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CuO Nanoparticles: Unveiling Photocatalytic Activity Through Comprehensive Review

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Abstract - Their stability and endurance even when washed indicates that it cannot be easy to eliminate them, therefore, efforts should be made to develop new products with attributes that will ensure they arrest the formation of dyes. In the present study, we propose a simple and one-pot synthetic approach for the synthesis of CuO NPs; furthermore, to carry out the mechanochemical process, we use the bioactive extract of Seriphidium oliverianum leaves as a stabilizing and reducing agent. The identification of CuO NPs was confirmed through using Fourier-transform infrared spectroscopy (FTIR), photoluminescence (PL), scanning electron microscopy (SEM) and X-ray diffraction (XRD). A use of the UV-Vis spectroscopy technique enabled the monitoring of the photocatalytic activity of CuO NPs. CuO nanoparticles showed remarkable ability to disperse some of the commercial colours soluble in water. Per cent degradation for methyl green (MG) was 64% whereas that of methyl orange (MO) was 45%. 34% ~ 0. 313 and 64. 128% ~ 0. 468, respectively. When CuO NPs synthesized by the biomechanochemical process, it was revealed that CuO NPs proved very efficient in removing dyes from water.

Key Words: CuO nanoparticles (CuO NPs), Mechanochemical process, Photocatalytic activity, Fourier-transform infrared spectroscopy, (FTIR), Bioactive extract of Seriphidium oliverianum, Dye degradation

1.INTRODUCTION

According to different authors, the threat of damaging the external environment has increasing with the development of industrialization [1]. The kind of trash that continues to make its way into water bodies is Can be a threat to aquatic life [2]. Many industries such as food processing, pharmaceuticals, leather, textiles, inks, cosmetics etc. are participating in this pollution problem by generating organic dyestuffs. On the negative effects on lit lives, it is realized that the release of tens of complex dyes into the water sources goes into tons every year [3]. According to existing studies, there are challenges when it comes to the identification of the mechanisms for degrading dyes [4]. The said strategies include ion exchange, ozonolysis, photocatalytic degradation, chemical oxidation, and coagulation based processes. There are many contaminants which can be removed by adsorption as stated by the references [5]. However, they still considered a very effective and eco-friendly technique for removing dyes from wastewaters; the photocatalytic degradation by a semiconductor photocatalyst. Bass depuration of organic dyes is attainable bylight activematerials and those with large surface areas [6]. Due to the availability of a small number or energy band, certain semiconductors and metal oxides can effectively be used under sunlight as photocatalysts. Band structure of CuO which is a p-type semiconductor has a relatively small band gap ranging from 2. 22 to 2. 69 eV. Concerning optical, mechanical and photolytic aspect they all exhibit satisfactory reception in CuO nanoparticles (NPs) [7]. Sol-gel synthesis, solvothermal synthesis, hydrothermal synthesis, microwave-assisted synthesis, arc-discharge synthesis, etc. are common techniques for synthesizing CuO NPs.

Therefore, the synthesis of CuO NPs through the use of plant extracts is one of the best solutions that are environmentally sound and viable. Due to their highest reactivity, bacteria, fungi, algae, and plants (such as Solanum americanum, Solanum nigram, Camellia japonica, Pterospermum acerifolium, Gum karaya, Soya bean etc.) can be employed as bioactive materials in biological techniques for CuO NPs synthesis.

In other experiments regarding the green synthesis of CuO NPs and characteristic of material, the biological action and phytochemicals of the production have also been studied [8]. Proteins especially enzymes, amino acids, polysaccharides, alkaloids, vitamins and alcoholic materials can stabilize and minimize nanoparticles. These include the reduction power of ions as well as the plant reduction capacity through biochemicals such as polyphenols, enzymes, and chelating agents leading to the final CuO NPs. Seriphidium oliverianum belongs to the family asteraceae and has been earlier used in traditional medicine. Flavonoids, terpenoids, tannins, anthraquinones, alkaloids, and cardenolides are some of the bioactive compounds present in this plant which mainly consists of carbohydrates. It has been demonstrated that biomolecules to some extent, can reduce the biological CuO NPs [9]. Many important products such as gasoline, chemicals and medicines, etc. their synthesis from cheap raw materials involve an essential catalysis-based operations. These processes are regarded of being driven by catalysts. The role that catalysis plays in our society is emphasized by estimates which show that business based on catalysis might produce goods worth several trillions of euros per annum. It is predicted that the total ales value will have a value of approximately 19 billion euros of catalytic materials. Owing to its suitability for the steady-state running, sustained performance, and catalyst recovery, heterogeneous catalysis is applied extensively in the chemical industry. Often, these catalyst materials possess complex structures and little is known about the active sites that are crucial to catalytic reactions. In the case of solid catalysts, this is especially true if we seek to obtain them through large-scale production. Catalyst synthesis is still viewed with a lot of scepticism as being more of an art form instead of technology despite this area being relatively technologically advanced.

Consequently, Catalysts are the center of stage; this demonstrates that Researchers do take the question regarding how to design catalysts rationally , being active, selective, and stable seriously. This is basic to the mass production of solid catalysts to ensure that the material produced would be stead and dependable in its operation. This has to increases people's perception that there is more of a qualitative components in catalyst synthesis than a quantitative component; given that the field is highly technological. Synthesis of catalysts is a significant area of focus because catalysts are synthesized after critical effort is

implemented in understanding how to synthesize catalysts that are active, selective, and stable in a logically synthesized manner.

At the current age, some of the most widespread techniques in the production of heterogeneous industrial catalysts while maintaining an adequate level of control over its properties is impregnation, deposition-precipitation, the hydrothermal method, and precipitation. Other potential approaches, for instance, are the fusing and the use of the solid-state reactions. However, since solution-based techniques are fundamentally different from deposit-based techniques, they invariable generate a considerable amount of solvent waste. Moreover, some of the precursors used contain nitrate or chloride metal salts and the following calcination processes will in turn generate toxic gases. That several of these gases escape into the atmosphere might require certain actions to avoid. A large number of researchers also view the wet chemistry methods as The present day industrially viable methods for preparing catalysts which can offer decent control over its characteristics and efficiency comprise of impregnation, deposition-precipitation, hydrothermal, and precipitation. Other methods include sintering and other solid-state processes which may also prove feasible. However, due to their propensity for generating large amounts of waste solvent, solution-based techniques are widely utilized.

This may lead to the following calcination steps producing poisonous gasses especially when precursors are in the form of nitrate or chloride metal salts. Possible fundamental measures that could prevent the release of these gases into the atmosphere are as follows. Here are certain activities that could be required to prevent these gases from being released into the atmosphere. Using wet chemistry processes, many people believe that the processes for a certain catalytic material composition are either time consuming or challenging to upscale. Furthermore, processes which include solution procedures and other subsequent processes that are performed at high temperatures rarely conform with modern environmental standards due to energy consumption and generation of dangerous waste materials. Hence, there is a vast incentive to come up with new synthetic methods that are less costly, more efficient, convenient, and easier to compare to the older methods.

Optimisations of the produced material or economic or environmental benefits of the procedures may make inventive synthetic techniques. The green synthesis of manufacturing catalysts is very vital since with the escalating effects of environmental degradation and rapidly depleting sources of energy [10]. Reactive extrusion and ball milling are two widely known, rapid, and effective ways of sintereing catalytic compositions.

The development of a low-energy, green synthetic strategy for producing nanomaterials has provided the mechanochemical methodology in the last few decades. Some of the many possibilities of the use of the metal oxide nanoparticles prepared by this method include generation of metal oxide nanoparticles to be used in environmental sensing, energy storage, conversion and biosensing. A homogeneous reaction may be easily achieved and the mechanochemical synthesis is an easily executable process to an industrial scale. An important reason for developing the modern interest in “green chemistry” is the possibility of a chemical reaction to occur without using a large amount of solvents and heat, and it is this idea that the field strives for.

To the best of out knowledge; no any work on the mechanical synthesis of CuO NPs using the extract of Seriphidium oliverianum has been reported. In the present work, I designed a simplo bio-mechanochemical method to synthesis CuO NPs using Seriphidium oliverianum leaf extract. We employed the electric mortar grinder mill for the purpose. Two water-soluble dyes methyl green (MG) and methyl orange (MO) were also subjected to the degradation experiments to determine the extent to which they could be degraded by the bacterial species.

2. RESULTS AND DISCUSSION

In this research, the crystalline qualitatively characterization of the synthesized CuO nanostructured material was analyzed through X-ray diffraction (XRD) analysis.

Mean size was 11.44 was done to get the overall mean size from all the classes available in the selected area. The crystallite size of the NPs was estimated to 11.44 nm. From figure 1, it can be realized that synthesised CuO NPs have many monoclinic structural peaks in the PXRD diffractogram.

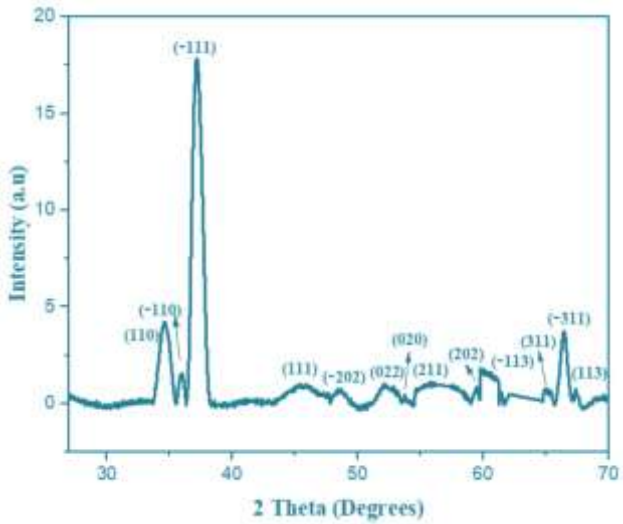

Fig. 1. For the XRD characterization of synthesized biogenic CuO NPs, a monoclinic phase of CuO is illustrated.

2.1 Using SEM Scanning (SEM)

Every precipitate was built up from small CuO nanoparticles and uniform in size. Nanoparticles possess high surface energy because a very high proportion of their volume has surface area. Nanoparticles themselves do aggregate because they prefer to have as little surface area as possible in terms of energy. Van der Waals forces acting on the particles with sufficiently low energy values are attractive and increase the likelihood of an uncontrollable particle aggregation. Grain sizes of 1. 68 m were typical for CuO NPs in the present study. Electrochemical synthesis of CuO NPs leads to the formation of small particles in an aggregated state as depicted in Figure 2.

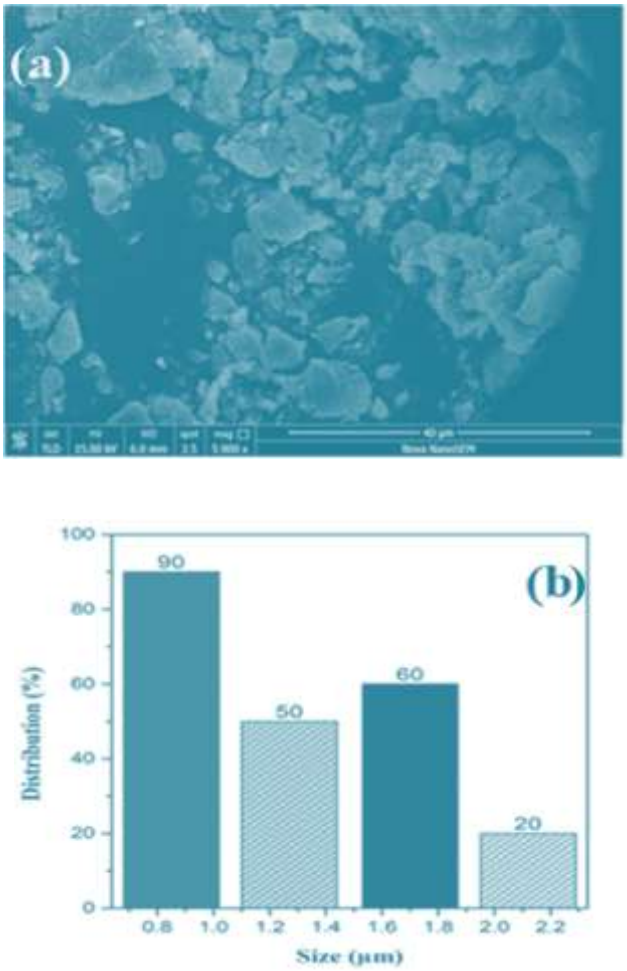

Fig 2. The synthesis of biogenic CuO NPs is presented as a SEM image (Figure 2 (a) and size distribution (Figure 2 (b)).

2.2 Fourier Transform Infrared (FTIR)

For the purpose of identifying the complete functional groups present in the bio-mechanochemically synthesized CuO NPs we used the Fourier Transform Infrared (FTIR) spectra at 390-3900 cm−1. This could be attributing to the fact that it was observed that Seriphidium oliverianum extract that was used to coat CuO NPs contributed to the strong vibrational bands observed in the FTIR of CuO NPs (Figure 3)Here, ${\text{O–H}}$ vibration of alcohol or phenolic compounds present on the surface of the NPs is represented by a broad band at 3468 cm−1 as shown in the Figure 3. Finally, the following complementary FTIR bands of the alkene group correspond to the aromatic bending vibrational frequency (C=C) at 1460 cm−1 and at 1414 cm−1.

This could be attributed to the bio components present in leaves that play their role in stabilizing and decreasing NPs. Also, the alkane frequencies in the C-H group contribute to the sharp peak at 1352 cm−1. This is well abbreviated in the alcoholic bio element group at 1176 cm−1 C-O stretching of the plant extract. The ring stretching vibration and bending frequency of the aromatic group is observed at 744 cm−1. The FTIR spectroscopy provides a confirmation on the existence of CuO NPs by the vibrational frequency range of 390 to 590 cm−1 attributed to Cu-O bond. This evidence relates with the presence of glycoalkaloid, tropane alkaloid and atropine functional groups in the phytochemicals of Seriphidium oliverianum, which has been confirmed as a reducing agent in the synthesis of CuO NPs.

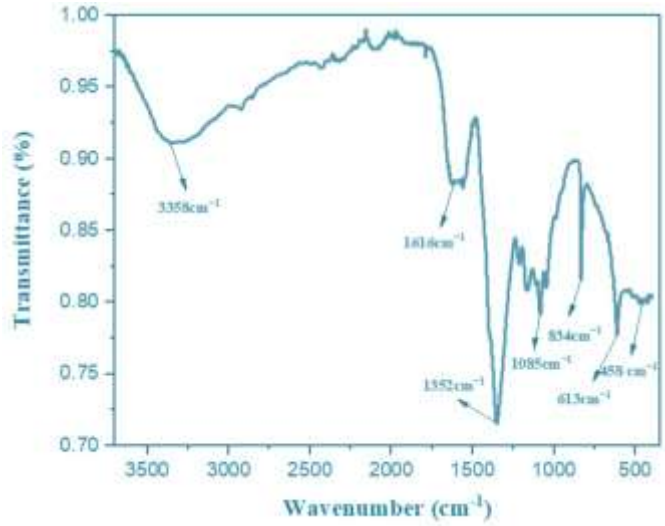

Fig 3.FTIR spectra of biogenic CuO NPs are presented below.

2.3 Photoelectron microscopy

The UV-Vis spectra of CuO NPs for the region 290 nm to 540 nm are depicted in Figure 4. The interband transition of the electrons in the Cu metal core results to the formation of a band at 346 nm while the CuO NPs demonstrated the predicted absorption band of 306 nm. The preparation of stable CuO NPs uses bio materials which are present in plant extract. The position of the absorption band in the UV-Vis spectrum may depend on such parameters as reaction time, temperature, concentration of the precursor salt and aqueous leaf extract, as well as nanoparticle form. A large concentration of nanoparticles is also evident from the sharp band.

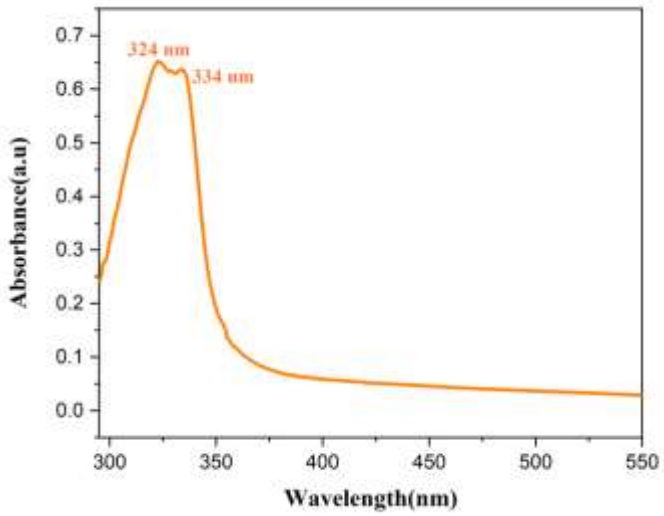

Fig 4. the biogenic CuO NPs' UVvis spectra.

2.4 Photoluminescence Spectroscopy (PL)

Potentially, the photocatalytic properties of CuO NPs including the photochemical characteristics, surface defects, optical emission data, and outer interstices may be understood with the help of PL. Both electron transport and separation, recombination, and photocatalysis phenomena can be studied through the fluorescence process. One type of photoluminescence mechanism is formation of a hole, which

enables an electron to move from the valence band to the conduction band upon absorption of energy. Hence recombination occurs when an electron is fired when at the same time it is transported back to the valence band. Moreover, the facet defect and oxygen vacancies are reflected for the small-sized particles which cause a high luminous peak.

The PL spectra of CuO NPs that were excited at 290 nm and 340 nm are shown in figure 5. Namely, for the wavelength of 290 nm only two peaks can be observed: at 418 and at 567 nm (Figure 5a). Specifically, the 322 nm band is ascribed to bound excitons whereas the 587 nm band is ascribed to band edge-free excitons. Because the particle size and surface defects of TiO2 nanoparticles are small, the PL spectra may have a strong peak value. It is also found that the high recombination rate is coupled with the intense band. By applying 340 nm wavelength, two distinct bands at 433 nm and 679 nm are obtained as depicted in figure 5b. The bands obtained at 300 nm (Figure 5a) and those obtained at other wavelengths are the various exictation processes. Before the absorbed radiant energies can be combined back into the valence band, some conditions have to be fulfilled to ensure that electron transformations occur on different energy levels as follows. Many ranges are found from the PL spectra. From the spectra profile, band edge-free and bound excitons were found to be more intense of the 344 nm excitation than in the 290 nm excitation.

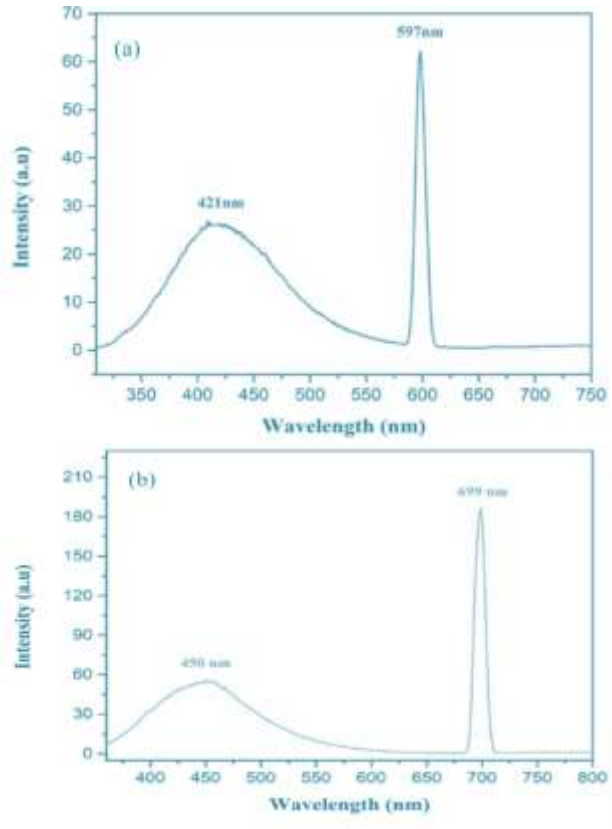

Fig 5. The PL spectra of synthesised Biogenic CuO NPs was recorded at 290 and 340 nm.

2.5 A Possible Route to Synthesize CuO Nanoparticles

Immediate bioc reduction of the precursor salt starts and change of color of the solution from blue to dark brown confirms the formation of CuO NPs. This study shows that the biochemicals within the plant extracts are important to stabilize CuO NP.

It has been postulated that flavonoids have many functional groups utilized in reductant processes that help in the synthesis of NPs [11]. During the conversion of enol flavonoids into keto flavonoids, hydrogen atoms are ejected, which reduces Cu ions into metal Cu NPs. Up to date, there is no clear understanding of how the extracts of plants facilitate the formation of CuO NPs. The synthesis of CuO NPs is believed due to oxidation process which explains the intensity of the colour of the nanoparticles when exposed to the open air after one hour. The oxidation can be attributed to presence of oxygen in the environment or reduced metal ion binding to biochemicals before forming stable compounds; this is just but a few of the many possibilities. In order to counter the electrostatic attraction metal oxide ions connect to each other thus stabilizing NPs as a way of avoiding formation of clusters. However, reduction of metal nanoparticles using plant extracts as reducing agents is safe, cost-effective, and green even though the mechanism of the process is not well understood. The following is the proposed process for preparation of CuO NPs as shown in FIG 6.

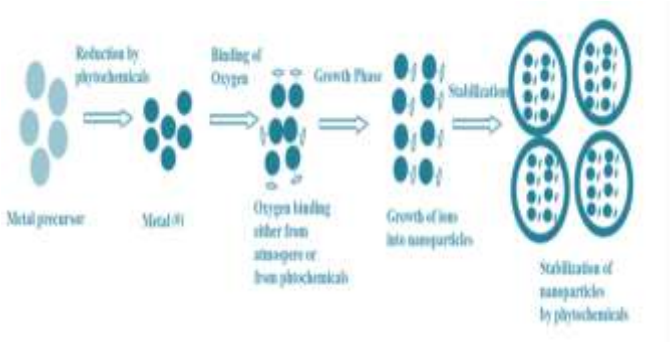

Fig 6. Synthesis mechanism for the CuO NPs.

3. MATERIAL AND METHODS

The chemical and precursor components were all from Sigma-Aldrich (98. 97%) and were used exactly as received. The precursor material used was Cu(NO3)2. 3H2O. It was not necessary to further purify any of the other compounds; all of them were of analytical reagent grade. For preparing the standard solutions, deionized water was used.

3.1 Extracting Seriphidium Oliverianum from Leaves:

The washed Seriphidium oliverianum leaves were left to air dry for a while then rinsed with distilled water. The dried leaves were then crushed into fine powder using a mortar and pestle. Four grams of powder was dissolved with forty-eight milliliters of deionized water. After that, it was allowed to stand for 23 hours without stirring and then heated at 69 ◦C for 28 min with stirring. The flocculated particles were then filtered twice on filter paper. The obtained leaves were left to be transported and used in other experiments in the laboratory. Since it is possible that the fresh leaves may have different morphology, size, and form, it is more appropriate to use the dried ones. Furthermore, heat stability during the drying of the leaves and the extraction process influences the number and the types of flavonoid groups. Moreover, no clear absorption band could be exhibited on the UV spectra if fresh leaves of the plant were used instead of the dried ones.

3.2 Culture of Copper Oxide Nanoparticles

Following the preparation of a fine copper nitrate powder, 38 mL of plant extract was prepared containing [Cu] of 0. 2 M) was added, and the mortar containing the mixture was then ground continuously for 2 hours at the speed of 69 rpm in an electric mortar grinder mill. The appearance of a new color reflected the presence of CuO NPs in the described solution. The following procedure involved the exposure of the mixture to natural light for an hour which made the sample change color from pale brown to dark brown. In this case, the mixture was centrifuged for 29 minutes them assuring 3990 rpm at room temperature to get rid of any excess of leaf extract or precursor salt. After that, it was rinsed with deionized water. /After that, it was washed with deionized water. This CuO NPs was then collected on a Petri plate and left to air dry. The whole procedure is summarized in Figure 7.

Fig 7. Synthesis of CuO-NPs by mechanochemical methods and sources of biogenic copper oxide nanoparticles.

3.3 Characterization

The optical characteristic of the synthesized CuO NPs was investigated in the ultraviolet-visible region of the wavelength ranging from 289 to 540 nm. In this study, a Fourier-transform infrared spectrophotometer with a vibrational frequency of 390-3990 cm−1 was employed to analyze the qualitative and quantitative characteristics of CuO NPs. The size, type, and phase description of CuO NPs was determined by using powder X-ray diffractometer using Cu-Kα radiation source with wave length of 1. 40579 Å. Morphological characteristics of the CuO NPs were also characterised by scanning electron microscopy using MIRA-III TESCON. Through photoluminescence (PL) spectrscopy, the surface deformities, photochemical, optical, and structure of the produced goods at the 290-340 nm range were determined.

3. CONCLUSIONS

This work demonstrated one novel biomechanical chemical method of synthesizing CuO NPs from the aqueous portion of Seriphidium oliverianum leaves without polluting the environment. The bio components discovered in the leaves of this plant aided in the stabilizing and reduction processes. A preferred monoclinic CuO structure along with the particle size of 11. The present study based on the PXRD investigation reveals the synthesized compound possesses 34 nm crystallite size. Au/SiO2-CuO NPs exhibited high photocatalytic activity due to the presence of OVs inside the CuO NPs which were confirmed by two bands at 418 nm and 565 nm in PLE spectra. The synthesised nanoscale material effectively reduced the MG and MO dyes under light conditions which points to its catalytic capabilities. Also, based on the findings, it was noted that the photocatalytic reduction process of both the MG and MO dyes obeyed pseudo-first-order kinetics, and the elimination rate was 55%. These innovative discoveries opened new prospects for the synthesis of cost-effective, green photocatalysts for the degradation of dyes from water.

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