



Engineering of *Foeniculum vulgare* with material science: La₂O₃-CeO₂-CuO nanocomposites to revolutionize photocatalysis and antimicrobial challenges

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ARTICLE INFO

Keywords:

Nanocomposite
Green synthesis
Antimicrobial activity
Photocatalysis
Methylene blue

ABSTRACT

The growing awareness of green avenues and the use of environmentally friendly technologies for crafting nanostructures leads to a remarkable shift in the fabrication approach. In this scenario, developing a highly crystalline heterojunction catalyst based on metal oxides is seen as a promising strategy. This study investigated the synthesis of nanocomposite La₂O₃-CeO₂-CuO and pure La₂O₃, CeO₂, CuO employing *Foeniculum vulgare* as a plant extract. The fabricated samples are characterized by X-ray diffraction (XRD), Fourier-Transform Infrared Spectroscopy (FTIR), Ultraviolet-Visible Spectroscopy (UV-Vis), Transmission Electron Microscopy (TEM), and Energy Dispersive X-ray Analysis (EDAX). The La₂O₃-CeO₂-CuO nanocomposite exhibits remarkable activity against *Escherichia coli* and *Staphylococcus aureus* with activity index and zone of inhibition of 93 % (31.90 ± 0.15 mm), and 92.33 % (27.7 ± 0.12 mm), respectively. Surprisingly, La₂O₃-CeO₂-CuO has a lower band gap, e⁻/h⁺ recombination, and enhanced charge transfer capability than pure La₂O₃, CeO₂, and CuO. The photodegradation efficiency of La₂O₃-CeO₂-CuO was recorded at 99.7 % after 100 min under sunlight radiation against methylene blue (MB), which was significantly higher than pure La₂O₃, CeO₂, and CuO. Our findings reveal that the La₂O₃-CeO₂-CuO nanocomposite is a highly effective antibacterial agent and photocatalyst formed in conjunction with *Foeniculum vulgare* as a plant extract. The bi-functionality of La₂O₃-CeO₂-CuO holds significant potential in achieving the ultimate clean environment.

1. Introduction

Nanomaterials are in the limelight because of their superior qualities over their bulk counterparts, which include more active sites, and a higher contact surface area. This is part of the hunt for materials that may satisfy society's expanding requirements [1–3]. Materials in the nano and small sizes are having an impact on photocatalytic, pharmaceutical, and medical applications [4–6]. Their applications are

growing, including as antimicrobials, contrast agents for imaging, and supports for the effectiveness of drugs and catalysts in breaking down harmful dyes [7–10].

Industrial pollution and microbial infections are serious risks to public health across the globe and are a major cause of death rates. Over a million people are thought to die each year as a result of *S. aureus* and *E. coli*, two of the most common bacteria that cause infection-related mortality. The proliferation of these bacteria is made more

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<https://doi.org/10.1016/j.jece.2025.118470>

Received 29 April 2025; Received in revised form 30 July 2025; Accepted 3 August 2025

Available online 5 August 2025

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detrimental by unclean surroundings and a lack of access to clean water, which may result in serious illnesses, including sepsis, infections of the digestive tract, and antibiotic resistance [11–13]. Pathogenic microorganisms can spread infections, migrate over massive distances, and create biofilms to increase pathogenicity in the human host [14]. It is the basis of diverse infectious diseases, including pyomyositis, endocarditis, bacteremia, osteomyelitis, cholera, lethal pneumonia, giardiasis, and infections of the skin and soft tissues [15,16]. Furthermore, industrial pollution introduces hazardous compounds that deteriorate water quality and pose long-term health hazards, especially from dye effluents. Organic pollutants, especially dyes, pose a serious threat to the environment because of their "high toxicity, stability, and capacity to cause mutations and cancer." Because it contains methyl bromide molecules, methylene blue, which is extensively utilized in textile manufacturing, is especially hazardous because of its toxicity and stability. It is essential to remove these substances from water to protect aquatic life and water resources from environmental hazards [17,18].

The combination of toxic pollutants and microbiological pollution highlights the urgent need for better public health interventions, more stringent environmental restrictions, and comprehensive water management measures to reduce the hazards implicated [19]. Using metal oxides to create new nanomaterials with dual uses as an antibacterial agent and photocatalyst is a widely recognized area of research [20]. The dynamic potentials of the nanocomposite made it possible to improve the characteristics of existing materials due to its ease of synthesis, size, shape, and doping with a wide variety of metal and non-metal materials at different concentrations [21]. Novel and effective nanocomposites that can function as biological agents to lessen the lethal impact of infectious bacteria and as photocatalysts for purifying water have been created and documented [22]. To obtain unique capabilities for biomedical and environmental applications, researchers and scientists are now working to produce superior, environmentally benign, multifunctional, nanostructure with sustainable qualities [23].

In this situation, tailored metal oxides (MO) are regarded as a significant class of materials that function as antibacterial and photocatalysts [24,25]. From the literature inspection, researchers have synthesized effective photocatalysts and antimicrobial agents like CuO–Co₃O₄ [26], Zn/Ce–CuO [27], ZnO/SnO₂–CeO₂/CuO [28], La₂Ti₂O₇ [29], La₂O₃/CeO₂ [30], La₂O₃–CuO [31], TiO₂@CeO₂ and CeO₂@TiO₂ [32], CeO₂/BiVO₄/g-C₃N₄ [33], Bi₂O₃/CeO₂ [34], TiO₂–Y₂O₃–V₂O₅ [35], CeO₂/CdO [36]. Hence, nanocomposites with widespread applications are significant in biological and environmental research fields that can offer effective catalytic sites for functioning. Among them, La₂O₃, CuO, and CeO₂ stand out owing to their distinctive structural and electrical features. CeO₂, an n-type semiconductor with a bandgap of roughly (~3.26 eV), is well-renowned for its excellent optical, chemical, antibacterial, electronic, and photocatalytic capabilities [37,38]. CuO, a p-type nanomaterial with a small bandgap (~1.20 eV), is widely recognized for its strong antibacterial activity and outstanding photocatalytic efficiency under visible light [39,40]. La₂O₃, with its intermediate bandgap (~4.5 eV), also exhibits antimicrobial potential while enhancing catalytic activity. However, regardless of outstanding features, these materials confront obstacles such as fast electron-hole recombination and restricted solar absorption owing to their bandgap restrictions [41]. The evolution of nanocomposites by combining narrow bandgap semiconductors (CuO) with wide bandgap materials (La₂O₃ and CeO₂) is an effective way to overcome these limitations [42]. It extends the absorbing capacity of solar light toward the visible spectrum, thereby improving catalytic efficiency through reduced recombination and improved charge separation [43,44].

One of the significant medicinal plants used in conventional medicine is *Foeniculum vulgare* [45]. Due to its numerous applications in the food, pharmaceutical, and health cosmetics industries, *Foeniculum vulgare* is currently grown on a large scale in most parts of the world, including southern and central Europe, Asia, many African nations, Brazil, and Argentina [46]. Belonging to the Umbelliferae family, the

plant *Foeniculum vulgare* is a popular zing and traditional remedy for a variety of ailments, including liver discomfort, gonorrhea, kidney stones, diaphoretic, fever, insomnia, renal issues, mouth ulcer, laxative, diuretic, Nosebleeds, and stomachache. Ketones, lignin, flavonoids, fiber, protein, saponins, carbohydrates, and vitamins are all abundant in the plant [47]. Because of this, it may potentially be investigated as a possible templating agent for La₂O₃, CeO₂, CuO, and La₂O₃–CeO₂–CuO synthesis.

The addition of bioactive compounds from *Foeniculum vulgare* further increases the nanocomposite's biopotential, making it an extremely effective candidate for environmental and biomedical applications. The synergistic interaction between these materials also improves antibacterial performance and increases pollutant degradation. In this work, we have fabricated a La₂O₃–CeO₂–CuO nanocomposite and systematically investigated it. To evaluate the photocatalytic activity of the La₂O₃–CeO₂–CuO nanocomposite, the photocatalytic degradation of Methylene Blue was used as a model reaction. A variety of parameters were used to evaluate the catalyst. Gram-positive (*Staphylococcus aureus*) and gram-negative (*Escherichia coli*) bacteria were used to elucidate the antibacterial activity of the fabricated La₂O₃–CeO₂–CuO nanocomposite. It offers substantial environmental implications to prevailing circumstances arising due to pathogenic bacteria and toxic pollutant draining into our ecosystem. The synergistic dual behavior of La₂O₃–CeO₂–CuO nanocomposite with tailored properties effectively degrades the harmful pollutants and destroy microbial colonies. Ultimately, this La₂O₃–CeO₂–CuO fabricated by *Foeniculum vulgare* delivers a pathway for cleaner water resources and better human health.

2. Methodology

2.1. Materials

All chemicals and reagents used in the experimentation were of analytical grade without any additional purification. Lanthanum nitrate hexahydrate (La (NO₃)₃·6 H₂O), Cerium nitrate hexahydrate (Ce (NO₃)₆·6 H₂O), and Copper nitrate hexahydrate (Cu (NO₃)₂·6 H₂O), Sodium hydroxide (NaOH) precursor salts used for the synthesis of the samples. Every chemical was purchased in a commercial grade (Sigma Aldrich) and was utilized accurately without any modifications. The entire chemicals used in the present research was 99 percent pure. Moreover, distilled water (DW) was used during the studies. In addition, organic pollutants employed in this study are Methylene Blue dye in the photodegradation test.

2.2. Collection and preparation of plant extract of *Foeniculum vulgare*

Foeniculum vulgare is taken from the native area of Bahawalpur, PAKISTAN. Fresh plant material, including fennel seeds, leaves, stems, and roots thoroughly washed and dried in a shaded area. Grind the dried plant material by using a pestle and mortar into a fine powder. Mix a 10 g measured amount of *Foeniculum vulgare* powder with 100 mL of water in a 1:10 ratio (w/v). Heat the mixture at 75–85°C for 40–70 min and allow it to stand for a few minutes at room temperature for cooling purposes. Allow the extract mixture to pass through a fine mesh, and the obtained extract solution is filtered through using Whatman filter paper. Store the plant filtrate in a clean, airtight reagent storage bottle at 4°C for further utilization. (Fig. 1)

2.3. Preparation of *Foeniculum vulgare* assisted La₂O₃–CeO₂–CuO nanocomposites

The synthesis process in brief of La₂O₃, CeO₂, CuO, and La₂O₃–CeO₂–CuO nanocomposites using the analogous experimental conditions was previously discussed in the literature [48]. In three separate reagent bottles, 80 mL of distilled water was combined with 0.01 M of the corresponding salts of lanthanum nitrate hexahydrate, cerium nitrate

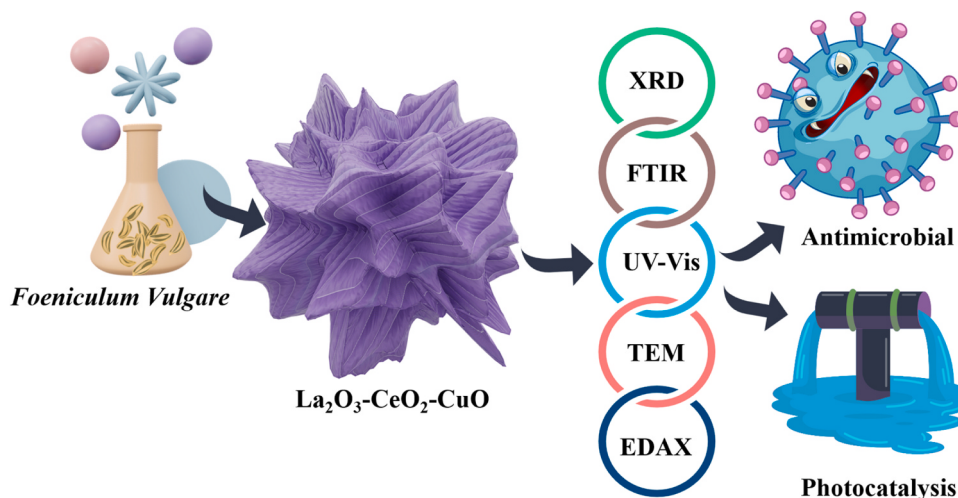


Fig. 1. Graphical representation of $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$.

hexahydrate, and copper nitrate hexahydrate to create a standard procedure for preparing La_2O_3 , CeO_2 , and CuO oxides. For fabricating the $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposite, the calculated amount with a molar ratio of 0.5:0.5:0.5 of each salt was mixed in H_2O . Add 50 mL of plant extract to the individual solution. The solution mixtures of each salt and nanocomposites were vigorously stirred for 30 min to dissolve the salts in water. Later, a freshly prepared NaOH solution was further added to the prepared relevant salt along with the extract solutions to maintain a pH level of 10. Subsequently, stirring of the reaction mixture is continued for 3 h and 50 min. The reaction mixture was centrifuged for 20 min at 6000 rpm. Washed thoroughly the resultant mixture with ethanol many times to remove undesirable ions, and desiccated at 85°C for 9 h in a drying incubator. The dried samples were finally La_2O_3 , CeO_2 , CuO , $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ annealed in a configurable Muffle Furnace at 650°C for 2 h duration and crushed into fine powder for characterization [49].

2.4. Photodegradation experiment

The fabricated pristine NPs and nanocomposites were assessed through the photodegradation of organic pollutants under direct visible light irradiation. The reaction was conducted for photocatalysis on October 15, 2024, from 12:00–2:00 p.m. at The Islamia University of Bahawalpur, Pakistan. The pyranometer (Kipp & Zonen CMP-11) assessed the recorded intensity to be between 580 and 602 W/m^2 . Before being exposed to light, the 20 mg catalyst was added to 50 mL of a dye-aqueous solution and agitated for 60 min in the dark to generate the adsorption-desorption phenomena. Following exposure to sunlight, 3 mL of the dye solution was taken out at predetermined intervals of 0, 20, 40, 60, 80, and 100 min and analyzed using the ultraviolet (UV) spectroscopy method. The MB absorption wavelengths of the dye were observed in nm. The photodegradation reaction of La_2O_3 , CeO_2 , CuO , $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ was evaluated through the following relation [50]:

$$\text{Degradation performance}(\eta) = \left[c_0 - \frac{c_t}{c_0} \right] \times 100 \% \quad (1)$$

C_0 is the initial concentration of the Mb dye, and C_t is the concentration of dye at time (t) under solar light irradiation. Different scavenger tests, such as EDTA-2Na , ASC , AgNO_3 and IPA were added to detect the ROS level that affects the photodegradation of dyes.

2.5. Antimicrobial activity

Antibacterial activity was examined for samples La_2O_3 , CeO_2 , CuO , $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$, utilizing the disc diffusion technique. The clinical

isolates of bacteria were cultured for a period of 24 h at 37°C in a medium (nutrient broth). The antimicrobial activity was assessed using a standardized inoculum concentration ($\text{OD}_{600} = 0.1$, or about 10^8 CFU/mL) against *E. coli* and *S. aureus*. Every experiment was carried out in triplicate under sterile conditions, and to guarantee statistical precision, $\pm$ standard deviation (SD) is provided. The samples La_2O_3 , CeO_2 , CuO , and $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ were dispersed with distilled water of various concentrations, ranging from 20, 40, and $60\text{ }\mu\text{g/mL}$. The filter paper disc of size (6 mm) was dipped in the fabricated sample solutions. Standard antibiotic ciprofloxacin ($0.2\text{ }\mu\text{g/mL}$) was used for the activity as a positive control. Nutrient agar solution was prepared in a weighted concentration of 2.85 g/100 mL . After adding 20 mL of nutrient agar to the Petri dishes and letting it firm, $100\text{ }\mu\text{L}$ of the test strain was then transferred to the agar surface. The agar surface was then topped with discs that had been soaked in the sample solutions. The Petri plates were parafilm-sealed and incubated at 37°C for the entire overnight. After 24 h of incubation, the inhibition zone (ZOI) was calculated [51].

$$\text{Activity index}(\%) = \left[\frac{\text{Zone of inhibition of sample}}{\text{Zone of inhibition of control}} \right] \times 100 \quad (2)$$

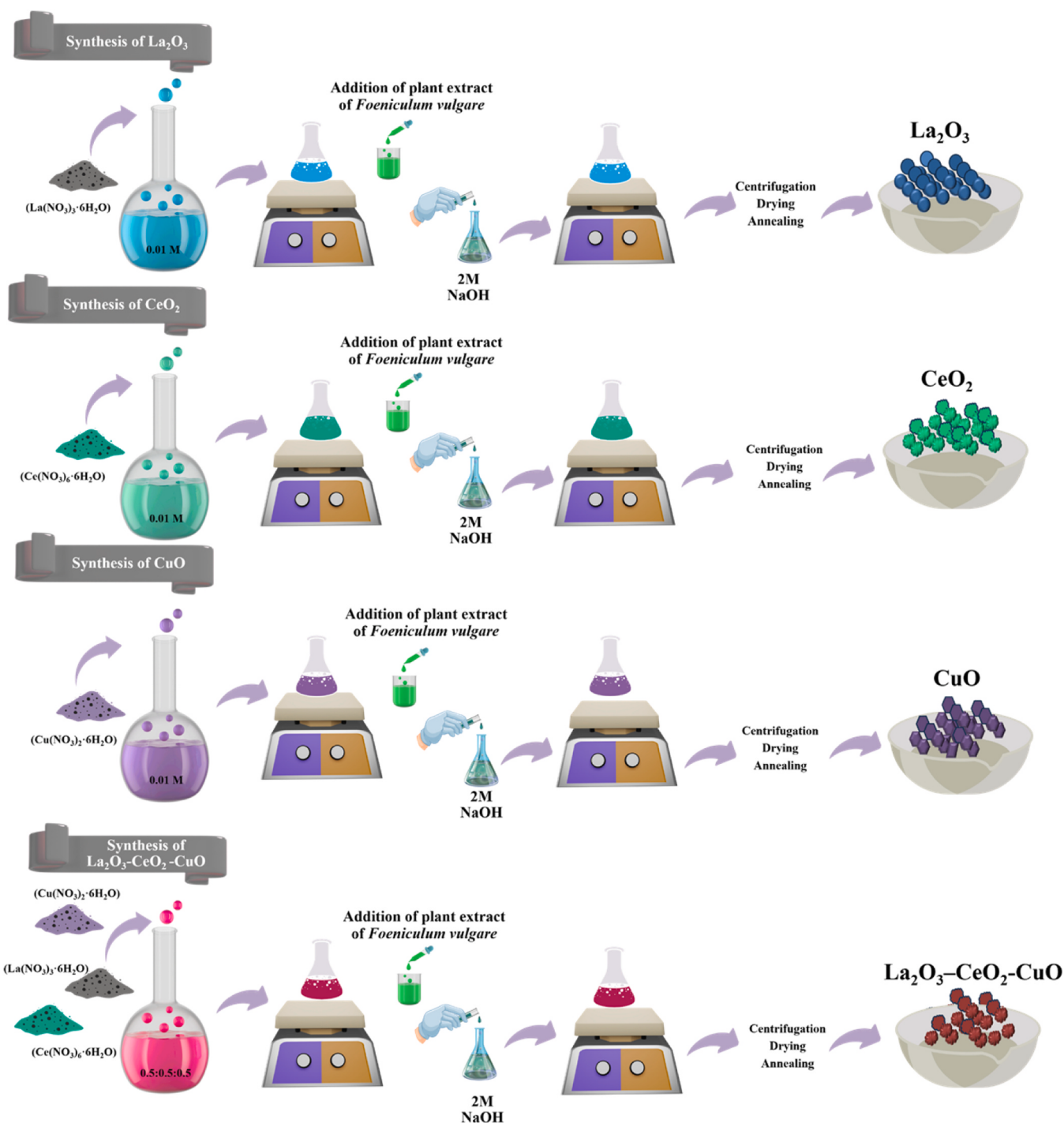
2.6. Characterization techniques

An Advanced Laboratory diffractometer (Bruker-D8, USA) was used to investigate the crystal structure and phase analysis of the fabricated samples. XRD $\text{CuK}\alpha$ was performed with $\lambda = 1.5406\text{ \AA}$, 40 kV/35 mA , and $1^\circ/\text{min}$ with a range of $20\text{--}80^\circ$. The *Foeniculum vulgare* assisted nanostructure's functional group analysis was examined using FTIR on a Bruker Tensor 27 Spectrometer (Germany) in the range of ($400\text{--}1000\text{ cm}^{-1}$). The optical patterns were measured using a dual-beam spectrophotometer (Cary-60 Agilent, USA), which has a UV-Vis range of $300\text{--}800\text{ nm}$. Transmission electron microscope (TEM) using the ThermoFisher (USA), and EDX (USA) was employed for detecting elemental analysis of the La_2O_3 , CeO_2 , CuO , $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$.

3. Results and discussion

3.1. Structural properties

The XRD pattern of the pure La_2O_3 , CeO_2 , CuO , $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ (Fig. 2). It comprises peaks corresponding to hexagonal La_2O_3 [JCPDS CARD NO.01-083-1344] and space group P-3m1. The diffractogram of La_2O_3 showed peaks at $2\theta = 26.12, 29.04, 30.02, 39.54, 46.14, 52.10, 55.34, 56.101$ are related to (100), (002), (011), (112), (110), (103),



Scheme1. Synthesis Illustration of La_2O_3 , CeO_2 , CuO , $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ by *Foeniculum vulgare*.

(112), (201). The corresponding planes and angles of hexagonal La_2O_3 are observed in the spectrum, confirming the synthesis of pure La_2O_3 nanoparticles. The diffractogram of CeO_2 showed peaks at $2\theta = 28.48, 32.99, 47.34, 56.15$, which are related to (111), (200), (220), (311). The CeO_2 spectrum with a cubic crystal system with definite angles and planes confirms the synthesis of pure CeO_2 nanoparticles. It comprises peaks corresponding to cubic CeO_2 [JCPDS CARD NO.03-065-5923] and space group Fm-3m. The diffractogram of CuO showed peaks at $2\theta = 35.54, 38.82, 48.59, 61.56, 66.13, \text{ and } 68.12$ are related to (-111), (200), (-202), (-113), (-311), and (220). The corresponding planes and angles of Monoclinic CuO are observed in the spectrum, confirming the synthesis of pure CuO nanoparticles. It comprises peaks corresponding

to Monoclinic CuO [JCPDS CARD NO.00-005-0661] and space group C2/C. The diffractogram of nanocomposite showed characteristics peaks at $2\theta = 28.54, 29.64, 35.96, 37.85, 39.66, 47.53, 52.17, 56.43, 61.55$ are related to (111), (011), (-111), (111), (012), (220), (103), (311), (-113). From diffractograms, the evaluation of $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ patterns is crystalline. The nanocomposite resultant peaks relate to hexagonal La_2O_3 [JCPDS CARD NO.01-083-1344], Monoclinic CuO [JCPDS CARD NO.00-005-0661], and cubic CeO_2 with [JCPDS CARD NO.03-065-5923]. The absence of any extraneous peaks in the pure La_2O_3 , CeO_2 , CuO nanoparticles, and $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ XRD diffractogram indicates the high purity of crystal growth and deduced values mentioned in (Table S1-S4). (Fig. 3)

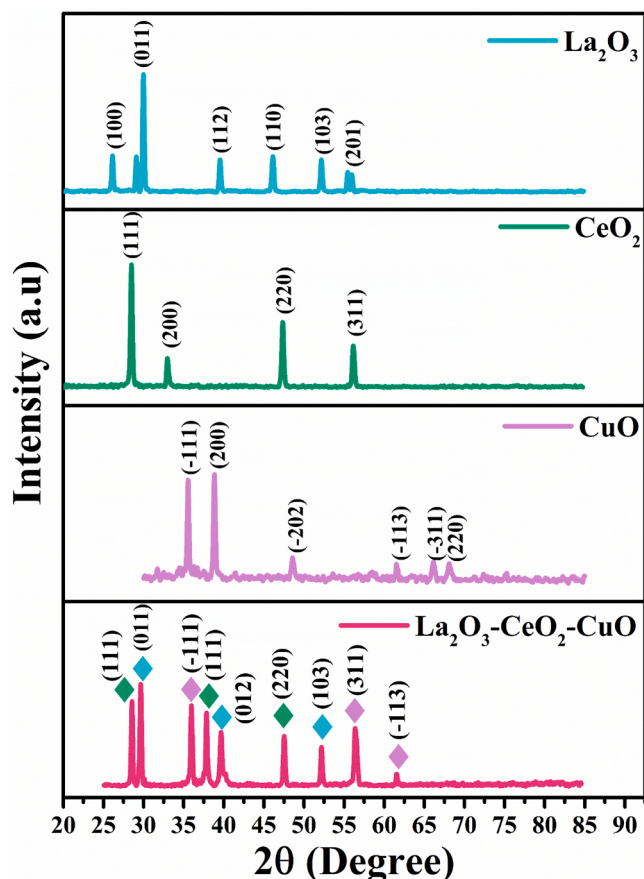


Fig. 2. XRD patterns of *Foeniculum vulgare* assisted La_2O_3 , CeO_2 , CuO , and $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$.

Using the Scherrer equation as mentioned in Eq. (3), the crystalline dimension of the produced pristine nanoparticles La_2O_3 , CeO_2 , CuO , and $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposite was identified [52].

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (3)$$

where β is the line broadening at full width at half-maximum (FWHM), which is calculated using a Gaussian single peak fit, D is the average crystal size, K is the constant, λ is the X-ray wavelength, and θ is Bragg's angle. The resulting microstructural parameters are achieved through the derivations mentioned in Table S5.

Fourier transform spectroscopy examines the molecular fingerprint of the materials by highlighting details about the functional groups that comprise the $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposite. The resultant signal encodes all of the infrared frequencies typical of the permitted vibrational modes of the substance under consideration [53]. A reliable technique for analyzing biodegradable and biocompatible polymer nanocomposites is Fourier transform infrared (FTIR). By interpreting the characteristics and dynamics of the material's characteristic vibrational bands, FTIR can detect conformational changes associated with the twisting, stretching, and bending of the polymer chain backbone. FTIR spectra of plant extract of *Foeniculum vulgare* show distinct peaks at 625 cm^{-1} that correspond to aromatic bending C-H groups vibrations [54,55]. The band at 1076 cm^{-1} , 1376 cm^{-1} , and 1585 cm^{-1} displays a characteristic of stretching and bending vibrations of alcohol and aromatic groups. Another band at 2368 cm^{-1} and 3737 cm^{-1} represent $\text{C}\equiv\text{C}$, $\text{C}\equiv\text{N}$ and O-H stretching [56,57]. FTIR spectra of La_2O_3 show distinct peaks at around 678.1036 cm^{-1} assigned to the stretching vibration of the La-O bond formed by oxidation reactions. The bond at 1135 cm^{-1} is distinct for C-O stretching typically from the esters and

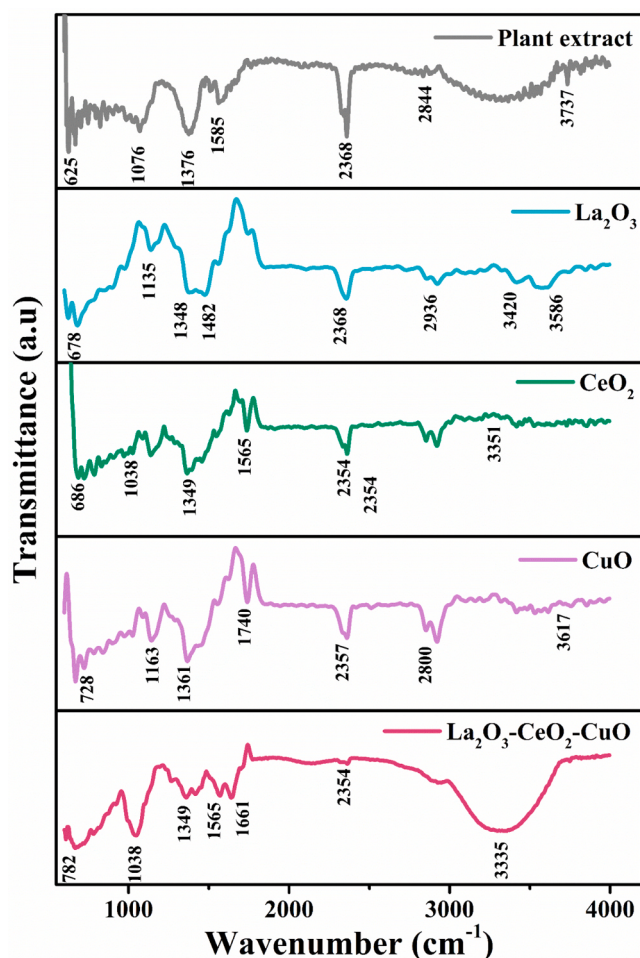


Fig. 3. FTIR patterns of *Foeniculum vulgare*, La_2O_3 , CeO_2 , CuO , and $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$.

alcohol from plant phytometabolite. A weak band at 1348 cm^{-1} and 1482 cm^{-1} is attributed to the deformation mode of OH groups. The peak is located in the region of 2368 cm^{-1} , which shows the incidence of atmospheric CO_2 in the sample. [58]. The value of the peak, ranging from 2300 to 2400 cm^{-1} is also responsible for the nitrile and cyanide group in the alkaloid metabolite of *Foeniculum vulgare*. A peak in the 2936 cm^{-1} range in *Foeniculum vulgare* synthesized is typically due to C-H stretching vibrations from organic compounds that are C-H stretching from aliphatic and aromatic plant metabolites, typically fatty acids and flavonoids. A peak in the 3420 cm^{-1} , and 3586 cm^{-1} range in is associated with O-H and N-H stretching from *Foeniculum vulgare* proteins and amines metabolites.

CeO_2 FTIR spectrum usually reveals distinctive absorption bands that correspond to different vibrational modes. The following are the main peaks frequently seen in the CeO_2 FTIR spectrum. The intense broad band observed at 686 cm^{-1} was assigned to the Ce-O bonds. The peaks observed at 1038 cm^{-1} , 1349 cm^{-1} , and 1420 cm^{-1} arise as a result of vibrational modes caused by defects, especially oxygen vacancies. Another band at 1565 cm^{-1} , 1661 cm^{-1} , and 2354 cm^{-1} represents the atmospheric moisture and centered position peaks in this range corresponding to the H-O-H bending. Weak absorbance bands in the range of 3351 cm^{-1} linked to hydroxylated in ceria surfaces (Ce-OH modes) and residue of *Foeniculum vulgare* metabolites from the synthesis process [59].

A peak in the 728 cm^{-1} range in *Foeniculum vulgare* synthesized can be attributed to M-O (Metal-Oxygen) that is Cu-O lattice vibrations in CuO . A well-defined peak appears in the region of 1163 cm^{-1} and

1361 cm^{-1} , signifying the C-O, C-N typically originating from ester, alcohol, and polyphenols. The band was observed at 1740 cm^{-1} due to the C=O stretching from Quinone, carboxylic acids, tannins, and aldehydes in *Foeniculum vulgare* metabolites. The peak is located in the region of 2357 cm^{-1} , which relates to the incidence of atmospheric CO_2 to CuO nanoparticles.

Another sharp peak in the CuO spectrum at 2800 cm^{-1} , and 2920 cm^{-1} is due to C-H stretching from fatty acids, carbohydrates, and terpenes, which originally came from the capping of plant extract. In the CuO spectrum, small peaks were observed at 3413 cm^{-1} , 3532 cm^{-1} , 3617 cm^{-1} , and 3853 cm^{-1} assigned to the -OH, -NH group originating from the plant metabolites anchoring the surface of the material.

In the La_2O_3 - CeO_2 -CuO nanocomposite, the metal-oxygen bond (M-O) arises at different peaks at 609 cm^{-1} , 664 cm^{-1} , 782 cm^{-1} that relate to the structural stability, and surface interaction of the nanocomposite with *Foeniculum vulgare* metabolite. Slight intense peaks were observed in the 790–1000 cm^{-1} region due to lattice distortion due to the incorporation of secondary elements of the plant that aid in the synthesis and capping. The peak around the 1038 cm^{-1} signifies the C-O-C, C-O stretching, and the metal phytochemical bonds due to plant flavonoids and alkaloids (M-O-C), while M represents the La, Cu, and Ce. The key vibrational assigned peaks at 1349 cm^{-1} and 1420 cm^{-1} denote the C-H bending typically (CH_2 , CH_3) associated with the plant-derived metabolites of *Foeniculum vulgare*. The sharp 1565 cm^{-1} and 1661 cm^{-1} bands represent C=C and C=O stretching vibrations from flavonoids, alkaloids, lignin, and associated aromatic compounds of the plant. The peaks around 2354 cm^{-1} and 3335 cm^{-1} are assigned to different functional groups related to ($\text{C}\equiv\text{C}$) or nitriles ($\text{C}\equiv\text{N}$).

3.2. Optical properties

Using UV-visible absorption spectroscopy of the La_2O_3 - CeO_2 -CuO nanocomposite, the optical response of the grown pristine and nanocomposite was investigated. The findings are displayed in Fig. (4). La_2O_3 , CeO_2 , and CuO have absorption edges at 298 nm, 532 nm, and

503 nm, respectively. Significantly, La_2O_3 - CeO_2 -CuO exhibits significant absorption peaks in the visible light area at 373, 420, and 540 nm. It indicates that the nanocomposite's close interfacial contact between La_2O_3 , CeO_2 , and CuO produces a cumulative effect that prolongs the visible light response. To estimate the variation in energy bandgap (E_g), Tauc's plot is used [60]: (Fig. 5).

$$\alpha h\nu = A(h\nu - E_g)^n \quad (4)$$

The computed values of the energy bandgap are 4.3, 3.32, 2.3, and 2.0 eV for La_2O_3 , CeO_2 , and CuO and La_2O_3 - CeO_2 -CuO, respectively [61]. Additionally, the energy bandgap has decreased in La_2O_3 - CeO_2 -CuO due to the formation of a heterojunction among the La_2O_3 , CeO_2 , and CuO oxides, which introduces defect states and facilitates interfacial charge transfer, as reported in the literature [62–64]. The reduced bandgap implies improved visible-light absorption, electron transition, and higher visible light-harvesting capacity, all of which are beneficial for photocatalytic applications [65].

3.3. Morphology and elemental analysis

The morphology and arrangement of the nanoparticles in La_2O_3 , CuO, CeO_2 , and La_2O_3 - CeO_2 -CuO obtained by TEM imaging. In Fig. 6 (a), La_2O_3 shows a diagonal square-shaped morphology. The CeO_2 in Fig. 6(b) showed an outgrowth of a circular sphere. The TEM image of the CuO of the sample shows almost spherical and large nanoparticles with controlled nucleation patterns, as in Fig. 6(c). The La_2O_3 - CeO_2 -CuO shows the agglomerated clusters forming flakes enclosing the mixtures of three oxides in a tri-phasic manner. The morphology of La_2O_3 - CeO_2 -CuO embedded with each other, forming a broad interface across the crystal lattice with improved catalytic properties, makes it a better candidate for biomedical and photocatalytic applications.

For the elemental composition of pristine fabricated La_2O_3 , CuO, CeO_2 , and La_2O_3 - CeO_2 -CuO nanocomposite, EDX was performed. The EDX spectrum with elemental mapping of pure and La_2O_3 - CeO_2 -CuO nanocomposite is displayed in Fig. 7(a-d). The pure nanoparticles La_2O_3 ,

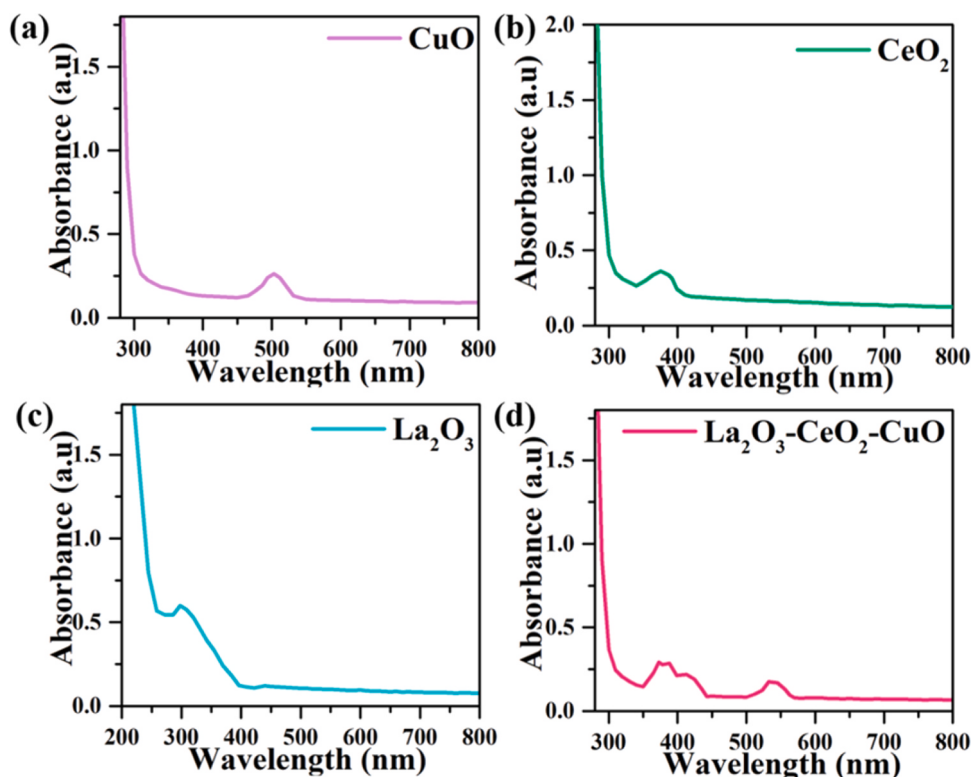


Fig. 4. UV-vis spectra of pure La_2O_3 (a), CeO_2 (b), CuO (c), and La_2O_3 - CeO_2 -CuO (d).

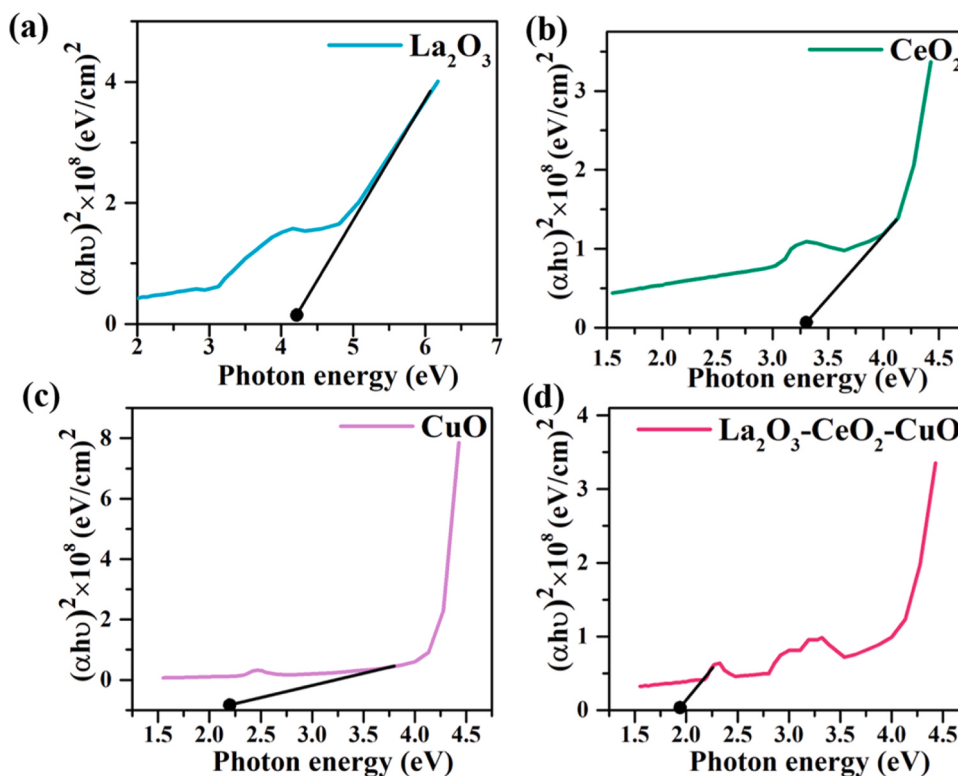


Fig. 5. Energy bandgap pattern of La_2O_3 (a), CeO_2 (b), CuO (c), and $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ (d).

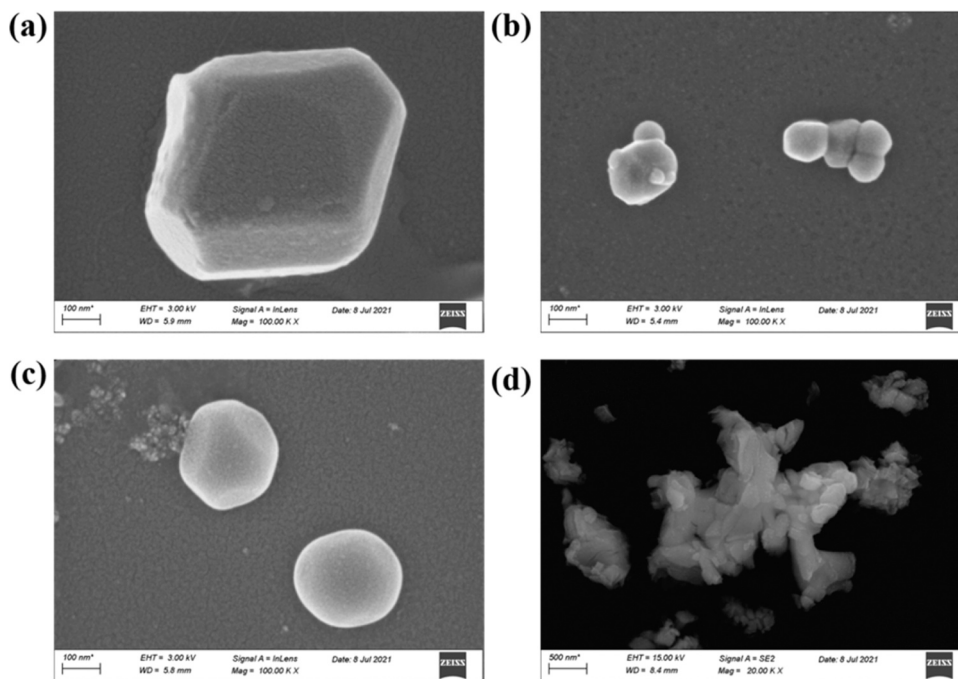


Fig. 6. TEM of pure La_2O_3 , CeO_2 , CuO nanoparticles, and $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$.

CeO_2 , and CuO EDX show the presence of La, Ce, and Cu, respectively. Fig reveals the uniform distribution of the lanthanum, cerium, copper, carbon, and oxygen, which were indicated with attached color mapping. The presence of La, Ce, Cu, and C elements without any other impurities is confirmed by the appearance of all the peaks of the manufactured La_2O_3 , CeO_2 , CuO , and $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ sample in the EDX bands. The Edax elemental composition of La_2O_3 , CuO , and CeO_2 , and $\text{La}_2\text{O}_3\text{-CuO}$

CeO_2 is tabulated in S-6. The TEM and EDX results demonstrated an excellent *Foeniculum vulgare* assisted nanocomposite $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$, which is beneficial for photocatalysis and anti-microbial applications.

3.4. Antimicrobial activity

The antibacterial activity of $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ and pure La_2O_3 , CeO_2 ,

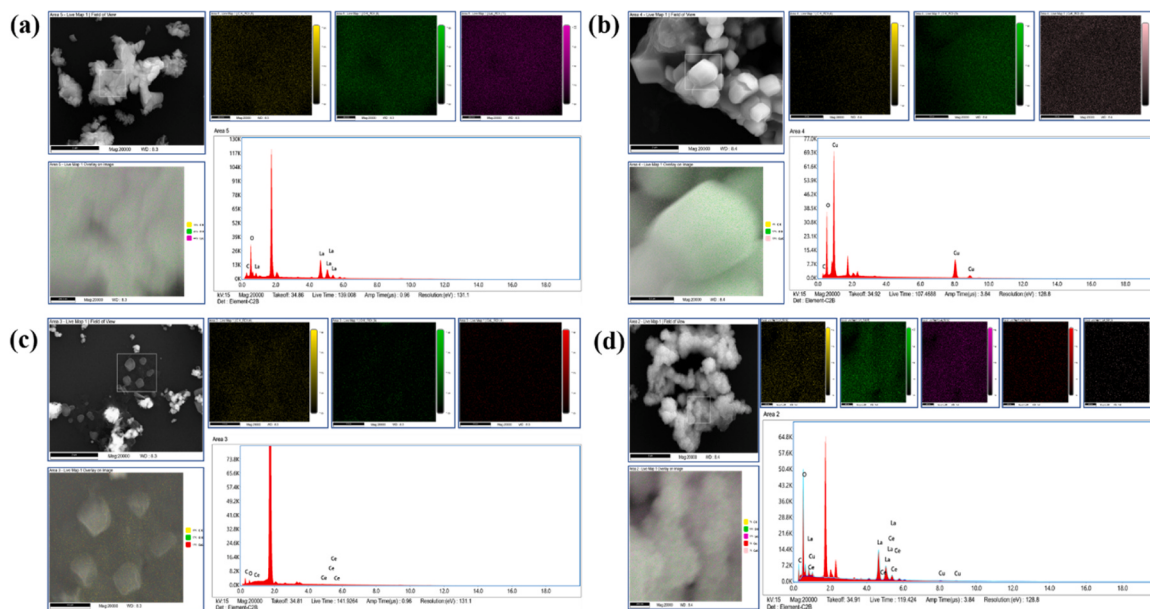


Fig. 7. EDAX Mapping of pure La_2O_3 , CeO_2 , CuO nanoparticles, and $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$.

and CuO was evaluated against certain bacterial strains using the disc diffusion technique [66]. The results depicted in Fig. 8(a, b) demonstrated efficient activity against *E. coli* within the concentration range of 40 mg/mL, as evidenced by the zone of inhibition. The antibacterial plates of respective *S. aureus* and *E. coli* strain are shown in Fig S1, S2. In comparison, the inhibitory effect against *S. aureus* species was minimal, with a slightly smaller zone of inhibition observed. The calculated diameter of the zone of inhibition increased progressively with every enhanced dosage of $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ and pure La_2O_3 , CeO_2 , and CuO across considered bacteria [67].

The obtained outcomes verified an outstanding antibacterial potential against the tested bacteria, namely, *S. aureus* (12 ± 0.25 mm), and *E. coli* (14 ± 0.24 mm), at a concentration of 20 $\mu\text{g/mL}$ for

La_2O_3 . At the dosage of 40 $\mu\text{g/mL}$, La_2O_3 exposed antibacterial efficacy in contrary to *S. aureus* (13.5 ± 0.28 mm) subsequent by *E. coli* ZOI (15.3 ± 0.22 mm). When applied at 60 $\mu\text{g/mL}$, La_2O_3 showed comparatively higher inhibitory effects against *S. aureus* (15.88 ± 0.23 mm), and *E. coli* (17.45 ± 0.3 mm). The positive control ciprofloxacin showed following ZOI as *S. aureus* (28 ± 0.3 mm), and *E. coli* (27 ± 0.2 mm). CeO_2 at a concentration of 20 $\mu\text{g/mL}$ showed substantial antibacterial activity against *S. aureus* (13 ± 0.5 mm), and *E. coli* (14.8 ± 0.25 mm) exhibited comparatively weaker inhibitory effects. At the dosage of 40 $\mu\text{g/mL}$, CeO_2 exhibited antibacterial activity against *S. aureus* (14.5 ± 0.5 mm), subsequent by *E. coli* ZOI (16 ± 0.5 mm). When applied at 60 $\mu\text{g/mL}$, CeO_2 showed comparatively higher inhibitory effects against *S. aureus* (17 ± 0.5 mm), and *E. coli* (19.45 ± 0.5 mm). The positive control ciprofloxacin showed following ZOI as *S. aureus* (28.5 ± 0.22 mm), and *E. coli* (29 ± 0.24 mm).

When CuO was administered at 20 $\mu\text{g/mL}$, it displayed a relatively higher antibacterial in contrary to *S. aureus* (16 ± 0.17 mm), and *E. coli* (18.8 ± 0.18 mm) than La_2O_3 , CeO_2 . At the dosage of 40 $\mu\text{g/mL}$, CuO exhibited antibacterial activity against *S. aureus* (17.54 ± 0.11 mm) subsequent by *E. coli* ZOI (19.23 ± 0.15 mm). When applied at 60 $\mu\text{g/mL}$, CuO showed comparatively higher inhibitory effects counter to *S. aureus* (20 ± 0.5 mm), and *E. coli* (21 ± 0.25 mm). The positive control ciprofloxacin, showed the following ZOI as *S. aureus* (29 ± 0.12 mm), and *E. coli* (30 ± 0.14 mm).

The $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposite showed remarkable antibacterial effects at various concentrations against *S. aureus*, and *E. coli*. At a concentration of 20 $\mu\text{g/mL}$, observed ZOI counter to *S. aureus* are (21 ± 1.1 mm), and *E. coli* (24 ± 1.0 mm). At 40 $\mu\text{g/mL}$ dosage,

$\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposite antibacterial activity counter to *S. aureus* (24 ± 0.18 mm) followed by *E. coli* ZOI (26 ± 0.15 mm). When applied at 60 $\mu\text{g/mL}$, $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ showed comparatively higher inhibitory effects counter to *S. aureus* (27.7 ± 0.12 mm), and *E. coli* (31.90 ± 0.15 mm). The positive control ciprofloxacin showed following ZOI as *S. aureus* (29 ± 0.19 mm), and *E. coli* (30 ± 0.12 mm).

The antibacterial properties of La_2O_3 nanoparticles were evaluated to recognize their efficacy as anti-bacterial agents. The La_2O_3 displayed percentage inhibition rates of *S. aureus* and *E. coli* at 20, 40, and 60 $\mu\text{g/mL}$ is 42.86 % 48.21 % 56.71 %, and 51.85 %, 56.67 %, 64.56 %. The CeO_2 displayed percentage inhibition rates of *S. aureus* and *E. coli* at 20, 40, and 60 $\mu\text{g/mL}$ is 46.43 %, 51.79 %, 60.71 % and 51.03 %, 55.17 %, 67.07 %. The CuO displayed percentage inhibition rates of *S. aureus*, and *E. coli* at 20, 40, and 60 $\mu\text{g/mL}$ is 55.17 %, 60.48 %, 68.97 % and 62.67 %, 64.43 %, 70 %. The $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ displayed percentage inhibition rates of *S. aureus*, and *E. coli* at 20, 40, and 60 $\mu\text{g/mL}$ is 70 %, 80 %, 92.33 %, and 73 %, 86.67 %, 93 %.

The potential of $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ in reducing bacterial viability with a maximum percentage index at 60 $\mu\text{g/mL}$, with a maximum 93 % inhibition zone against *E. coli*. The antibacterial activity of $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposite at 20, 40, and 60 $\mu\text{g/mL}$ was noticeable in its ability to inhibit the growth of common pathogenic bacteria, with *E. coli* being the most sensitive [66,68]. These findings suggest that $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ could serve as an effective claimant for antimicrobial treatments. The interaction mechanism of the $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposite is largely influenced by its unique size and shape. The unique round spherical-shaped crystalline structure helps in its antibacterial activity [69]. The antibacterial mechanism works by the generation of reactive oxygen species (oxygenated moieties) in Fig. 8 (c). The small size of the nanocomposite, as discussed in our XRD findings able to cross the membrane barrier. The ions produced by the nanomaterial, such as La, Ce, and Cu (positive) interact with the negatively charged membrane of bacteria. The interaction is accompanied by an electrostatic interaction, and it disrupts the membrane integrity with loss of cellular content [70]. Furthermore, *Foeniculum vulgare* derived $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ boosts antibacterial activity by providing a bioactive phenolic, amine group, as confirmed by FTIR findings that help the nanocomposite break bacterial membranes. In the cytoplasm, the logged nanocomposite crops Reactive Oxygen Species (ROS), which creates an environment strained with oxidative stress [71]. The Reactive Oxygen Species disturb the whole cellular homeostasis and oxidation of proteins,

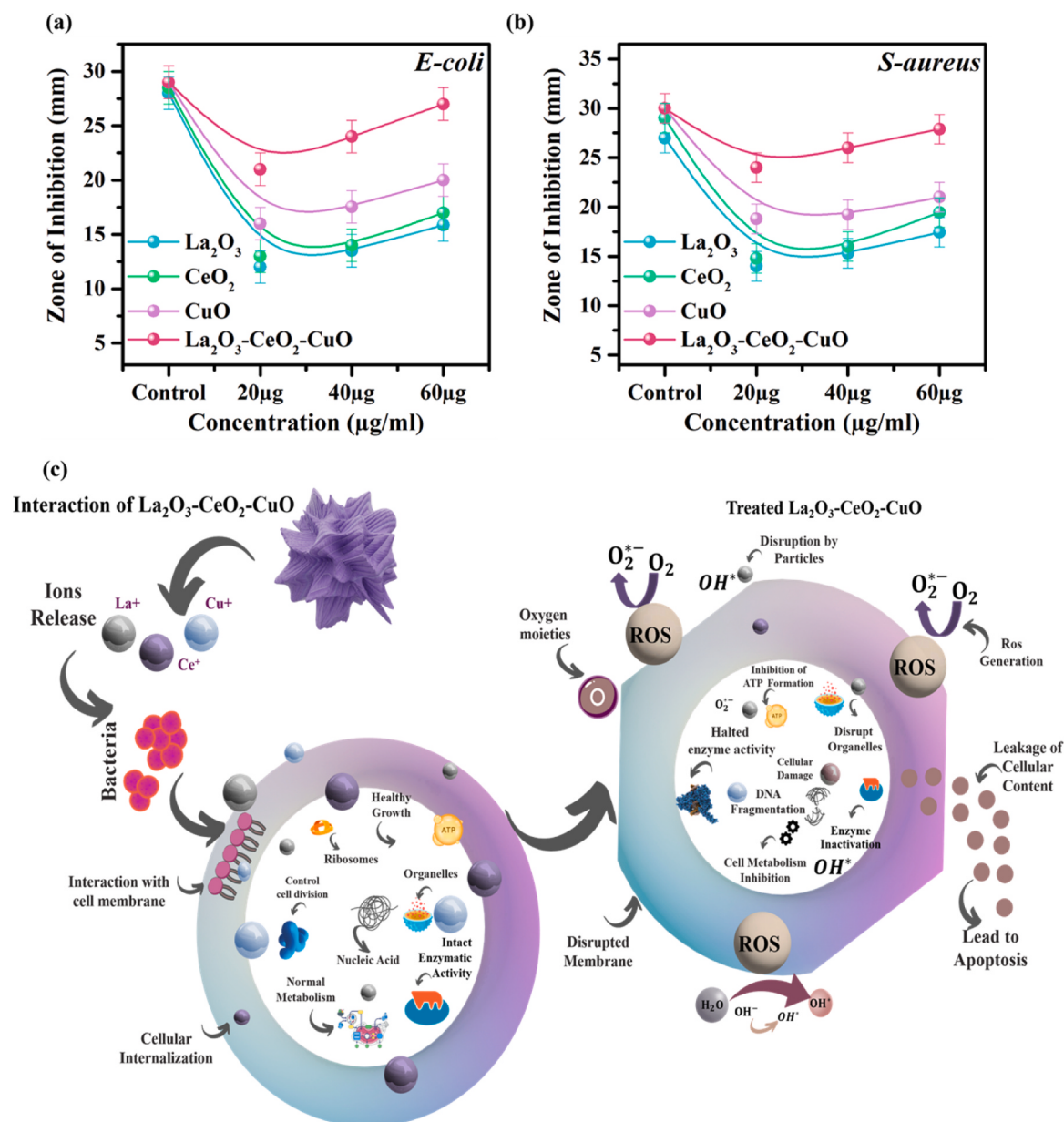


Fig. 8. Antibacterial activity of (a) *E. coli*, (b) *S. aureus* of pure La_2O_3 , CeO_2 , CuO nanoparticles, and $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ and (c) Mechanism of Antibacterial action.

then lipids, and trigger mitochondrial hemorrhaging. ROS, in particular, causes major alterations such as deactivation of enzymes, along with denaturation of DNA, which eventually leads to cell death [72]. The mechanistic *Foeniculum vulgare* derivative $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ enhances its antibacterial properties by activating these pathways. Therefore, our work proved the prospect of fabricating $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ with considerable antibacterial activity against both gram-positive and gram-negative bacteria [73].

3.5. Photocatalysis Pathways and Mechanism

Synthetic pollutants in the form of Methylene blue dyes were used to assess the photodegradation traits of La_2O_3 , CeO_2 , CuO , and $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ under solar stimulation. A prevalent organic contaminant, Methylene Blue is a dye that is cationic with a complicated molecular structure that may enter the water system via industrial effluents used to color cotton, wool, and textiles. In order to remove environmentally hazardous substances, this study uses La_2O_3 , CeO_2 , CuO , and $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ to check the photodegradation efficacy of MB. Since no

notable byproducts were produced during the reaction time, the degradation assessment of MB dye was carried out using UV-vis spectroscopy. The periodic progression of the absorbance spectrum changes of MB for photocatalytic experiments conducted at different times is shown in Fig. 9(a, b, c, d). The intensity of the MB characteristic absorption peak (665 nm) dropped sequentially in the presence of La_2O_3 , CeO_2 , and CuO catalysts, but more quickly in the presence of $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$. After 100 min of exposure to sunlight, full degradation was attained. After the dark reaction, absorption spectrum measurements of blank dye were taken to track the role of degradation [74]. Further, a degradation pattern of MB under *Foeniculum vulgare* assisted nanocomposite was observed during regular intervals of 0, 10, 20, 40, 60, 80, and 100 min. The proportion of degradation efficiency (%) for *Foeniculum vulgare* assisted La_2O_3 , CeO_2 , CuO , and $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ catalysts is depicted in Fig. 9(e). This validates that photocatalysis serves a significant part in the photodegradation reaction for MB dye eradication. The photodegradation efficiency of La_2O_3 , CeO_2 , CuO $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ reaches 68 %, 73 % 91 %, 99.7 % against MB after 100 min under sunlight illumination.(Table 1)

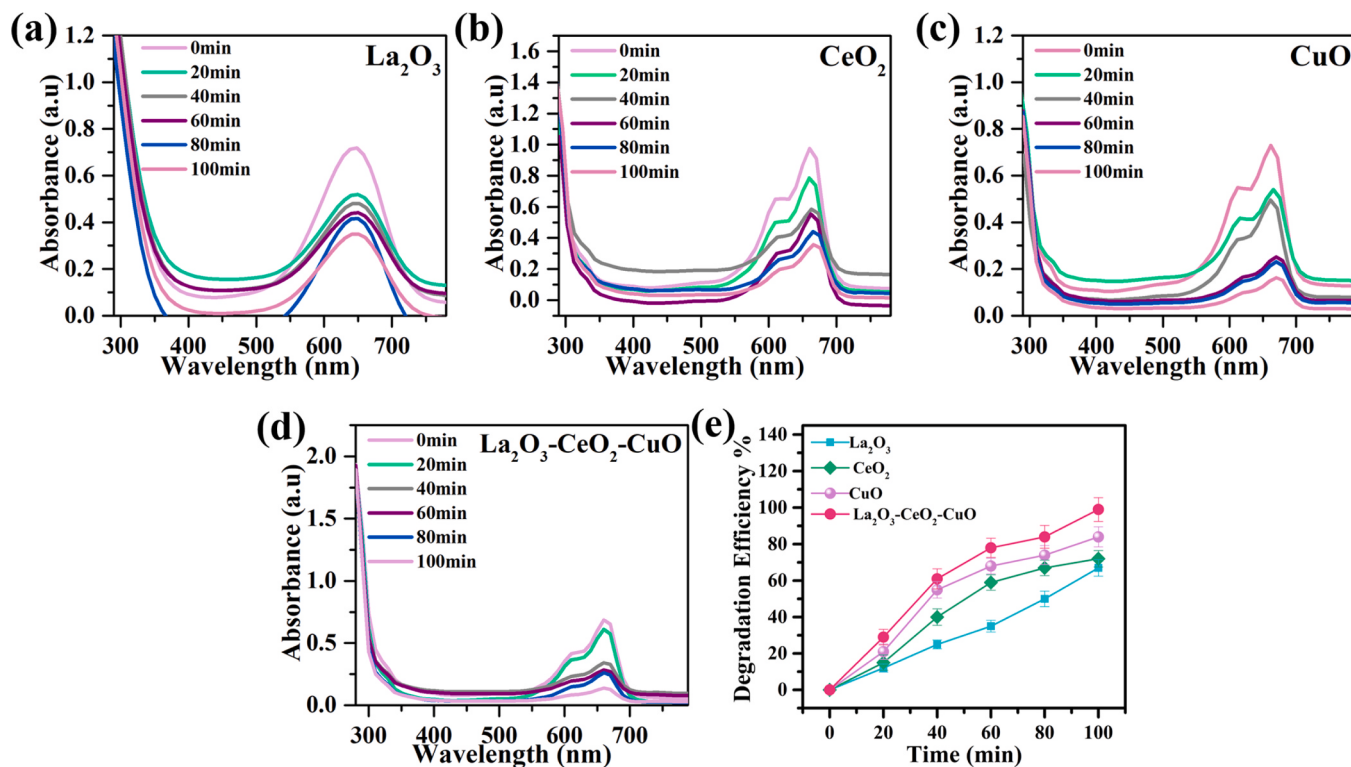


Fig. 9. Photocatalytic activity absorption spectra of pure La_2O_3 , CeO_2 , CuO nanoparticles, and $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ against MB dye (a, b, c, d), degradation efficiency (e).

Table 1

The antibacterial activity comparison with other reported nanocomposites.

Nanocomposite	Strain	ZOI	Reference
Au/MgO	<i>S-aureus</i>	19	[88]
CdS/ZnO		22	[89]
NiO-CeO ₂ -ZnO		14	[89]
TiO ₂ -ZnO-MgO		15.16	[90]
CS@Ag/CeO ₂		16	[91]
CeO ₂ /GO		10.6	[92]
CeO ₂ -CuO-ZnO		14	[93]
Ni/ZnO		23	[94]
$\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$		27.7	Present work
Se/ZnO/CuO	<i>E-coli</i>	30.7	[95]
Cu/TiO ₂		25	[96]
Cu-Zn-Mn		16	[97]
g-C ₃ N ₄ /TiO ₂		17	[98]
Pt/ZnO		21	[99]
Ag/V2O5-curdlan		18	[100]
GA@CuO-ZnO		21	[101]
$\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$		31.90	Present work

Moreover, the degradation process was also studied by a pseudo-first-order kinetic model, as given below [75]:

$$C_t = C_0 e^{-kt} \quad (5)$$

$$\Rightarrow \ln(C_0/C_t) = kt \quad (6)$$

The rate constant is k. A straight line is produced by plotting the natural logarithm of concentration against various irradiation times (t), as seen in Fig. Plotting $\ln(C_0/C_t)$ against irradiation time and slope yields the rate constant value. The reduction kinetics curve, $\ln(C_0/C_t)$ vs. t(time)), is obtained from Fig. 10(a). Compared to individual oxide catalysts, $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ has a higher rate constant of 0.03609 min^{-1} , (La_2O_3) 0.01126 min^{-1} , (CeO_2) 0.01456 min^{-1} , and (CuO) 0.02155 min^{-1} . (Table 2)

The higher photocatalytic performance of solar-driven photo-

catalysts generally requires higher separation effectiveness, redox ability, and light-capturing capacity, as depicted in Fig. 10(b) [76]. While degrading ability depends on the photocatalyst's band locations, light-capturing ability is correlated with bandgap [77]. Therefore, it is necessary to estimate the energy levels of the valence and conduction bands of the fabricated samples. The following empirical formulas were used to predict the band positions: The pathways followed by the nanocomposite are summarized in the following reactions in which the pollutant is converted into degraded products.

$$E = X - E - 0.5E \quad (7)$$

$$EV.B. = EC.B. + E_g \quad (8)$$



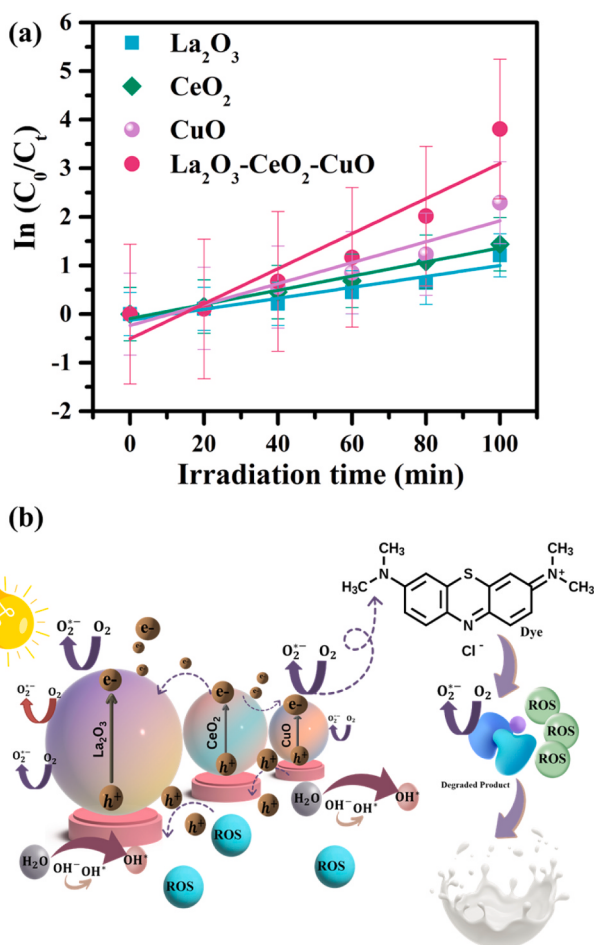
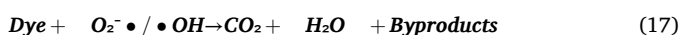
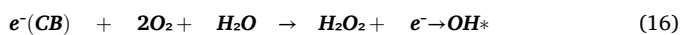
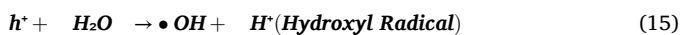
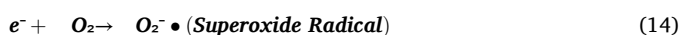
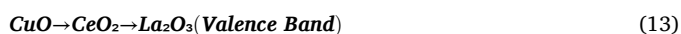


Fig. 10. Rate constant of La_2O_3 , CeO_2 , CuO , $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ (a), Photocatalytic mechanism of La_2O_3 , CeO_2 , CuO , $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ against MB dye (b).



3.5.1. Effect of catalyst dosage

Using the appropriate amount of catalyst in the degradation of pollutants plays a crucial role. The experiment for $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposite was performed at different concentrations [78]. The degradation efficiency of $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposite catalysts having concentrations of 10, 20, 30, and 40 mg is 94.0 %, 99.5 %, 91 %, and 86 %, respectively. The photodegradation pattern of the dye under solar light irradiation can be strongly influenced by the catalyst dose of $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposites. Fig. 11(a) shows the degradation efficiency of $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposites. Results show that

fabricated $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposites at a dose of 20 mg have supreme degradation efficiency. The 10 mg catalyst dosage has the least efficiency due to the less active site available for the catalyst and poor absorption rate. While at higher concentrations, the particle tends to agglomerate, and charge recombination increases. This is due to less diffusion of pollutant molecules to the $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ catalyst surface.

3.5.2. Effect of pH

The wide variety of pollutants from various sectors makes it difficult to adjust pH for photocatalytic processes. There is currently no information on $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ photocatalyst that demonstrates an effective breakdown of pollutants over a broad pH range [79]. By altering the dye solution pH, many studies looked at the impact of pH. To test the efficacy of the catalysts, the pH of the synthesized $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ has been adjusted [80]. The characteristics of surface charge and photocatalyst aggregation are significantly influenced by pH. In the mechanistic approach of photocatalytic MB degradation, it is essential to optimize the value range at which it performs well. As the pH rises, the $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ photocatalyst surface produces a large number of hydroxyl radicals. These radicals interact with the dye and transform into benign, less toxic moieties. It indicates that high pH levels encourage dehydrogenation, which increases MB dye elimination. $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposites are utilized in an alkaline environment, which exhibits comparatively higher degradation efficiencies. The photodegradation efficiency examined against various pH values of 6, 8, 10, and 12 is displayed in Fig. 11(b), with degradation efficiencies of 84, 88, 94, and 99 %, respectively. These findings confirm that the photodegradation results of plant mediated $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ at pH = 12 have a supreme photodegradation rate. The results of $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ clearly show that an increment in pH value intensifies the degradation efficiency.

3.5.3. Effect of dye concentrations

The degrading efficiency of $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposites is influenced by the initial dye concentration. Fig. 11(c). Demonstrate the degradation competence of *Foeniculum vulgare* assisted nanocomposites by varying the concentration from 20, 30, 40, and 50 ppm. The findings explicitly show that as the dye concentration increased, the degradation declined [81]. The proportion of MB degradation decreases as dye concentration rises because fewer photons access the reaction and decrease electron-hole production. Saturation of the active site occurs when significant amounts of organic contaminant molecules accumulate on the catalyst surface. The rise in dye concentration quenches the electron hole before the reaction with water and oxygen to form ROS. The formation of by-products shades the active catalytic site for the dye molecules to interact and increase the charge recombination rate. As a result, there is limited charge carrier mobility and less catalyst diffusion to the catalytic surface. To improve degradation efficiency, the photodegradation rate was thus optimized.

Table 2

Comparison table of Degradation of Methylene blue by different nanocomposite.

ZnO-CuO-graphene	Methylene Blue	81 %	[102]
ZnO/Fe ₂ O ₃ /MnO ₂		93 %	[103]
CuO/ZnO	-	96.57 %	[104]
Sm ₂ O ₃ -WO ₃ -La ₂ O ₃	-	99.0	[105]
TiO ₂ -silica	-	97.66 %	[106]
CeO ₂ /GO-PAM	-	90 %	[107]
CQDs@ZIF-8	-	93 %	[108]
AC-ZrO ₂ /CeO ₂	-	97.91 %	[109]
CeO ₂ /CdS	-	98.9359 %	[110]
Ce-TiO ₂ /g-C ₃ N ₄	-	93 %	[111]
Ag-doped CeO ₂ /ZnO	-	98.90 %	[112]
rGO/Gd ₂ WO ₆	-	92 %	[113]
Gd ₂ O ₃ -La ₂ O ₃	-	84.80 %	[114]
ZnIn ₂ S ₄ -Ag-LaFeO ₃	-	95 %	[115]
La ₂ O ₃ -CeO ₂ -CuO	-	99.7 %	Present work

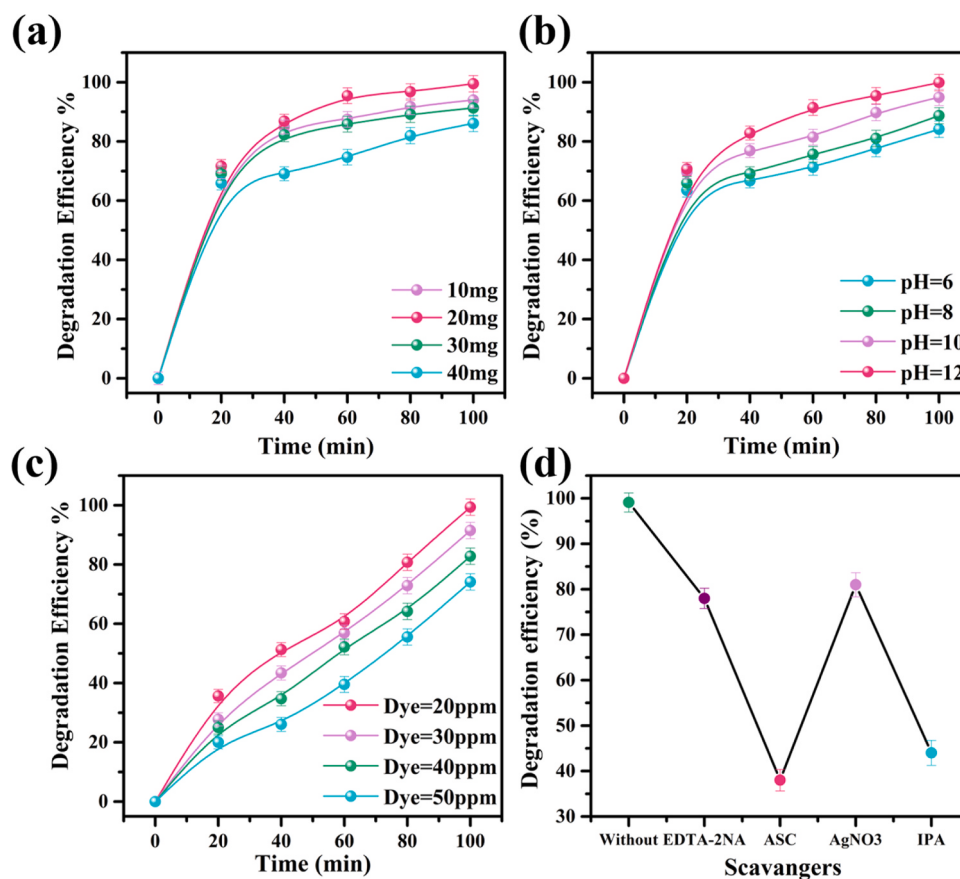


Fig. 11. Photocatalytic activity of $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ effect on (a) catalyst dosage, (b) dye concentration, (c) pH, and scavengers (d).

3.5.4. Scavengers experiment

$\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ trapping studies were conducted to examine the production of reactive oxygen species that contribute to dye degradation [82,83]. Numerous studies were carried out to investigate the main reactive species, hydroxyl radical, hole, and superoxide radical anion, as well as the effect of additives on dye degradation, using a range of scavenger tests. EDTA-2Na, ASC, AgNO_3 , and IPA are employed as scavengers in this experiment. To examine the impact of scavengers, reaction conditions were added to the solution: catalyst $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ (20 mg) with MB-dye (10 ppm), and pH (10). The results show that the largest amount of MB dye degradation occurs in the absence of a scavenger test. Additionally, the effect of hydroxyl radicals is examined using isopropyl alcohol (IPA), and the findings indicate a considerable reduction in MB breakdown. When superoxide moieties and hydroxyl

(OH) radical scavenger's cast-off instead of electron or hole scavengers, the degradation efficiency is significantly reduced. This suggests that $\text{O}_2^{\bullet-}$ and $\bullet\text{OH}$ are the main species that cause the methylene blue degradation process. Different scavengers like EDTA-2Na, ASC, AgNO_3 , and IPA have different effects on degradation efficiency. The percentage (%) degradation efficiency without scavenger, or by adding EDTA-2Na, ASC, AgNO_3 , and IPA was 99.1 %, 78 %, 38 %, 81 %, and 44 %, respectively, as in Fig. 11(d).

3.5.5. Reusability test

A multicycle MB dye degradation experiment was used to evaluate the $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ catalyst's stability and reusability. Additionally, the stability test was assessed for seven cycles. The composite durability and reusability were demonstrated in Fig. 12(a). Throughout several

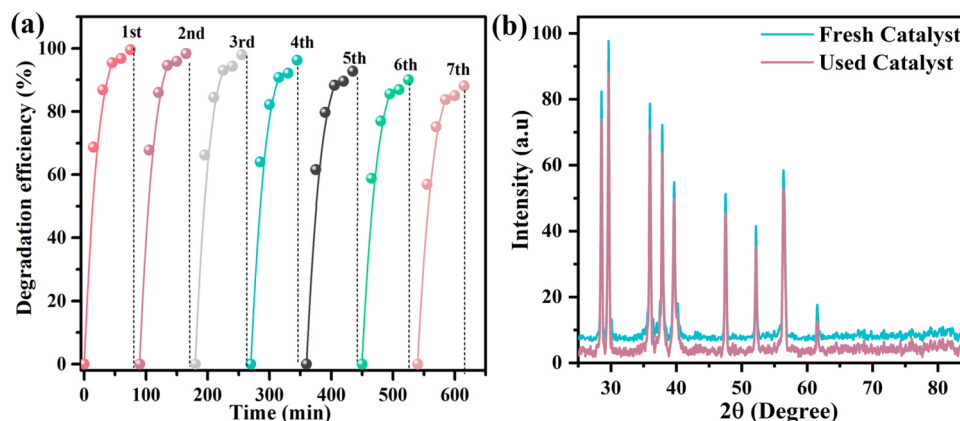


Fig. 12. Efficiency of the recycling ability of $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ (a), XRD pattern of fresh and used catalyst $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ (b).

cycles, the $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ composite retained its photocatalytic activity, indicating that it may find use in wastewater treatment without undergoing noticeable performance degradation [84,85]. The $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ photodegradation efficiencies are 99.5 % (1st), 98.34 % (2nd), 97.99 % (3rd), 96.2 % (4th), 92.74 % (5th), 91.73 % (6th), and 88.74 % (7th), as shown in Fig. 12 (a). Fig. 12 (b) shows the $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposite photocatalysts' XRD pattern both before and after degradation cycles. The XRD patterns of the fresh and used $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ catalysts showed no alterations, suggesting that the crystal's nanocomposite structure remained stable throughout the cycle process. $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ capacity to endure prolonged, repeated usage while retaining efficiency is essential for industrial applications as it increases the process's viability and cost-effectiveness [86,87].

4. Conclusion

$\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposites and pure oxide nanostructures were successfully synthesized by the green chemistry route. The XRD, FTIR, UV-Vis, TEM, and EDAX data confirmed the formation of $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposites and pure oxide La_2O_3 , CeO_2 , CuO . The $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposite showed enhanced antimicrobial and photocatalytic potential compared to the pure. The photodegradation efficiency of $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ reaches 99.7 % against MB after 100 min under sunlight illumination. The $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ assisted microbial inhibition ability against *S. aureus*, and *E. coli* with maximum inhibition zone diameters 27.7 ± 0.12 mm and 31.90 ± 0.15 mm, respectively. The catalyst $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ dose of 20 mg, dye concentration of 20 ppm, and pH 12 were optimized for maximum photodegradation. The $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ assisted photodegradation in the absence of scavengers have the highest percentage of degradation of MB. In addition to its reusability and cyclability, this hybrid composite showed an efficient photodegradation of MB, making it appropriate for use in water purification applications. This study provides an enlightening parameter for designing highly potent antimicrobial agents. Overall, fabricated $\text{La}_2\text{O}_3\text{-CeO}_2\text{-CuO}$ nanocomposite via *Foeniculum vulgare* proposed as an effective strategy for therapeutic and sustainable environmental remediation applications. To evaluate clinical applicability, future research should concentrate on toxicity testing, the active compound isolation, and in vivo validations.

CRedit authorship contribution statement

Calvyn Howells: Visualization, Validation, Methodology, Investigation. **Iftikhar Ahmed:** Visualization, Software, Resources, Methodology, Formal analysis. **Muhammad Saqib Saif:** Writing – original draft, Validation, Methodology, Investigation. **Muhammad Waqas:** Validation, Software, Resources, Methodology. **Tuba Tariq:** Resources, Formal analysis, Data curation, Conceptualization. **Yanjun Duan:** Methodology, Investigation, Formal analysis, Conceptualization. **Li Haitao:** Supervision, Software, Project administration, Methodology. **Mansour Ghorbanpour:** Writing – review & editing, Resources, Project administration, Investigation. **Mumtaz Hussain:** Software, Resources, Investigation, Formal analysis. **Murtaza Hasan:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Sana Batool:** Resources, Methodology, Investigation, Data curation. **Ghazala Mustafa:** Writing – review & editing, Visualization, Validation, Supervision, Conceptualization.

Declaration of Competing Interest

All the authors declared that there is no conflict of interest in this research article

Acknowledgements

We warmly thank the Department of Biotechnology, The Islamia

University of Bahawalpur, Pakistan for providing space and all instruments and chemical to complete these studies.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2025.118470.

Data availability

Data will be made available on request.

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