nanocomposites, are able to optimize their photo catalytic properties and contribute to sustainable waste water treatment solutions.

2.4. Green Synthesis of metal doped SnO₂/g-C₃N₄ Nano composite photocatalytic degradation of dye

Over the last few years, the novel synthesis of nonmaterials such as metal, metal oxide, and metal sulfide nanoparticles has gained much attention. Metal, metal oxide, and their composites have become an exciting area in nanoscience and technology due to the many applications in versatile fields and even proven promise in human life aspects (Mourdikoudis.S, Kostopoulou.A.andLaGrow. A. P., 2021).Synthesis of nanoparticles through eco-friendly routes attracted much awareness in recent years because of its environment-friendly nature, that is, nontoxic to the environment, reaction process, short time, low temperature, and safe, mild reaction conditions (Singh, J.*et al.*, 2018).

However, modifying the surface area of the nanoparticles through the natural reducing and capping agents remains challenging.Nevertheless, nanoparticles can be generated by green chemical agents that are plant extracts that possess even higher stability. The green process synthesis of metal oxide nanoparticles, particularly tin oxide nonmaterial using plant extract, is an alternative method to the chemical synthesis that could control the chemical toxicity to the environment and control the sizeand shape of the nonmaterial (Shamaila, S.*et al.*, 2016).

Moreover, green synthesized nanomaterials are gaining interest in the research fields, environmental sciences, synthetic chemistry, nanobiotechnology, and material chemistry, respectively (Mazari, S. *et al.*, 2021).Among various nanomaterials, SnO₂nanomaterials are considered an alternative source for the degradation of water purification/environmental pollutants because they possess outstanding UV light absorption and generate reactive oxygen species (ROS) that lead to the degradation of environment pollutant dye molecules (Palanisamy, G.*et al.*, 2021).Tin oxide nanoparticles (SnO₂ NPs) are widely used in several fields such as photocatalyticactivity, energy storage application, and organic transformation used as catalysts in various fields. Tin oxide nanoparticles (SnO₂ NPs) are widely used in several fields such as photocatalytic activity, energy storage application, and organic transformation used as catalysts in various fields (Suthakaran, Dhanapandian.S, Krishnakumar.N and Ponpandian, N, 2019).

In fact, plant extracts have various photo chemical constituents, that is, secondary metabolites such as alkaloids, terpenoids, flavonoids, antioxidants, and amino acids, respectively, which exist in fruits, peels, seeds, and leaves that permit the replacement of the traditional toxic chemicals for the synthesis of nano materials(Yuliarto, B.*et al.*, 2019).

Currently, photocatalysis applications for addressing environmental issues such as environmental pollution and energy crises have attracted more and more attention and gradually become a research hotspot. The most common pollutants identified in urban and industrial areas are volatile organic compounds such as toluene, benzaldehyde, benzyl alcohol, and chlorinated derivatives (A. J.Pal, V. K.andKannan, K., 2021).Volatile organic compounds are dangerous for human health, and they are toxic, mutagenic, and carcinogenic to all human beings. Nowadays, research has mostly been focused on the toxicity of volatile organic compounds sources or the degradation conditions rather than the byproducts generated during the treatment procedures(Rueda-Marquez, *et al.*, 2020).

2.5. Photo degradation of Methylene Blue

Over the last few decades, multi-component photocatalysis of organic pollutants using semiconducting NPs has received increased attention because it is a cost-effective, environmentally-friendly, and easy technique for waste water treatment containing hazardous pollutants (Chandra, R.*et al.*, 2020). The lower cost of catalysts and the utilization of renewable energy in this technology are much more attractive when compared to other techniques.The oxidation of MB to H₂O and CO₂ through a photocatalyst is an imperative technique to remove the dye from industrial wastewater (Shaban, M.*et al.*, 2020).

Photodegradation is an oxidation process in which the chemical down of complex molecules transforms into simple, nontoxic, and lower molecular weight fragments due to light exposure (Saeed, K.and Khan, I., 2017). This is an emerging and promising technology for waste effluent treatment, having the capability to decolorize and degrade the dye moleculesinto simple and nontoxic inorganic species such as CO₂ and H₂O (Khan, I.*et al.*,2019).The process is performed in the presence of a photocatalyst; a semiconductor material activated by adsorbing photons, and can accelerate a reaction without being consumed(Khan, I. *et al.*,2017).

MB is a representative organic dye and stable under visible light irradiation (Rashad, M., Shaalan, N.M. and Abd-Elnaiem, A.M., 2016). Due to its stability, it cannot be degraded efficiently just by photolysis or catalysis alone. It was reported that 7.9% of Methylene Blue dye was removed through photolysis after 10 hr irradiation time (Siong, V.L.E. *et al.*, 2019), and only 10% degradation of MB occurred after 24 hr. in the presence of a catalyst without light irradiation (León, E.R. *et al.*, 2016). It was also observed that no negligible decomposition occurred without a catalyst under visible light. Similarly, no degradation was observed in the acidic and neutral medium in the dark and under sunlight irradiation without using a catalyst. In the basic medium, photolysis occurs rapidly because of the formation of the hydroxyl ions, which is a key radical for dye degradation.

3. MATERIAL AND METHODOLOGY

3.1. Experimental site

All laboratory work was done at the Salale university chemistry department laboratory room. XRD, SEM, FTIR, and UV were conducted at Adama Science and Technology university chemistry department.

3.2. Materials

Urea, Tin (IV) chloride dihydrate ($\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$), Sodium hydroxide (NaOH), Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), Methylene blue, distilled water, 2, 2-diphenyl-1-picrylhydrazyl (DPPH) and, Ethanol.

3.3 Preparation *Cal Pura Aurea* Leaf Extract

The leaves of the *calpura Aurea* were washed thoroughly with distilled water to remove dust and other particles. The plant part is then dried at room temperature and The dried leaf were ground into powder through an electric mixer. 15 g of powder was added to 100 ml of distilled water and stirring in a magnetic stirrer at 50 °C for 30 min to prepare the aqueous extract. Eventually, the extract was cooled at room temperature and filtered through what man filter paper



Figure 1. calpuraAurea leaf

dry calpuraAurea leaf

3.4. Preparation of Graphitic Carbon Nitride

Graphitic carbon nitride (g-C₃N₄) was prepared by hydrothermal method (K. Zhu.*et al.*2019). 18 g urea was initially ground well into fine powder with pastel for 10 min and then dried over hot plate for 30 min at 50 °C. Then after; the dried powder was placed on a covered silica crucible in a muffle furnace at 550 °C for 2 hr. A light brown colored powder of g-C₃N₄ was achieved. Brown-colored powder was cooled down to room temperature, and grounded well into a fine powder.

3.5. Preparation of Copper doped Tin Oxide Nanoparticles

To synthesize 5% of Copper doped tin oxide (Cu-SnO₂), 3.4 g of Tin chloride dihydrate (SnCl₂.2H₂O) and 1.2 g copper nitrate trihydrate (Cu (NO₃)₂.3H₂O) were dissolved in 100 ml of distilled water on vigorous and constant stirring with the magnetic stirrer. Stirring continued until they formed a homogenous solution (Parthibavarman, M., 2019), and subsequently 25 ml of *Cal Pura Aurea* aqueous extract was added drop-wise with continuous stirring using a magnetic stirrer and form a foam. After 25 min 4 g of NaOH added to the stirring solution by adjusting the pH of the solution 10 at 50 °C for 2 hr. gradually formed apaste and was cooled at room temperature. The solution was filtered and washed with ethanol again and again to remove chloride ions. Subsequently centrifuged for 3 min and eventually dried in oven at 120 °C for 2 hr. The resulting dried solid was calcined at 500 °C for 2 hr in a muffle furnace. A gray-colored solid of Cu-SnO₂ was achieved. Cu-SnO₂ was ground in a pestle to obtain Cu-SnO₂ powdered nanoparticles.

3.6. Preparation of Cu-SnO₂/g-C₃N₄ Nanocomposites

3.4 g of Tin chloride dihydrate (SnCl₂.2H₂O) and 1.2 g copper nitrate trihydrate (Cu (NO₃)₂.3H₂O) were dissolved in 100 ml of distilled water on vigorous and constant stirring with the magnetic stirrer. Stirring continued until they formed a homogenous solution was observed and 1.4 g of graphitic carbon nitride dissolved in 100 ml of ethanol and sonicated for 25 min separately. After 25 min, g-C₃N₄ solution was put on the stirrer solution, and subsequently 25 ml of *Cal Pura A urea* aqueous extract was added drop-wise with continuous stirring using a magnetic stirrer and form like foam. After 25 min 4 g of NaOH was added to the stirring solution by adjusting the pH of the solution 10 at 50 °C for 2 hr. The solution gradually formed apaste and was cooled at room temperature and the solution

filtered with filter paper and was washed with distilled water to remove chloride ions. After washing, the precipitates were dried in an oven at 60 °C for 3 hr. Dried material was then placed into the muffle furnace at 550 °C for 3 hr. Cu-SnO₂/g-C₃N₄ nanocomposites were ground to a fine powder in a mortar and pestle.

3.7. Material Characterization

Cu-SnO₂ nanoparticle, g-C₃N₄ and Cu-SnO₂/g-C₃N₄ nanocomposites were characterized by using various techniques. The crystalline structure was determined by a powder XRD (SHIMADZU Corporation, Japan, and its model XRD-7000). The surface morphology of synthesized materials was examined by SEM. FTIR analysis to obtain the functional group study was carried out on FTIR spectra in the range of 4000–500 cm⁻¹. The photo catalytic degradation efficacy of samples was measured by a UV-visible spectrophotometer (Shimadzu UV-3600) with a wavelength range of 320–800 nm.

4. RESULT AND DISCUSSION

4.1 RTIR Analysis

Fourier-transform infrared spectroscopy (FTIR) is a useful technique (Taqiullah, S.M.*et al.*, 2022).for characterizing g-C₃N₄ due to its ability to provide information about the chemical structure and bonding of materials. When analyzing g-C₃N₄ using FTIR, several key characteristics can be observed. In the FTIR spectra, the characteristic bands with high intensity at the wave number about 1632,1468,1304 and 1219 are related to the stretching modes of C=N and C–N heterocycles. These values were very close to the reported values (Geng, Y.*et al.*, 2021).Besides, the strong peaks at 799 cm⁻¹ are attributed to the s-triazine units (L. Li, S.-Q. Sun, Y.-X. Wang, and C.-Y., 2017).The broad range peak between 3000 cm⁻¹ and 3500 cm⁻¹ is due to the N-H stretching vibration and the remaining water molecules in the structure, very close to the reported value (Li, F.*et al.*, 2019). Overall, FTIR analysis of g-C₃N₄ provides valuable information about its chemical composition, bonding structure, and functional groups, making it a powerful tool for characterizing this unique carbon nitride material.

Characterization by FTIR of Cu-SnO₂ prepared from plant extraction can provide valuable information about the chemical composition and bonding structure of the material. In the FTIR spectrum of Cu-SnO₂ several characteristic peaks can be observed. The presence of tin oxide can be confirmed in absorption band is 889 cm⁻¹, corresponding to the stretching vibrations of Sn-O bonds. The peak at 3363 cm⁻¹ is due to the O–H stretching vibration of water molecules absorbed from the environment by SnO₂ nanoparticles and which may present in the surface of the SnO₂ nanoparticles (Tazikeh S,*et al.*, 2014).Another band is observed at 1631 cm⁻¹, which represents the vibration peak of C=O.A peak at 1087 cm⁻¹ has also appeared which represents C-O bond stretching. The peak at 1373 cm⁻¹ is due to the aromatic (C-C) stretching band. The presence of copper doping can also be detected in the FTIR spectrum. Copper dopant ions typically introduce additional absorption FTIR peaks change after Cu doping, showing that the Cu ion has been integrated into the SnO₂. Furthermore, due to the modest quantity of copper concentration utilized, the peak position and intensity for Cu-SnO₂ changed. Shifting of metal-oxygen peak from 889 to 740 cm⁻¹, corresponding to the stretching vibrations of Cu-O bonds. Characterization by FTIR of Cu-

SnO₂/g-C₃N₄ nano composite synthesized from plant extraction can provide valuable insights into the chemical composition and bonding structure of the material. In the FTIR spectrum of the Cu-SnO₂/g-C₃N₄ nano composite, several characteristic peaks can be observed. The presence of tin oxide and graphitic carbon nitride can be confirmed by specific absorption bands in the spectrum. For the tin oxide component the bands 889 cm⁻¹ can be observed, corresponding to the stretching vibrations of Sn-O bonds, indicating the presence of tin oxide in the nanocomposite. The occurrence of peak at (500-1000) cm⁻¹ the FTIR band was related to metal-oxygen (M-O) bonds which corroborate with the report of (Senthil Kumar, *p et al.*, 2015). The peak at 3411 cm⁻¹ is due to the O-H stretching vibration, Another band is observed at 1622 cm⁻¹, which represents the vibration peak of C=O. A peak at 1066 cm⁻¹ has also appeared which represents C-O bond stretching. This may occur due to the release of CO₂ during annealing in the furnace. A peak of Sn-OH is also observed at 1381 cm⁻¹

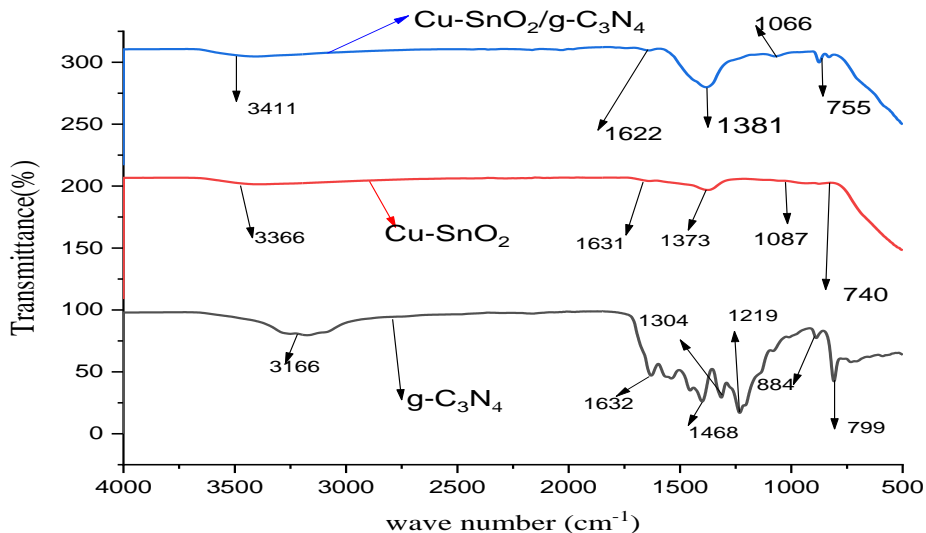


Figure 2. FTIR analysis of g-C₃N₄, Cu-SnO₂ and Cu-SnO₂/g-C₃N₄

4.2 XRD Analysis

Characterization by X-ray diffraction (XRD) Figure 3 shows the XRD patterns of as-prepared g-C₃N₄, Cu-SnO₂ nanoparticles and Cu-SnO₂/g-C₃N₄ nanocomposites. From Figure 3 there are three diffraction peaks around 12.8°, 27.5° and 37.7° which were accorded to the (100) and (002) planes of g-C₃N₄, which is close to the XRD pattern of g-C₃N₄ JCPDS No. 87-1526) (A. Priya, R. A. *et al.*, 2020.) These two peaks are likely to be attributed to the

structure of the tri-s-triazine unit with interplanar spacing and the conjugated aromatic system, respectively (Paul, D.R. *et al.*, 2019). It can be concluded that g-C₃N₄ was synthesized successfully. As observed from the Cu-SnO₂/g-C₃N₄ nanocomposite curves, there are seven distinct diffraction peaks around 26.55°, 29.27°, 30.6°, 31.66°, 33.88°, 35.5° and 38.8 ° which correspond to the (110),(101),(111),(211),(221),(022) and (121) planes of (JCPDS Card No.048-1588) respectively. However, Figure 3a–b shows that there are no diffraction peaks of g-C₃N₄ observed in the curves. This is due to the relatively small content of g-C₃N₄ in the nanocomposites or the peak around 27.5° of g-C₃N₄ is covered by the peak around 26.55° or peak broadening with a slight shift towards at 27.5° to 26.66° was observed which confirms the successful synthesis of the nanocomposite Cu-SnO₂/g-C₃N₄.

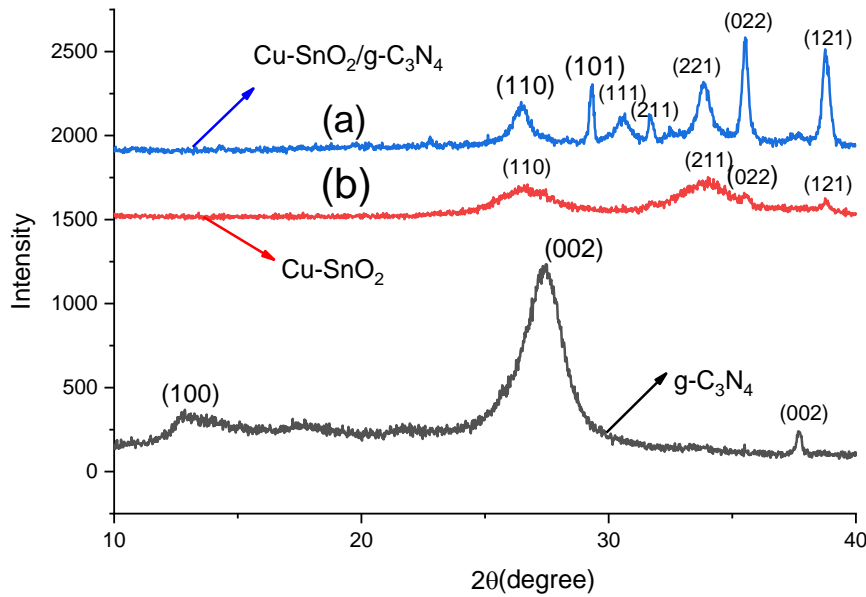


Figure 3. XRD pattern of g-C₃N₄, Cu-SnO₂ and Cu-SnO₂/g-C₃N₄

In order to calculate the crystallite size of g-C₃N₄, Cu-SnO₂ and Cu-SnO₂/g-C₃N₄ Nano composite from the XRD patterns the average crystallite size of g-C₃N₄, Cu-SnO₂ and Cu-SnO₂/g-C₃N₄ were 1.75 nm, 26.42 nm and 8.15 nm. The three peaks of g-C₃N₄, 2θ and FWHM have equal values to 68.69626 and 54.8692 respectively. Similarly, the three peaks of 2θ and FWHM of Cu-SnO₂ nanoparticle and Cu-SnO₂/g-C₃N₄ nanocomposite values were 33.95102, 3.14417 and 33.6324 and 10.2508 respectively.

we used Scherer's equation. $D = k\lambda / \beta \cos(\theta)$(1)

where D is the crystallite size, k is the Scherer's coefficient (0.9), λ is the X-ray wavelength, θ is the Bragg angle, and β is the full width at half-maximum (FWHM) intensity.

Sample	2 θ	FWHM value	FWHM in radian.	Cos θ	Crystallite Size
g-C ₃ N ₄	68.69626	54.8692	0.957163	0.825625	1.75nm
Cu-SnO ₂	33.95102	3.14417	0.0548483	0.95642964	26.42nm
Cu-SnO ₂ /g-C ₃ N ₄	33.6324	10.25084	0.1788202	0.95723774	8.15nm

Table 1.crystallite size calculated

The crystallite size calculated for g-C₃N₄, Cu-SnO₂, and Cu-SnO₂/g-C₃N₄ using the Scherer equation from XRD data was found to be 1.75 nm, 26.42 nm, and 8.15 nm respectively.

4.3 SEM Analysis

Characterization by SEM of Cu-SnO₂/g-C₃N₄ nanocomposite prepared from plant extraction involves a detailed analysis of the surface morphology, particle size distribution, structural features, and elemental mapping of the material. The SEM analysis provides valuable insights into the physical and chemical properties of the nanocomposite, shedding light on its unique characteristics resulting from the plant extraction process. The surface morphology analysis using SEM allows for the observation and examination of the nanocomposite surface features, including particles, aggregates, pores, and any other structural elements present in material. SEM analysis was used to study the morphology of g-C₃N₄, Cu-SnO₂ and Cu-SnO₂/g-C₃N₄ nanocomposites at different resolutions. Figures -4 show the morphology of Cu-SnO₂, revealing uniform and smooth sheets of g-C₃N₄ and aggregation of particles as an outcome of Cu-SnO₂ nanoparticle on g-C₃N₄ sheets. it can be seen that Cu-SnO₂ is dispersed irregularly in the form of small spherical particles on the surface of g-C₃N₄ sheets. The coupling of Cu-SnO₂ and g-C₃N₄ reveals that the coupling has not affected the morphology of Cu-SnO₂/g-C₃N₄ spheres. Instead, Cu-SnO₂ the aggregates got attached to the surface of

g-C₃N₄. These SEM images illustrate those agglomerates of Cu-SnO₂ were successfully anchored over g-C₃N₄. In the presence of Cu, the agglomeration and stacking of particles were enhanced as compared to simple SnO₂/g-C₃N₄. Similar results of doping and coupling we also reported (R. Saher., 2021).

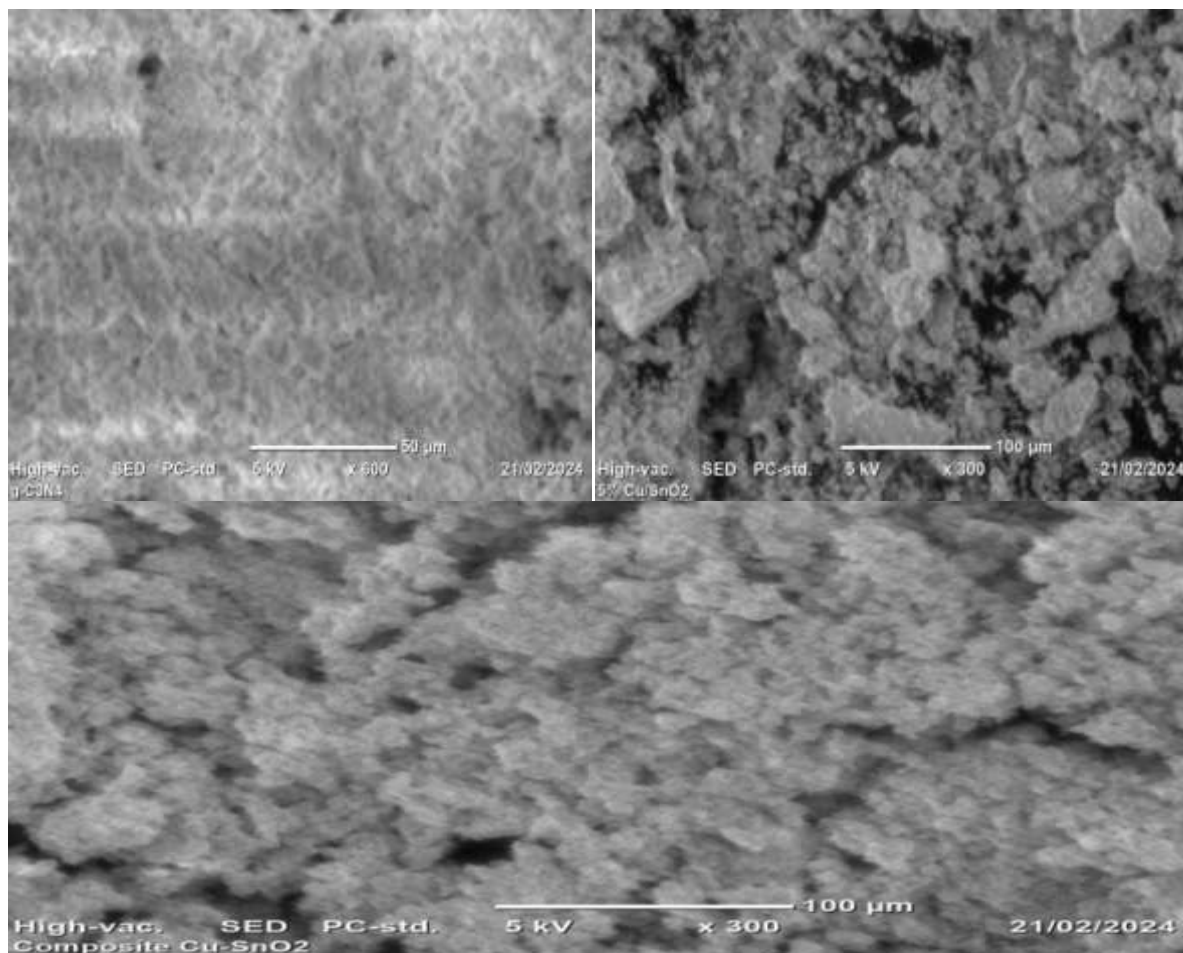


Figure 4. SEM images g-C₃N₄, Cu-SnO₂ and Cu-SnO₂/g-C₃N₄ nanocomposite

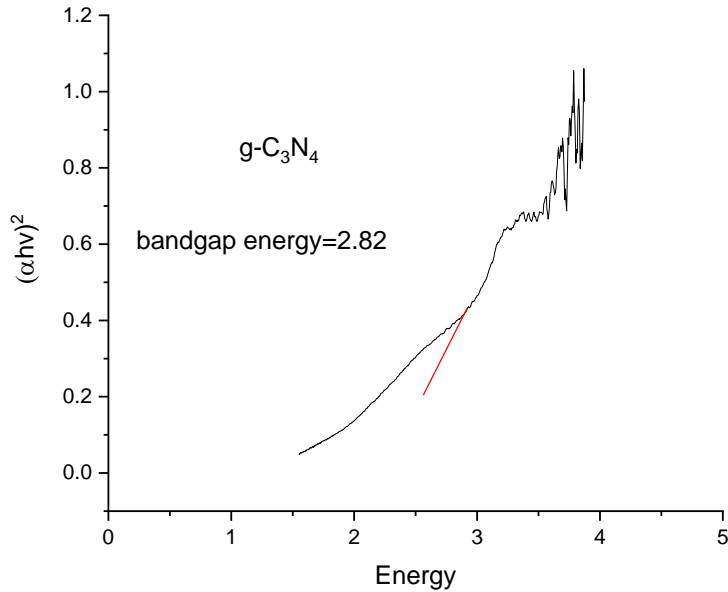
4.4 UV-Visible Analysis

The UV-Vis spectroscopy characterization of the green-synthesized Cu-SnO₂/g-C₃N₄ nanocomposites for photocatalytic degradation involves a detailed analysis of its optical properties during the degradation process. UV-vis absorption spectrums of the samples in the band range 320-800 nm. Initially, the UV-Vis spectrum of the Cu-SnO₂/g-C₃N₄ nanocomposites before photo catalysis provides insights into its absorption features, such as band gap energy and absorption peaks, which are influenced by the presence of copper

dopants and the combination with graphite carbon nitride. g-C₃N₄, Cu-SnO₂ and Cu-SnO₂/g-C₃N₄ were red shift in absorption in UV–vis absorption spectra. which correlates with the report of (M. Gholami, M. Shirzad-Siboni, and J.-K Yang., 2016). Band edge shift in UV–vis absorption spectral lines for g-C₃N₄, Cu-SnO₂ and Cu-SnO₂/g-C₃N₄ nanocomposite are represented in Table 2. The band gap energy values for the synthesized materials were evaluated by plotting Tauc's plots. The bandgap energy values for the prepared samples were estimated by applying given typical equation (2) (J.Thomas., 2018).

$$(\alpha h\nu) = A(h\nu - E_g)^n \dots\dots\dots 2$$

where $h\nu$ is the photon energy, E_g is the bandgap, A is the parameter and α is the absorption coefficient. The bandgap energy values for the g-C₃N₄, Cu-SnO₂ and Cu-SnO₂/g-C₃N₄ nanocomposite were determined from the Tauc plot drawn between $(\alpha h\nu)$ versus $h\nu$, and extrapolating the straight-line part to $(\alpha h\nu)$. band gap energy of g-C₃N₄ was 2.82, the value which is close to by reported (GuoW, *et al.*, 2019).



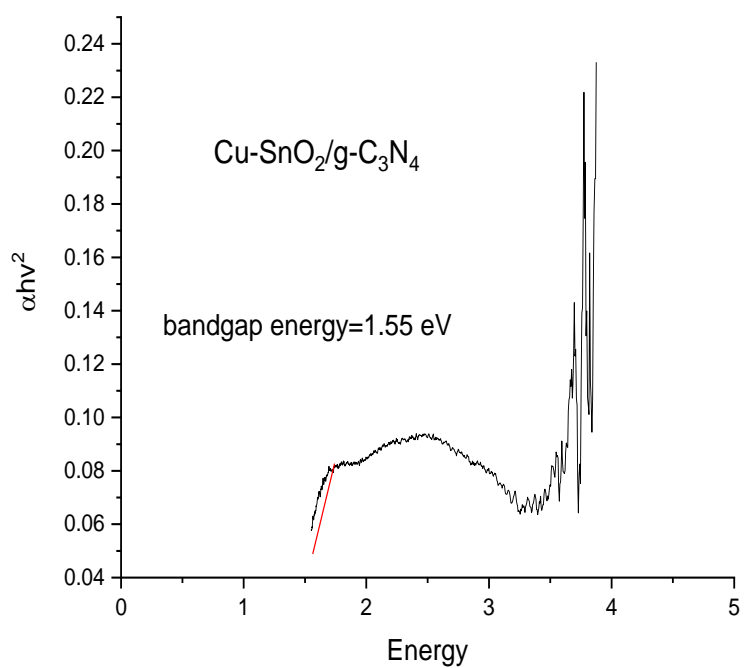
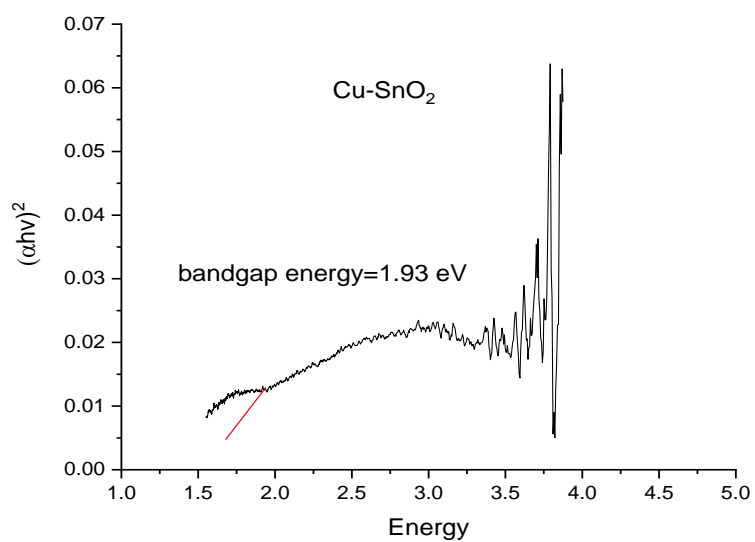


Figure 5. band gap of g-C₃N₄, Cu-SnO₂ and Cu-SnO₂/g-C₃N₄

Photo catalytic degradation efficiency of material is influenced by its band gap. From figure-5 the band gap of Cu-SnO₂/g-C₃N₄ nano composite is 1.55 eV which is less than that of band gap g-C₃N₄ and Cu-SnO₂. The decrease in the band gap energy for Cu-SnO₂/g-C₃N₄

nanocomposite can be attributed to the effective interaction between Cu-SnO₂ and g-C₃N₄. Moreover, the reduced bandgap energy values for the Cu-SnO₂/g-C₃N₄ nanocomposite in compare to Cu-SnO₂ and g-C₃N₄ could lead to enhance light absorption in the visible region that has increased the generation of more electron-hole pairs (N. Li, *et al.*, 2018). Additionally, due to the coupling interactions g-C₃N₄ and Cu-SnO₂ could create nanocomposite that inspiring transfer of carriers due to which recombination of electrons–holes is delayed (M.Wu *et al.*, 2019). Consequently, the photocatalytic degradation performance of Cu-SnO₂/g-C₃N₄ nanocomposite is enhanced under visible-light irradiation. The maximum degradation efficiency is determined for the nanocomposite of Cu-SnO₂/g-C₃N₄, since the band gap energy (1.55 eV).

Catalyst	Absorption (nm)	Bandgap(eV)
g-C ₃ N ₄	374	2.82
Cu-SnO ₂	375	1.93
Cu-SnO ₂ /g-C ₃ N ₄	385	1.55

Table-2 Band gap energy and absorption spectra values of g-C₃N₄, Cu-SnO₂ and Cu-SnO₂/g-C₃N₄

4.5. Effect of Reaction Parameters on Photocatalytic Activity of Catalyst

4.5.1 Effect of initial dye concentration

The initial dye concentration is an essential feature of the photocatalytic process. To determine the optimized value of dye concentration, the photocatalytic performance of the green synthesis Cu-SnO₂/g-C₃N₄ nano composite was investigated against the MB dye degradation at 20-35 mg/L of dye concentrations under the visible light irradiation for 60 min using 20 mg of catalyst amount. The photodegradation efficiency of Cu-SnO₂/g-C₃N₄ nano composite against the MB dye is calculated as 90.49%, 92.92%, 97.6%, and 95.4% for the 20, 25, 30, and 35 mg/L of dye concentrations respectively.

The maximum degradation efficiency is observed for the 30 mg/L concentration, which is selected as an optimal dye concentration for the next studies. At a lower initial concentration of dye, the less efficiency may be due to less amount of dye adsorbed on the catalyst surface

(H.Osman,Z. Su, X. Ma, 2017).However, at a higher concentration of dye, the decrease in the degradation efficiency may be due to the decreasing of penetration of light photons or suppression path length photo(R.C. Pawar.*et al.*,2018).



Figure 6.20 mg Cu-SnO₂/g-C₃N₄ nano composite in 20 mg, 25 mg, 30 mg and 35 mg MB dye solution in sun light radiation for 60 min

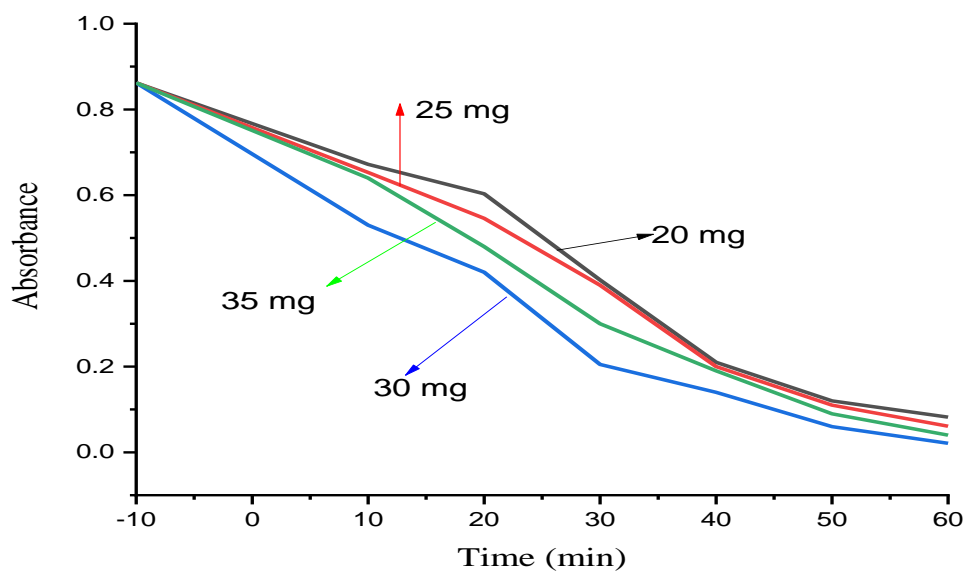


Figure 7.Effect of initial dye concentration on photo degradation of MB over the Cu-SnO₂/g-C₃N₄ nano composite

4.5.2 Effect of pH of the solution

The influence of solution pH on the photocatalytic performance for the MB dye over Cu-SnO₂/g-C₃N₄ nano composite is investigated by changing the pH value from 4 to 12 in a 50mL of dye solution with 30 mg/L dye concentration and 20 mg catalyst amount under 60 min of visible light radiation. At pH=4 the 82.6% of the MB is degraded which is increased to 86.07% on increasing the pH value to 6. In contrast, when pH is changed into an alkaline medium from the normal pH condition, the photo degradation efficiency is increased considerably at pH=8 is 93.03% and maximum degradation performance is at pH=10 is 97.6%. However, in a strongly alkaline medium at pH=12 is 94.2%, the photodegradation efficiency is decreased.

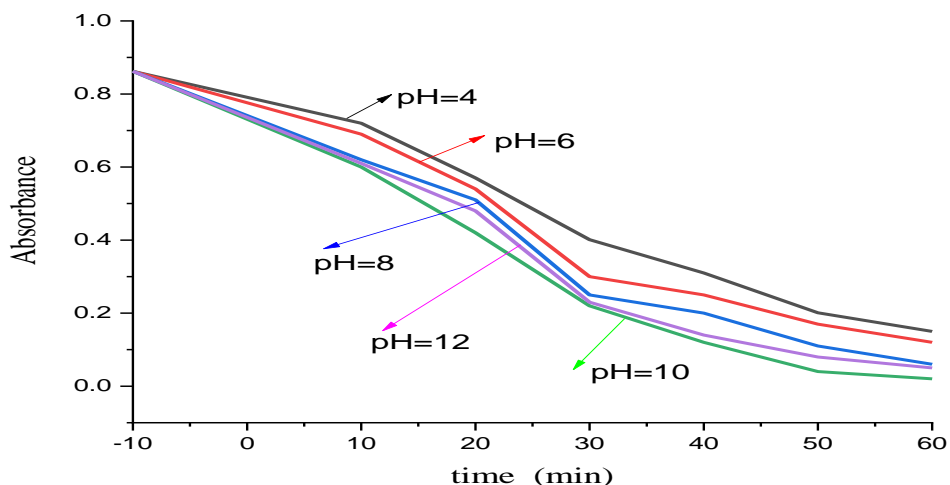


Figure 8. Effect of pH on photo degradation of MB over the Cu-SnO₂/g-C₃N₄ nano composite

In the acidic medium, at lower pH, the catalyst surface is positively charged due to the adsorption of excess of H⁺ ions, which electro-statically repel the cationic dye MB molecules, due to which lower degradation efficiency is determined. But in an alkaline medium above the pH seven catalyst surfaces acquire a negative charge due to the adsorption of OH⁻, which attracts electrostatically to the cationic dye molecules that lead to an increase in the adsorption of MB dye. Due to this, the degradation of MB dye would be further enhanced (I.-H. Tseng, Y.M. Sung, P.Y. Chang, C.Y. Chen., 2019). Moreover, in alkaline pH OH⁻ ions can produce hydroxyl (•OH) radicals that also trigger the degradation rate of dye. However, at

higher pH in a stronger alkaline medium, the degradation activity decreased due to the competition between dye molecules and OH^- for the adsorption on the catalyst surface.

4.5.3. Effect of catalyst dose amount

The influence of catalyst dose amount on the photodegradation performance of MB dye under visible light exposure is studied by varying the catalyst dose amount from 10 to 25 mg in 50 ml of dye solution at pH=10 and room temperature conditions. The photodegradation efficiency is increased from 86.25% to 97.6%, on increasing the dose amount of catalyst from 10 to 20 mg. However, efficiency is decreased to 93.83% on a further increase of the dose amount of catalyst to 25 mg. At a lower amount of catalyst, the available free active sites are less, on increasing dose amount of catalyst free active sites on the surface increase, and because of this photodegradation activity is enhanced. However, furthermore increase in catalyst amount the degradation activity declined due to the scattering of light photons and poor penetration.



Figure 9.10mg, 15mg, 20mg and 25 mg $\text{Cu-SnO}_2/\text{g-C}_3\text{N}_4$ nano composite in 30mg MB solution in sun light radiation for 60min

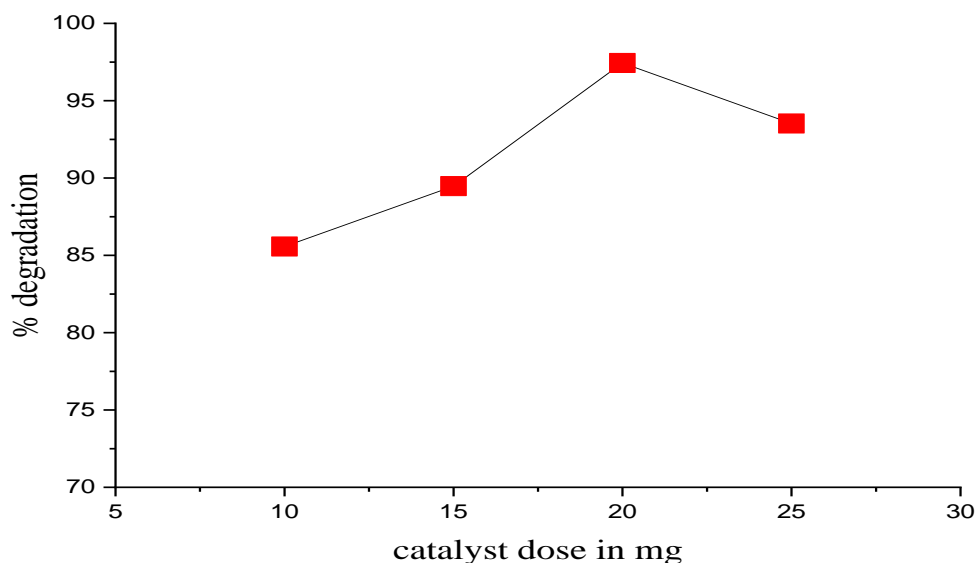


Figure 10. Effect of dose amount of Cu-SnO₂/g-C₃N₄ nano composite on photo degradation of Methylene Blue dye

4.6. Photocatalytic Activity

The composite material was prepared using environmentally friendly methods. Maximum methylene blue (MB) photocatalytic degradation was seen with the 5% Cu-SnO₂ NPs compared to other (1%, 2%, 3% and 4%) Cu-SnO₂ Nano particles. 1%, 2%, 3% and 4% and 5% Cu-SnO₂ are all of the photo catalysts used for degradation of organic pollutants. All are prepared by the same procedure by keeping the parameters like pH=10 and the prepared sample to evaluate the photo catalytic degradation over MB dye exposure to sun light for 60 min, with 10 min interval to measure the absorbance of each sample by using of UV spectrometer at 665 nm, about 0.169, 0.144, 0.129, 0.110 and 0.094 for 1% Cu-SnO₂, 2% Cu-SnO₂, 3% Cu-SnO₂, 4% Cu-SnO₂ and 5% Cu-SnO₂ respectively. 5% Cu-SnO₂ has lower absorbance since has high photo catalytic degradation efficiency.

The main difference between them is the concentration of Cu in the SnO₂ matrix. 1%, 2%, 3%, 4% have a lower concentration of copper compared to 5% Cu-SnO₂. This difference in copper concentration can affect the photocatalytic activity of the material. Higher concentrations of copper can lead to increased photo-catalytic activity due to enhanced

electron-hole separation and improved redox reactions. In terms of degradation efficiency, it is likely that the 5% Cu-SnO₂ would exhibit higher efficiency compared to the other. This is because the higher concentration of copper in the 5% Cu-SnO₂ can lead to more active sites for catalytic reactions, resulting in faster and more efficient degradation of organic pollutants.



Figure 11. 2%,3%,4% and 5% Cu-SnO₂ with MB dye in sun light radiation



Figure 12. 5% Cu-SnO₂ after 60 min in sun light radiation

The percentage photo degradation of organic dyes was determined by the following equation.

$$\% \text{ degradation} = \frac{C_0 - C_t}{C_0} \times 100 = \frac{A_0 - A_t}{A_0} \times 100 \dots \dots \dots (3)$$

Where C_0 and C_t are the initial and concentration of dye at a certain time interval and A_0 and A_t are the absorbance at initial and at t time.

$$\% \text{ degradation of 1\% Cu-SnO}_2 = \frac{A_0 - A_t}{A_0} \times 100 = \frac{0.862 - 0.169}{0.862} \times 100 = 0.693/0.862 \times 100 = 80.39\%$$

$$\% \text{ degradation of 2\% Cu-SnO}_2 = \frac{A_0 - A_t}{A_0} \times 100 = \frac{0.862 - 0.144}{0.862} \times 100 = 0.718/0.862 \times 100 = 83.29\%$$

$$\% \text{ degradation of 3\% Cu-SnO}_2 = \frac{A_0 - A_t}{A_0} \times 100 = \frac{0.862 - 0.129}{0.862} \times 100 = 0.733/0.862 \times 100 = 85.03\%$$

$$\% \text{ degradation of 4\% Cu-SnO}_2 = \frac{A_0 - A_t}{A_0} \times 100 = \frac{0.862 - 0.110}{0.862} \times 100 = 0.752/0.862 \times 100 = 87.24\%$$

$$\% \text{ degradation of 5\% Cu-SnO}_2 = \frac{A_0 - A_t}{A_0} \times 100 = \frac{0.862 - 0.094}{0.862} \times 100 = 0.768/0.862 \times 100 = 89.09\%$$

The photocatalytic performance of the green synthesized 5% Cu-SnO₂/g-C₃N₄ and Cu-SnO₂/g-C₃N₄ nano composite was assessed by the photo degradation of MB dye under visible light exposure. Before testing the photocatalytic abilities of the prepared samples, the adsorption capacities for MB dye were evaluated. The MB dye solution with catalyst was stirred in dark for 30 min to achieve the adsorption-desorption equilibrium before being exposed to visible light. All the photocatalytic experiments in the presence of catalysts were conducted under the optimized conditions of pH, initial dye concentration, and catalyst dose amount at room temperature. The residual concentration of MB dye at different time intervals was evaluated from intensities of UV-vis. absorption spectral peaks at 665 nm. The results of the photo degradation experiments are shown in Fig.13.

The self-degradation of MB dye is slight under the exposure of visible light, which represents that the MB dye is significantly stable in the absence of a catalyst under visible light. The apparent degradation of MB is observed under visible light exposure over the pure Cu-SnO₂, g-C₃N₄ and Cu-SnO₂/g-C₃N₄ catalysts. The catalytic performance of the green synthesis of Cu-SnO₂ nano particle was changed with a composite of g-C₃N₄ and the maximum photodegradation efficiency is determined for Cu-SnO₂/g-C₃N₄ nano composite photo

catalyst. The increase in the photocatalytic performance of Cu-SnO₂ with the g-C₃N₄ might be due to the enhancement in visible-light absorption due to the modification of band gap energy and interruption in recombination rate of the electrons-holes in comparison to g-C₃N₄ with the Cu-SnO₂ catalysts.

Additionally, the presence of more surface-active sites onto g-C₃N₄ increases the adsorption rate of dye molecules, and the layered structure of g-C₃N₄ increases the transfer of photo-generated electron-hole from g-C₃N₄ to Cu-SnO₂ due to the formation of the composite. Conversely, in the presence of more or less amount of Cu-SnO₂ than that of the optimized amount, the photodegradation performance of the prepared nanocomposite is determined relatively less, because of poor absorption of visible light radiations under similar reaction conditions due to the large bandgap energy value.

The photocatalytic performances of g-C₃N₄, Cu-SnO₂, and Cu-SnO₂/g-C₃N₄ nanocomposite were examined against the degradation of MB dye solutions with 30 mg/L dye concentrations and 20 mg of catalyst dose amounts at pH=10 under visible light and in the 60 min of visible light irradiation 50.7%, 89.09% and 97.6% of MB is photocatalytic degraded by g-C₃N₄, Cu-SnO₂ and Cu-SnO₂/g-C₃N₄ respectively. This photocatalytic degraded by g-C₃N₄, Cu-SnO₂, and Cu-SnO₂/g-C₃N₄ over MB dye is calculated as follow.

$$\% \text{ degradation g-C}_3\text{N}_4 = \frac{A_0 - A_t}{A_0} \times 100 = \frac{0.862 - 0.425}{0.862} \times 100 = 50.7\%$$

$$\% \text{ degradation Cu-SnO}_2 = \frac{A_0 - A_t}{A_0} \times 100 = \frac{0.862 - 0.094}{0.862} \times 100 = 89.09\%$$

$$\% \text{ degradation Cu-SnO}_2/\text{g-C}_3\text{N}_4 = \frac{A_0 - A_t}{A_0} \times 100 = \frac{0.862 - 0.021}{0.862} \times 100 = 97.6\%$$

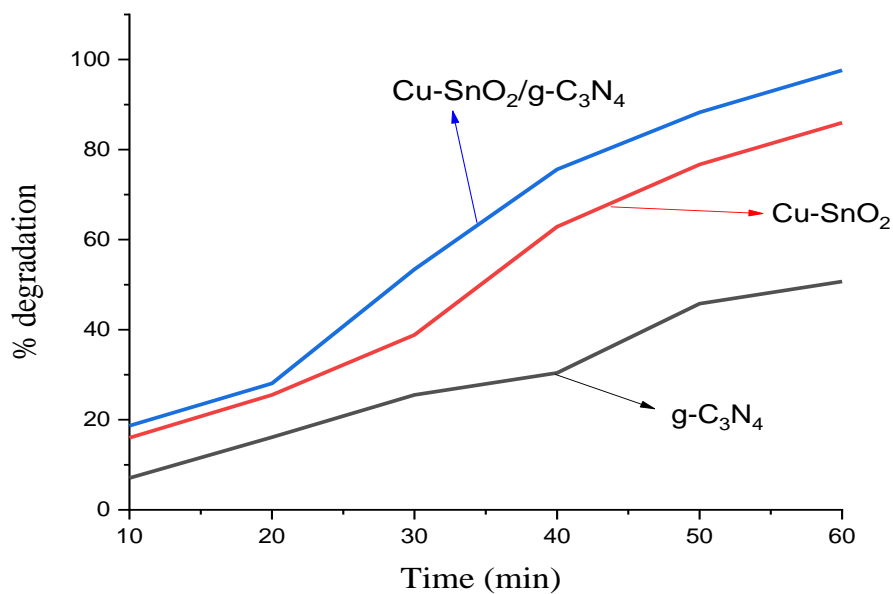


Figure 13. photo degradation of MB dye over g-C₃N₄, Cu-SnO₂ nano particle and Cu-SnO₂/g-C₃N₄ nano composite

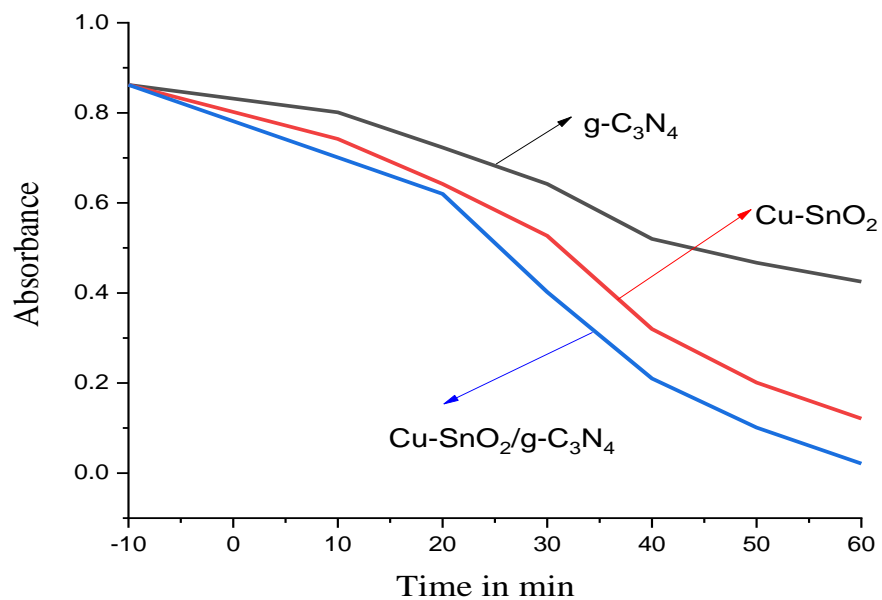


Figure 14. Photo degradation of MB dye over g-C₃N₄, Cu-SnO₂ nano particle and Cu-SnO₂/g-C₃N₄ nano composite

4.7 Reusability

The ability to reuse the catalyst in subsequent synthesis cycles reduces the overall cost of production by minimizing the need for fresh catalyst materials. This sustainability aspect aligns with green chemistry principles, promoting resource efficiency and waste reduction in nano particle synthesis. The photo stability and reusability of the Cu-SnO₂/g-C₃N₄ nano composite catalyst is studied by performing the recyclability and reusability photocatalytic experiments for MB dye for four cyclic runs under visible light exposure. The used photo catalyst is recollected by centrifugation at the end of each experimental run of use, washed with distilled water and ethyl alcohol, and dried in the oven for 2 hr at 100 °C before utilize in the next run of use under similar reaction conditions.

The photocatalytic performance of the Cu-SnO₂/g-C₃N₄ nano composite catalyst is determined to be nearly the same for each run of use. After four runs of reuse, in the photo degradation efficacy of the catalyst, a slight decrease. However, the efficiency of the catalyst was 90.4% for MB dye under visible-light irradiation. The slight decrease in the photocatalytic activity of the catalyst could be accredited to the loss in the amount of photocatalyst during the process of recollection and deposition of intermediate species on the active sites formed during the degradation of MB dyes.

4.8 Photodegradation Mechanism

The basis of the results of reactive species scavenger experiments and valance band (VB) edge potential (EVB) and conduction band (CB) edge potential (ECB) values, the plausible photo degradation mechanism for the degradation of MB dye over the Cu-SnO₂/g-C₃N₄ nano composite photo catalyst can be projected. The EVB and ECB values for g-C₃N₄ and Cu-SnO₂ can be determined using the relation

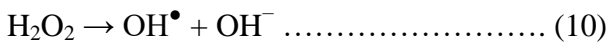
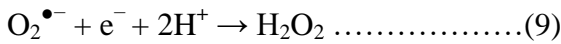
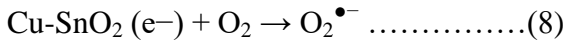
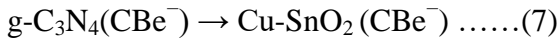
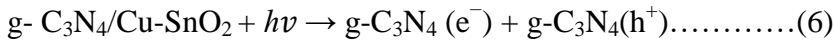
$$E_{VB} = x - E_e + 0.5E_g \dots\dots\dots (4) \text{(X. Linet } al., 2007)$$

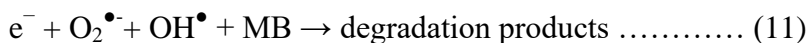
$$E_{CB} = E_{VB} - E_g \dots\dots\dots (5)$$

where x is the absolute electronegativity of g-C₃N₄ and Cu-SnO₂, values of x were 2.55eV and 3.6eV for g-C₃N₄ and Cu-SnO₂ respectively (from Pauling scale), E_e is the energy of free electrons on the hydrogen scale (≈ 4.5 eV) and E_g is the band gap energy values. The band

gap energy values determined for the g-C₃N₄ and Cu-SnO₂ are 2.82 eV and 1.93eV respectively. Therefore, the EVB and ECB values are calculated as -0.53 eV and -3.38 eV for g-C₃N₄ and 0.07 eV and -1.87 eV for Cu-SnO₂. Under visible light exposure, only the g-C₃N₄ is excited and the photogenerated electron-holes are produced in the VB of g-C₃N₄. The photo-generated electrons move from VB of g-C₃N₄ to the corresponding CB. Due to the creation of heterojunction between g-C₃N₄ and Cu-SnO₂, and more negative value of the CB edge potential of g-C₃N₄ (-3.38eV vs. NHE) (M. A. Qamaret *al.*, 2020) than that of Cu-SnO₂(-1.87eV) (M. A. Qamaret *al.*, 2020) the photogenerated electrons from the CB of g-C₃N₄ could transfer to the CB of Cu-SnO₂.

The accumulated electrons on the CB of Cu-SnO₂ move to the surface of the heterojunction and reduce dissolved O₂ molecules into superoxide radicals (O₂•⁻) because the CB edge potential of the Cu-SnO₂ (-1.87 vs. NHE) is more negative than the standard redox potential (O₂/•O₂⁻) (-0.33 eV vs. NHE) (W. Liu, *et al.*, 2013). In this way, the produced superoxide radicals degrade the MB dye molecules into non-hazardous products. On the other hand, the photo-generated holes stay in the VB of g-C₃N₄, but could not oxidize OH⁻ or H₂O to •OH radicals, since the VB edge potential of g-C₃N₄ (-0.53eV vs. NHE) is more negative than that of the standard redox potential of E (•OH/OH⁻) (1.99 eV vs. NHE) (W. Liu, *et al.*, 2013). However, the holes are capable of decomposing dye molecules directly. In this manner, the transfer of charge carriers is improved and the rate of recombination of the photo-generated electron-hole pairs is effectively suppressed by the doping of Cu-SnO₂. Consequently, the photocatalytic performance of the prepared Cu-SnO₂/ g-C₃N₄ is enhanced against MB dye molecules in comparison to the components of (g-C₃N₄ and Cu-SnO₂) of the heterojunction. The relevant reactions are listed.





4.9 Anti-Oxidant Activities

DPPH test to determine the radical scavenging activity, 0.1 mill molar (mM) solution of 2,2-diphenyl-1-picrylhydrazyl (DPPH) was generated by dissolving 4 mg of DPPH in 100 ml of ethanol for making stock solution. 2 mg of Cu-SnO₂/g-C₃N₄ added into 25 ml DPPH solution. The solution was well shaken and then stored in the dark at room temperature for one hour. The absorbance of 0.140 was measured at a wavelength of 517 nm after one hour. A control sample consisting of 3 ml of DPPH was used and the absorbance at 517 nm was 0.698. The % radical scavenging activity of the Cu-SnO₂/g-C₃N₄ was calculated using the following formula.

$$\%RSA = \frac{\text{Abs.control} - \text{Abs.Sample}}{\text{Abs.Control}} \times 100 \dots\dots\dots (12)$$

Where, RSA is the Radical Scavenging Activity; Abs control is the absorbance of DPPH solution, Abs sample is the absorbance of the sample(catalyst).

DPPH is a stable nitrogen-based free radical that has a violet color in the solution that changes to pale yellow after reduction by Cu-SnO₂/g-C₃N₄ nano composite the process of hydrogen or electron transfer substances, which are able to execute this reaction can be considered as antioxidants and therefore a radical scavenger, the radical form of the DPPH molecule has an absorbance at 517 nm which is the change from 0.698 to 0.140 after accepting of an electron or hydrogen radical from anti-oxidant. The sequence of DPPH radical scavenging effectiveness of the sample and ascorbic acids (vitamin C) as follows, 2 mg (83.9%) Ascorbic acid > 2 mg (79.9%) in 25 ml DPPH solution.

5. CONCLUSION AND RECOMMENDATIONS

In conclusion, the green synthesis of copper-doped tin oxide graphitic carbon nitride Nano composite has shown promising results in photo-catalytic degradation of methylene blue. By using aqueous leave extract of *Cal Pura A urea*. The use of environmentally friendly synthesis methods and the incorporation of copper into the composite material have enhanced its photo-catalytic activity. The dye degradation results of a series of Cu-SnO₂ samples were compared via UV-visible spectroscopy, and it was found that by increasing the concentration of copper in SnO₂ nanoparticles, the rate of degradation was enhanced regularly.

The band gap g-C₃N₄, Cu-SnO₂, and Cu-SnO₂/g-C₃N₄ narrowed from 2.83 eV to 1.55 eV by Cu-doping of SnO₂ and making composite with g-C₃N₄. In order to achieve the highest degradation in a short period of time the Cu-SnO₂ Nano particle makes a composite with the best catalytic efficiency of g-C₃N₄. The photocatalytic performance of the green synthesis Cu-SnO₂/g-C₃N₄ nano composite is determined much higher in compare to the g-C₃N₄ and Cu-SnO₂. The optimized Cu-SnO₂/g-C₃N₄ photo catalyst is 97.6% of MB dye is degraded in 60 min of visible light irradiation at pH=10. The degradation of methylene blue under visible light irradiation demonstrates the potential of this composite material for waste water treatment application.

I recommend the use of Cu-SnO₂/g-C₃N₄ nano composite by using plant extraction for visible-light photo catalytic degradation of methylene blue dye, the working life and recycle ability of the Cu-SnO₂/g-C₃N₄ photocatalyst should not be ignored, because long-term stability and durability are necessary for large-scale practical applications. It must be mentioned that although the experimental research of Cu-SnO₂/g-C₃N₄ photocatalyst has made great progress, it still has a long way to go before practical application. Because the actual application environment is more demanding and various influencing factors should be considered comprehensively, including cost, effectiveness, durability, etc. we should continue to be committed to solving the above problems, so that theoretical research can be transformed into practical applications to achieve greater value in the future.

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