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HUZURIDAGI ILMIY DARAJALAR BERUVCHI
DSc.03/06.11.2025.K/FM.10.09 RAQAMLI ILMIY KENGASH**

FUNDAMENTAL VA AMALIY TADQIQOTLAR INSTITUTI

SIRAJUL HAQ

**ATROF-MUHITNI MUHOFAZA QILISH MAQSADLARI UCHUN BIR
KOMPONENTLI METALL OKSIDLAR ASOSIDA
FUNKSIONALLASHTIRILGAN KO‘P KOMPONENTLI
NANOMATERIALLAR PLATFORMASI**

**02.00.04 - Fizik kimyo
(Kimyo fanlari)**

**E‘LON QILINGAN ILMIY ISHLAR BO‘YICHA DISSERTATSIYASIZ
KIMYOFANLARI BO‘YICHA FAN DOKTORI (DSc) ILMIY DARAJASINI OLISH
UCHUN TAQDIMNOMA**

Toshkent – 2026

**Presentation on awarding the scientific degree of Doctor of Science (DSc) on
the basis of published papers without a dissertation**

**E'lon qilingan ilmiy ishlar bo'yicha dissertatsiyasiz fan doktori (DSc) ilmiy
darajasini olish uchun taqdimnoma**

**Представление на соискание ученой степени доктора наук (DSc) без
диссертации на основе опубликованных научных трудов**

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на основе однокомпонентных оксидов металлов для экологических
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**SCIENTIFIC COUNCIL DSc.03/06.11.2025.K/FM.10.09 ON AWARD OF A
SCIENTIFIC DEGREE AT THE INSTITUTE OF FUNDAMENTAL AND
APPLIED RESEARCH UNDER THE NATIONAL RESEARCH
UNIVERSITY “TIAME”**

INSTITUTE OF FUNDAMENTAL AND APPLIED RESEARCH

SIRAJUL HAQ

**A MULTICOMPONENT NANOMATERIAL PLATFORM
FUNCTIONALIZED FROM SINGLE-COMPONENT METAL OXIDES
FOR ENVIRONMENTAL APPLICATIONS**

**02.00.04 - Physical Chemistry
(Chemical Sciences)**

PRESENTATION

**On awarding the scientific degree of Doctor of Science (DSc) in chemical sciences on the
basis of published papers without a dissertation**

Tashkent - 2026

The subject of the DSc research is registered by the Supreme Attestation Commission of the Cabinet of Ministers of the Republic of Uzbekistan under B2026.3.DSc/K274.

The research work results have been carried out at Institute of Fundamental and Applied Research, TIAME National Research University (Uzbekistan).

Presentation abstract of scientific research in three languages (English, Uzbek and Russian (only introduction and conclusions)) is posted on the webpage at the address www.ifar.uz and information-educational portal “Ziyonet” (www.ziyonet.uz).

Research advisor:

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Doctor of Chemical Sciences

Presentation of the scientific research will take place on the “____” “____” 2026 at _____ in the meeting of the Scientific Council No. DSc.03/06.11.2025.K/FM.10.09 at the Institute of Fundamental and Applied Research under the “TIAME” National Research University (Address: 100000, Tashkent city, Qori Niyaziy Street 39, Institute of Fundamental and Applied Research, Hall 108; Tel.: 71237-09-61.; email: info@ifar.uz).

The DSc presentation abstract can be looked through at the Information Resource center of the Institute of Fundamental and Applied Research under the “TIAME” National Research University (registered under No _____) (Address: 100000, Tashkent city, Qori Niyaziy Street 39, Institute of Fundamental and Applied Research, Hall 105; Tel.: 71 237-09-61).

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INTRODUCTION (Presentation Abstract)

Relevance of the topic. The research presented in this report addresses one of the most critical environmental challenges of our time: the contamination of water resources by organic dyes. According to the UNESCO report presented at the UN 2023 Water Conference in New York, approximately 2 billion people worldwide constituting 26% of the global population lack access to safe drinking water. This is not merely a statistic but a daily reality affecting the health, economic productivity, and human dignity of billions. Water pollution contributes to 70% of mortality from diarrheal diseases, along with significant percentages of typhoid fever (8%), paratyphoid fever (20%), and lower respiratory tract infections (2%). The textile industry alone discharges approximately 10-25% of textile dyes into freshwater reservoirs annually, with global dye production reaching 1.3 million tons per year. These dyes contain aromatic compounds such as naphthalene and benzamine that are toxic, carcinogenic, and mutagenic, causing bladder cancer, central nervous system disorders, dermatitis, allergic conjunctivitis, rhinitis, occupational asthma, and various other allergic reactions.

The World Health Organization has listed antimicrobial resistance (AMR) among the top ten global public health threats, leading to approximately 1.27 million deaths annually. Multi-drug resistant bacterial strains have emerged worldwide due to the overuse and misuse of antibiotics, rendering conventional treatments ineffective. The development of new antibiotics has stalled, with few novel classes reaching the market in recent decades. The economic burden of AMR is estimated to reach \$100 million by 2050 if no action is taken. The antibacterial nanomaterials developed in this research offer a fundamentally different approach to combating bacterial infections. Unlike antibiotics that typically target specific cellular processes (enabling bacteria to develop resistance through single mutations), metal oxide nanoparticles employ multiple simultaneous mechanisms of action: physical disruption of bacterial cell membranes through direct contact, release of metal cations (Zn^{2+} , Cu^{2+} , Ag^{+} , Ni^{2+} , Fe^{3+}) that interact with vital bacterial enzymes containing thiol groups, generation of reactive oxygen species that cause oxidative damage to cellular components, and penetration of bacterial cells by small nanoparticles causing internal structural damage. The rGO-ZSF nanocomposite achieved inhibition zones of 31 mm against *E. coli* and 29 mm against *S. aureus*, significantly exceeding the standard antibiotic control (21 mm and 20 mm respectively), demonstrating potential to combat even resistant bacterial strains.

Oxidative stress is the imbalance between excessive formation of reactive oxygen/nitrogen species and the ability of antioxidant defense mechanisms to scavenge them underlies numerous chronic diseases including cancer, cardiovascular disease, diabetes, neurodegenerative disorders (Alzheimer's, Parkinson's), asthma, premature aging, and inflammatory conditions. When reactive oxygen species (hydroxyl radicals, superoxide anions, atomic oxygen) and reactive nitrogen species

(peroxynitrite) are produced in excess, they damage DNA (causing mutations and cancer), proteins (inactivating enzymes), and cellular membranes (disrupting integrity and function). The antioxidant activities demonstrated by these nanomaterials with IC₅₀ values as low as 11.25 µg/mL for GO against ABTS and 15.98 µg/mL against DPPH approach or exceed those of standard antioxidants like ascorbic acid (IC₅₀ 44.67 µg/mL). The mechanisms include radical adduct formation on sp²-hybridized carbon sites, electron transfer, and hydrogen donation from functional groups, providing multiple pathways for radical neutralization.

Necessity of the topic. The necessity of this research is driven by the accelerating rate of environmental degradation and its direct impact on human health. Global water consumption has increased six-fold over the past century, twice the rate of population growth, while pollution has rendered vast water resources unusable. Industrialization without adequate environmental safeguards has led to widespread contamination of rivers, lakes, and groundwater. In developing countries, over 80% of wastewater is discharged untreated into water bodies, creating a cycle of pollution and disease that perpetuates poverty. The economic cost of water pollution is staggering: lost fishing and agricultural productivity, increased healthcare expenditures, reduced property values, and expensive water treatment infrastructure. Conventional treatment technologies are failing to keep pace with the volume and complexity of industrial pollutants. The textile industry alone produces over 10,000 different synthetic dyes, many of which are designed to resist degradation (light-fast, wash-fast, chemically stable). These same properties that make them useful for coloring fabrics make them persistent environmental pollutants. Advanced oxidation processes (AOPs) using photocatalysis offer the only viable route to complete mineralization of these recalcitrant compounds. The development of efficient, cost-effective, solar-activated photocatalysts is therefore not merely academically interesting but environmentally necessary.

The necessity of this research is also driven by the alarming rise of antimicrobial resistance. The "post-antibiotic era" is no longer a theoretical concern but a present reality. Carbapenem-resistant Enterobacteriaceae (CRE), methicillin-resistant *S. aureus* (MRSA), vancomycin-resistant *Enterococcus* (VRE), and multidrug-resistant *P. aeruginosa* are now common in hospitals worldwide. The development of new antibiotics has been economically unattractive for pharmaceutical companies, with several new classes of antibiotics developed in the past 30 years. Nanomaterials offer a fundamentally different paradigm: rather than developing new molecular entities that bacteria can eventually develop resistance against, nanomaterials use physical mechanisms of action (membrane disruption, oxidative stress) that are much more difficult for bacteria to evolve resistance against. The development of effective antibacterial nanomaterials is therefore a public health necessity.

The necessity of antioxidant research is driven by the global burden of chronic diseases. Cardiovascular disease causes 17.9 million deaths annually (32% of all global deaths). Cancer causes 9.6 million deaths annually. Diabetes causes 1.6 million deaths annually, with millions more suffering from complications including blindness, kidney failure, and lower limb amputation. All of these diseases have oxidative stress as a common pathogenic mechanism. Effective antioxidants that can be safely delivered to target tissues could dramatically reduce the burden of these diseases. The nanomaterials developed in this research, with IC₅₀ values as low as 11.25 µg/mL, offer potential for therapeutic antioxidant applications.

International context of the research. This research positions itself within the international research landscape on nanomaterials for environmental and biomedical applications. According to Web of Science data, publications on "photocatalytic degradation" have grown from ~500 in 2000 to over 10,000 in 2023. Publications on "green synthesis nanoparticles" have grown from ~100 in 2005 to over 5,000 in 2023. Publications on "antibacterial nanomaterials" have grown from ~200 in 2005 to over 8,000 in 2023. This research contributes to these rapidly growing fields by addressing specific gaps: the limited research on MWCNT-modified trimetallic oxides, the limited research on green synthesis using *C. maxima*, *D. kaki* and *S. chirayita*, the limited research on LDHs with four metal cations, and the limited integration of photocatalytic, antibacterial, and antioxidant functions in single nanomaterials. This research directly contributes to multiple United Nations Sustainable Development Goals, providing an international framework for its significance. The research opens several international research directions: pilot-scale studies with real industrial wastewater in multiple countries to validate performance under different environmental conditions; clinical trials for antibacterial and anticancer nanomaterials following international regulatory standards (FDA, EMA); life cycle assessment and techno-economic analysis to demonstrate sustainability and economic viability for different regions; technology transfer to developing countries through capacity building and knowledge exchange programs; standardization of synthesis, characterization, and testing protocols to enable international comparison and regulatory approval; and exploration of additional applications (e.g., hydrogen production, CO₂ reduction, sensing) to expand the impact of these multifunctional nanomaterials.

Aim of the research. The overarching aim of this research is to develop efficient, cost-effective, and environmentally sustainable multifunctional nanomaterials through innovative synthesis approaches (green synthesis, mechanochemical methods, and modified sol-gel processes) for the remediation of organic pollutants from wastewater and for antibacterial and chemical antioxidant analysis, while establishing comprehensive structure-property-performance correlations to guide rational material design.

Tasks of the research. The main objectives of this research are:

1. **Synthesis and fabrication:** Develop diverse nanomaterials including single metal oxides (ZnO, Fe₂O₃), bimetallic oxides (CuO-ZrO₂, CuO-Fe₂O₃, CuO-NiO, and Zr-doped NiO-ZnO), Co-Cu-Zn-Layered Hydroxides, trimetallic oxides (Ag₂O-CuO-ZnO, TiO₂-doped SnO₂-ZrO₂, SnO₂-NiO-CuO), Co-Cu-Zn-Layered Hydroxides, layered double hydroxides (Cr/Ni/Mg/Al-LDH), and their advanced composites with graphene oxide, reduced graphene oxide, and multi-walled carbon nanotubes using green synthesis (*M. acuminata peels*, *D. kaki*, *S. chirayita*, *C. maxima* extracts), solvent-free mechanochemical grinding, modified Hummers' method, co-precipitation, and modified sol-gel techniques.
2. **Comprehensive characterization:** Investigate structural, morphological, optical, compositional, thermal, and textural properties using XRD, SEM, TEM, EDX, EDS, FTIR, DRS, and BET surface area analysis to establish detailed structure-property correlations.
3. **Photocatalytic degradation:** Evaluate photocatalytic efficiency against various organic dyes (MO, R-6G, brilliant green (BG), fluorescein, 4-nitrophenol) under solar/UV light irradiation, including kinetic analysis and mechanistic studies.
4. **Antibacterial activity:** Assess bactericidal potential against Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria using the agar well diffusion method, establishing concentration-dependent activity profiles.
5. **Antioxidant activity:** Evaluate free radical scavenging capacity against ABTS and DPPH radicals, calculating IC₅₀ values and establishing structure-activity relationships.
6. **Optimization studies:** Systematically examine effects of calcination temperature (uncalcined to 900°C), pH (2-12), catalyst dose (5-30 mg), initial concentration (5-30 ppm), and recycling stability (4-5 cycles) on material performance.

Scientific novelty of the research. This research presents several significant scientific novelties that advance the field of nanomaterials for environmental and biomedical applications. First, the research reports several first-time syntheses of novel nanocomposite systems that have never been reported in the literature. MWCNT-modified Ag₂O/CuO/ZnO trimetallic nanocomposites were synthesized for the first time using a modified sol-gel method, demonstrating exceptional multifunctional properties as a photocatalyst, antibacterial agent, and antioxidant agent. Similarly, rGO-ZnO-SnO₂-Fe₂O₃ quaternary nanocomposite represents a novel combination where reduced graphene oxide is integrated with three distinct metal oxides for enhanced biological applications. Zr-doped NiO/ZnO nanocomposites were fabricated for the first time using *D. kaki* leaf extract, introducing a new green synthesis approach for doped bimetallic oxides. TiO₂-doped

SnO₂-ZrO₂ nanocomposites using *S. chirayita* plant extract represent a novel combination of materials with heterojunction formation. Cr/Ni/Mg/Al layered double hydroxides with multiple metal cations (Cr³⁺, Ni²⁺, Mg²⁺, Al³⁺) and the Co-Cu-Zn-LHs was prepared using the *C. maxima* leaves extract were synthesized and investigated for MO degradation, which was previously underexplored in the literature.

Second, the research introduces innovative synthesis methodologies that advance sustainable nanomaterial production. The mortar-pestle-assisted mechanochemical solvent-free synthesis for bimetallic oxide nanocomposites (CuO-ZrO₂, and CuO-Fe₂O₃) represents a greener alternative to conventional solvothermal methods, being more efficient, faster, straightforward, scalable, and environmentally friendly while eliminating hazardous solvents. Green synthesis using various plant extracts (*M. acuminata* peels, *D. kaki* leaves, *S. chirayita*, and *C. maxima*) as reducing and capping agents eliminates hazardous chemicals, promotes waste valorization of agricultural byproducts, and yields nanoparticles with superior biological activities due to adsorbed phytochemicals.

Third, the research establishes novel multifunctional platforms where single nanomaterials demonstrate simultaneous photocatalytic, antibacterial, and antioxidant capabilities. The integration of comprehensive biological evaluation (photocatalytic, antibacterial, and antioxidant) in single nanocomposite systems represents a holistic approach to material development that is rarely reported. The synergistic combination of graphene oxide with trimetallic oxides (rGO-ZSF, GO-SNC) and MWCNTs with bimetallic/trimetallic oxides (MWCNTs@CuO-NiO, MWCNTs@Ag₂O/CuO/ZnO) demonstrated enhanced properties through improved charge separation, electron transfer, and surface area.

Fourth, the research provides fundamental mechanistic insights through systematic correlation of structure-property-performance relationships. The trade-off between surface area and crystallinity with increasing calcination temperature was clearly demonstrated across multiple systems, revealing that surface area is the dominant factor governing photocatalytic activity despite lower crystallinity. The doping dilemma was elucidated, showing that increasing dopant concentration from 0.5% to 1% in Zr-NiO/ZnO unexpectedly reduced photocatalytic activity (86.45% → 67%) and increased band gap (3.43 → 3.66 eV), challenging the assumption that "more doping equals better performance." The MWCNT double-edged sword was characterized, where MWCNT incorporation consistently enhanced photocatalytic and antioxidant properties while sometimes reducing antibacterial activity, revealing that different applications require different surface modifications.

Fifth, the research provides unprecedented comparative performance data with green-synthesized nanoparticles consistently outperforming chemically synthesized counterparts, suggesting that adsorbed phytochemicals contribute directly to biological activities rather than merely controlling size and morphology. The

superior performance of Cr/Ni/Mg/Al-LDH (89.23% MO degradation in 30 min with a rate constant of 0.07427 min^{-1}) compared to literature-reported LDHs (requiring 90-180 min) demonstrates significant advancement.

Reliability of research results. The reliability of research findings in this study is established through multiple complementary characterization techniques applied consistently across all studies, ensuring data accuracy and reproducibility. XRD provided phase identification using standard JCPDS reference cards, crystallite size calculations via the Debye-Scherrer equation ($D = K\lambda/\beta\cos\theta$), and lattice strain analysis, with all peaks matched to reference cards ensuring correct phase identification. SEM and TEM revealed morphology, particle size distribution, and microstructure, with ImageJ software used for size estimation from multiple images to ensure statistical significance. EDX confirmed elemental composition and purity, with spectra showing expected peaks for all constituent elements and absence of unexpected impurities.

FTIR identified functional groups and confirmed metal-oxygen bond formation, with consistent band positions across multiple samples and systematic intensity changes with calcination temperature. Diffuse reflectance spectroscopy (DRS) determined optical properties and band gap energies through Tauc plots ($\alpha h\nu = A(h\nu - E_g)^n$), with multiple measurements confirming reproducibility. BET surface area analysis quantified surface area, pore size, and pore volume using N_2 adsorption-desorption isotherms, following IUPAC classification standards. Thermogravimetric analysis provided thermal stability profiles with consistent weight loss patterns across multiple heating cycles.

Reproducible synthesis methods with detailed experimental procedures including controlled parameters (temperature, pH, concentration, time, stirring rate, calcination conditions) ensure that findings can be replicated by independent researchers. All syntheses were repeated multiple times (3-5 times) to verify reproducibility, with consistent results within $\pm 5\%$ variation. Statistical analysis of biological activities includes standard deviation, variance, IC_{50} values, and correlation coefficients, demonstrating data reliability. For antibacterial activity, multiple wells per plate (minimum 3) and multiple plates per experiment (minimum 3) were used, with standard deviation values typically ranging from 1.09 to 1.83 mm, indicating good precision. For antioxidant activity, IC_{50} values were calculated from dose-response curves with R^2 values typically >0.98 , and standard deviation values ranged from 1.51 to 1.75, indicating consistency.

Comparative analysis with literature data and standard controls (ascorbic acid for antioxidant, ciprofloxacin/antibiotics for antibacterial) validates the significance of findings. Kinetic modeling of photocatalytic and drug release data fitted to pseudo-first-order and pseudo-second-order models with high regression coefficients ($R^2 > 0.98$) confirms the appropriateness of proposed mechanisms. Reusability studies over 4-5 cycles demonstrate catalyst stability and practical applicability, with

consistent degradation patterns across cycles. Systematic optimization of influencing factors (pH, dose, concentration, temperature, calcination temperature) ensures comprehensive understanding of material performance under various conditions. Control experiments (catalyst-only, light-only) were performed for photocatalytic studies to confirm that degradation was indeed due to photocatalysis rather than adsorption or photolysis alone.

Significance of the research results. The research demonstrates exceptional environmental remediation capabilities with significant practical implications. Photocatalytic degradation efficiencies reach up to 99.61% for R-6G using MWCNTs@Ag₂O/CuO/ZnO, 99.42% for R-6G using green-synthesized iron oxide nanoparticles, 95.37% using MWCNTs@CuO-NiO, and 93.57% for 4-nitrophenol using SnO₂-ZrO₂, representing superior performance compared to literature-reported values. Rate constants as high as 0.10012 min⁻¹ (MWCNTs@Ag₂O/CuO/ZnO) and 0.07427 min⁻¹ (Cr/Ni/Mg/Al-LDH) indicate rapid degradation kinetics suitable for practical wastewater treatment. Solar light activation reduces energy requirements and operational costs, making the technology accessible for developing regions where both water contamination and energy poverty coexist.

Biomedical applications show promising results with significant therapeutic potential. Antibacterial activity with inhibition zones up to 31 mm (rGO-ZSF against *E. coli*) demonstrates effectiveness against both Gram-positive and Gram-negative bacteria, addressing the global challenge of antimicrobial resistance. The superior activity of uncalcined samples (31 mm vs 29 mm for calcined) and GO-supported nanocomposites (24-31 mm) compared to bare metal oxides (7-24 mm) and standard antibiotics (16-20 mm) provides multiple strategies for combating drug-resistant bacteria. Enhanced antioxidant activity with IC₅₀ values as low as 11.25 µg/mL (GO against ABTS) and 15.98 µg/mL (GO against DPPH) indicates strong free radical scavenging capacity for combating oxidative stress-related diseases including cancer, cardiovascular disease, diabetes, and neurodegenerative disorders. The exceptional performance of GO (IC₅₀ 11.25 µg/mL) compared to ascorbic acid (IC₅₀ 44.67 µg/mL) represents a 4-fold improvement, opening new avenues for antioxidant therapeutics.

Materials science advances include fundamental understanding of calcination temperature effects on crystallinity, surface area, and band gap, establishing structure-property-performance correlations essential for rational material design. The clear demonstration that uncalcined samples showed the highest activity despite lower crystallinity, while CuO-ZrO₂ showed increased activity with calcination (77.27% at 900°C), reveals that different material systems have different dominant factors, and optimization must be material-specific rather than assuming universal trends. The correlation between decreased surface area (152.53 → 1.78 m²/g) and decreased photocatalytic activity (88.95% → 59.19%) for CuO-Fe₂O₃ further confirms that surface area is the dominant factor.

The green synthesis advantage is clearly demonstrated, with *M. acuminata*-derived iron oxide nanoparticles achieving 99.42% R-6G degradation, outperforming many chemically synthesized counterparts. The use of agricultural waste (banana peels) and medicinal plants (*D. kaki*, *S. chirayita*, *C. maxima*) provides sustainable, low-cost, and locally adaptable production routes. The mechanochemical approach offers advantages including solvent-free operation, energy efficiency, environmental friendliness, scalability, and simplicity, making it a compelling alternative for sustainable photocatalyst development. Alignment with UN Sustainable Development Goals 3 (good health) and 6 (clean water) positions this research within the global framework for addressing pressing humanitarian challenges.

Implementation of research results. The scientific results obtained during this DSc. research have been published in high-impact international journals and have received significant recognition from the global scientific community, as evidenced by the citation metrics obtained from Scopus. The paper entitled "Solar light-induced degradation of hazardous organic pollutants using Diospyros kaki mediated green synthesized zirconium doped nickel oxide-zinc oxide nanocomposite," published in *Materials Research Express* (2024), has received 3 citations and is ranked at the 60 percentile with a Field-Weighted Citation Impact (FWCI) of 0.35. The paper entitled "Antibacterial and antioxidant screening applications of reduced-graphene oxide modified ternary SnO₂-NiO-CuO nanocomposites," published in *Arabian Journal of Chemistry* (2023), has received 21 citations and is ranked at the 89 percentile with an FWCI of 1.40, indicating a citation impact significantly above the global average for its field and publication year. The paper entitled "Fabrication and structural analysis of CuO-NiO and MWCNTs@CuO-NiO hybrid nanostructures: versatile materials for environmental and biomedical remediation," published in *RSC Advances* (2025), has received 5 citations and is ranked at the 82 percentile with an FWCI of 0.71. The paper entitled "Unveiling the physicochemical, photocatalytic, antibacterial and antioxidant properties of MWCNT-modified Ag₂O/CuO/ZnO nanocomposites," published in *RSC Advances* (2025), has received 11 citations and is ranked at the 95 percentile with an FWCI of 2.38, representing the highest citation impact among the published works and indicating that this research has been cited more than twice the global average for its field. The paper entitled "Enhanced Photocatalytic Performance of Cr/Ni/Mg/Al Layered Double Hydroxides against Methyl Orange in Aqueous Solution," published in *Desalination and Water Treatment* (2024), has received 6 citations and is ranked at the 75 percentile with an FWCI of 0.75. The paper entitled "Solvent free fabrication and thermal tuning of copper oxide-zirconium dioxide nanocomposite for enhanced photocatalytic efficacy," published in *Materials Research Express* (2024), has received 7 citations and is ranked at the 75 percentile with an FWCI of 0.70. Collectively, these publications have received a total of 53 citations from independent researchers worldwide, demonstrating that the scientific

results of this DSc research have been recognized, cited, and utilized by the international scientific community in high-impact journals. The research findings have been cited in subsequent publications in journals such as *Scientific Reports*, *RSC Advances*, *Heliyon*, *Materials Science and Engineering: B*, *Journal of Environmental Chemical Engineering*, and *Pharmaceuticals*, among others. This citation record confirms the scientific quality, international relevance, and practical significance of the research results, and demonstrates that the developed nanomaterials and synthesis approaches have made a meaningful contribution to the fields of environmental remediation and biomedical therapeutics.

Pulications of research results. The results obtained in the frame of this DSc research work are presented in 12 peer-reviewed articles published in prestigious journals recommended by the Superme Attestation Commission of the Republic of Uzbeksiatn for the publication of he main scientific results of D.Sc presentation and displayed in the *Web of Science* database.

MAIN CONTENTS

PART 1: SINGLE METAL OXIDE NANOMATERIALS

1.1 Zinc oxide nanoparticles (ZnO-NPs). Zinc oxide nanoparticles were synthesized using an economical precipitation method with $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ precursor and KOH as a precipitating agent. The synthesis involved dissolving zinc chloride in distilled water with ethanol, heating at 60°C , and adding KOH dropwise until pH 10 was achieved. The resulting precipitates were washed with warm distilled water and dried at 100°C , producing white powdered ZnO-NPs. XRD analysis revealed a hexagonal crystal structure with characteristic diffraction peaks at 31.90° (100), 34.45° (002), 36.27° (101), 47.59° (102), 56.63° (110), 62.97° (103), and 68.11° (112), matching JCPDS card 01-079-0205. The crystallite size was calculated as 25.84 nm using the Debye-Scherrer equation, with a lattice strain of 0.323%.

SEM at low magnification showed significant agglomeration with particles forming an irregular network on a flat surface, while high magnification revealed nearly spherical particles with sizes ranging from 88 to 121 nm and an average size of 99.62 nm. TEM provided detailed morphological insights, showing particle sizes ranging from 25 to 60 nm with both spherical and polyhedral morphologies. Some regions exhibited particle fusion forming sheet-like structures due to high surface energy, while other areas maintained distinct particle boundaries despite close packing. EDX confirmed the elemental composition with sharp signals at 0.9, 8.70, and 9.60 keV for zinc and at 0.24 keV for oxygen, showing weight percentages of 80.3% Zn and 19.7% O, confirming high purity without impurities. FTIR revealed O-H stretching vibrations in the range of $3539\text{--}3376\text{ cm}^{-1}$, O-H bending at 1626.92 cm^{-1} , M-OH vibration at 1379.56 cm^{-1} , O-Zn-O stretching at 1027.44 cm^{-1} , and Zn-O stretching and bending vibrations at 673.71 and 478.33 cm^{-1} .

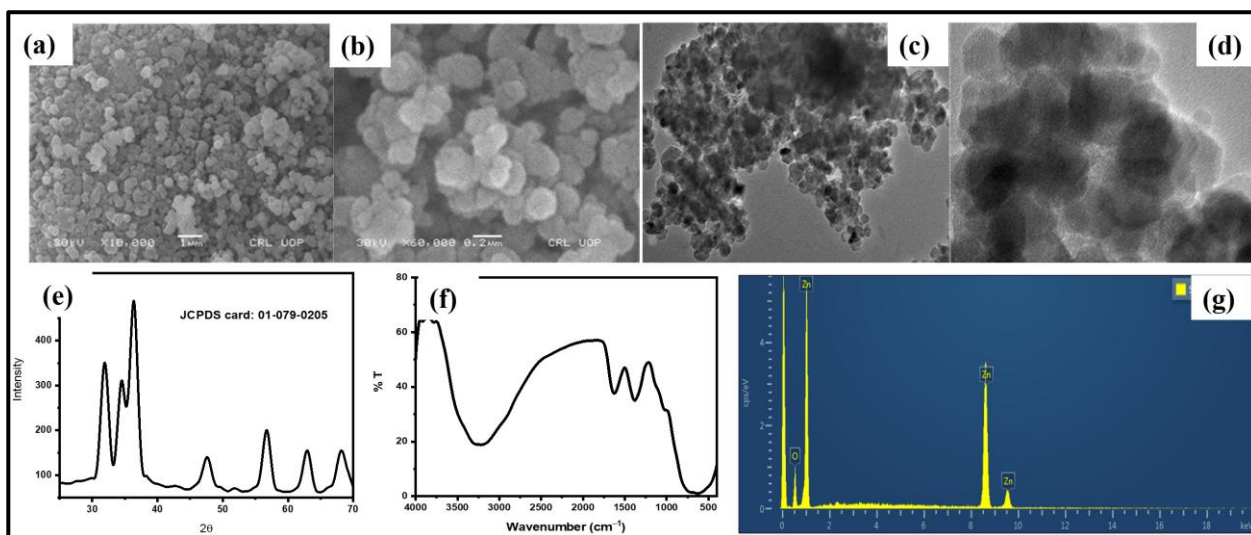


Figure 1: SEM micrograph (a, b), TEM image (c, d), XRD pattern (e), FTIR spectrum (f), and EDX spectrum (g) the ZnO-NPs synthesized by precipitation method (Azeem et al., 2024).

The antibacterial activity of ZnO-NPs was evaluated against *S. aureus* (Gram-positive) and *E. coli* (Gram-negative) using the agar well diffusion method with varying concentrations from 20 to 100 μ L of nanoparticle dispersion (1 mg/mL in DMSO). The results showed that growth inhibitory activity increased with increasing concentration of ZnO suspension in the wells, indicating greater effectiveness at higher concentrations. ZnO-NPs demonstrated stronger growth inhibitory effect against *E. coli* compared to *S. aureus*, with inhibition zones of 14 mm and 10 mm at 100 μ L, respectively. This variance was attributed to the different chemical interactions of ZnO-NPs in aqueous environments and the distinct chemical compositions of the bacterial outer membranes. The strong linkage between Zn^{2+} ions and *E. coli* surfaces occurs through phospholipids and lipopolysaccharides, while the weaker interaction with *S. aureus* is due to the partial negative charge imparted by teichoic acid in the Gram-positive cell wall. The antibacterial mechanism involves the release of Zn^{2+} ions that disrupt bacterial membrane integrity, interact with vital bacterial enzymes containing thiol groups, and generate reactive oxygen species that cause oxidative damage to cellular components.

Table 1. The bactericidal results of ZnO-NPs extracted from the agar well diffusion experiment (Azeem et al., 2024).

Species	Volume of ZnO-NPs in μ L					-ve control
	20	40	60	80	100	
<i>S. aureus</i>	0.5	01	04	07	10	00
<i>E. coli</i>	1	02	07	10	14	00

The antioxidant activity of ZnO-NPs was assessed through ABTS free radical scavenging assay, with results compared to ascorbic acid as a standard. The study showed a gradual increase in radical scavenging activity with increasing concentrations of both samples. ZnO-NPs exhibited activity increasing from 40.23% at 50 µg/µL to 98.01% at 300 µg/µL, with an IC₅₀ value of 83.89 µg/µL, while ascorbic acid showed 99.56% activity at 300 µg/µL with an IC₅₀ of 77.35 µg/µL. The increase in antioxidant activity at higher concentrations was attributed to the larger number of ZnO-NPs available to interact with and scavenge free radicals, effectively reducing their levels and preventing cellular damage. The IC₅₀ value, representing the concentration that inhibits 50% of free radicals, indicated that ZnO-NPs possess considerable antioxidant activity comparable to the standard. Statistical analysis showed variance of 2.26 and standard deviation of 1.51 for ZnO-NPs, indicating consistency in the results. This study successfully demonstrated that ZnO-NPs synthesized through a straightforward, cost-effective method possess strong crystalline structure, uneven particle distribution, high purity, dose-dependent antibacterial activity with greater efficacy against *E. coli*, and significant antioxidant potential, making them promising candidates for biomedical applications targeting drug-resistant bacterial strains and oxidative stress-related conditions.

Table 2. Antioxidant activity of ZnO-NPs against ABTS free radicals (Azeem et al., 2024).

Sample	Concentration (µg/µL)	Activity (%)	IC ₅₀ (µg/µL)	Variance (S ²)	STD Dev.
ZnO-NPs	50	40.23	83.89	2.26	1.51
	100	54.02			
	200	81.34			
	300	98.01			
Ascorbic acid	50	41.34	77.35	2.25	1.51
	100	55.78			
	200	83.55			
	300	99.56			

1.2 Iron oxide nanoparticles (IO-NPs) from *Musa acuminata* peel extract.

IO-NPs were synthesized using an eco-friendly green approach utilizing *M. acuminata* (banana) peel extract as both reducing and stabilizing agent, representing a single-pot, low-temperature process that eliminates hazardous chemicals and promotes waste valorization. The peel extract was prepared by boiling clean waste *M. acuminata* peels in distilled water at 80 °C for 2 h, producing a light yellow crude extract that was filtered and stored. For nanoparticle synthesis, FeSO₄·7H₂O was dissolved in distilled water to create a 15 mM solution, which was mixed with the peel extract and stirred at 250 rpm and 50 °C for 45 min, producing brick-red precipitates that were aged for 6 h, filtered, washed with hot distilled water, and dried

at 140 °C. The peel of *M. acuminata* is an abundant agricultural waste product rich in bioactive substances including antioxidants, flavonoids, and polyphenols that serve as organic reducing and stabilizing agents, donating electrons to reduce iron ions and subsequently adsorb onto the nanoparticle surface, forming a stabilizing organic moiety that controls size and morphology while preventing agglomeration.

XRD analysis revealed a slightly noisy diffractogram indicating some amorphous content from phytochemicals alongside the crystalline phase, with characteristic diffraction peaks matching JCPDS card 01-071-4918 confirming the formation of Fe₂O₃ crystallites with cubic geometry. The average crystallite size calculated from XRD data was 38.42 nm, with a lattice strain of 0.149%. SEM at low magnification showed most particles appearing round or nearly round with irregular distribution, with the lower left portion slightly agglomerated forming larger particles while small particles resided upon the surface of larger ones. High magnification images revealed three perfect spherical particles with well-defined boundaries alongside several nearly spherical particles that seemed fused with one another without forming larger agglomerates, a phenomenon attributed to high surface energy causing particle fusion. TEM provided better understanding of morphology, showing nearly spherical particles with porous surfaces and a particle size of 56.22 nm, nearly double the crystallite size due to the organic coating from plant extract.

EDX confirmed the presence of iron with peaks at 0.6, 6.40, and 7.12 keV, and oxygen with a sharp signal at 0.50 keV, giving weight percentages of 78.21% Fe and 21.79% O. The presence of carbon from the carbon tape used for sample streaking was also noted. Thermogravimetric analysis showed a two-stage weight loss pattern, with the first weight loss of 9.71% occurring between 48 and 130 °C due to evaporation of moisture and physisorbed water, followed by a second weight loss of 12.02% between 220 and 535°C caused by loss of chemisorbed water. FTIR confirmed the formation of pure IO-NPs with bands corresponding to non-bonding water molecules at 3742.51 cm⁻¹, O-H stretching vibrations in the 3394.72-3038.59 cm⁻¹ range, O-H bending at 1639.28 cm⁻¹, metal-oxygen stretching and bending vibrations at 1054.72, 755.63, and 726.76 cm⁻¹, and lattice vibrations involving iron-oxygen bonds at 473.90 and 435.24 cm⁻¹. UV-visible spectroscopy showed a strong absorbance band at 312.35 nm associated with direct band-to-band transition, and Tauc's plot analysis gave a band gap energy of 3.20 eV, indicating the minimum energy required to transfer electrons from the valence band to the conduction band, enabling effective charge transport and electron-hole pair generation for photocatalytic processes.

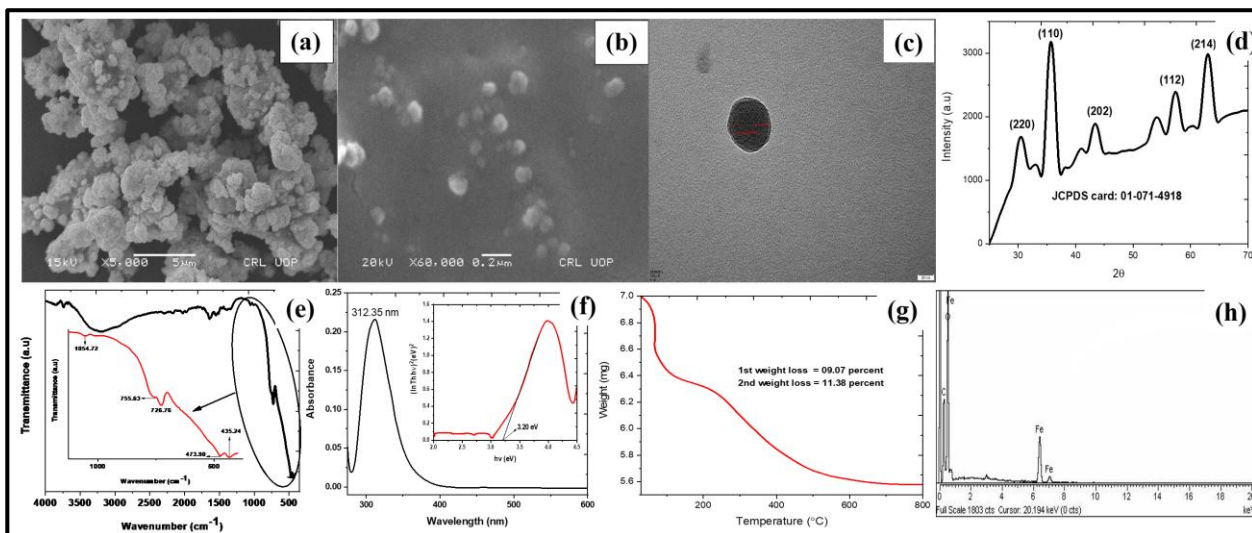


Figure 2: SEM micrograph (a and b), TEM image (c), XRD pattern (d), FTIR spectrum (e), UV-Vis spectrum (f), TGA plot (g) and EDX spectrum (h) the IO-NPs synthesized by *M. acuminata* peels extract (Hedfi et al., 2025).

The photocatalytic efficacy of IO-NPs was evaluated against MO and R-6G under simulated solar light. For MO degradation, a 15 ppm solution was treated with 20 mg of IO-NPs, stirred for 30 min in the dark to achieve adsorption-desorption equilibrium, then exposed to solar light. The bright orange color faded with time, confirmed by UV-Vis analysis showing a continuous decrease in absorbance maxima at 464 nm. The degradation profile showed a sharp decrease followed by a steady decrease, attributed to initial free binding sites on the catalyst surface becoming engaged with dye molecules, followed by limited degradation after maximum binding site occupation. After 160 min, 79.87% of MO was degraded with a rate constant of 0.00873 per min. For R-6G, the same procedure at 526 nm showed even higher efficiency with 99.42% degradation in 160 min and a rate constant of 0.03012 per min. The photocatalytic mechanism involves absorption of photons with energy higher than the semiconductor band gap, exciting electrons from the valence band to the conduction band, leaving holes in the valence band. These photogenerated electron-hole pairs migrate to the nanoparticle surface and participate in redox reactions with adsorbed species. Electrons combine with adsorbed oxygen to form superoxide radicals, while holes react with water molecules to produce hydroxyl radicals. Both superoxide and hydroxyl radicals are highly reactive species that oxidize organic dye molecules, causing their breakdown into simpler, less hazardous substances like CO₂ and H₂O.

Optimization studies revealed that solution pH significantly affected degradation efficiency, with maximum degradation occurring at pH 6 where the catalyst surface is positively charged due to protonation, resulting in electrostatic attraction with anionic MO. At higher pH, the surface becomes negatively charged due to deprotonation, causing electrostatic repulsion and decreased activity. Catalyst dose optimization showed maximum degradation at 20 mg, with lower doses

providing insufficient active sites and higher doses causing particle aggregation that blocks binding sites and impedes dye molecule travel toward active sites. Initial concentration studies showed optimal degradation at 15 ppm, with higher concentrations causing light blockage where maximum radiation is absorbed by dye molecules, limiting photon strike on the catalyst surface for activation. Reusability studies over five consecutive cycles showed a gradual decrease in degradation efficiency from 79.87% to 38.65%, attributed to surface saturation, decreased light penetration due to accumulated by-products, and structural and chemical changes limiting binding site availability and efficacy. Comparative analysis with literature-reported IO-NPs demonstrated superior performance of the green-synthesized nanoparticles, achieving higher degradation percentages in shorter times with lower catalyst doses compared to materials synthesized through conventional methods, highlighting the effectiveness of the green synthesis approach and the potential of utilizing naturally derived precursors for developing sustainable photocatalytic materials for wastewater treatment applications.

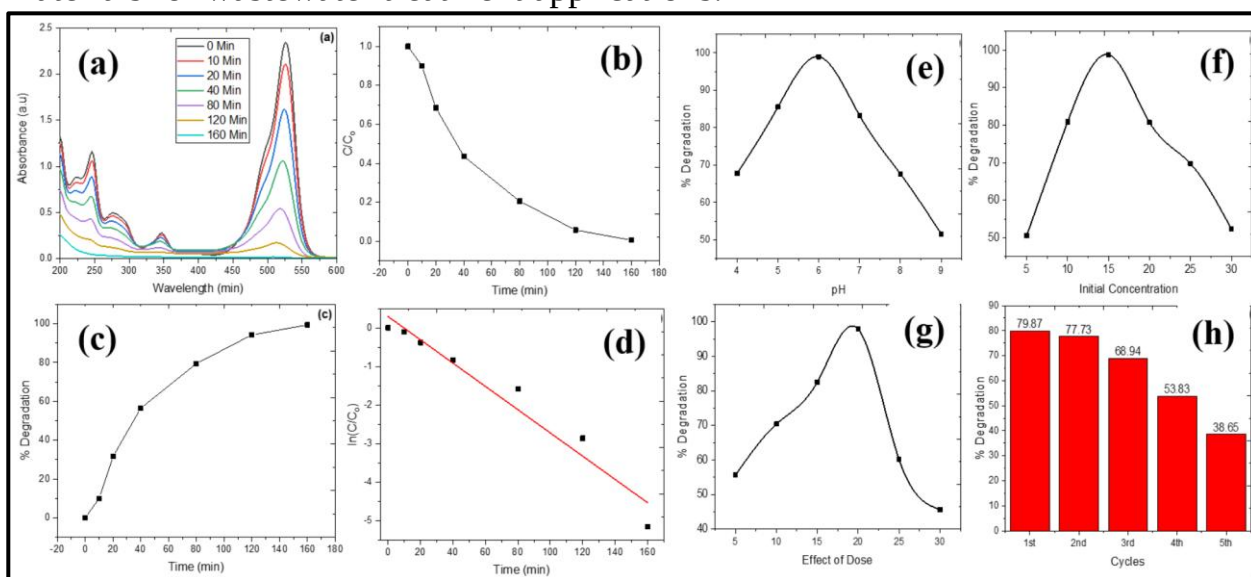


Figure 3: Photocatalytic data of the R-6G degradation of in the presence of IO-NPs under simulated solar light; Degradation profile (a), linear plot (b), Percent degradation (c), rate constant (d), effect of pH (e), effect of initial concentration (f), effect of dose (g) and reuse efficacy (h) of the IO-NPs during the photocatalytic experiment (Hedfi et al., 2025).

Green synthesis offers environmental advantages (elimination of hazardous chemicals, low energy consumption, waste valorization), economic advantages (low cost, simple equipment, scalability), and performance advantages (enhanced biological activity). Phytochemicals (flavonoids, polyphenols, terpenoids) serve dual functions: as reducing agents, they donate electrons to reduce metal ions (e.g., $\text{Fe}^{3+} \rightarrow \text{Fe}^0$) through oxidation of hydroxyl groups to quinones; as capping agents, the oxidized phytochemicals adsorb onto nanoparticle surfaces via -OH, -COOH, and -C=O groups, creating electrostatic and steric stabilization that prevents

agglomeration and controls particle size (15-60 nm). The adsorbed organic layer also enhances biocompatibility and provides additional biological activity, explaining why green-synthesized nanoparticles consistently outperform chemically synthesized counterparts.

PART 2: BIMETAL OXIDE NANOCOMPOSITES

2.1 CuO-ZrO₂ nanocomposites via mechanochemical synthesis. Copper oxide-zirconium dioxide nanocomposites were fabricated through an innovative solvent-free mechanochemical process using mortar and pestle grinding, representing a simple, eco-friendly, and scalable approach that integrates mechanical and chemical interactions at the molecular level. For the first time, this mortar-pestle-assisted mechanochemical process was introduced for bimetallic nanopowder fabrication, offering advantages over conventional solvothermal and sol-gel methods including simplicity, scalability, environmental friendliness, reduced risk of solvent contamination, and simplified purification process. Copper(II) hydroxide and zirconium(IV) hydroxide precursors in equal amounts (1 g each) were ground continuously for six hours, during which observable physical transformations occurred from granular appearance to powdered form, with stickiness developing around three hours due to hydroxide bond breakdown and moisture presence, then reverting to powdered form as metal oxides formed. The final product underwent calcination in a muffle furnace at 300, 600, and 900 °C to investigate temperature effects on structural and photocatalytic properties.

XRD analysis revealed diffraction bands for CuO at 32.61°, 35.58°, 38.72°, 48.78°, 53.44°, 61.61°, 65.86°, 66.24°, 68.15°, and 75.35° corresponding to Miller indices (110), (11T), (111), (20), (020), (113), (022), (311), (220), and (22), matching JCPDS card 96-901-6106 for monoclinic CuO (tenorite mineral) with space group C12/c1. Unit cell dimensions were $a=4.6833$ Å, $b=3.4208$ Å, $c=5.1294$ Å with interfacial angles α and γ at 90° and β at 99.57°, density 6.51 g/cm³, and volume 81.00×10^6 pm³. Crystallite size for uncalcined CuO was 28.3 nm with 0.402% lattice strain, increasing to 42.4 nm for samples calcined at 300, 600, and 900 °C with lattice strains of 0.268%, 0.266%, and 0.266% respectively. For ZrO₂, Bragg's reflections appeared at 24.01°, 28.18°, 31.55°, 34.08°, 40.71°, 44.78°, 49.24°, 50.19°, 55.29°, 58.39°, 59.82°, 62.96°, 64.06°, 71.06°, 72.57°, 76.50°, and 78.00° corresponding to (011), (11T), (111), (002), (21T), (112), (022), (220), (221), (22), (131), (31), (023), (32), (213), (41T), and (104) planes, matching JCPDS card 96-230-0297 for monoclinic ZrO₂ with space group p21/c. Unit cell dimensions were $a=5.1477$ Å, $b=5.2096$ Å, $c=5.3164$ Å with α and γ at 90° and β at 99.21°, density 5.82 g/cm³, and volume 140.61×10^6 pm³. ZrO₂ crystallite size increased with calcination temperature from 20.8 nm (uncalcined) to 41.6 nm (300 °C), 44.9 nm (600 °C), and 55.3 nm (900 °C), with corresponding lattice strain decreasing from 0.680% to 0.342%, 0.301%, and 0.257%. FTIR showed broad bands at 3462.38 cm⁻¹ for O-H stretching, 1622.16

cm^{-1} for H-O-H bending, 1395.63 cm^{-1} for surface OH groups in M-OH, 1329.95 cm^{-1} for out-of-plane O-H bending, 1169.90 cm^{-1} for O-M-O stretching, 746.38 cm^{-1} for M-O-M stretching, and broad bands at $586\text{--}423 \text{ cm}^{-1}$ for M-O stretching modes. The uncalcined sample showed a significant peak at 530 cm^{-1} for Zr-O, while distinctive peaks at 522 and 590 cm^{-1} signaled Cu-O stretching vibrations. Calcination caused progressive intensity reduction in all bands, with significant decreases at 3462.38 , 1622.16 , 1329.95 , and 1169.90 cm^{-1} , and merging of peaks in the $586\text{--}423 \text{ cm}^{-1}$ region into a broad band, resulting from condensation reactions causing water evaporation and metal hydroxide conversion to metal oxides.

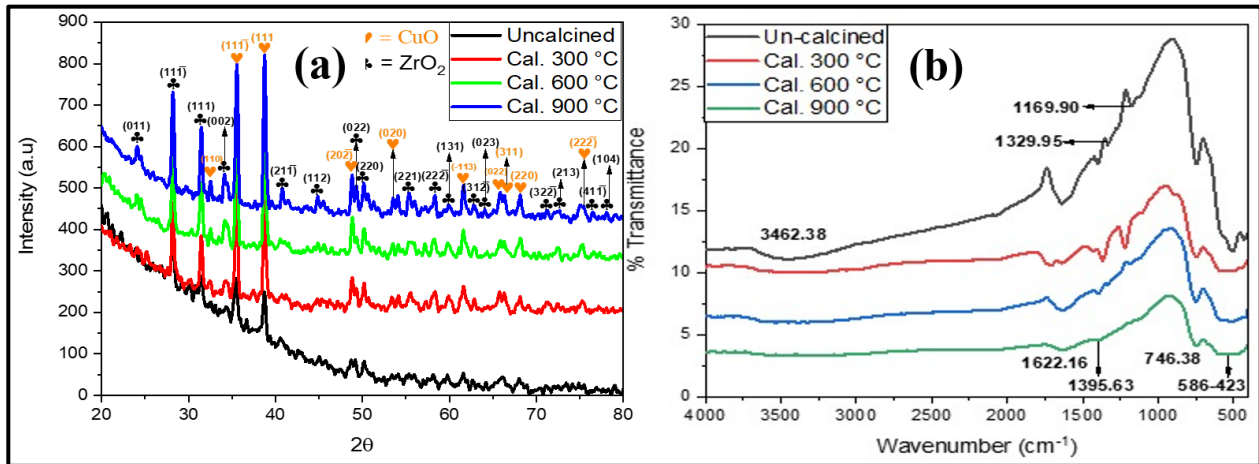


Figure 4: XRD patterns (a) and FTIR spectra (b) of CuO-ZrO₂ NCs (uncalcined and calcined at 300, 600 and 900 °C) (Zain et al., 2024).

SEM revealed dynamic morphological changes during calcination. The as-prepared uncalcined sample showed unevenly distributed granular particles with no specific morphological shape, grain sizes between 35.47 and 52.81 nm , and average size 44.43 nm . At 300°C , grain size increased to $37.60\text{--}53.11 \text{ nm}$ (average 47.43 nm) with small grains fusing together due to high surface energy, forming larger particles with some nearly spherical shapes. At 600°C , the sample became more condensed with further grain size increase to $35.50\text{--}72.47 \text{ nm}$ (average 47.43 nm), accompanied by reduced empty spaces as grains filled voids, and more defined morphology though still lacking uniformity. At 900°C , specific morphological shapes became clearer with spherical, nearly spherical, oval, and elongated shapes, grain sizes ranging $55.98\text{--}75.3 \text{ nm}$ (average 63.23 nm), and aggregate formation due to particle fusion contributing to significant overall grain size increase.

EDX showed peaks at 0.5 keV for oxygen, 0.9 , 8.05 , and 8.9 keV for copper, and 2.1 and 2.5 keV for zirconium. With increasing calcination temperature, copper weight percent increased from 16.79% (uncalcined) to 35.79% (900°C), while zirconium decreased from 53.27% to 38.89% . This compositional shift was attributed to thermally-induced transformations including phase transitions, crystal growth, and evaporation of volatile components. The initial precursor amounts of 0.011 moles $\text{Cu}(\text{OH})_2$ and 0.006 moles $\text{Zr}(\text{OH})_4$ meant that at elevated temperatures, condensation

reactions caused H₂O evaporation, with larger number of hydroxyl groups in Cu(OH)₂ per mole leading to greater mass loss and relatively higher copper weight percent. Crystal growth kinetics also favored faster nucleation and growth of CuO, physically hindering ZrO₂ crystal growth and leading to lower zirconium abundance.

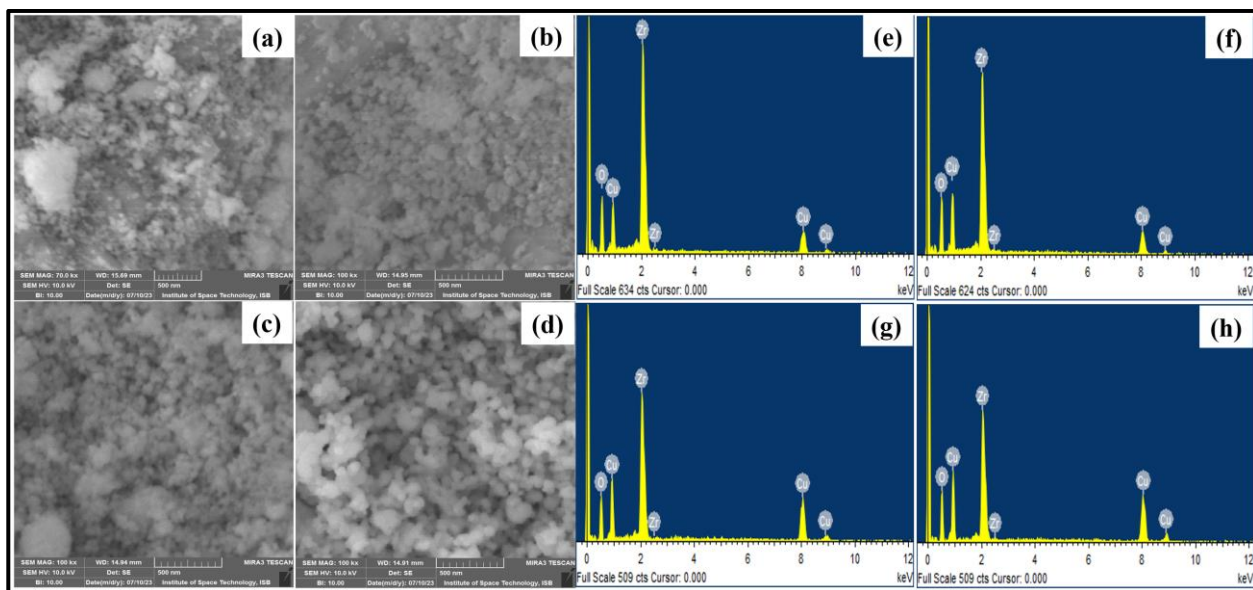


Figure 5: The SEM micrographs (a-d) and EDX spectra (e-h) of CuO-ZrO₂ NCs (uncalcined and calcined at 300, 600 and 900 °C) showing structural variation with increasing calcination temperature (Zain et al., 2024).

Photocatalytic activity against fluorescein dye under natural sunlight from June 15-30, 2023 between 11 a.m. and 3 p.m. showed degradation percentages of 50.83% for uncalcined sample, 58.33% at 300 °C, 67.5% at 600 °C, and 77.27% at 900 °C, with corresponding rate constants of 0.00744, 0.0089, 0.01402, and 0.0153 per min. The sample calcined at 900°C exhibited highest activity due to enhanced crystallinity and homogeneity despite larger particle size and reduced surface area. The photodegradation mechanism involves solar light absorption by CuO-ZrO₂ semiconductor, elevating electrons from valence band to conduction band, creating electron-hole pairs. Excited electrons accumulate in CuO conduction band while positive holes gather in ZrO₂ valence band. Hydroxyl radicals are produced through reaction of photogenerated holes with water molecules, while photogenerated electrons reduce oxygen molecules to form superoxide radicals that further react with hydrogen to generate hydroxyl radicals. Highly reactive hydroxyl radicals attack adsorbed fluorescein molecules, breaking chemical bonds and mineralizing dye into water and carbon dioxide.

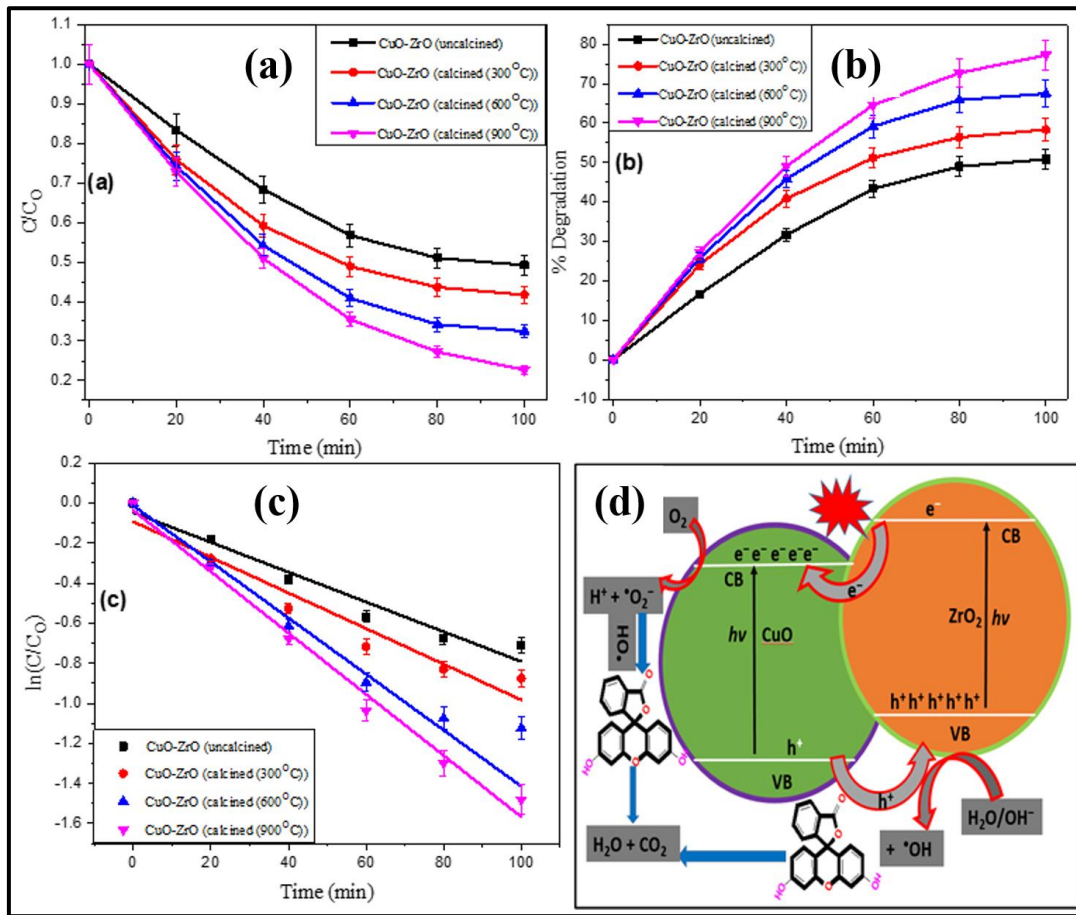


Figure 6: The photodegradation data of the Fluorescein dye in presence of CuO-ZrO₂ NCs and solar light: a) degradation profile, b) percentage degradation, c) kinetic rate constant and d) proposed degradation mechanism (Zain et al., 2024).

Optimization studies on the 900°C calcined sample showed maximum degradation at pH 6 (77.27%), with lower degradation at acidic and alkaline pH due to surface charge effects. ZrO₂ exhibits positive charge under acidic conditions and negative charge in alkaline environments, while fluorescein exists in monoanionic form at pH 4.3-6.4 and dianionic form above pH 6.4, with attractive forces between cationic catalyst and anionic dye favoring adsorption and degradation at pH 6. Catalyst dose optimization showed degradation increasing from 44.55% to 77.27% as dose increased from 5 to 20 mg, then declining to 72.86% at 25 mg due to increased total surface area providing more active sites at optimal dose, while higher doses caused agglomeration, reduced photon interaction, and less efficient light absorption. Initial concentration studies showed degradation percentages of 70.56%, 77.27%, 68.95%, and 56.21% at 10, 15, 20, and 25 ppm respectively, with maximum at 15 ppm and decrease at higher concentrations due to active site saturation and interference with light-catalyst surface interaction. Reusability studies over four consecutive cycles showed degradation percentages of 77.27%, 71.28%, 62.71%, and 49.68% for cycles 1 through 4, with initial high efficiency due to pristine catalyst

state and gradual decline due to surface contamination, structural alterations, catalyst deactivation, and dye absorption on photocatalyst surface during recycling.

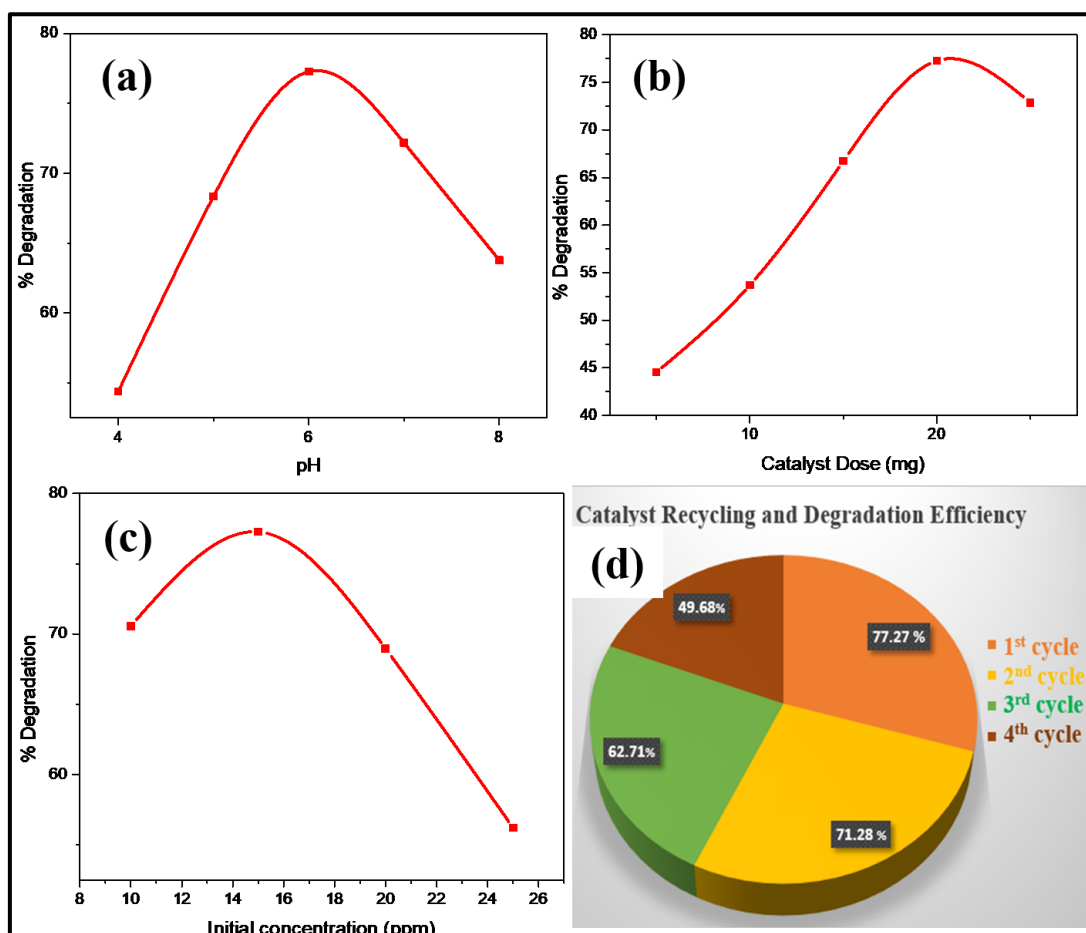


Figure 7: Factors effecting the photocatalytic activity of CuO-ZrO₂ NCs; effect of pH (a), effect of catalyst dose (b), effect of initial concentration (c) and reuse efficacy (d) (Zain et al., 2024).

2.3 CuO-Fe₂O₃ nanocomposites via mechanochemical synthesis. This research successfully demonstrates a simple, solvent-free mechanochemical approach for synthesizing CuO-Fe₂O₃ nanocomposites (NCs) using a mortar and pestle, followed by calcination at 300°C, 600°C, and 900°C. The study investigates how calcination temperature influences the structural, morphological, optical, and textural properties of the bimetallic oxide system and its subsequent photocatalytic performance for fluorescein dye degradation under solar light irradiation. For synthesis, equal amounts (1 g each) of copper(II) hydroxide and iron(II) hydroxide precursors were ground together for 6 h, during which the mixture transformed from granular to sticky to powdered form as metal oxides developed. The final product was calcined at three different temperatures in a muffle furnace. Photocatalytic testing involved adding 25 mg of each NC sample (uncalcined and calcined at 300°C, 600°C, and 900°C) to 100 mL of 15 ppm fluorescein solution, stirring for 30 min in the dark to achieve adsorption-desorption equilibrium, then exposing to simulated

solar radiation (250 W) while monitoring absorbance decrease at 475 nm using a double-beam UV-Vis spectrophotometer.

The XRD patterns revealed distinct diffraction peaks corresponding to both CuO and Fe₂O₃ phases. CuO peaks appeared at 35.49° (002), 38.72° (111), 48.87° (-202), 53.28° (020), 58.16° (202), 61.62° (113), and 68.10° (220), matching JCPDS card 01-80-1268 for monoclinic CuO with space group C2/c. The unit cell parameters were $a = 4.6833 \text{ \AA}$, $b = 3.4208 \text{ \AA}$, $c = 5.1294 \text{ \AA}$, with $\alpha = \gamma = 90^\circ$ and $\beta = 99.5678^\circ$. Fe₂O₃ (hematite) peaks were observed at 33.13° (104), 65.88° (531), 70.08° (208), 72.40° (119), 73.91° (533), and 75.32° (217), matching JCPDS card 01-097-1741 for rhombohedral geometry with space group R-3c. The unit cell had $a = b = 5.0343 \text{ \AA}$, $c = 13.7460 \text{ \AA}$. Importantly, peak intensity increased with higher calcination temperatures, indicating enhanced crystallinity, while no peak shifting occurred, confirming that no phase transformation took place with calcination temperature. All samples exhibited notable absorption in the visible region, making them suitable for solar light photocatalysis. A bathochromic shift (shift toward longer wavelength) was observed in absorbance maxima with increasing calcination temperature, accompanied by significant enhancement in absorbance peak intensity. Band gap energies decreased with calcination: direct band gaps were 1.53 eV (uncalcined), 1.30 eV (300°C), 1.24 eV (600°C), and 1.18 eV (900°C); indirect band gaps were 1.44 eV (uncalcined), 1.13 eV (300°C), 1.09 eV (600°C), and 1.03 eV (900°C). This decrease is attributed to increased crystallinity, reduced defects/vacancies, and evaporation of impurities at elevated temperatures. FTIR spectra showed a broad band at 3438.57 cm⁻¹ (O-H stretching), bands at 1712.91 cm⁻¹ (absorbed water on Fe₂O₃), 1639.39 cm⁻¹ (H-O-H bending), 1416.96 cm⁻¹ (O-H bending with Cu), 1345.25 cm⁻¹ (CO₂ and H₂O on CuO surface), 1214.22 cm⁻¹ (M-OH vibration), 1087.00 cm⁻¹ (terminal M-OH), 1039.39 cm⁻¹ (Cu-O bending), 902.32 cm⁻¹ (O-M-O bridging), 793.98 cm⁻¹ (M-O-M bending), 699.58 cm⁻¹ (Fe-O), 524.76 cm⁻¹ (Fe-O vibration), and 441.21 cm⁻¹ (Cu-O stretching). Band strength gradually weakened with calcination, confirming condensation reactions converting metal hydroxides to metal oxides.

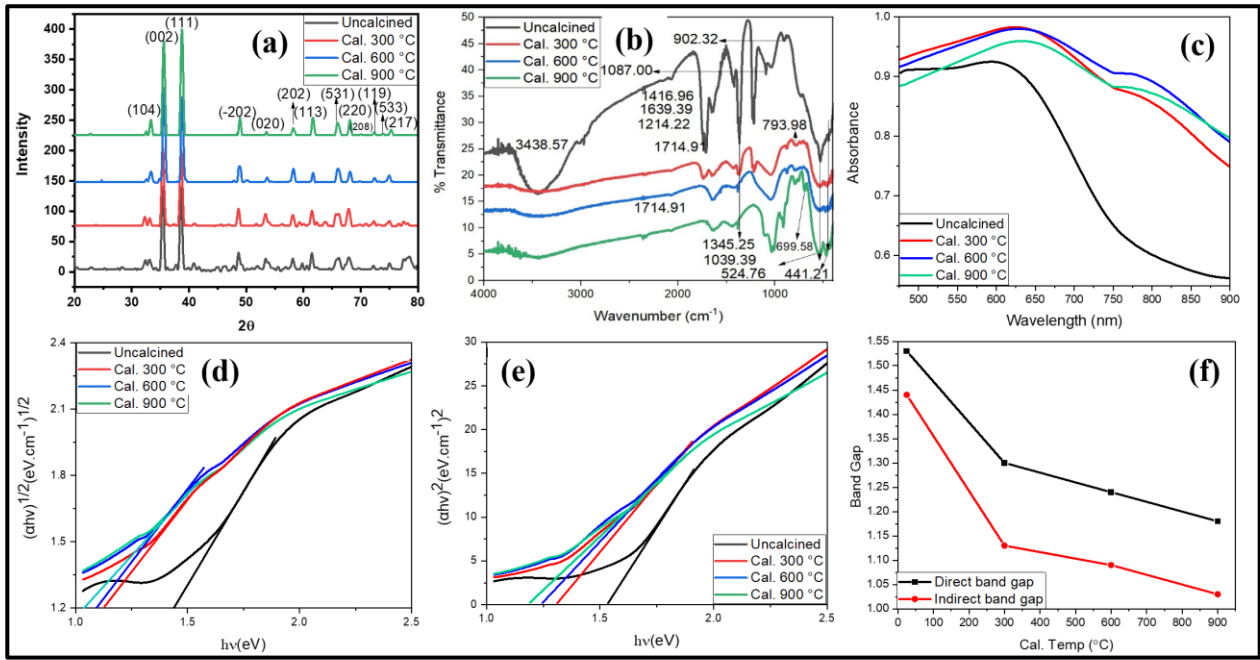


Figure 8: XRD patterns (a), FTIR spectra (b), DRS spectra (c), Tauc's plots for direct (d), indirect (e) and comparative band gap energies curves (f) of CuO-Fe₂O₃ NCs (uncalcined and those calcined at 300, 600 and 900 °C (Zain et al., 2025).

Type IV isotherms with H2 hysteresis loops confirmed mesoporous nature with complex porous networks. Surface area decreased dramatically with calcination: 152.53 m²/g (uncalcined), 123.86 m²/g (300°C), 43.77 m²/g (600°C), and 1.78 m²/g (900°C). Pore diameter initially increased from 69.53 nm (uncalcined) to 83.26 nm (300°C) then decreased to 78 nm (600°C) and 67 nm (900°C). Pore volume was 0.199 cc/g (uncalcined), 0.224 cc/g (300°C), 0.148 cc/g (600°C), and 0.025 cc/g (900°C). High calcination temperatures promote nanostructure growth and particle coalescence, reducing surface area and causing pore collapse under heat stress. EDX spectra confirmed the presence of oxygen (peak at 0.4 keV), iron (peaks at 0.6, 6.4, and 7.1 keV), and copper (peaks at 0.9, 8.1, and 8.9 keV). The atomic percentages varied with calcination temperature: uncalcined sample showed 12.83% Cu, 19.55% Fe, 67.62% O with Cu:Fe ratio of 0.66; at 300°C: 22.31% Cu, 24.69% Fe, 53.00% O with ratio 0.90; at 600°C: 21.82% Cu, 42.45% Fe, 35.73% O with ratio 0.51; at 900°C: 25.60% Cu, 40.15% Fe, 34.25% O with ratio 0.64. The 300°C sample showed Cu:Fe ratio closest to the initial 1:1 precursor ratio, while higher temperatures caused deviations due to metal diffusion, surface segregation, or agglomeration. SEM micrographs revealed significant morphological evolution with calcination temperature. The uncalcined sample displayed a mixture of elongated, semi-spherical, nearly triangular, plate-like, and star-like shapes with agglomerates and numerous small particles on larger agglomerate surfaces, showing uneven particle distribution and multiple cavities. At 300°C, increased agglomeration and reduced cavities were observed, with various agglomerates dispersed above a single

substantial structure. At 600°C, particles formed smaller agglomerates with more cavities and diverse shapes due to sintering effects breaking down larger agglomerates. At 900°C, some areas showed heavy agglomeration with particle fusion, reduced cavities, and blurred boundaries, while other areas exhibited smooth surfaces and mixed morphologies, with smaller agglomerates fusing back into larger structures.

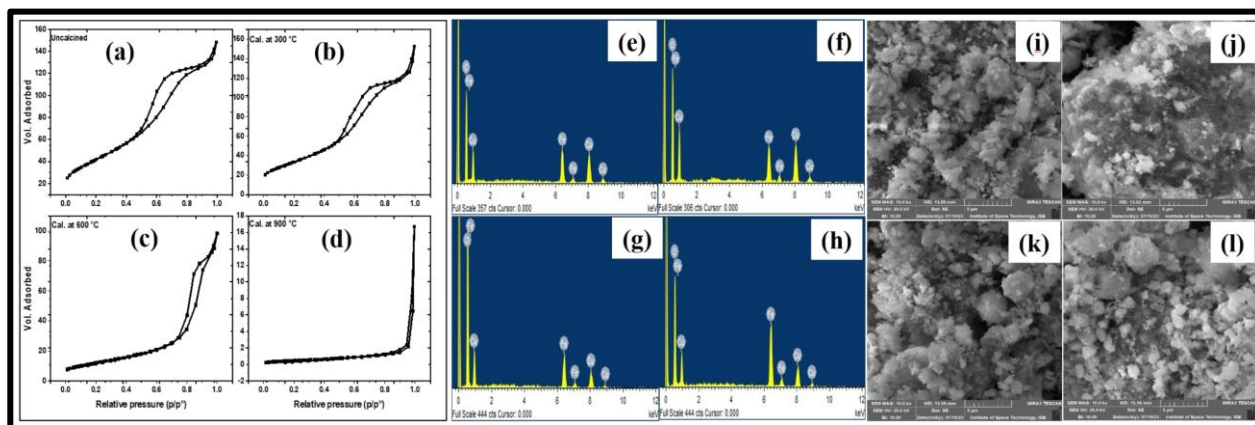


Figure 9: BET plots (a-d), EDX spectra (e-h) and SEM micrographs (i-l) of CuO-Fe₂O₃ NCs (uncalcined and those calcined at 300, 600 and 900 °C (Zain et al., 2025)).

The photocatalytic performance of CuO-Fe₂O₃ NCs was evaluated for fluorescein degradation under direct sunlight (June 15-30, 11 a.m. to 3 p.m.). The degradation profile showed a slow decline in absorbance maxima at 475 nm with rising calcination temperature. The uncalcined sample exhibited the greatest decrease in absorbance peak, achieving 88.95% degradation of fluorescein, while samples calcined at 300°C, 600°C, and 900°C showed 82.67%, 70.06%, and 59.19% degradation respectively. Rate constants followed the same trend: 0.02177 min⁻¹ (uncalcined), 0.01757 min⁻¹ (300°C), 0.01242 min⁻¹ (600°C), and 0.00905 min⁻¹ (900°C), with regression coefficients ranging from 0.9859 to 0.9994. When CuO-Fe₂O₃ absorbs sunlight photons, electrons are excited from the valence band to the conduction band, forming electron-hole pairs. Excited electrons reside in CuO's CB while holes accumulate in Fe₂O₃'s VB. Due to different CB/VB positions, electrons migrate from the oxide with higher CB to the one with lower CB, while holes move in the opposite direction, facilitating efficient charge separation and slowing recombination. Holes react with water to produce hydroxyl radicals (•OH), while electrons reduce oxygen to superoxide radicals (O₂⁻). These highly reactive species attack adsorbed fluorescein molecules, breaking chemical bonds and mineralizing the dye into CO₂ and H₂O.

pH studies showed maximum degradation (88.96%) at pH 6, with acidic conditions favoring catalyst-dye attraction (cationic catalyst, anionic dye) and alkaline conditions causing repulsion. Catalyst dose optimization revealed 25 mg as

optimal (51.69% to 88.96% from 10 to 25 mg, then decreasing to 76.25% at 30 mg due to aggregation and light scattering). Initial concentration studies showed 15 ppm as optimal (61.07% to 88.96% from 5 to 15 ppm, then decreasing at higher concentrations due to active site saturation and light blockage). Reusability over five cycles showed gradual decrease from 88.96% to 51.46%, attributed to surface contamination, structural changes, and active site loss. The uncalcined CuO-Fe₂O₃ NC exhibited the highest photocatalytic activity (88.95%) despite lower crystallinity, demonstrating that surface area (152.53 m²/g) is the dominant factor governing photocatalytic performance. While calcination improved crystallinity and narrowed the band gap, the substantial reduction in surface area proved more detrimental to activity. The mechanochemical synthesis approach offers distinct advantages over conventional chemical methods, including solvent-free operation, energy efficiency, environmental friendliness, scalability, and simplicity, making it a compelling alternative for sustainable photocatalyst development despite slightly lower efficiency compared to some chemically synthesized counterparts.

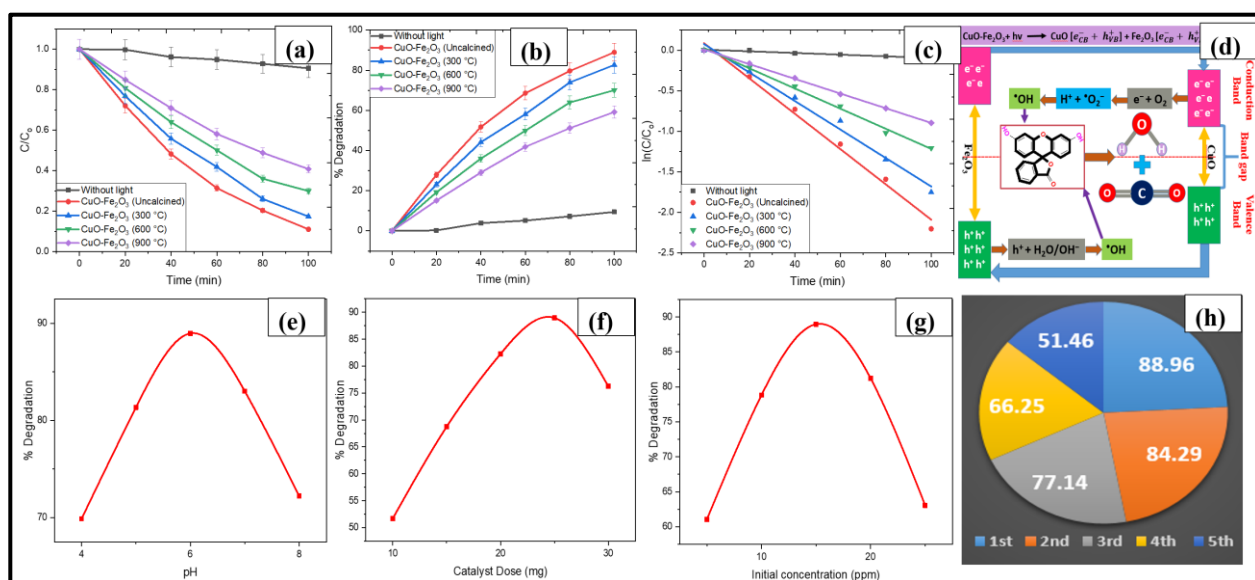


Figure 10: Photocatalytic data of the R-6G degradation of in the presence CuO-Fe₂O₃ NCs under simulated solar light; linear plot (a), Percent degradation (b), rate constant (c), effect of calcination temperature (d), effect of pH (e), effect of initial concentration (f), effect of catalyst dose (g), and reuse efficacy (g) of the photocatalyst (Zain et al., 2025).

A comprehensive four-panel comparative figure overlaying surface area, crystallite size, band gap energy, and photocatalytic degradation efficiency for bimetallic systems (CuO-ZrO₂, CuO-Fe₂O₃) across calcination temperatures (uncalcined, 300 °C, 600 °C, 900 °C) would clearly illustrate the trade-offs between surface area and crystallinity. Panel A (Surface Area vs Temperature) would show dramatic decrease for all systems, with CuO-Fe₂O₃ showing highest initial (152.53 m²/g) and steepest decline. Panel B (Crystallite Size vs Temperature) would show

opposite trend-crystallite size increases with temperature. Panel C (Band Gap Energy vs Temperature) would show gradual decrease with temperature. Panel D (Photocatalytic Degradation Efficiency vs Temperature) would reveal that CuO-Fe₂O₃ show highest activity at uncalcined (88.95% respectively) despite lower crystallinity, while CuO-ZrO₂ shows highest activity at 900°C (77.27%) due to enhanced crystallinity and homogeneity. The key trade-off analysis shows that for CuO-Fe₂O₃, surface area dominates over crystallinity as the determining factor for photocatalytic performance, while for CuO-ZrO₂, crystallinity and homogeneity dominate over surface area. This demonstrates that material-specific optimization is essential and no universal rule applies to all material systems. The conclusion from this figure is that the dominant factor governing photocatalytic activity varies between material systems and must be empirically determined, with surface area being the primary factor for some materials while crystallinity dominates for others.

PART 3: TRIMETAL OXIDE NANOCOMPOSITES

3.1 Amorphous bio-capped Co-Cu-Zn-layered hydroxides. The eco-friendly synthesis of tri-metal (Co-Cu-Zn) layered hydroxides using *Citrus maxima* leaf extract as a multifunctional reducing and capping agent. Copper(II) nitrate (99.0%), cobalt(II) nitrate (97-98%), zinc nitrate (99%), methyl orange, and sodium hydroxide were used as received. The plant extract was prepared by collecting *C. maxima* leaves from Muzaffarabad, AJK, Pakistan, rinsing them twice with tap water and deionized water, drying at room temperature for 4 hours, chopping 20 g of leaves, and boiling them in distilled water in an airtight bottle for 12 hours. The extract was filtered through simple filter paper and then Whatman No. 1 filter paper, and the strained extract was preserved for subsequent utilization. For the synthesis of tri-metal layered hydroxides, three different stock solutions of Zn(NO₃)₂ were prepared by dissolving 0.13, 0.29, and 0.40 g along with 5 mM stock solutions of Co(NO₃)₂ (0.915 g) and Cu(NO₃)₂ (0.938 g) in 1 L deionized water. For a typical reaction, 30 mL each of Co(NO₃)₂ and Cu(NO₃)₂ stock solutions along with 30 mL of Zn(NO₃)₂ stock solution were mixed with 20 mL of plant extract in separate reactors, and the pH was fixed at 12 by addition of NaOH solution. Each mixture was heated and stirred separately until a thick gel formed, displaying respective metal ion colors. Following 60 minutes of aging, all three gels were combined in a reactor, heated and stirred for 5 hours without further additions, and aged for 24 hours at ambient temperature. The product was collected by centrifugation, washed thoroughly with hot deionized water, dried in an oven at 120°C, and marked as S1-LH. For S2-LH and S3-LH with different Zn contents, the same procedure was followed with the sole modification being the concentration of Zn(NO₃)₂ stock solution.

SEM analysis revealed a clear dependence of morphological changes on Zn content, which acts as a structural modifier fundamentally altering growth and aggregation patterns. S1-LH showed relatively large, irregular, blocky, and

monolithic aggregates with fewer visible surface pores, while S3-LH exhibited highly porous, fluffy architectures with increased interfacial active sites. The EDS mapping results confirmed the homogeneous distribution of Co, Cu, Zn, and O throughout the sample matrix, indicating that the three metal ions were uniformly integrated into the hydroxide framework without significant phase segregation or elemental clustering. This uniform distribution is critical for photocatalytic applications because it ensures that the multi-metal heterojunctions are evenly distributed, maximizing the spatial charge separation and reactive oxygen species generation. The EDX spectra confirmed the presence of cobalt, copper, zinc, and oxygen as the principal elemental constituents in all three samples (S1-LH, S2-LH, and S3-LH), with no detectable impurities, validating the high purity of the biogenic synthesis approach. The elemental composition showed systematic variation in zinc content across the three samples, consistent with the intended compositional design, where S1-LH had the lowest Zn content, S2-LH had intermediate Zn content, and S3-LH had the highest Zn content.

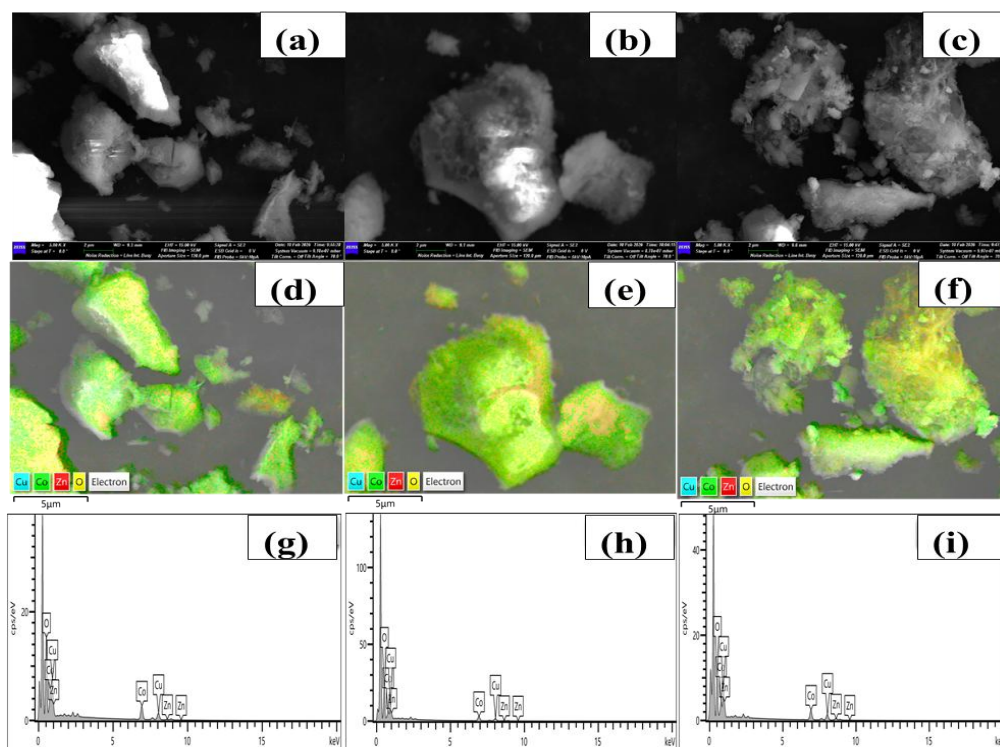


Figure 11: SEM (a-c), EDS mapping (d-f) and EDX spectra (g-i) of the Amorphous Bio-capped Co-Cu-Zn-Layered Hydroxide (Othman et al., 2026).

XRD patterns showed noisy profiles reflecting noncrystalline/semi-amorphous structural characteristics, with the first-order basal reflection at $2\theta = 11.42^\circ$ indexed to (003) plane and basal spacing $d_{003} = 7.74 \text{ \AA}$, indicating successful accommodation of bulky phytochemical organic species alongside co-intercalated water molecules. The broad peak at $2\theta = 23.18^\circ$ was assigned to (006) plane. Other distinct low-crystallinity hydroxide phases included orthorhombic $\text{Cu}(\text{OH})_2$ (JCPDS 00-013-0420) at 16.55° and 21.99° , orthorhombic $\epsilon\text{-Zn}(\text{OH})_2$ (JCPDS 00-038-0385)

at 34.39° and 46.23°, and hexagonal β -Co(OH)₂ (JCPDS 00-030-0443) at 38.99°, 50.27°, and 59.37°. The broad diffraction profiles indicated that incorporation of three metal ions and bio-derived surface species strongly disrupts long-range periodicity while preserving local metal-hydroxide coordination. Raman analysis showed noisy and featureless spectra for S1-LH and S2-LH, revealing primarily amorphous phase with lack of long-range atomic order, while S3-LH exhibited a distinctive sharp peak at 917 cm⁻¹ ascribed to δ -OH bending vibration, suggesting that increased Zn content promotes localized atomic order and facilitates formation of rigid, ordered vibrational domains that overcome fluorescence masking from plant extract. DRS analysis demonstrated broad and intense light-harvesting capabilities spanning 200-800 nm, with three characteristic absorption edges at approximately 230, 540, and 800 nm, corresponding to transition energies of ~5.4, ~2.3, and ~1.6 eV. The high-energy UV region yielded fundamental bandgap of ~5.4 eV assigned to metal-to-ligand charge transfer bands and $\pi \rightarrow \pi^*$ transitions of aromatic rings from phytochemical capping agents. The visible region transition at ~2.3 eV was governed by ligand-to-metal charge transfer of O²⁻ $\rightarrow$ M²⁺, while the low-energy absorption at ~1.6 eV was indexed to spin-allowed d-d electronic transitions of octahedrally coordinated Co²⁺ ions alongside split Jahn-Teller states of lattice-confined Cu²⁺. BET analysis showed specific surface area increased progressively from 42.31 m²/g (S1-LH) to 52.97 m²/g (S2-LH) and peaked at 84.87 m²/g for S3-LH, with pore volume increasing from 0.26 to 0.78 cm³/g. This systematic expansion strongly corroborated structural alterations confirmed via SEM, where introduction of higher zinc content drove controlled formation of ultra-small, semi-amorphous Zn(OH)₂ surface nanoclusters that pin grain boundaries and restrict long-range dense grain crystallization, leading to morphological fragmentation into highly open, high-surface-area aggregate networks.

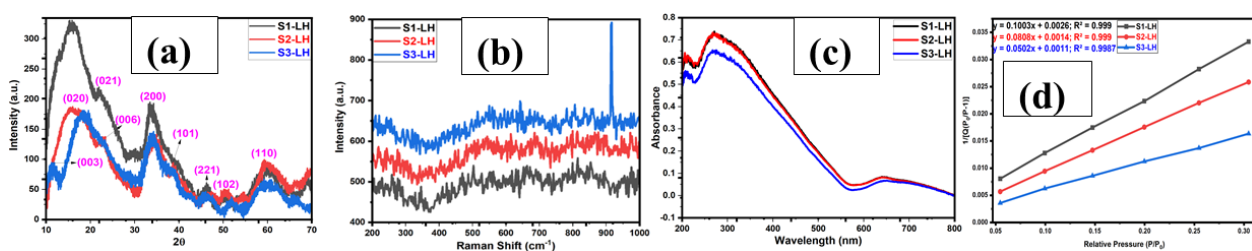


Figure 12: XRD patterns (a), Raman spectra (b), DRS spectra (c), N2 adsorption analysis (d) of the Amorphous Bio-capped Co-Cu-Zn-Layered Hydroxides (Othman et al., 2026).

Photocatalytic analysis showed MO degradation reached 65.31% for S1-LH, 81.74% for S2-LH, and 92.98% for S3-LH after 60 minutes of UV exposure. The superior performance of S3-LH was tied to systematically expand optical bandgap and optimized absolute band edge realignments, generating robust thermodynamic overpotential for hydroxyl radical production. Control experiments validated that degradation is a unique synergistic, light-activated catalytic phenomenon: light only

exhibited negligible self-photolysis; dark control with S3-LH accounted for minor 10.68% decrease due to physical adsorption; when both catalyst and light were applied, degradation dramatically accelerated to 92.98%. The proposed mechanism involves initial sequestration of anionic MO molecules onto catalyst surface through electrostatic attraction between negatively charged sulfonate group and protonated, positively charged metal hydroxide layers. Upon illumination, catalyst undergoes photoexcitation, promoting e^- to CB and leaving h^+ in VB. Multi-metal composition facilitates enhanced charge separation by creating intermediate energy states that trap charge carriers. The h^+ reacts with hydroxyl groups/surface-adsorbed water to generate $\bullet OH$, whereas excited electrons reduce dissolved oxygen to superoxide radicals. These ROS attack MO structure, with degradation starting with N-demethylation and hydroxylation of aromatic ring. Decolorization occurs by cleavage of central azo bond ($-N=N-$), leading to fragmentation into sulfonic acid and N,N-dimethyl-p-phenylenediamine. Prolonged exposure leads to oxidative ring opening into low-molecular-weight organic acids, ultimately resulting in complete mineralization into H_2O , CO_2 , SO_4^{2-} , and NO_3^- . Radical trapping with IPA confirmed that degradation is predominantly mediated via $\bullet OH$ radical pathways, with degradation collapsing to 28.11% upon IPA introduction. Operational parameters showed percentage degradation rose from 79.64% to 92.8% as concentration increased from 0.02 to 0.06 mM. Catalyst dose displayed optimal threshold at 100 mg/L, and maximum degradation of 92.98% was achieved at pH 4, declining to 78.04% at pH 6 due to competitive adsorption between OH^- ions and MO molecules. Reusability showed gradual decline due to accumulation of recalcitrant degradation intermediates blocking binding sites. Kinetic analysis showed data fit well with both pseudo-zero-order and pseudo-first-order kinetics. High R^2 for pseudo-zero-order (0.996 for S1-LH) was attributed to porous and disordered amorphous structure providing excess accessible active sites. Overall degradation trajectory was best described by pseudo-first-order model following Langmuir-Hinshelwood pathway. The highest-efficiency sample (S3-LH, 92.98% with $k_1 = 0.04763 \text{ min}^{-1}$) suggested transition from surface-reaction-limited to diffusion-limited kinetics due to highly porous morphology. Comparative evaluation showed S3-LH catalyst exhibits competitive high-performance degradation metrics under challenging conditions. While traditional multi-metal structures like MgAlCu-LDH (96.5%) and CuAl-LDH (93%) achieved comparable efficiencies, they rely on conventional hydrothermal methods requiring high power consumption and harsh precursors. The S3-LH catalyst achieves 92.98% MO degradation within 60 minutes using eco-friendly biogenic process.

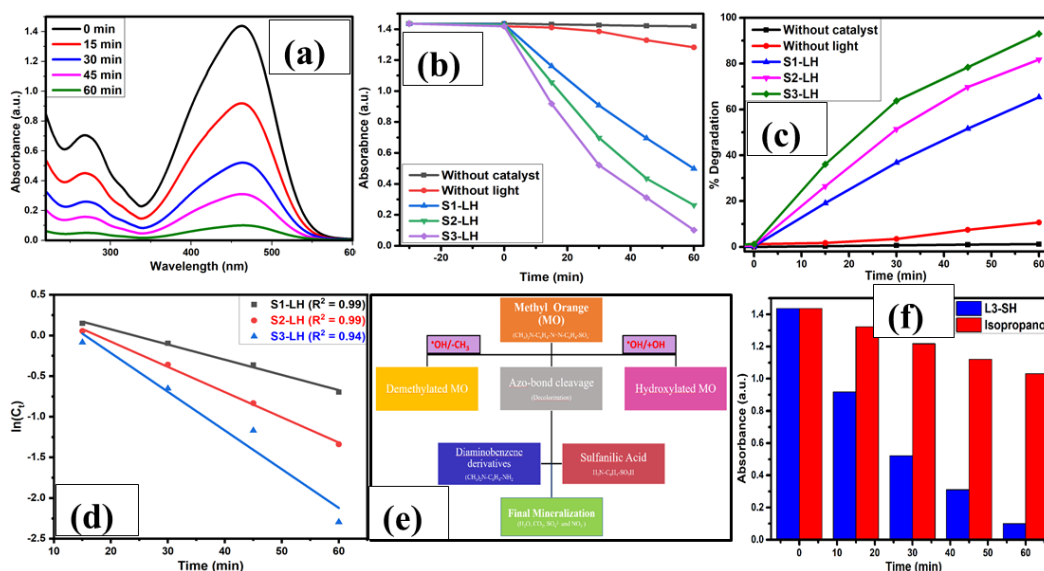


Figure 13: Photocatalytic data of the MO degradation of in the presence Amorphous Bio-capped Co-Cu-Zn-Layered Hydroxide under UV light; degradation profile (a), linear plots (b), Percent degradation (c), rate constant (d), degradation pathway (e) and radicals trapping data (f) (Othman et al., 2026).

3.2 Zr-Doped NiO-ZnO nanocomposites (green synthesis). Zirconium-doped nickel oxide/zinc oxide nanocomposites were synthesized using an eco-friendly green approach with *D. kaki* leaf extract serving as reducing and stabilizing agent, representing the first report of this combination for photocatalytic applications. *D. kaki* leaves were collected, washed, shade-dried, and boiled in distilled water for three hours to prepare the extract. For NiO-ZnO NC synthesis, Zn(OH)₂ and Ni(OH)₂ gels were prepared separately by dissolving zinc sulfate hexahydrate and nickel sulfate hexahydrate in distilled water, adding leaf extract, and heating at 60 °C for 30 min. The gels were mixed, vigorously stirred, and heated at 70 °C for 4 h to ensure homogeneous distribution. The product was filtered, washed with ethanol and water, dried at 150 °C for 24 h. For Zr doping, 0.95 g of prepared NiO-ZnO NC was dissolved in distilled water, vigorously stirred, and 0.05 g (0.5%) or 0.1 g (1%) zirconium chloride was added as dopant, stirred for 5 h at 60 °C with pH adjusted to 10 using NaOH. The product was filtered, washed, dried at 150 °C, ground, and calcined at 500 °C for 2 h.

XRD analysis showed only prominent peaks of hexagonal ZnO phase with less intense NiO peaks due to overlap of diffraction peaks, and no peaks for zirconium dopant, indicating well-integrated dopant into hexagonal lattice of ZnO without disturbing crystal structure or creating secondary phases. This behavior was attributed to small amount of zirconium dopant sufficient to occupy interstitial sites or substitute for Zn²⁺ or Ni²⁺ ions without disrupting host lattice. Diffraction peaks were slightly shifted to higher angle due to accumulation of ZnO on NiO. Peak intensity increased with increasing doping from 0.5% to 1%, resulting from increase in crystallite size. Average crystallite size calculated using Debye-Scherrer formula was 35.5 nm for 0.5% Zr-NiO/ZnO and 49.4 nm for 1% Zr-NiO/ZnO. FTIR showed

broad absorption peaks in 3700-3000 cm^{-1} range from O-H stretching vibrations of adsorbed water, peaks around 1500 cm^{-1} from O-H bending, peaks at 1370 cm^{-1} from aromatic C-C from plant extract moieties, peaks around 1030-1070 cm^{-1} from C-O bond vibrations. For 0.5% Zr-NiO/ZnO, peaks at 713, 590, and 500 cm^{-1} arose from stretching vibrations of Ni-O, Zn-O, and Zr-O bonds respectively. For 1% Zr-NiO/ZnO, peaks at 598, 561, and 517 cm^{-1} corresponded to metal-oxygen stretching vibrations, confirming formation of metal-oxygen bonds and effective role of phytochemicals as capping agent. DRS showed higher absorbance in UV region, indicating synthesized NCs require high-energy photons for electron excitation. The spectrum of 0.5% Zr-NiO/ZnO exhibited bands around 580 nm and 900 nm from adsorbed organic moieties from plant extract. Band gap energy estimated using Tauc plot method was 3.43 eV for 0.5% Zr-NiO/ZnO and 3.66 eV for 1% Zr-NiO/ZnO, showing band gap widening with increased dopant concentration. SEM showed less agglomeration of particles in 0.5% Zr-NiO/ZnO compared to 1% Zr-NiO/ZnO, with microstructures of irregular morphologies unevenly distributed in both cases. Less aggregated nanoparticles offer increased surface area positively impacting photocatalytic performance. EDX showed weight percentages for 0.5% doped product: carbon 16.30%, nickel 7.24%, zinc 32.56%, oxygen 42.70%, zirconium 1.20%. For 1% doped product: carbon 12.21%, nickel 6.32%, zinc 41.15%, oxygen 38.13%, zirconium 2.19%. Higher percentage of Zn in both nanocomposites validated XRD results, reflecting that during synthesis, less $\text{Ni}(\text{OH})_2$ formed compared to $\text{Zn}(\text{OH})_2$, resulting in higher Zn content. TEM showed less aggregation of particles with more defined boundaries and less overlap in 0.5% Zr-NiO/ZnO, while 1% Zr-NiO/ZnO appeared more aggregated forming larger, densely packed clusters. Average particle size was 14.67 nm for 0.5% Zr-NiO/ZnO and 17.40 nm for 1% Zr-NiO/ZnO.

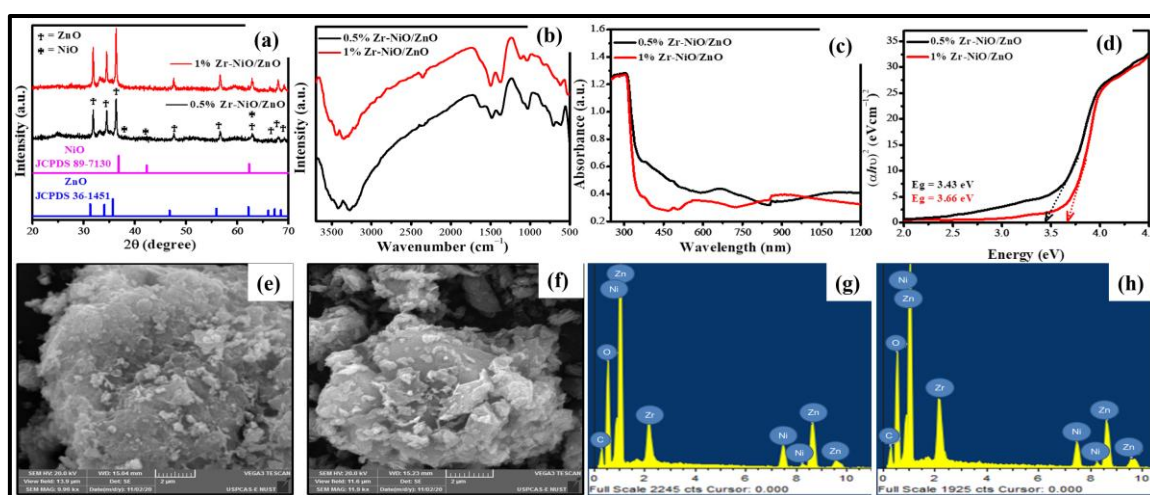


Figure 14: XRD patterns (a), FTIR spectra (b), DRS spectra (c), Tauc's plots (d), SEM micrographs (e, f), and EDX spectra (g, h) of pure and Zr doped NiO/ZnO NC (Haq et al., 2024).

Photocatalytic activity against brilliant green dye showed 86.45% degradation in 90 min for 0.5% Zr-NiO/ZnO with rate constant 0.024 min^{-1} , while 1% Zr-

NiO/ZnO achieved 67% degradation with rate constant 0.011 min^{-1} . For 4-nitrophenol, 0.5% Zr-NiO/ZnO achieved 89% degradation in 60 min with rate constant 0.044 min^{-1} , while 1% Zr-NiO/ZnO achieved only 51% degradation with rate constant 0.015 min^{-1} . The superior performance of 0.5% Zr-NiO/ZnO was attributed to lower band gap (3.43 eV) leading to higher rate of electron-hole generation, and less agglomerated nanostructures providing higher surface area for photocatalysis. The photocatalytic mechanism involves solar light irradiation on Zr-NiO/ZnO NC surface generating photo-excited electrons transferring from valence band to conduction band. The conduction band of zirconium is higher (more negative) than ZnO and NiO, while conduction band of nickel oxide is more negative than ZnO, so electrons transfer from Zr conduction band to ZnO and NiO conduction bands, and from NiO conduction band to ZnO conduction band. At ZnO and NiO conduction bands, atomic oxygen is reduced to O_2^- which reacts with pollutants causing degradation. Simultaneously, holes from valence band of ZnO and NiO migrate to Zr valence band, and from ZnO valence band to NiO valence band, oxidizing OH^- to $\bullet\text{OH}$ which reacts with pollutants. This simultaneous electron and hole transfer reduces recombination chance, leading to increased photocatalytic performance. Higher Zr doping (1% vs 0.5%) reduces photocatalytic activity due to four mechanisms: (1) Band gap widening (3.43 eV $\rightarrow$ 3.66 eV), requiring higher energy photons for electron excitation, resulting in fewer electron-hole pairs; (2) Defect formation, where excess Zr^{4+} creates lattice strain and mid-gap states that act as recombination centers; (3) Surface segregation, where excess Zr^{4+} blocks active Zn^{2+} and Ni^{2+} sites; (4) Reduced crystallinity (crystallite size increased from 35.5 nm to 49.4 nm but with broader peaks indicating higher defect density). This demonstrates that doping is a delicate optimization where "more is not always better," with optimal concentration at 0.5%.

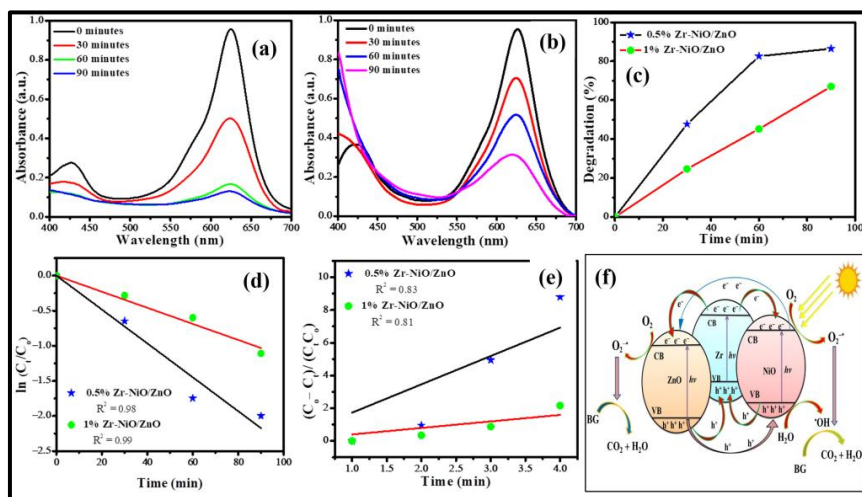


Figure 15: Photocatalytic data of brilliant green degradation of in the presence pure and Zr doped NiO/ZnO NCs under simulated solar light; Degradation profile (a, b), Percent degradation (c), rate constant (d, e) and proposed mechanism (f) respectively (Haq et al., 2024).

3.3 TiO₂-Doped SnO₂-ZrO₂ nanocomposites (green synthesis). Titanium dioxide-doped tin dioxide-zirconium dioxide nanocomposites were synthesized using an eco-friendly green method with *S. chirayita* leaf extract as capping and stabilizing agent, representing the first use of this plant extract for nanocomposite synthesis. *S. chirayita*, an annual medicinal herb belonging to Gentianaceae family, contains natural products such as terpenoids, iridoids, flavonoids, xanthonenes, and secoiridoid glycosides that serve as effective reducing and stabilizing agents. Plant extract was prepared by boiling washed *S. chirayita* in distilled water at 60 °C for 3 h, cooling, and filtering. For Sn(OH)₂ synthesis, SnCl₂ was dissolved in water, plant extract added as stabilizing agent, heated with stirring for 45 min, and NaOH added to adjust pH, producing precipitated nanoparticles that were filtered, washed with distilled water and ethanol, and dried at 90°C. Similar procedure was followed for Zr(OH)₂ using ZrCl₂. For SnO₂-ZrO₂ NC synthesis, synthesized Sn(OH)₂ and Zr(OH)₂ (0.5 g each) were hydrolyzed in distilled water, 0.1 M NaOH added to attain pH 10, mixture heated and stirred for 4 h, aged 12 h at room temperature, washed, oven-dried at 100°C. For TiO₂@SnO₂-ZrO₂ NC, 1 g SnO₂-ZrO₂ NC was hydrolyzed in distilled water, titanium isopropoxide added for 0.5% doping, heated and stirred for 4 h, aged 12 h, washed, oven-dried, and stored.

XRD analysis showed diffraction bands for SnO₂ at 26.5° (110), 33.86° (101), and 51.8° (211) confirming tetragonal geometry matching JCPDS card 01-077-0448. ZrO₂ Bragg reflections appeared at 31.9° (012), 34.1° (111), 43.1° (022), 45.1° (121), and 52.1° (113) confirming rhombohedral geometry matching JCPDS card 00-033-1483. For TiO₂-doped sample, additional diffraction peaks at 25.9° (101), 37.86° (004), 54.3° (211), and 62.5° (204) confirmed anatase phase of titanium dioxide matching JCPDS card 01-071-1167. Separate sets of diffraction peaks for ZrO₂, SnO₂, and TiO₂ indicated formation of heterojunction. FTIR showed broad band at 3500-3000 cm⁻¹ for O-H stretching, band at 2335 cm⁻¹ for surface-absorbed CO₂, peak at 1628 cm⁻¹ for O-H bending, band at 895 cm⁻¹ for Sn-O-Zr bond, absorption band at 626 cm⁻¹ characteristic of tin oxide, band at 532 cm⁻¹ for terminal oxygen vibration of SnO₂. In TiO₂-doped composite, band at 1622 cm⁻¹ indicated Ti-OH bending vibration, bands at 1346 and 586 cm⁻¹ attributed to Zr-O bond. DRS showed transmittance edges at 300.78 nm for SnO₂-ZrO₂ and 294.14 nm for TiO₂-doped sample, with slight shift to longer wavelength after doping due to quantum size effect and creation of oxygen vacancies. Direct band gap energies calculated from Tauc plots were 3.41 eV for SnO₂-ZrO₂ and 3.47 eV for TiO₂-doped sample. TiO₂ doping leading to increased band gap indicated potential phase mismatch, with TiO₂ incorporation forming separate poorly integrated phase or inducing lattice strain, creating energy barriers at interfaces hindering smooth transfer of photogenerated charge carriers and promoting recombination. BET surface area analysis using N₂ adsorption showed surface area of 96.04 m²/g for SnO₂-ZrO₂ NC and 29.75 m²/g for TiO₂-doped SnO₂-ZrO₂ NC. Decrease after doping was attributed to surface coverage

of $\text{SnO}_2\text{-ZrO}_2$ NC preferentially occupying surface sites (pores), reducing accessibility of surface area for adsorbent to adsorb, and TiO_2 insertion inducing structural changes affecting growth and crystallinity, leading to larger crystallite formation reducing surface area-to-volume ratio. SEM of pure $\text{SnO}_2\text{-ZrO}_2$ NC showed predominant large compact structure with multiple smaller agglomerates dispersed across surface, mixed morphological shapes with elongated shapes dominant, smaller agglomerates either nearly spherical, elongated, or polyhedral-shaped unevenly distributed leading to cavity formation, with smooth non-porous surface. Particle size ranged 51.68-64.38 nm with average 56.09 nm. $\text{TiO}_2@\text{SnO}_2\text{-ZrO}_2$ NC showed slightly different morphology with numerous compact structures, reduced cavities, multiple smaller agglomerates over compact structure surface, multifaceted agglomerates with distinct boundaries. Particle size ranged 56.85-61.68 nm with average 59.48 nm. Reduction in surface cavities, formation of more compact structure, and increased average particle size upon TiO_2 doping indicated that TiO_2 precursors did not form uniform dopant layer but instead led to partial aggregation and pore blockage.

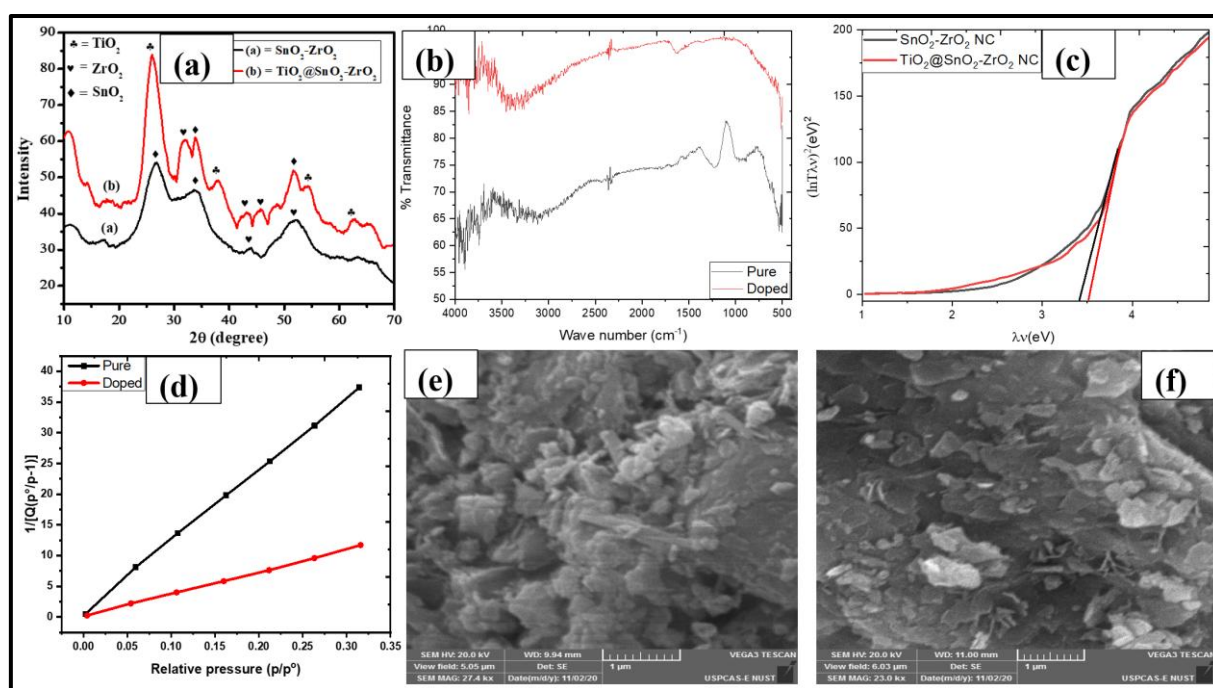


Figure 16: XRD patterns (a), FTIR spectra (b), Tauc's plots (c), BET plots (d), and SEM micrographs (e, f) of pure and TiO_2 -doped $\text{ZrO}_2\text{-SnO}_2$ NC (Haq, Mushtaq, et al., 2026).

Photocatalytic activity against brilliant green and 4-nitrophenol under solar light from 11 a.m. to 2 p.m. on June 18, 2024 showed gradual decrease in absorbance maxima for both pollutants, with sharper decrease for 4-nitrophenol indicating higher degradation potential. For brilliant green in 120 min, $\text{SnO}_2\text{-ZrO}_2$ NC achieved 80.9% degradation with rate constant $1.373 \times 10^{-2} \text{ min}^{-1}$, while $\text{TiO}_2@\text{SnO}_2\text{-ZrO}_2$ NC achieved 77% degradation with rate constant $1.211 \times 10^{-2} \text{ min}^{-1}$. For 4-nitrophenol in

60 min, SnO₂-ZrO₂ NC achieved 93.57% degradation with rate constant $4.56 \times 10^{-2} \text{ min}^{-1}$, while TiO₂@SnO₂-ZrO₂ NC achieved 71.70% degradation with rate constant $2.78 \times 10^{-2} \text{ min}^{-1}$. The higher activity of undoped sample was attributed to larger surface area and lower band gap. Variation in activity between pollutants was due to molecular structure and reactivity, with 4-nitrophenol having simpler structure with electron-withdrawing nitro group making it more susceptible to hydroxyl radical attack, while brilliant green has more complex structure with multiple substituted benzene rings making it more resistant. The photocatalytic mechanism involves nanocomposite exposure to solar light with photon energy greater than band gap generating electron-hole pairs in valence band of all three counterparts (SnO₂, TiO₂, ZrO₂). Photoexcited electrons migrate from valence band to conduction band, leaving positively charged holes in valence band. Excited electrons gather in TiO₂ conduction band while generated holes shift to ZrO₂ valence band. Holes oxidize organic dye molecules adsorbed on surface forming radical cations, while electrons in conduction band reduce oxygen molecules to form superoxide radicals. Highly reactive radical cations and superoxide radicals attack organic dye molecules adsorbed on catalyst surface, breaking down chemical structure into smaller less harmful molecules like CO₂ and H₂O. Dopants like zirconium dioxide and tin dioxide help reduce recombination rate by trapping photoexcited electrons and holes, prolonging their lifetime.

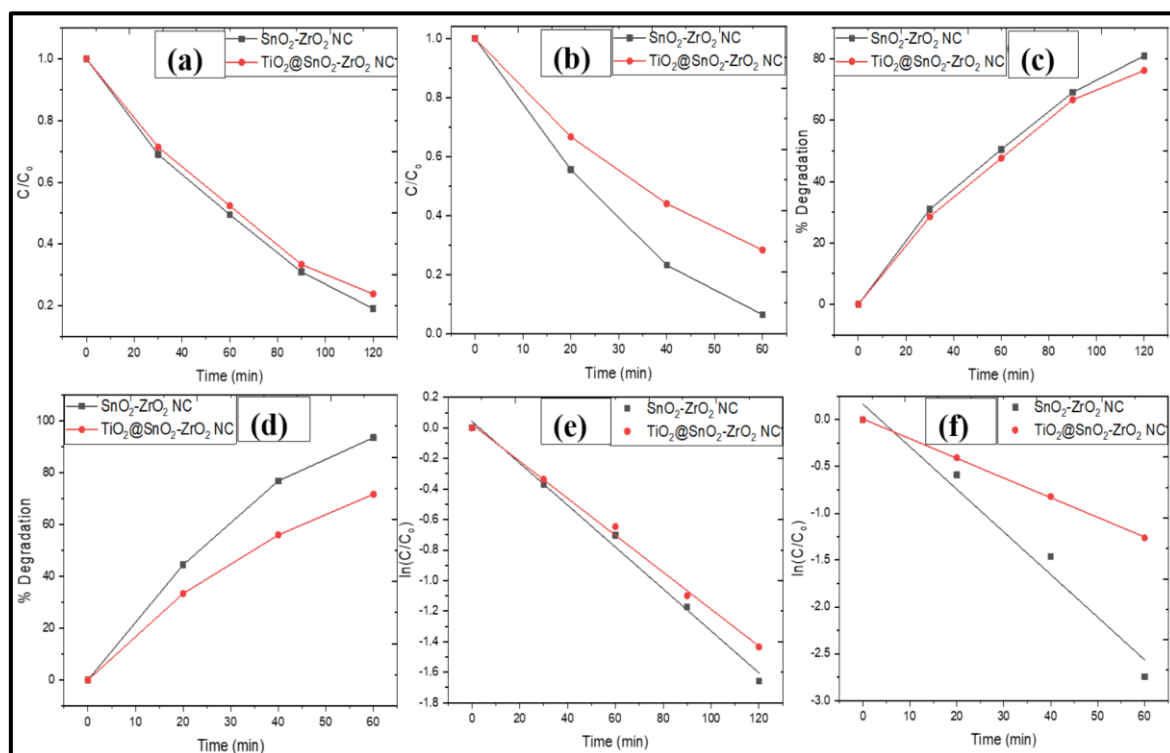


Figure 17: Photocatalytic data of brilliant green, and 4-nitrophenol degradation of in the presence pure and TiO₂-doped ZrO₂-SnO₂ NCs under simulated solar light; linear plot (a, b), Percent degradation (c, d), and rate constant (e, f) respectively (Haq, Mushtaq, et al., 2026).

3.4 Cr/Ni/Mg/Al layered double hydroxides. This section include the synthesis and enhanced photocatalytic performance of Cr/Ni/Mg/Al layered double hydroxides (LDHs) for the degradation of MO, an anionic dye widely used in textiles, cosmetics, and healthcare products. The study modified Mg/Al-LDHs by incorporating Ni and Cr to improve their photocatalytic efficiency, leveraging the large surface area, strong anionic exchange capacity, and tunable composition of LDH materials. Four LDH samples were synthesized using the hydrothermal co-precipitation method: LDH-1 (Mg/Al-LDH), LDH-2 (Ni/Mg/Al-LDH), LDH-3 (Cr/Mg/Al-LDH), and LDH-4 (Ni/Cr/Mg/Al-LDH). For LDH-1, 0.01 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.01 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 20 mL deionized water with 0.04 M $\text{CO}(\text{NH}_2)_2$ as co-precipitating agent, followed by calcination at 400 °C for 2 h. LDH-2 and LDH-3 were obtained by adding 0.01 M $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.01 M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to the Mg/Al-LDO, followed by hydrothermal reaction at 120 °C for 24 h. LDH-4 was synthesized by dispersing 0.5 g each of LDH-2 and LDH-3 in 50 mL deionized water with urea, followed by hydrothermal treatment at 120°C for 24 h. Photocatalytic testing involved adding 20 mg of each LDH sample to 100 mL of 15 ppm MO solution, stirring for 30 min in the dark to achieve adsorption-desorption equilibrium, then exposing to sunlight (12 p.m. to 1 p.m. in June) while monitoring absorbance decrease at 464 nm using a double-beam UV-Vis spectrophotometer at 15 min intervals.

The XRD patterns of all four LDH samples revealed prominent diffraction peaks indexed to (003), (006), (012), and (015) crystal planes, corresponding to Mg/Al hydrotalcite-like materials according to JCPDS card 35-0965, confirming successful formation of the desired LDH structure. Additional peaks at higher angles (approximately $2\theta = 60^\circ$) corresponding to (018), (110), and (113) planes indicated the presence of Ni^{2+} and Al^{3+} metal cations within the LDH host layer (JCPDS 15-0087), confirming successful incorporation of these metals into the layered structure. The d-spacing values for the (003) plane were calculated as 0.779 nm (LDH-1), 0.762 nm (LDH-2), 0.779 nm (LDH-3), and 0.789 nm (LDH-4). The increased interlayer spacing for LDH-4 suggests the influence of larger ionic radii of Cr^{3+} and Ni^{2+} compared to Mg^{2+} and Al^{3+} , reflecting alterations in composition and arrangement of the LDH structure. FTIR spectra displayed broad absorption bands in the range of 3100–3600 cm^{-1} attributed to OH stretching vibrations linked to basal hydroxyl groups and interlayer water. Broad bands around 1653 cm^{-1} reflected bending vibrations of interlayer H_2O . O–C–O asymmetric stretching vibrations were observed between 1363 and 1507 cm^{-1} . Bands at lower wavenumbers (approximately 567 cm^{-1}) corresponding to metal-oxygen M–O–H vibration and O–M–O stretching supported the successful formation of LDHs.

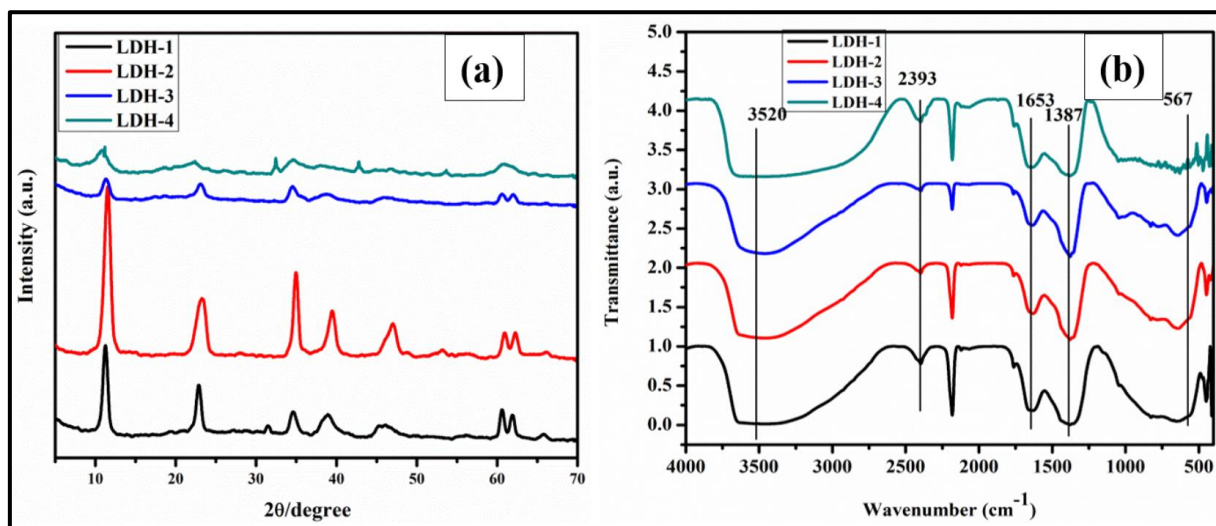


Figure 18: XRD patterns (aa) and FTIR spectra (b) of prepared LDH-1, LDH-2, LDH-3, and LDH-4 (Waheed et al., 2024).

SEM micrographs revealed distinct morphological features for each LDH sample. LDH-1 showed a compact solid structure formed by agglomeration of small individual particles arranged in closely packed layers, with morphological shape difficult to identify due to high agglomeration degree. LDH-2, after $\text{Ni}(\text{OH})_2$ incorporation, exhibited mixed morphology with thin fibers irregularly dispersed on the surface of a solid structure. LDH-3, with $\text{Cr}(\text{OH})_3$ incorporated into the LDH-1 matrix, formed fiber-like structures closely arranged to create a complex porous structure resembling a beehive (bee yard). LDH-4, formed by combining LDH-2 and LDH-3, showed mixed morphological shape with a layered bee yard-like structure in the background, where irregularly shaped and sized aggregates or larger particles were randomly distributed on the surface. All samples exhibited layered-type structures closely packed together, forming complex morphological architectures. TEM images revealed that all samples possessed a jelly-like structure with embedded fibers. LDH-1 consisted of narrow fiber-like structures connecting to form a complex network leading to larger undefined structures, with monodisperse fibers in some regions and dense polydisperse fibers in others. LDH-2 was composed of both fibers and thin sheets randomly distributed, forming dense shapes with the lower region more porous than the upper region. LDH-3 consisted of narrow fibers unevenly distributed, forming multilayered structures with no definite morphological shape, appearing more porous than LDH-2. LDH-4 showed clearer and almost monodispersed fiber shapes, with fiber width increasing progressively from LDH-1 to LDH-4, though fiber size and shape remained non-uniform throughout the series.

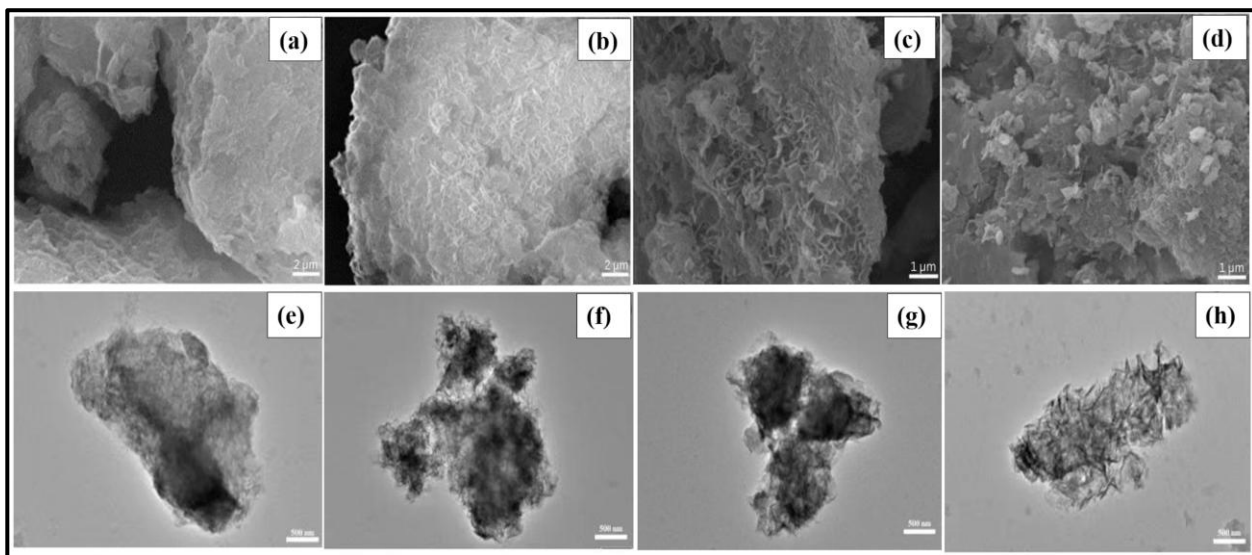


Figure 19: SEM images (a-d) TEM images (e-h) of LDH-1 (a), LDH-2 (b), LDH-3 (c), and LDH-4 (d) respectively (Waheed et al., 2024).

The solar light-induced photocatalytic potential of the synthesized LDH samples was evaluated against MO under natural sunlight in June between 12 p.m. and 1 p.m. The bright orange color of the reaction mixture faded with time, indicating dye mineralization, confirmed by UV-Vis analysis showing continuous decrease in absorbance maxima at 464 nm. The degradation profile showed a sharp decrease followed by a steady decrease, attributed to surface coverage of LDHs. Initially, all binding sites on each LDH surface were free, allowing maximum dye attachment. After 15 min, most binding sites became engaged, resulting in limited degradation in subsequent intervals. The four LDH samples showed significantly different degradation efficiencies: LDH-1 degraded only 12.63% of MO, LDH-2 achieved 65.10%, LDH-3 reached 83.92%, and LDH-4 demonstrated the highest performance with 89.23% degradation. The results followed the order: LDH-4 > LDH-3 > LDH-2 > LDH-1. The superior performance of LDH-4 is attributed to its highly porous structure providing increased surface area and the synergistic effect of multiple metal cations (Ni, Cr, Mg, Al) enhancing charge separation and providing multiple active sites. Rate constants calculated using the pseudo-first-order kinetic model were 0.0045 min^{-1} (LDH-1), 0.03509 min^{-1} (LDH-2), 0.06090 min^{-1} (LDH-3), and 0.07427 min^{-1} (LDH-4). LDH-4 exhibited the highest rate constant, approximately 16.5 times higher than LDH-1, indicating significantly faster degradation kinetics. The high regression coefficients confirmed good fit to the kinetic model. Upon photon absorption by LDH, electrons shift from the valence band (VB) to the conduction band (CB), creating electron-hole pairs. The excited electrons in the CB react with O_2 to form superoxide anions (O_2^-), while holes in the VB oxidize H_2O or OH^- to produce hydroxyl radicals ($\bullet\text{OH}$). Both generated species are highly reactive and attack MO molecules, breaking them down into smaller non-toxic molecules such as CO_2 and H_2O . The inclusion of multiple metal cations (Cr^{3+} , Ni^{2+} , Mg^{2+} , Al^{3+})

enhances photocatalytic efficiency by providing multiple active sites and improving charge separation, with Cr addition causing new energy levels within the band gap.

Percentage degradation increased with increasing MO concentration up to 15 ppm due to greater number of MO molecules available for redox reactions. Further increase caused light blockage, where maximum light radiation was absorbed by dye molecules, limiting photons striking the catalyst surface. Highest activity was observed at 20 mg catalyst dose. At 10 mg, insufficient active sites limited degradation. At 20 mg, sufficient active sites effectively interacted with MO molecules. Further increase caused particle aggregation, blocking binding sites and impeding MO molecule travel toward active sites. Highest activity was observed at pH 4, with steadfast decrease as pH increased. In acidic medium, LDH-4 surface becomes positively charged due to protonation, resulting in electrostatic attraction with anionic MO. At neutral pH (7), surface charge approaches isoelectric point with moderate interaction. In basic medium, surface becomes negatively charged due to deprotonation, causing electrostatic repulsion and decreased activity. Over four consecutive cycles, LDH-4 showed gradual decrease in degradation percentage, attributed to surface saturation, decreased light penetration due to accumulated by-products, and structural/chemical changes, all contributing to limited availability and efficacy of binding sites on the catalyst surface.

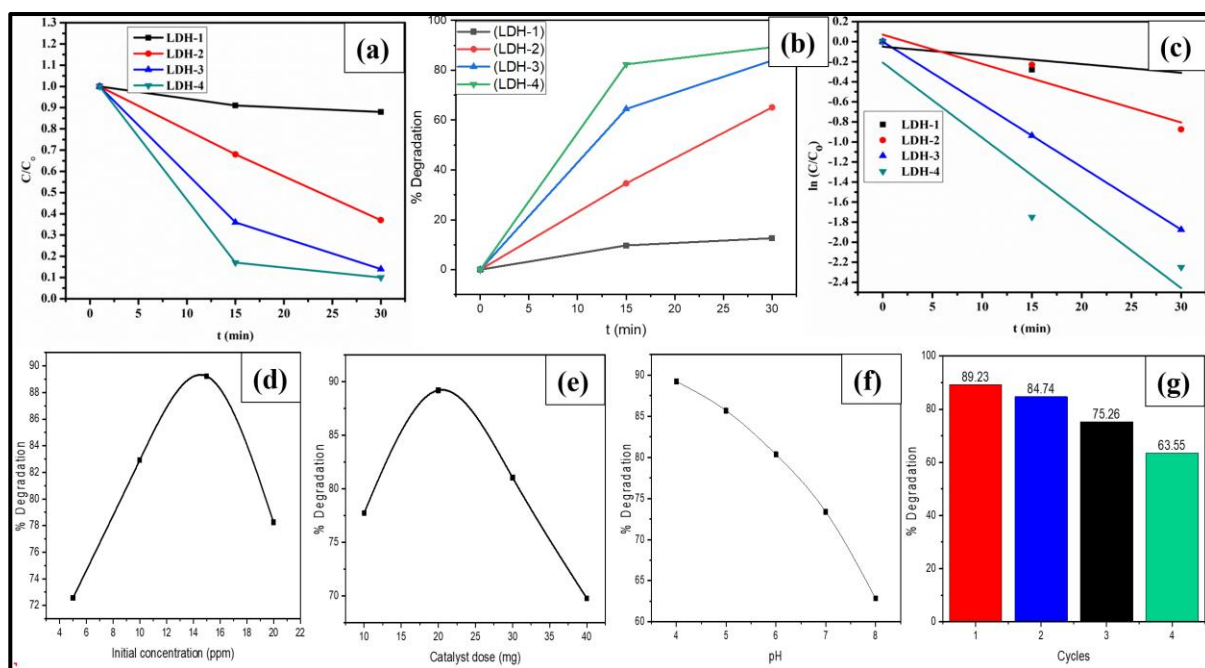


Figure 20: Photocatalytic data of the MO degradation of in the presence prepared LDHs samples under simulated solar light; linear plot (a), Percent degradation (b), rate constant (c), effect of initial concentration (d), effect of catalyst dose (e), effect of pH (f), and reuse efficacy (g) of the photocatalyst (Waheed et al., 2024).

PART 4: GRAPHENE OXIDE-METAL OXIDE NANOCOMPOSITES

4.1 rGO-ZnO-SnO₂-Fe₂O₃ (rGO-ZSF) nanocomposite. Reduced graphene oxide-zinc oxide-tin oxide-iron oxide quaternary nanocomposite was synthesized combining graphene oxide with three metal oxides for enhanced biological applications, representing a novel combination to the best of available knowledge. Graphene oxide was prepared by modified Hummers' method using graphite flakes, H₂SO₄, H₃PO₄, and KMnO₄. The mixture was stirred in ice bath at 10 °C for 10 min, graphite and KMnO₄ added, stirred for 6 h until dark green color appeared, then H₂O₂ added to remove excess KMnO₄ with intense care due to exothermic nature. After cooling, HCl and deionized water were added, mixture centrifuged, washed, and dried. For ZSF NC synthesis, SnCl₂·2H₂O, FeSO₄·7H₂O, and ZnSO₄·7H₂O were separately dissolved in deionized water and methanol mixture, 2 M NaOH added to pH 10, mixtures agitated at 50 °C for 30 min forming stable suspensions, then all three suspensions mixed in beaker and stirred at 300 rpm for 4 h at 50 °C, filtered, washed with deionized water, dried at 100 °C, and calcined at 450 °C for 2 h. For rGO-ZSF NC, the same metal salt solutions were prepared, then 1 g GO was ultrasonically dispersed in deionized water and stirred for 2 h to obtain rGO, metal hydroxide suspensions slowly added to GO suspension with vigorous stirring for 6 h, seasoned for 24 h, filtered, washed with deionized water, dried at 100 °C, and half the product calcined at 450 °C for 2 h.

XRD of rGO showed diffraction peak at 11.01° corresponding to interlayer d-spacing of 8.18 Å associated with (111) plane matching JCPDS card 01-082-2261, density 2.12 g/cm³, cell volume 2834.35×10⁶ pm³, and additional peak at 42.43° from (622) plane indicating residual graphite. ZSF NC showed Fe₃O₄ diffraction peaks at 35.06° (311), 37.09° (222), and 42.57° (400) matching JCPDS card 01-079-1849 for cubic magnetite with space group Fd3M, crystallite size 57.93 nm, lattice strain 0.419%, microstrain 2.2×10⁻³, dislocation density 2.98×10⁻⁴ nm⁻². SnO₂ peaks at 18.40° (001), 29.92° (101), and 61.99° (202) matching JCPDS card 01-072-1012 for square-based geometry with space group P4/nmm, crystallite size 35.33 nm, lattice strain 0.256%, microstrain 6.6×10⁻³, dislocation density 8.02×10⁻⁴ nm⁻². ZnO peaks at 31.96° (101), 36.38° (101), and 56.40° (110) matching JCPDS card 01-079-0205 for hexagonal shape with space group P6₃mc, crystallite size 29.56 nm, lattice strain 0.419%, microstrain 4.9×10⁻³, dislocation density 1.1458×10⁻³ nm⁻². rGO-ZSF NC showed GO peaks at 32.67° (101) and 58.18° (200) matching JCPDS card 01-076-2378 for hexagonal carbon oxide, GO crystallite size 24.10 nm, dislocation density 1.722×10⁻³ nm⁻², microstrain 6.11×10⁻³. Fe₃O₄ peaks at 29.50° (220), 42.66° (400), and 53.70° (422) with crystallite size 21.15 nm, microstrain 7.35×10⁻³, dislocation density 2.237×10⁻⁴ nm⁻². ZnO peaks at 34.91° (002), 36.46° (101), 46.83° (102), and 56.25° (110) with crystallite size 17.31 nm, microstrain 7×10⁻³, dislocation density 3.341×10⁻³ nm⁻². SnO₂ peaks at 52.75° (101) and 61.48° (222) confirming

orthorhombic geometry matching JCPDS card 00-029-1484, crystallite size 15.25 nm, microstrain 35.42, and dislocation density $4.303 \times 10^{-3} \text{ nm}^{-2}$.

FTIR of rGO showed C-H stretching at 2918.19 and 2873.80 cm^{-1} , C=C bonds of aromatic groups at 1587 cm^{-1} , C-O group at 1043.22 cm^{-1} , C-O and O-H bending vibrations at 946.92 and 1402.36 cm^{-1} . ZSF NC showed O-H stretching at 3383.94 cm^{-1} , O-H bending at 1631.49 cm^{-1} , out-of-plane O-H at 1366.96 cm^{-1} , terminal OH at 1115.69 cm^{-1} , metal-oxygen bridging at 1069.08 and 974.97 cm^{-1} , O-M-O at 740.22 cm^{-1} , M-O-M at 706.73 cm^{-1} , Zn-O at 685.24 cm^{-1} , Fe-O at 621.52 cm^{-1} , Sn-O at 557.05 cm^{-1} . Calcination caused intensity diminution in water/hydroxyl vibrations indicating water removal and hydroxide conversion to oxides. rGO-ZSF NC showed O-H stretching at 3555.45 cm^{-1} and broad band $3491\text{--}3195 \text{ cm}^{-1}$, O-H bending at 1643.11 cm^{-1} , surfactant CH_2/CH_3 deformation at 1478.1 cm^{-1} , aromatic ring stretching at 1367.4 cm^{-1} , carbonyl groups at 1080.94 cm^{-1} , M-O-M at 724.58 cm^{-1} , Zn-O at 660.47 cm^{-1} , Fe-O at 589.40 cm^{-1} , Sn-O at 562.05 cm^{-1} . Calcination decreased hydroxyl group vibrations and shifted peaks due to particle size changes and increased crystallinity.

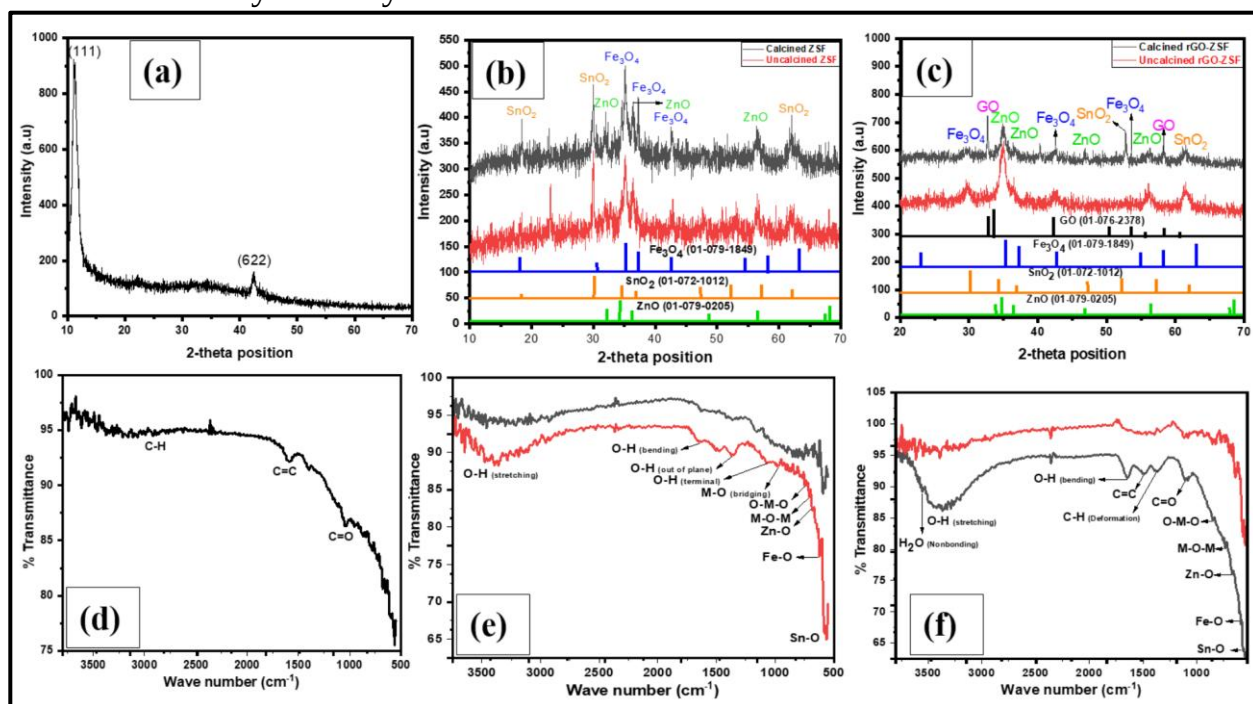


Figure 21: XRD patterns GO (a), uncalcined and calcined SF (b), uncalcined and calcined rGO-ZSF (c); FTIR spectra of GO (d), uncalcined and calcined SF (e), uncalcined and calcined rGO-ZSF (f) (Haq, Ashrabi, et al., 2026).

SEM of rGO confirmed layer-like structure with small-sized sheets, irregular surface morphology, micro-size clearly visible, uneven distribution causing surface roughness along voids, no sharp edges detected. ZSF NC low magnification showed bright and dull particles forming irregular network with irregular distribution. High magnification revealed modest agglomeration with small particles forming larger aggregates with no clear boundaries, larger aggregates having wide size range with

diverse morphological shapes, some individual particles on aggregate surface with different sizes and shapes, cavities from improper particle configurations. Aggregate size ranged 6.31-44.29 nm with mean 16.02 nm. rGO-ZSF NC showed separate blocks/larger cloudy aggregates representing graphene oxide structure with embedded trimetallic oxide nanocomposite, spotted particles and elongated particles implanted in graphene oxide, cloudy structures with varied sizes and shapes randomly distributed leading to cavity formation. High resolution showed solid particles embedded in graphene oxide matrix with particles far apart due to prolonged stirring during synthesis, shapes and sizes distinct and irregularly dispersed, particles ranging 4.29-49.89 nm with average 22.5 nm.

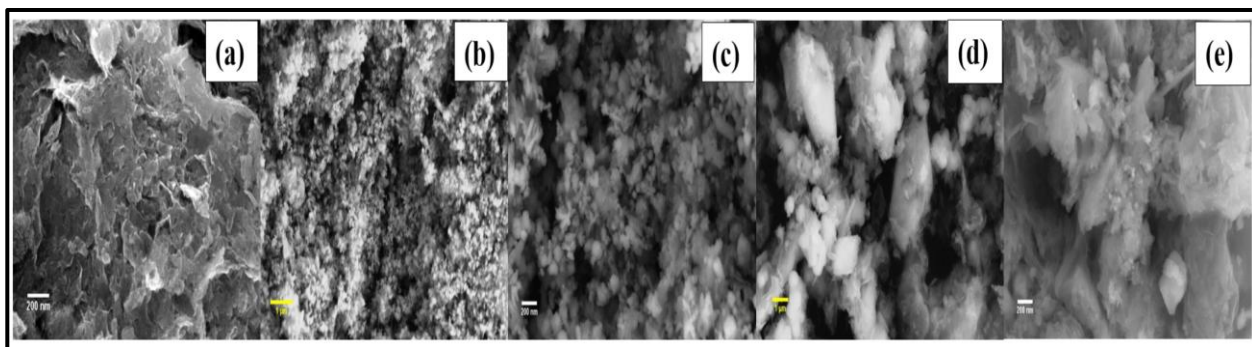


Figure 22: SEM images of GO (a), as-synthesized (b) and calcined (c) of ZSF; as-synthesized (d) and calcined (e) of rGO-ZSF NC (Haq, Ashravi, et al., 2026).

Antibacterial activity against *S. aureus* and *E. coli* using agar well diffusion at concentrations 10-60 $\mu\text{g/mL}$ showed activity enhanced with increasing concentration due to larger sample amounts producing more reactive species (metal cations and radicals) that interact with bacterial surface and vital bacterial enzymes containing thiol groups, disturbing survival activities and causing cell death. rGO-ZSF nanocomposites showed higher activity than ZSF nanocomposites against both bacterial strains, with rGO-ZSF uncalcined showing 31 mm (*E. coli*) and 29 mm (*S. aureus*), calcined rGO-ZSF 29 mm (*E. coli*) and 27 mm (*S. aureus*), ZSF uncalcined 24 mm (*E. coli*) and 23 mm (*S. aureus*), calcined ZSF 23 mm (*E. coli*) and 22 mm (*S. aureus*), antibiotic 21 mm (*E. coli*) and 20 mm (*S. aureus*), GO 7 mm (*E. coli*) and 6 mm (*S. aureus*), graphite no activity. Graphene acts as substrate showing more antibacterial activity than metal oxide nanocomposites without graphene, with graphene sheet edges penetrating bacterial cells upon direct contact causing pore formation and cytoplasmic content leakage, and bacteria ensnared within graphene sheets leading to inactivation. Uncalcined samples more active due to smaller size and greater exterior surface resulting in robust interactions with bacterial cell surface. Larger inhibition zones against *E. coli* due to thin peptidoglycan layer in Gram-negative bacteria facilitating sample entry, while Gram-positive bacteria have thick peptidoglycan coating inhibiting nanocomposite entry. *E. coli* surface carries strong negative charge due to lipopolysaccharides and phospholipids providing strong

binding sites for metal cations, while *S. aureus* surface exhibits only partial negativity due to teichoic acid.

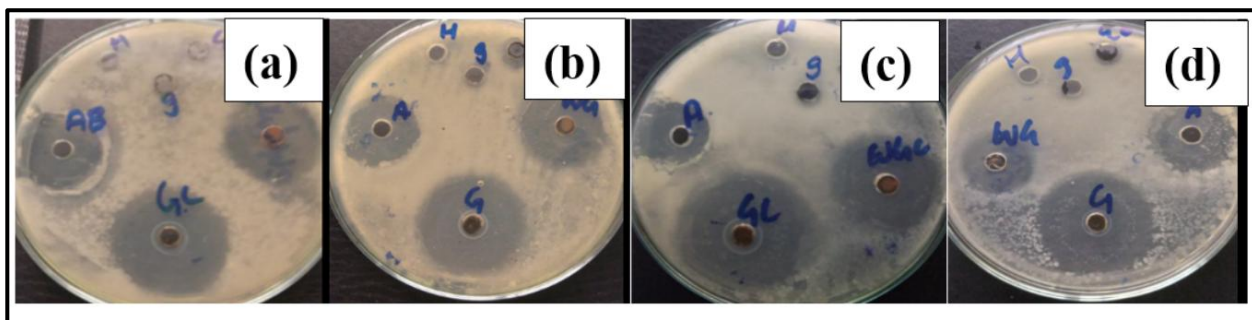


Figure 23: Antibacterial activity of uncalcined and calcined ZSF and rGO-ZSF NCs; H=-ve control (solvent), AB=+ve control (Antibiotic), GO=graphene oxide, G= rGO-ZSF, WG= ZSF, GC=calcined rGO- ZSF, and WGC=calcined ZSF (Haq, Ashravi, et al., 2026).

Antioxidant activity assessed using DPPH and ABTS free radical scavenging assays showed sample absorbance declined as sample suspension quantity increased, with higher quantity contributing to greater antioxidant activity by effectively counteracting more reactive oxygen species. For DPPH assay, GO showed 88.91-98.25% RSA with IC_{50} 21.55 $\mu\text{g/mL}$; rGO-ZSF uncalcined 77.04-94.16% with IC_{50} 36.92 $\mu\text{g/mL}$; ZSF uncalcined 56.03-75.87% with IC_{50} 42.65 $\mu\text{g/mL}$; rGO-ZSF calcined 58.36-80.73% with IC_{50} 43.56 $\mu\text{g/mL}$; ZSF calcined 50.19-90.66% with IC_{50} 46.76 $\mu\text{g/mL}$; ascorbic acid 68.87-76.84% with IC_{50} 25.25 $\mu\text{g/mL}$. For ABTS assay, GO showed 83.92-94.73% RSA with IC_{50} 27.51 $\mu\text{g/mL}$; rGO-ZSF uncalcined 51.46-93.86% with IC_{50} 46.92 $\mu\text{g/mL}$; ZSF uncalcined 33.91-81.87% with IC_{50} 47.37 $\mu\text{g/mL}$; rGO-ZSF calcined 28.65-67.83% with IC_{50} 48.94 $\mu\text{g/mL}$; ZSF calcined 26.90-76.60% with IC_{50} 49.97 $\mu\text{g/mL}$; ascorbic acid 42.39-60.82% with IC_{50} 43.75 $\mu\text{g/mL}$. Higher antioxidant activity of rGO-ZSF compared to ZSF was attributed to radicals forming adducts on sp^2 -hybridized carbon sites causing spin delocalization across conjugated graphene backbone, triggering radical annihilation by electron transfer and hydrogen donation from functional groups, and interactions between metal components and graphene oxide leading to more reactive oxygen species formation. Uncalcined samples had higher scavenging activity than calcined ones due to smaller particle size and higher surface area providing more active sites to stabilize free radicals.

Table 3: %RSA and IC₅₀ values of uncalcined and calcined rGO-ZSF and ZSF nanocomposite against DPPH and ABTs radical scavenging assay (Haq, Ashravi, et al., 2026).

Sample	Concentration mg/mL	%RSA	IC ₅₀	Sample	Concentration mg/ml	%RSA	IC ₅₀
GO	0.005	88.91	21.55	GO	0.005	83.92	27.51
	0.010	94.16			0.010	88.59	
	0.015	96.69			0.015	92.10	
	0.020	98.25			0.020	94.73	
rGO-ZSF (Uncalcined)	0.005	77.04	36.92	rGO-ZSF (Uncalcined)	0.005	51.46	46.92
	0.010	85.60			0.010	77.19	
	0.015	89.88			0.015	90.35	
	0.020	94.16			0.020	93.86	
ZSF (Uncalcined)	0.005	56.03	42.65	ZSF (Uncalcined)	0.005	33.91	47.37
	0.010	61.28			0.010	56.14	
	0.015	68.09			0.015	72.80	
	0.020	75.87			0.020	81.87	
rGO-ZSF (calcined)	0.005	58.36	43.56	rGO-ZSF (calcined)	0.005	28.65	48.94
	0.010	62.64			0.010	39.76	
	0.015	72.17			0.015	61.11	
	0.020	80.73			0.020	67.83	
ZSF (calcined)	0.005	50.19	46.76	ZSF (calcined)	0.005	26.90	49.97
	0.010	74.51			0.010	41.23	
	0.015	83.46			0.015	64.91	
	0.020	90.66			0.020	76.60	
Ascorbic acid	0.005	68.87	25.25	Ascorbic acid	0.005	42.39	43.75
	0.010	71.01			0.010	50.87	
	0.015	73.73			0.015	55.55	
	0.020	76.84			0.020	60.82	

4.2 rGO-modified ternary SnO₂-NiO-CuO nanocomposites (GO-SNC).

This section report the synthesis, characterization, and biological applications of reduced graphene oxide modified ternary SnO₂-NiO-CuO nanocomposites (GO-SNC) and their unmodified counterparts (SNC). Graphene oxide was fabricated by modified Hummers' method using graphite flakes, H₂SO₄, H₃PO₄, and KMnO₄ under carefully controlled exothermic conditions, followed by thermal reduction to obtain rGO. The ternary SnO₂-NiO-CuO nanocomposite was prepared by dissolving 3.78 g SnCl₂·2H₂O, 4.48 g NiSO₄·6H₂O, and 3.93 g CuSO₄·5H₂O in 50 mL deionized water and 10 mL methanol, adjusting pH to 10 with 2M NaOH, stirring at 50°C for 30 min, combining all three mixtures, stirring for 3 h at 50 °C, filtering, and drying at 100°C. GO-SNC was prepared by ex-situ hybridization, where 1.0 g of GO was thermally

reduced by sonication in 100 mL deionized water at 100 °C for 2 h, and the rGO solution was slowly poured into the previously prepared metallic nanocomposite solution with continuous stirring for 4 h. Both SNC and GO-SNC were calcined at 450 °C for 2 h in a muffle furnace. The antibacterial activity was evaluated against Gram-negative (*E. coli*) and Gram-positive (*S. aureus*) using agar well diffusion method with sample concentrations ranging from 10 to 60 mg/3mL, using ciprofloxacin as positive control and deionized water as negative control. Antioxidant activity was assessed against ABTS and DPPH free radicals at concentrations of 5, 10, 15, and 20 µg in 5 mL deionized water, with ascorbic acid as standard, measuring absorbance at 734 nm (ABTS) and 517 nm (DPPH).

The XRD pattern of synthesized GO exhibited a diffraction peak at 10.78° corresponding to interlayer d-spacing of 8.17 Å, associated with the (111) plane according to reference card 01-082-2261, with determined density of 2.12 g/cm³ and cell volume of 2834.35×10⁶ pm³. The absence of graphite peaks confirmed complete conversion of graphite to GO. The uncalcined SNC pattern showed a sharp signal at 36.55° ascribed to (551) plane but was otherwise noisy, indicating mostly amorphous nature. Upon calcination, several reflections appeared at 2θ angles of 23.26°, 33.06°, 36.55°, 42.46°, 47.41°, and 61.76° corresponding to Miller planes (422), (444), (551), (660), (664), and (1200), matching reference card 00-030-0496, confirming synthesis of Cu₉NiSn₃ nanocomposite with cubic geometry (space group F-43m, a = 1.801 nm, α = β = γ = 90°). Average crystallite size calculated by Debye-Scherrer equation was 14 nm with 0.75% lattice imperfection. For GO-SNC, no shift in diffraction band positions was observed, confirming that Cu₉NiSn₃ was incorporated onto graphene oxide sheets without chemical linkage formation. However, d-spacing for the (551) plane decreased from 2.523 Å (pure SNC) to 2.458 Å (GO-SNC), confirming incorporation of graphene oxide. This decrease was attributed to reorganization of lattice positions after mixing, where carbon atoms with smaller ionic radius adjusted between larger metal atoms (Cu²⁺, Ni²⁺, Sn⁴⁺). Average crystallite size increased from 14 nm to 57.45 nm, while lattice strain reduced to 0.59%, indicating the nanocomposite became more stable after GO incorporation. FTIR of GO showed peaks at 3404.10 cm⁻¹ (O-H stretching), 2929.68 and 2834.47 cm⁻¹ (symmetric and asymmetric C-H stretching), 2308.34 cm⁻¹ (C=O or O=C=O), 1717.37 cm⁻¹ (C=C vibrations), 1607.38 cm⁻¹ (aromatic C=C), 1381.66 cm⁻¹ and 1118.19 cm⁻¹ (C=C and C-O moieties), and 600.27 cm⁻¹ (out-of-plane C-H bending). For SNC, peaks were observed at 3524.18 cm⁻¹ (non-bonding water molecules), 3473 cm⁻¹ (OH stretching, decreasing after calcination due to water evaporation), 1385.83 cm⁻¹ (C=O stretching), 1044.60 cm⁻¹ (Cu-O-Cu vibration), 571.72 cm⁻¹ (Ni-O stretching), and 887.58 cm⁻¹ (C-C vibration). For GO-SNC, FTIR showed wide band at 3398.46 cm⁻¹ (O-H stretching, decreasing after calcination), 1624.89 cm⁻¹ (C=O vibration), 1490.30 cm⁻¹ (C-O-C vibration), 1362.47 cm⁻¹ (O-C=O group), 1028.36

cm^{-1} (Cu-O-Cu vibration), 544.63 cm^{-1} (Ni-O vibration), and 799.27 cm^{-1} (Sn-O stretching vibration).

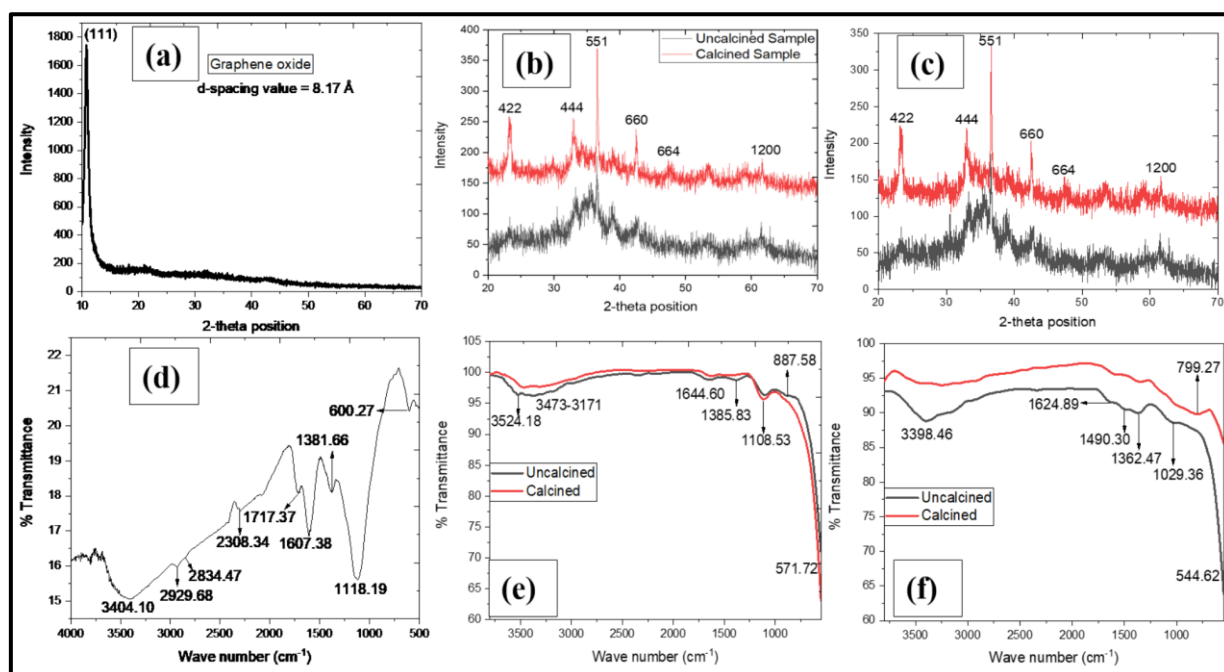


Figure 24: XRD patterns GO (a), uncalcined and calcined SNC (b), uncalcined and calcined GO-SNC (c); FTIR spectra of GO (d), uncalcined and calcined SNC (e), uncalcined and calcined GO-SNC (f) (Haq et al., 2023).

SEM images of GO revealed layer-type structures with multilayers, high surface roughness, and cavities/cracks possibly due to sample grinding after dehydration. The as-synthesized SNC showed snowball-like structures (grains) resulting from aggregation of smaller particles formed during synthesis, with irregular dispersion and clumping together forming larger structures. High degree of agglomeration was observed in the background due to high surface energy holding particles together. Grain size for as-synthesized SNC ranged from 40.75 to 98.93 nm with average of 84.55 nm. Upon calcination at 450°C , individual snowball-like structures grew through diffusion-driven processes including grain boundary migration and recrystallization, increasing average grain size to 101 nm (range 68-123 nm), with cavities of distinct size formed due to irregular arrangement of grains. For GO-SNC, morphology completely changed after mixing metals with GO, with metal nanocomposite deeply incorporated into GO layers. The as-synthesized GO-SNC showed grains embedded in GO layers, where majority of cavities seen in SNC were filled due to GO deposition. Upon calcination, GO layers became more prominent and converted to semi-porous sheets, with boundaries between Cu_9NiSn_3 grains almost disappearing.

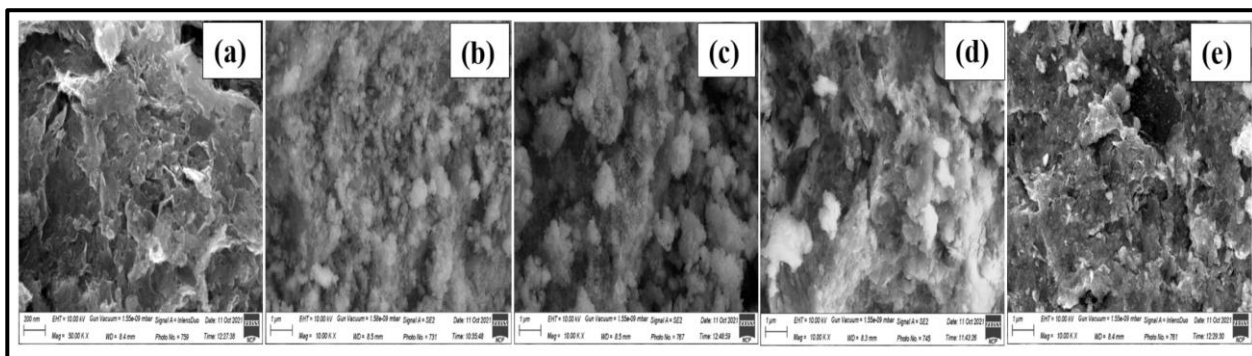


Figure 25: SEM images of GO (a), as-synthesized (b) and calcined (c) of SNC; as-synthesized (d) and calcined (e) of GO-SNC (Haq et al., 2023).

The antibacterial activity of uncalcined and calcined SNC and GO-SNC was evaluated against *E. coli* (Gram-negative) and *S. aureus* (Gram-positive) using agar well diffusion method at concentrations of 10, 20, 30, 40, 50, and 60 $\mu\text{g/mL}$. Bacterial activity was directly related to sample concentration, as increasing concentration per mL generated more reactive species including metal cations, hydroxyl radicals, and superoxide radical anions in aqueous solution. These cations react with thiol groups of fundamental bacterial enzymes, causing inactivation of cell activities leading to cell death, while radicals interact with negatively charged cell surfaces, causing cell wall rupture and loss of cell content. At the highest concentration tested (60 mg/3mL), GO-SNC showed inhibition zones of 24 mm against *E. coli* and 21 mm against *S. aureus*, while calcined GO-SNC showed 9 mm (*E. coli*) and 12 mm (*S. aureus*). SNC showed 21 mm (*E. coli*) and 7 mm (*S. aureus*), while calcined SNC showed 11 mm (*E. coli*) and 15 mm (*S. aureus*). The positive control (ciprofloxacin antibiotic) showed 16 mm against *E. coli* and 20 mm against *S. aureus*, while GO alone showed 6 mm against *E. coli* and 11 mm against *S. aureus*.

GO-SNC showed higher antibacterial activity than SNC against both bacterial strains, attributed to GO-supported metallic nanocomposites exhibiting enhanced activity due to oxygen vacancies on GO surface acting as sorption centers for water molecules, reacting to form hydroxyl radicals. The edges of graphene sheets penetrate bacterial cells upon direct contact, causing pore formation and leakage of cytoplasmic content, while bacteria can also be ensnared within graphene sheets leading to inactivation. Uncalcined samples showed greater activity than calcined counterparts because calcination increases particle size, reducing surface-to-volume ratio and number of binding sites available for interaction with bacterial surfaces. Higher activity was observed against *E. coli* compared to *S. aureus* due to differences in cell wall composition. Gram-negative *E. coli* has a thin peptidoglycan layer with outer membrane containing lipopolysaccharides and phospholipids that impart strong negative charge, providing strong binding sites for metal cations. Gram-positive *S. aureus* has a thick peptidoglycan layer with teichoic acid imparting only partial negative charge, resulting in weaker interactions and greater resistance.

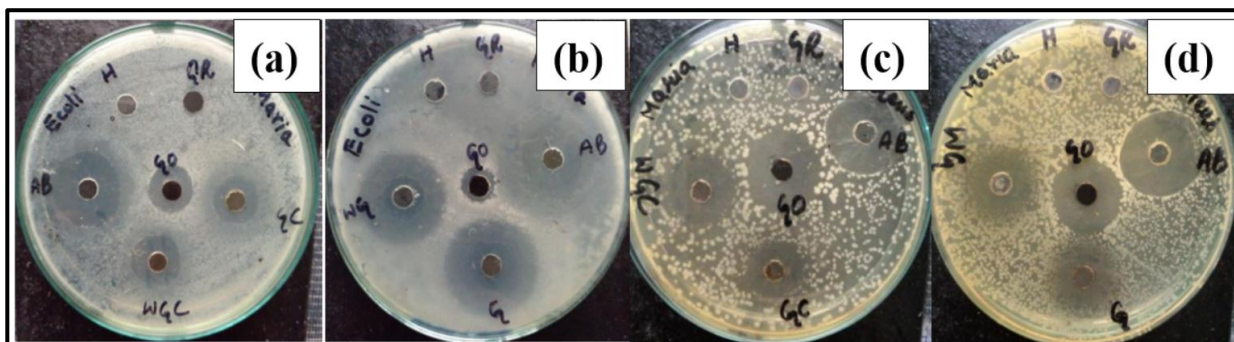


Figure 26: Antibacterial activity of uncalcined and calcined SNC and GO-SNC; H=-ve control (solvent), AB=+ve control (Antibiotic), GO=graphene oxide, G= GO-SNC, WG= SNC, GC=calcined GO-SNC, and WGC=calcined SNC (Haq et al., 2023).

The antioxidant potential of calcined and uncalcined SNC and GO-SNC was evaluated against ABTS and DPPH free radicals at concentrations of 5, 10, 15, and 20 μg in 5 mL deionized water, with ascorbic acid as standard. For ABTS radical scavenging, GO showed increasing activity from 74.46% (5 μg) to 96.11% (20 μg) with IC_{50} of 11.25 $\mu\text{g/mL}$. Uncalcined SNC showed 44.78-86.33% (IC_{50} 36.84 $\mu\text{g/mL}$), calcined SNC showed 38.68-77.65% (IC_{50} 41.03 $\mu\text{g/mL}$), uncalcined GO-SNC showed 56.65-91.69% (IC_{50} 28.95 $\mu\text{g/mL}$), calcined GO-SNC showed 31.73-67.82% (IC_{50} 48.56 $\mu\text{g/mL}$), and ascorbic acid showed 34.60-58.67% (IC_{50} 44.67 $\mu\text{g/mL}$). For DPPH radical scavenging, GO showed 89.68-99.02% (IC_{50} 15.98 $\mu\text{g/mL}$), uncalcined SNC showed 73.93-88.91% (IC_{50} 36.55 $\mu\text{g/mL}$), calcined SNC showed 53.51-65.17% (IC_{50} 36.98 $\mu\text{g/mL}$), uncalcined GO-SNC showed 76.85-90.86% (IC_{50} 33.68 $\mu\text{g/mL}$), calcined GO-SNC showed 42.02-68.09% (IC_{50} 46.18 $\mu\text{g/mL}$), and ascorbic acid showed 69.26-76.45% (IC_{50} 22.33 $\mu\text{g/mL}$).

In both assays, uncalcined samples showed higher percentage scavenging activity than calcined samples, with lower IC_{50} values indicating higher antioxidant potential. This is because calcination increases particle size, decreasing number of nanoparticles in solution and reducing available active sites for stabilizing free radicals. GO exhibited the highest antioxidant activity among all samples, attributed to radicals forming adducts on sp^2 -hybridized carbon sites with spin delocalization across conjugated graphene backbone, electron transport, and hydrogen donation from hydroxyl functional groups. GO-SNC showed higher antioxidant activity than SNC due to synergistic effects between SNC and GO, where the combination may form reactive oxygen species that donate electrons to free radicals, making them stable. The percentage radical scavenging activity increased with increasing sample dose in all cases, indicating that higher concentrations provide more nanoparticles available to interact with and neutralize free radicals.

Table 4: Antioxidant activity of the GO, SNC and GO-SNC against ABTS and DPPH free radicals (Haq et al., 2023).

Samples	Concentration mg/mL	%RSA	IC ₅₀	Samples	Concentration mg/mL	%RSA	IC ₅₀
GO	0.005	90.35	14.82	GO	0.005	89.68	15.98
	0.010	92.39			0.010	94.94	
	0.015	93.57			0.015	97.08	
	0.020	98.25			0.020	99.02	
SNC	0.005	83.04	32.43	SNC	0.005	73.93	36.55
	0.010	89.18			0.010	76.07	
	0.015	93.86			0.015	81.32	
	0.020	96.78			0.020	88.91	
SNC calcined	0.005	41.52	42.33	SNC calcined	0.005	53.51	36.98
	0.010	67.25			0.010	57.97	
	0.015	75.73			0.015	61.28	
	0.020	81.58			0.020	65.17	
GO-SNC	0.005	83.92	24.56	GO-SNC	0.005	76.85	33.68
	0.010	86.84			0.010	79.96	
	0.015	88.59			0.015	81.71	
	0.020	93.86			0.020	90.86	
GO-SNC calcined	0.005	52.22	45.43	GO-SNC calcined	0.005	42.02	46.18
	0.010	59.35			0.010	50.39	
	0.015	62.86			0.015	59.14	
	0.020	82.46			0.020	68.09	
Ascorbic acid	0.005	33.04	41.81	Ascorbic acid	0.005	69.26	22.33
	0.010	37.42			0.010	71.40	
	0.015	40.35			0.015	73.92	
	0.020	44.15			0.020	76.45	

PART 5: MWCNTs-METAL OXIDE NANOCOMPOSITES

5.1 CuO-NiO and MWCNTs@CuO-NiO nanocomposites. Copper oxide-nickel oxide nanocomposite and its multi-walled carbon nanotube-modified

counterpart were synthesized using a modified sol-gel method representing an enhanced version of the traditional sol-gel process. For CuO-NiO NC synthesis, nickel(II) nitrate hexahydrates and copper(II) nitrate pentahemihydrate were separately dissolved in deionized water under continuous stirring for 30 min, then mixed and heated at 60 °C for 30 min with vigorous stirring. Sodium hydroxide solution was added until pH 10 was achieved, and the mixture was continuously stirred and heated at 60 °C for 3 h. After cooling and aging for 24 h, the mixture was filtered, rinsed three times with deionized water, and the solid residue was calcined at 350 °C for 4 h in a muffle furnace. For MWCNTs@CuO-NiO NC synthesis, carboxylic acid-functionalized MWCNTs were ultrasonically dispersed in deionized water and added to the metal nitrate mixture before pH adjustment. The reaction was maintained at 80 °C with continuous stirring for 5 h, aged for 24 h, filtered, washed four times with hot distilled water, dried at 100 °C, and calcined at 350 °C for 4 h. This modified sol-gel method represents an efficient, faster, and more straightforward approach for synthesizing bimetallic oxide nanoparticles and carbon nanotube-modified composites.

SEM of CuO-NiO NC revealed a cloudy appearance from particle agglomeration and limited surface resolution, with multiple cavities formed from solvent removal during the sol-gel method or shrinkage during drying. Heavy agglomeration occurred due to nanoparticle attraction common in metal oxides, creating a dense appearance from overlapping particles. Some elongated or needle-like structures indicated anisotropic growth, while irregular shapes suggested non-homogeneous nucleation and growth during the sol-gel process. Flaky structures resulted from solvent evaporation. When MWCNTs were incorporated, significant morphological changes occurred as MWCNTs acted as a scaffold with high surface area, strongly interacting with CuO and NiO nanoparticles and consolidating them into a dense, compact structure with smooth surface and minimized cavities. Agglomeration increased significantly as MWCNTs and metal oxide particles clustered together due to strong van der Waals forces, creating a unified structure where individual particle boundaries merged into a continuous phase with bulges from nanoparticle clustering and a non-porous compact structure from MWCNTs filling gaps. EDX confirmed elemental composition with signals at 0.14 keV for carbon, 0.5 keV for oxygen, 0.93, 8.1, and 8.9 keV for copper, 0.81 and 7.5 keV for nickel, and 2.3 keV for sulfur from SDS surfactant. MWCNT incorporation enhanced oxygen signals by improving dispersion of CuO and NiO particles, increasing surface exposure and detectability. Copper signals increased as CNTs prevented particle agglomeration and ensured uniform dispersion. Carbon content significantly increased due to CNT incorporation with their high surface area and conductivity. Nickel signals decreased as CNTs bonded preferentially with CuO and altered composite morphology. EDS mapping confirmed the presence and distribution of elemental constituents, showing slight agglomeration of Cu, Ni, and O elements

while CNTs appeared monodispersed and uniformly distributed throughout the sample, confirming successful formation of CuO-NiO nanoparticles and incorporation of MWCNTs.

XRD analysis showed noisy patterns for both samples, indicating significant amorphous content alongside crystalline phases, attributed to peak broadening of CuO and NiO nanoparticles due to the Scherrer effect where smaller crystallite sizes result in broader, less intense peaks, and overlapping of multiple phases (MWCNTs, CuO, and NiO) contributing to pattern complexity. Diffraction peaks at 26.81° and 42.10° were linked to the (002) and (100) planes of MWCNTs according to JCPDS card 00-041-1487, corresponding to interlayer spacing and in-plane carbon atom structure in the hexagonal lattice. Bragg's reflections at 33.38° and 38.67° were linked to the (110) and (111) planes of CuO with monoclinic crystal system, space group Cc, showing varied coordinate lengths ($a=4.6927 \text{ \AA}$, $b=3.4283 \text{ \AA}$, $c=5.1370 \text{ \AA}$) with interfacial angles α and γ at 90° and β at 99.5460° . The diffraction peak at 62.29° was linked to the 220 plane of NiO with cubic system, space group Fm3m, showing equal three-dimensional distances ($a=b=c=3.1700 \text{ \AA}$) with all interfacial angles at 90° . FTIR revealed broad bands centered at 3337.57 cm^{-1} along with bands at 3443.32 and 3252.97 cm^{-1} associated with tensile collision of H-O-H and hydroxyl incorporation. A weak band at 3013.82 cm^{-1} was contributed to asymmetric C-H stretching, while C-H stretching modes of CNTs appeared at 2936.24 cm^{-1} . A peak at 2929.04 cm^{-1} was attributed to 2D oscillation mode of bridging hydroxyl groups involved in hydrogen bonding. A minor band at 2365.16 cm^{-1} resulted from atmospheric CO_2 adsorbed on the nanocomposite surface. In-plane bending of H-O-H coordinated water molecules was responsible for the medium band at 1646.12 cm^{-1} . C=C stretches of CNTs gave rise to slightly intense bands at 1613.72 and 1518.95 cm^{-1} , while C-H bending vibrations caused the weak band at 1477.36 cm^{-1} . Lattice M-OH vibrations were identified as the source of the weak band at 1420.57 cm^{-1} , while O-C-O asymmetric vibrations caused the intense band at 1364.95 cm^{-1} . Bands at 1251.81 and 1244.61 cm^{-1} resulted from O-M-O ($M=\text{Cu}$) vibrations. The intense band at 1181.43 cm^{-1} was caused by C-O bond vibrations, while bands at 1054.25 cm^{-1} with varying intensities were ascribed to M-O-M vibrations. The band at 1004.67 cm^{-1} was generated by bending vibrations of Cu-O bonds, while M-O vibrations produced another weak band at 913.49 cm^{-1} . Out-of-plane C-H deformation mode was responsible for the band at 856.70 cm^{-1} , while the band at 849.50 cm^{-1} was ascribed to M-O-C vibrations. Stretching of Cu-O within the monoclinic lattice led to a band at 779.12 cm^{-1} , while bands of different intensities at 631.15 and 575.16 cm^{-1} were produced by Ni-O vibrations. Cu-O stretching vibrations produced bands at 525.57 and 462.39 cm^{-1} . MWCNT incorporation caused variations in band intensities, appearance and disappearance of some bands, and enhanced features in the fingerprint region due to new interactions between

CNTs and metal oxides, altered bonding environments, enhanced dispersion of particles, introduction of new vibrational modes, and improved vibrational coupling.

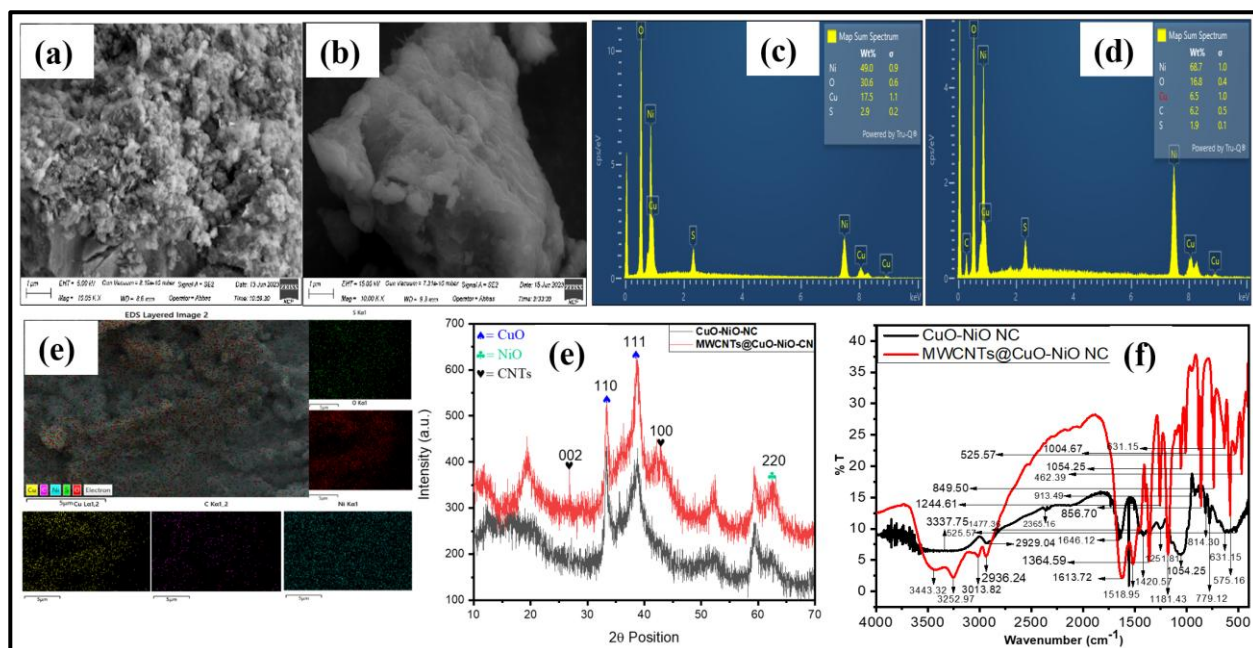


Figure 27: SEM micrograph (a, b), DX spectra(c, d), EDS mapping (e), XRD pattern (g), and FTIR of the CuO-NiO and MWCNTs@CuO-NiO Nanocomposites (Lone, Rehman, Haq, Shahzad, et al., 2025).

Photocatalytic activity was assessed against R-6G under solar light irradiation from June 3 to 14, 2024 between 11 a.m. and 3 p.m. The bright brown color of the reaction mixture gradually faded during deterioration, with a rapid decline in absorbance maximum at 526 nm indicating chromophore breakdown. The catalyst-free sample showed negligible decrease, while catalyst-containing samples showed significant decrease, particularly in the MWCNT-modified sample. The degradation profile showed a sharp and substantial decrease in maximum absorption in the initial 20 min, followed by reduced rate in all samples. CuO-NiO NC achieved 80.09% degradation, while MWCNTs@CuO-NiO NC achieved superior degradation of 95.37%. Control experiments with only light (no catalyst) and only catalyst (no light) resulted in 3.52% and 10.45% degradations respectively, highlighting the synergistic effect of both light and catalyst. Rate constants were 0.02737 min^{-1} for CuO-NiO NC and 0.0477 min^{-1} for MWCNTs@CuO-NiO NC, with the catalyst-free sample showing 5.99312 min^{-1} . Photocatalytic Activity Index values were calculated as 0.13×10^{-4} and 0.22×10^{-4} for CuO-NiO NC and MWCNTs@CuO-NiO NC respectively, clearly indicating that MWCNT integration significantly improved photocatalytic activity.

The photocatalytic mechanism involves R-6G degradation through a series of steps with attack of generated hydroxyl radicals and reactive oxygen species. When the catalyst absorbs solar light, valence electrons are excited to the conduction band, generating positive holes in the valence band. Holes react with $\text{OH}^-/\text{H}_2\text{O}$ to generate

hydroxyl radicals attached to ethyl groups and the xanthene ring. Simultaneously, excited electrons react with oxygen, forming reactive oxygen species responsible for conjugated bond breakage. N-de-ethylation is the initial and most prominent step, where highly reactive hydroxyl radicals attack ethyl groups attached to nitrogen atoms of the xanthene core, generating N-de-ethylated intermediates responsible for initial solution decolorization. Further attack by reactive oxygen species on the xanthene ring structure leads to conjugated double bond breakage, while electrophilic attack by hydroxyl radicals on aromatic rings forms smaller aromatic fragments. Further oxidative attacks lead to C-C, C-N, and C-O bond breakage, resulting in simpler molecules like H_2O , CO_2 , NH_4^+ , and NO_3^- .

pH effect studies showed degradation rates of 56.02% at pH 4, 69.83% at pH 5, 83.29% at pH 6, 95.37% at pH 7, 85.02% at pH 8, and 72.17% at pH 9, with maximum at neutral pH. R-6G exists in both ionic (R6G^+) and non-ionic forms, with higher solution pH causing cationic dye molecules to convert to neutral forms, preventing attractive interaction with the negatively charged nanocomposite surface and decreasing degradation above pH 7. Below pH 7, protonation of nitrogen in the secondary amine group causes cationic dye molecules to become hydrophilic, producing fewer radicals than under neutral conditions. Catalyst dose optimization showed degradation increasing from 78.36% to 95.37% as dose increased from 10 to 20 mg, then decreasing to 89.01% at 25 mg and 81.03% at 30 mg due to increased total surface area providing more active sites for dye interaction at optimal dose, while higher doses caused nanoparticle aggregation, reduced photon interactions, and less efficient photon absorption. Initial concentration studies showed degradation rates of 73.42%, 84.26%, 95.37%, 87.16%, and 76.97% at 5, 10, 15, 20, and 25 ppm respectively, with maximum at 15 ppm and decrease at higher concentrations due to reactive center saturation and interference with light irradiation. Reusability studies over five consecutive cycles showed degradation percentages of 95.37%, 88.34%, 81.69%, 75.04%, and 61.21% for cycles 1 through 5, with initial high efficiency due to fresh catalyst form and gradual decrease due to surface contaminants, structural changes, catalyst deactivation, and dye adsorption on the photocatalyst surface during recycling.

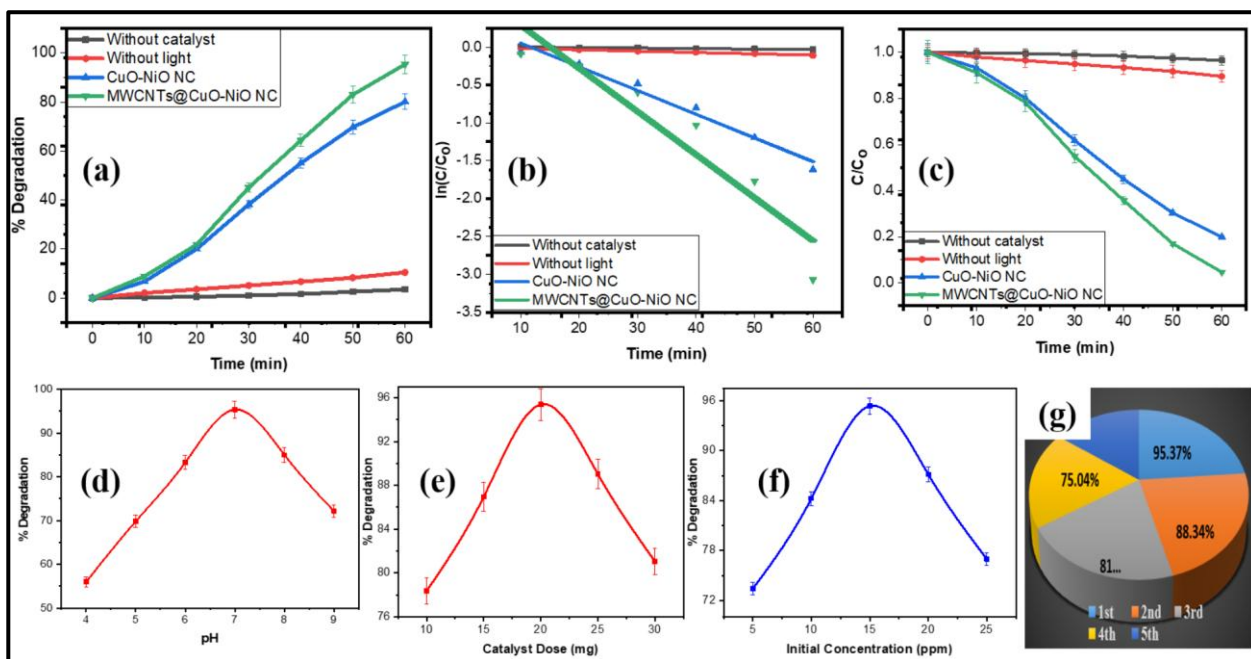


Figure 28: Photocatalytic data of the R-6G degradation of in the presence of CuO-NiO and MWCNTs@CuO-NiO Nanocomposites under simulated solar light; Percent degradation (a), rate constant (b), linear plot (c), effect of pH (d), effect of catalyst dose (e), effect of initial concentration (f) and reuse efficacy (g) of the MWCNTs@CuO-NiO NC during the photocatalytic experiment (Lone, Rehman, Haq, Shahzad, et al., 2025).

Antibacterial activity evaluated against *S. aureus* and *E. coli* using agar well diffusion method showed that CuO-NiO NC exhibited high activity against both bacteria, with *E. coli* found more resistant due to its outer membrane structure providing stronger defense. The activity of CuO-NiO NC was higher than the standard drug, indicating potential as effective antibacterial agent. The solvent did not interfere with antibacterial activity, confirming that observed effects were solely due to the nanocomposites. MWCNTs@CuO-NiO nanocomposite showed reduced antibacterial activity compared to bare CuO-NiO NC, despite still demonstrating significant activity. The incorporation of MWCNTs may shield or block active sites of CuO-NiO nanoparticles, reduce direct interaction with bacterial cells, lead to agglomeration reducing effective surface area, and alter surface chemistry as metal ions bind to functional sites on MWCNTs, reducing metal oxide affinity for bacterial cell walls.

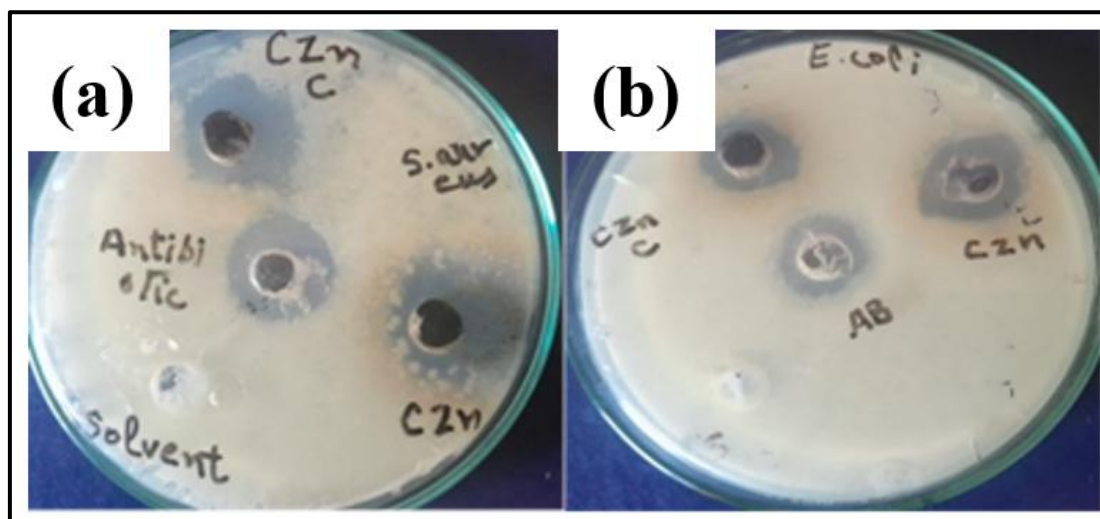


Figure 29: Experimental photographs showing the antibacterial activity of CuO-NiO NC and MWCNTs@CuO-NiO NC (Lone, Rehman, Haq, Shahzad, et al., 2025).

Antioxidant activity assessed against ABTS⁺ solution compared to vitamin C as reference showed that both samples exhibited increasing activity with increasing concentrations. At concentrations from 5 to 400 $\mu\text{g/mL}$, CuO-NiO NC showed scavenging activity from 22.076% to 82.336% with IC₅₀ value of 116.52 $\mu\text{g/mL}$, while MWCNTs@CuO-NiO NC showed scavenging activity from 24.14% to 90.924% with IC₅₀ value of 84.61 $\mu\text{g/mL}$, compared to ascorbic acid IC₅₀ of 92.74 $\mu\text{g/mL}$. The anionic NCs' electron-donor surface may be responsible for trapping ABTS free radical species, with higher antioxidant activity occurring because more reactive oxygen species could be combined. Standard deviation values of 1.68, 1.69, and 1.75 for CuO-NiO NC, MWCNTs@CuO-NiO NC, and ascorbic acid indicated that CuO-NiO NC produced the most accurate and consistent findings. Variance values of 2.82, 2.84, and 3.09 respectively indicated that CuO-NiO NC varied least among samples. Correlation between dose and % RSA was 0.098, 0.108, and 0.102 respectively, showing ascorbic acid had the strongest relationship where higher doses were associated with increased % RSA. MWCNT incorporation facilitated efficient electron transfer, augmented active sites, and stabilized reactive species, enhancing composite antioxidant performance through SPR effects, redox cycling, and metal-ligand interactions.

Table 5: Antioxidant activity of the synthesized NC against ABTS free radicals (Lone, Rehman, Haq, Shahzad, et al., 2025).

Samples	Concentration ($\mu\text{g/mL}$)	%RSA	IC ₅₀ ($\mu\text{g/mL}$)	Variance (S ²)	Standard deviation (S)	Correlation between dose and %RSA
CuO-NiO NC	5	22.076	116.52	2.82	1.68	0.098
	25	30.188				
	50	43.228				
	100	59.916				
	200	74.004				
	400	82.336				
MWCNT@ CuO-NiO NC	5	24.144	84.61	2.84	1.69	0.108
	25	33.432				
	50	49.796				
	100	65.124				
	200	79.612				
	400	90.924				
Ascorbic acid	5	21.92	92.74	3.09	1.75	0.102
	25	33.58				
	50	47.956				
	100	57.396				
	200	83.976				
	400	94.068				

5.2 Ag₂O/CuO/ZnO and MWCNTs@Ag₂O/CuO/ZnO nanocomposites.

Silver oxide/copper oxide/zinc oxide trimetallic nanocomposite and its MWCNTs-modified counterpart were synthesized using a modified sol-gel method, representing the first report of MWCNT-modified Ag₂O/CuO/ZnO nanocomposites with multifunctional applications as photocatalyst, antibacterial agent, and antioxidant agent. For ACZ-NC synthesis, Zn(NO₃)₂·5H₂O, AgNO₃, and Cu(NO₃)₂·5H₂O were individually dissolved in deionized water under constant stirring for 30 min, mixed with vigorous stirring, heated at 60 °C for 30 min, then 1 M NaOH was added to adjust pH to 10 for 3 h with continuous heating and stirring. After cooling for 24 h, the mixture was filtered, washed with deionized water, dried at 100 °C for 8 h, and calcined at 350 °C for 4 h. For MWCNTs@ACZ-NC, carboxylic acid-functionalized MWCNTs were ultrasonically dispersed and added to the metal nitrate mixture

before pH adjustment, with reaction maintained at 80 °C for 5 h, aged 24 h, filtered, washed four times with hot distilled water, dried at 100 °C, and calcined at 350 °C for 4 h.

XRD analysis showed Bragg's reflections corresponding to Ag₂O, CuO, ZnO, and CNTs. A diffraction peak at 44.39° from (111) plane confirmed CNTs existence matching JCPDS card 01-080-0017. Ag₂O diffraction peaks at 17.31° (001), 27.93° (110), 33.59° (100), and 38.24° (011) confirmed hexagonal geometry with space group P3m1, lattice parameters $a=b=3.0720$ Å, $c=4.9410$ Å, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$, crystallite size 14.25 nm with 0.074% lattice strain. CuO diffraction peaks at 29.43° (020), 32.35° (200), 46.25° (-112), 60.83° (125), and 64.54° (141) confirmed orthorhombic configuration with space group Bmm2, unit cell dimensions $a=5.3510$ Å, $b=6.0200$ Å, $c=9.3400$ Å, all interfacial angles 90°, crystallite size 14.02 nm with 0.089% lattice strain. ZnO diffraction peaks at 30.38° (100), 34.87° (002), 54.93° (110), 55.59° (022), and 63.20° (103) confirmed hexagonal crystallite with space group P6₃mc, unit cell dimensions $a=b=3.3520$ Å, $c=5.2260$ Å, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$, crystallite size 60.3 nm with 0.192% lattice strain. FTIR showed broad bands centered at 3380.30 and 3220.25 cm⁻¹ for O-H stretching, band at 2933.79 cm⁻¹ for C-H stretching modes of MWCNTs, band at 2703.15 cm⁻¹ for C-H stretching vibration, intense band at 1634.47 cm⁻¹ for H-O-H bending, faint band at 1516.28 cm⁻¹ for C=C stretching of MWCNTs, mild band at 1417.78 cm⁻¹ for M-OH vibrations, sharp band at 1369.36 cm⁻¹ for out-of-plane O-H bending, band at 1264.30 cm⁻¹ for C-O stretching, band at 1187.96 cm⁻¹ for C-H flexural vibration, band at 1054.10 cm⁻¹ for M-OH vibrations, band at 915.46 cm⁻¹ for O-M-O vibrations, band at 866.21 cm⁻¹ for M-O-M vibrations, band at 817.79 cm⁻¹ for M-O-M vibrations, band at 748.02 cm⁻¹ for C-O-M bond, band at 678.25 cm⁻¹ for Cu-O stretching, band at 636.39 cm⁻¹ for Ag-O bending, bands at 545.28 and 468.13 cm⁻¹ for ZnO bending and stretching. MWCNT incorporation caused new absorption bands, shifts in existing bands, intensity changes, broadening, and potential new functional group formation due to interactions between MWCNTs and metal oxides, altered local electronic environment, enhanced dispersion, improved interfacial bonding, and increased polarizability from π -electrons. Energy dispersive X-ray mapping confirmed presence of carbon from CNTs and metallic components including silver, copper, zinc, and oxygen corresponding to Ag₂O, CuO, and ZnO phases, with no significant impurities detected. EDX spectra showed oxygen peak at 0.5 keV from oxides of Ag, Zn, and Cu; silver peaks at 3.08 keV; copper peaks at 0.9 and 8.05 keV; zinc peaks at 1.05, 8.7, and 9.6 keV; chlorine peak at 2.62 keV; carbon peak at 0.21 keV confirming MWCNT incorporation. DRS showed absorbance edges at 720.56 nm for ACZ-NC and 765.70 nm for MWCNTs@ACZ-NC, with redshift upon CNT incorporation indicating broader visible light absorption. Band gap energies calculated from Tauc plots showed slight decrease

with MWCNT incorporation due to interaction between electronic structure and conductive π -electron networks of MWCNTs.

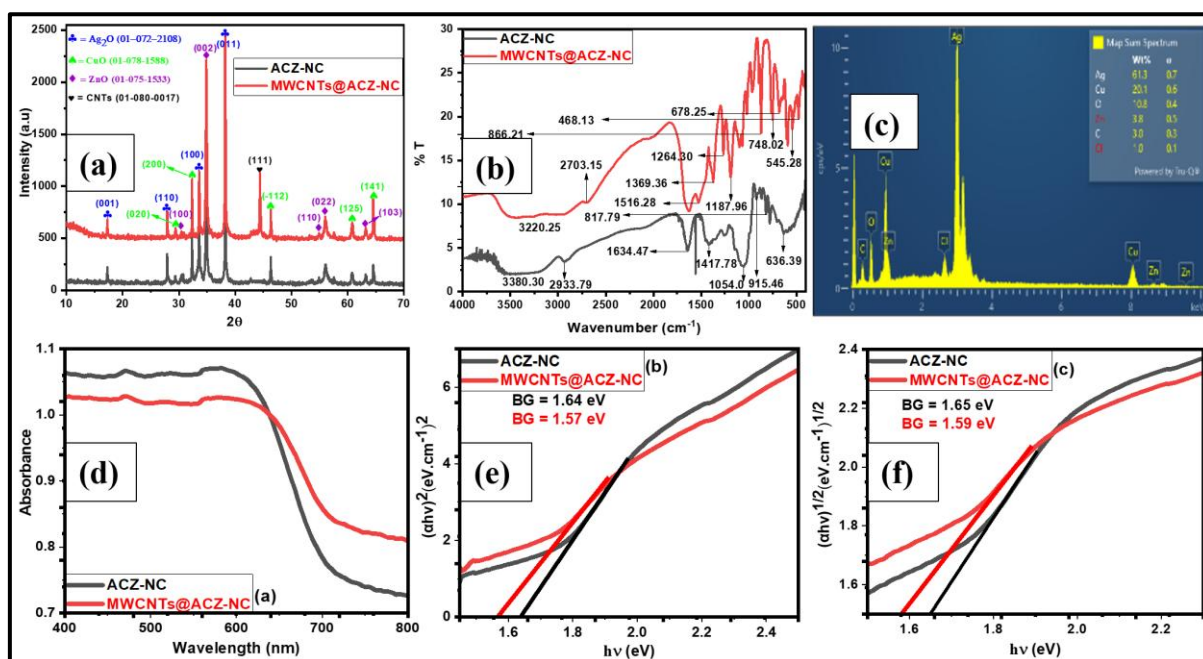


Figure 30: XRD patterns (a), FTIR spectra (b), EDX spectrum (c), DRS spectra (d), Tauc's plpts for direct (e), indirect (f) of ACZ-NC and MWCNTs@ACZ-NC (Lone, Rehman, Haq, Alkhuriji, et al., 2025).

FE-SEM of ACZ-NC showed non-uniform particle size and shape with both individual particles and larger aggregates. Individual particles exhibited spherical, nearly spherical, slightly elongated fiber-like, and polyhedral morphologies, with non-uniformity leading to several defects. Cavity formation resulted from solvent evaporation and volatile byproduct removal during drying. Individual particles had wide size distribution ranging 15-110 nm, while larger aggregates exceeded 160 nm. MWCNTs@ACZ-NC showed distinct elongated morphology with tube-like structures apparent, ACZ-NC particles visible on surface of elongated tube-like structures but with non-uniform distribution. Cavities reduced as MWCNTs filled voids in original nanocomposite, with elongated tube-like structures regularly distributed and surfaces appearing smooth and non-porous. Elemental mapping showed uniform distribution across CNT matrix, indicating well-integrated nanocomposite structure with good interaction between CNTs and metal oxide nanoparticles.

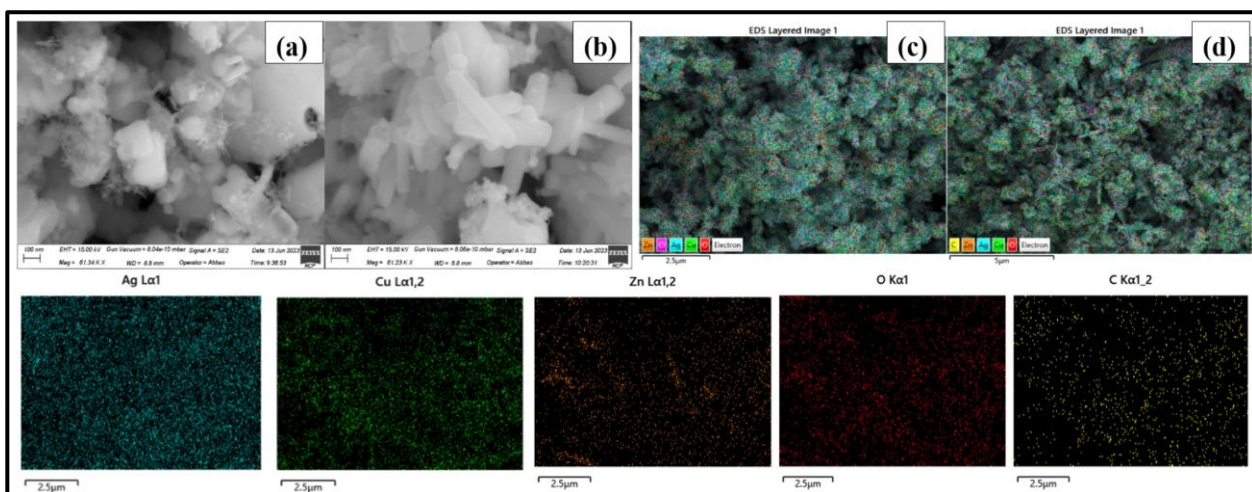


Figure 31: SEM micrographs (a, b), and EDS mapping (c, d) of ACZ-NC and MWCNTs@ACZ-NC (Lone, Rehman, Haq, Alkhuriji, et al., 2025).

Photocatalytic activity against R-6G under solar light from June 3-14, 2024 showed ACZ-NC achieved 97.31% degradation, MWCNTs@ACZ-NC achieved 99.61% degradation, and catalyst-free sample showed only 3.52% degradation. Rate constants were 0.05368 min^{-1} for ACZ-NC, 0.10012 min^{-1} for MWCNTs@ACZ-NC, and 5.90528 min^{-1} for catalyst-free sample. The superior performance of MWCNT-modified sample was attributed to increased conductivity and improved electron-hole separation. pH effect studies on MWCNTs@ACZ-NC showed degradation percentages of 68.38% at pH 4, 72.59% at pH 5, 76.91% at pH 6, 81.1% at pH 7, 85.334% at pH 8, 89.4% at pH 9, 93.74% at pH 10, 97.21% at pH 11, 99.61% at pH 12, and 96.76% at pH 13. Degradation rate increased with increasing pH due to binary existence of R-6G in ionic (R6G^+) and non-ionic forms, with non-ionic form increasing reactivity in basic environment allowing greater dye accessibility during cavity contraction and extreme cavitation accelerating decomposition. Lower degradation at pH 13 compared to optimal pH was due to rapid hydroxyl radical scavenging at very high pH levels reducing availability for specific oxidation. Catalyst dose optimization showed degradation increasing from 78.96% to 99.61% as dose increased from 10 to 20 mg, then decreasing to 91.67% at 25 mg and 80.25% at 30 mg due to increased total surface area providing more active sites at optimal dose, while higher doses caused nanoparticle agglomeration, reduced photon interaction, and less efficient light absorption. Initial concentration studies showed degradation percentages of 72.97%, 89.26%, 99.61%, 92.79%, and 83.05% at 5, 10, 15, 20, and 25 ppm respectively, with maximum at 15 ppm and decrease at higher concentrations due to reactive center saturation and interference with light-catalyst surface interaction. Reusability studies over five consecutive cycles showed degradation percentages of 99.61%, 98.21%, 93.74%, 87.65%, and 81.96% for cycles 1 through 5, with initial high efficiency due to pristine catalyst state and gradual decrease due to catalyst deactivation, structural alterations, surface impurities, and dye adsorption during recycling.

Main factors contributing to catalyst deactivation over 4-5 cycles include: (1) surface saturation and fouling by adsorbed dye molecules and intermediates; (2) pore blockage from accumulated by-products (confirmed by BET showing pore volume decrease); (3) structural changes and leaching of active metal ions (Zn^{2+} , Cu^{2+} , Ni^{2+}); (4) nanoparticle agglomeration; (5) light penetration reduction from colored by-products. Strategies to improve long-term stability include: thermal treatment at 300-400°C to burn off organic residues; chemical washing with dilute acid or base; catalyst immobilization on supports (graphene, biochar); surface coating with PEG or silica; optimized washing using ethanol-water mixtures; and process optimization (pH 6-7, reduced reaction time, lower catalyst doses).

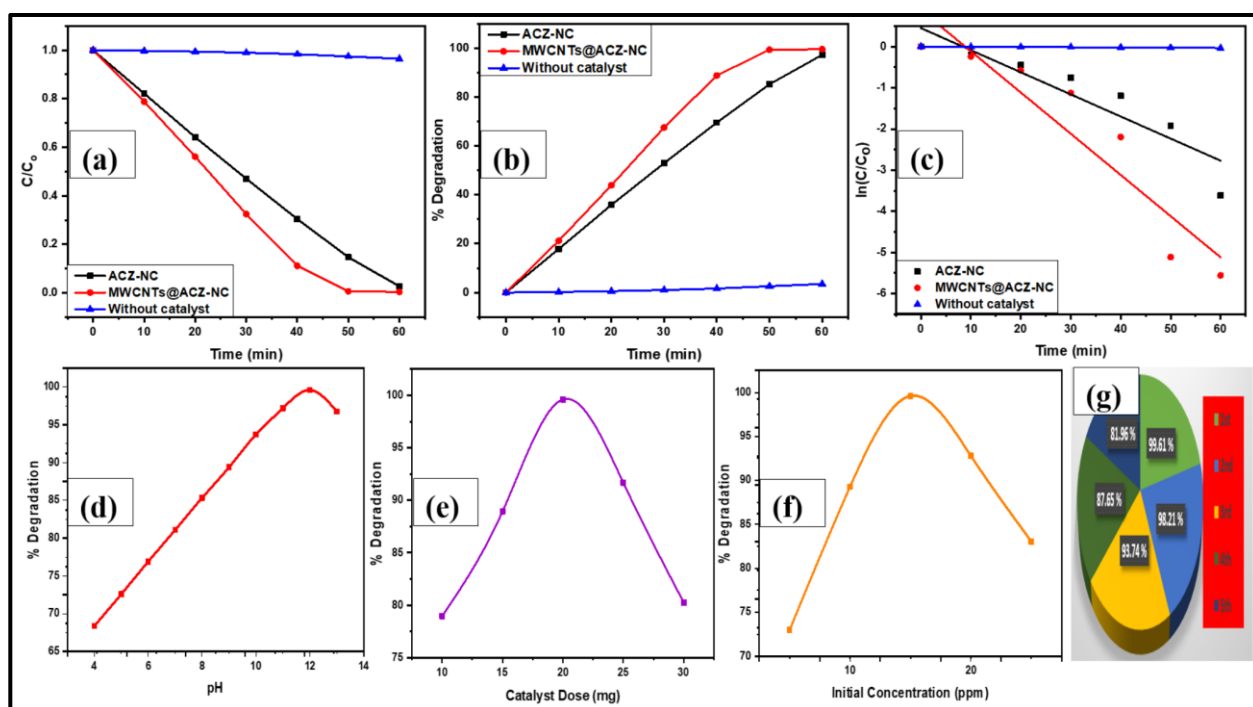


Figure 32: Photocatalytic data of the R-6G degradation of in the presence of ACZ-NC and MWCNTs@ACZ-NCs under simulated solar light; Percent degradation (a), rate constant (b), linear plot (c), effect of pH (d), effect of catalyst dose (e), effect of initial concentration (f) and reuse efficacy (g) of the MWCNTs@ACZ-NC during the photocatalytic experiment (Lone, Rehman, Haq, Alkhuriji, et al., 2025).

Antibacterial activity against *S. aureus* and *E. coli* showed ACZ-NC activity higher than MWCNTs@ACZ-NC, with inhibition zones of 22.5 mm (*S. aureus*) and 18.3 mm (*E. coli*) for ACZ-NC, and 20 mm (*S. aureus*) and 16 mm (*E. coli*) for MWCNTs@ACZ-NC, compared to standard drug showing 19.5 mm (*S. aureus*) and 19 mm (*E. coli*). MWCNT incorporation reduced activity due to CNTs occupying/covering binding sites responsible for direct interaction with bacterial cell, altering surface morphology, surface charge, and chemical functionality, and increasing particle size hindering ability to effectively penetrate bacterial cells.

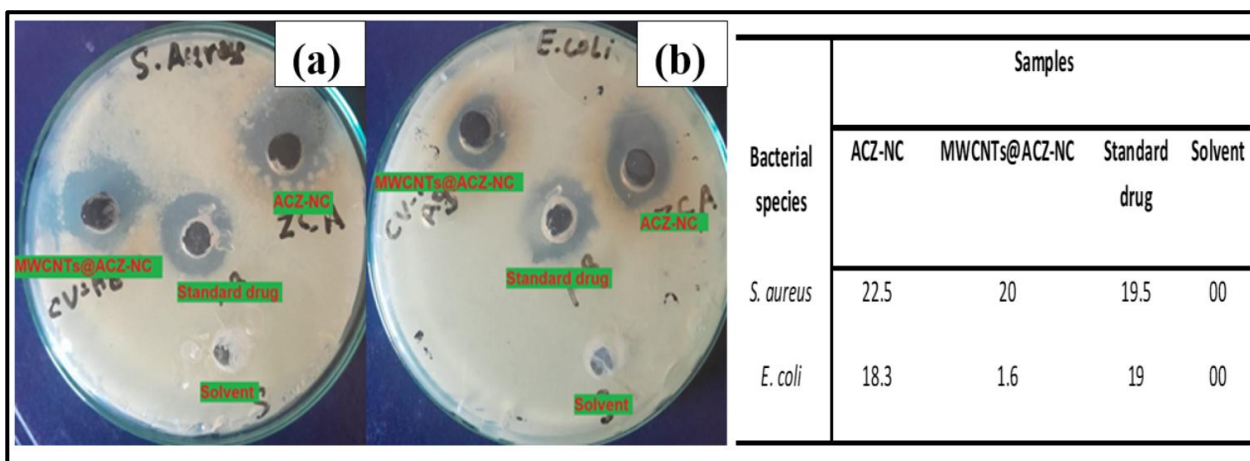


Figure 33: Antibacterial activity of the synthesized nanocomposites against *S. aureus* (a) and *E. coli* (b) (Lone, Rehman, Haq, Alkhuriji, et al., 2025).

Antioxidant activity against ABTS⁺ solution showed ACZ-NC scavenging activity from 26.076% to 91.336% at concentrations 5-400 $\mu\text{g/mL}$ with IC₅₀ 80.65 $\mu\text{g/mL}$, MWCNTs@ACZ-NC from 27.144% to 95.924% with IC₅₀ 59.22 $\mu\text{g/mL}$, and ascorbic acid IC₅₀ 49.79 $\mu\text{g/mL}$. Enhanced activity of MWCNT-modified sample was attributed to increased electron transfer, augmented active sites, and stabilized reactive species. Statistical analysis showed standard deviation 1.63, 1.64, and 1.75 for ACZ-NC, MWCNTs@ACZ-NC, and ascorbic acid, with variance 2.65, 2.71, and 3.09 respectively, indicating ACZ-NC demonstrated highest precision and consistency. Correlation between dose and % RSA was 0.110, 0.119, and 0.102 respectively, showing ascorbic acid strongest relationship.

Table 6: Antioxidant activity of ACZ-NC and MWCNTs@ACZ-NC against the ABTS free radicals (Lone, Rehman, Haq, Alkhuriji, et al., 2025).

Samples	Concentration ($\mu\text{g/mL}$)	%RSA	IC ₅₀ ($\mu\text{g/mL}$)	Variance (S ²)	Standard deviation (S)	Correlation between dose and %RSA
ACZ-NC	5	26.076	80.65	2.65	1.63	0.110
	25	34.188				
	50	48.228				
	100	65.916				
	200	81.004				
	400	91.336				
MWCNT@ACZ-NC	5	27.144	59.22	2.71	1.64	0.119
	25	36.432				
	50	53.796				
	100	71.124				
	200	84.612				
	400	95.924				
Ascorbic acid	5	21.92	92.74	3.09	1.75	0.102
	25	33.58				
	50	47.956				
	100	57.396				
	200	83.976				
	400	94.068				

MWCNT incorporation in metal oxide nanocomposites consistently enhanced photocatalytic and antioxidant properties while having variable effects on antibacterial activity. The enhancement mechanisms include acting as electron highways accelerating charge separation and prolonging carrier lifetimes for photocatalysis, providing conductive pathways for efficient electron transfer, filling gaps between nanoparticles creating denser more compact structures, introducing new vibrational modes and enhanced fingerprint regions in FTIR, and stabilizing reactive species for antioxidant applications. The decrease in antibacterial activity when observed was attributed to shielding of active sites preventing direct bacterial interaction, altered surface chemistry and charge affecting bacterial membrane interaction, increased particle size hindering bacterial cell penetration, and agglomeration reducing effective surface area. These findings demonstrate that MWCNT modification is a valuable strategy for enhancing specific properties of metal oxide nanocomposites, with the choice of application determining whether MWCNT incorporation is beneficial.

MWCNTs act as "electron highways" or "electron sinks" that facilitate rapid transfer of photogenerated electrons away from the metal oxide surface. When the semiconductor absorbs photons ($h\nu \geq E_g$), electrons are excited from valence band to conduction band, creating electron-hole pairs. Due to the high electrical conductivity of MWCNTs and heterojunction formation, electrons are quickly transferred to the MWCNT network, significantly reducing electron-hole recombination probability. This directional electron movement increases charge carrier lifetime, leading to enhanced photocatalytic activity. Quantitative evidence: MWCNTs@CuO-NiO achieved 95.37% degradation vs 80.09% (rate constant +74.3%); MWCNTs@Ag₂O/CuO/ZnO achieved 99.61% vs 97.31% (rate constant +86.5%).

CONCLUSIONS

1. This study successfully demonstrates the development of diverse multifunctional nanomaterials for environmental and biomedical applications through innovative synthesis approaches including green synthesis using agricultural waste (*M. acuminata* peels) and medicinal plant extracts (*C. maxima*, *D. kaki*, *S. chirayita*), solvent-free mechanochemical grinding, modified Hummers' method, co-precipitation, and modified sol-gel techniques.

2. Single metal oxides (ZnO, Fe₂O₃) showed promising antibacterial (inhibition zones 14 mm for *E. coli*) and photocatalytic (99.42% R-6G degradation) activities, demonstrating the effectiveness of utilizing agricultural waste for nanomaterial synthesis.

3. Bimetallic oxides including CuO-NiO, CuO-ZrO₂, CuO-Fe₂O₃ and Zr-NiO/ZnO exhibited enhanced photocatalytic properties strongly influenced by calcination temperature, doping concentration, and synthesis method.

4. The critical trade-off between surface area and crystallinity was clearly demonstrated, with uncalcined Co-Cu-Zn-LHs showing highest activity (92.98 %) due to maximum surface area (84.87 m²/g) despite lower crystallinity, while CuO-ZrO₂ showed increased activity with calcination (77.27% at 900°C) due to enhanced crystallinity and homogeneity.

5. Trimetallic oxides including Co-Cu-Zn-LHs, Ag₂O-CuO-ZnO, TiO₂-doped SnO₂-ZrO₂, and SnO₂-NiO-CuO demonstrated multifunctional capabilities with exceptional photocatalytic activities up to 99.61% and strong antioxidant properties.

6. Layered double hydroxides proved highly effective, with Cr/Ni/Mg/Al-LDH (LDH-4) exhibiting 89.23% MO degradation with rate constant of 0.07427 min⁻¹ (approximately 16.5 times higher than undoped LDH-1), attributed to highly porous structure, increased surface area, synergistic effects of multiple metal cations, and enhanced charge separation with Cr addition causing new energy levels within the band gap.

7. Graphene oxide-metal oxide composites (rGO-ZSF, GO-SNC) demonstrated exceptional antibacterial activity with inhibition zones up to 31 mm due to synergistic effects between graphene sheets (providing bacterial cell penetration and entrapment) and metal oxide nanoparticles (providing metal cation release and ROS generation).

8. For antioxidant activity, GO showed exceptional radical scavenging (IC₅₀ 11.25 µg/mL for ABTS, 15.98 µg/mL for DPPH), outperforming SNC, GO-SNC, and even ascorbic acid standard (IC₅₀ 44.67 µg/mL).

9. MWCNTs-metal oxide composites (MWCNTs@CuO-NiO, MWCNTs@Ag₂O/CuO/ZnO) consistently enhanced photocatalytic and antioxidant properties through improved charge separation and electron transfer, with rate constants increasing from 0.02737 to 0.0477 min⁻¹ and IC₅₀ values decreasing from 116.52 to 84.61 µg/mL, while antibacterial effects varied depending on surface modification.

10. The mechanochemical synthesis approach offers distinct advantages including solvent-free operation, energy efficiency, environmental friendliness, scalability, and simplicity.

11. Green synthesis methods using plant extracts provide eco-friendly alternatives to chemical methods, reducing environmental impact and promoting sustainable development, with the added benefit that adsorbed phytochemicals contribute directly to biological activities.

12. The successful demonstration of multifunctional nanomaterials capable of simultaneous photocatalytic degradation, antibacterial activity, and antioxidant

protection opens new avenues for integrated environmental and biomedical solutions addressing global health challenges.

13. The research provides clear structure-property-performance correlations that guide rational material design, establishes scalable and cost-effective production routes, and demonstrates real-world applicability through reusability studies and optimization of practical parameters.

14. These developed nanomaterials show excellent potential for industrial wastewater treatment, drinking water purification, antibacterial and antioxidant applications, contributing significantly to sustainable development goals for clean water (SDG 6) and good health (SDG 3).

**“TIQXMMI” MTU HUZURIDAGI FUNDAMENTAL VA AMALIY
TADQIQOTLAR INSTITUTI HUZURIDAGI ILMIY DARAJALAR
BERUVCHI**

DSc.03/06.11.2025.K/FM.10.09 RAQAMLI ILMIY KENGASH

FUNDAMENTAL VA AMALIY TADQIQOTLAR INSTITUTI

SIRAJUL HAQ

**ATROF-MUHITNI MUHOFAZA QILISH MAQSADLARI UCHUN BIR
KOMPONENTLI METALL OKSIDLAR ASOSIDA
FUNKSIONALLASHTIRILGAN KO‘P KOMPONENTLI
NANOMATERIALLAR PLATFORMASI**

**02.00.04 - Fizik kimyo
(Kimyo fanlari)**

**E‘LON QILINGAN ILMIY ISHLAR BO‘YICHA DISSERTATSIYASIZ KIMYO
FANLARI BO‘YICHA FAN DOKTORI (DSc) ILMIY DARAJASINI OLISH UCHUN
TAQDIMNOMA**

Toshkent – 2026

Kimyoviy fanlar bo'yicha fan doktori (DSc) Taqdimnoma mavzusi O'zbekiston Respublikasi Vazirlar Mahkamasi huzuridagi Oliy attestatsiya komissiyasi B2026.3.DSc/K274 raqami bilan ro'yxatga olingan

Taqdimnoma "TIQXMMI" MTU huzuridagi Fundamental va amaliy tadqiqotlar institutida bajarilgan.

Taqdimnoma uch tilda ingliz, o'zbek va rus (rezyume) Ilmiy Kengashning internet sahifasida www.ifar.uz va "Ziyonet" axborot-ta'lim portalida (www.ziyonet.uz) joylashtirilgan.

Ilmiy maslahatchi:

Razzokov Jamoliddin Inotullayevich

Kimyo fanlari doktori

Taqdimnoma "TIQXMMI" MTU huzuridagi Fundamental va amaliy tadqiqotlar instituti huzuridagi ilmiy darajalar beruvchi DSc.03/06.11.2025.K/FM.10.09 raqamli Ilmiy Kengashning "____"- "____" 2026-yil soat ____ dagi majlisda bo'lib o'tadi (Manzil: 100000, Toshkent shahri, Qori Niyoziy ko'chasi, 39A, Tel.: 71 237-09-61; e-mail: info@ifar.uz).

Taqdimnoma bilan "TIQXMMI" MTU huzuridagi Fundamental va amaliy tadqiqotlar instituti Axborot-resurs markazida tanishish mumkin (No ____ raqam bilan ro'yxatga olingan). (Manzil: 100000, Toshkent shahri, Qori Niyoziy ko'chasi, 39A, IFAR, Xona-105, Tel.: 71 237-09-61).

Taqdimnoma 2026-yil "____" _____ kuni tarqatildi.

(2026-yil "____" _____ reestr bayonnomasi.

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KIRISH

Mavzuning dolzarbligi. Ushbu taqdimnomada keltirilgan tadqiqot zamonamizning eng dolzarb ekologik muammolaridan biri – suv resurslarining organik bo‘yoq moddalar bilan ifloslanishi masalasiga bag‘ishlangan. UNESCO tomonidan BMTning 2023-yilda Nyu-York shahrida o‘tkazilgan Suv konferensiyasida taqdim etilgan hisobotga ko‘ra, dunyo bo‘yicha taxminan 2 milliard kishi, ya’ni Yer aholisi umumiy sonining 26 foizi, xavfsiz ichimlik suvi bilan ta’minlanmagan. Bu shunchaki statistik ko‘rsatkich emas, balki milliardlab insonlarning salomatligi va munosib hayot kechirish imkoniyatiga har kuni salbiy ta’sir ko‘rsatayotgan global muammodir. Suvning ifloslanishi diareya kasalliklari oqibatidagi o‘limlarning 70 foizga, shuningdek, qorin tifi (8%), paratif (20%) va quyi nafas yo‘llari infeksiyalari (2%) bilan bog‘liq o‘lim holatlariga sabab bo‘lmoqda. To‘qimachilik sanoatining o‘zi har yili ishlab chiqarilgan bo‘yoqlarning taxminan 10–25 foizini chuchuk suv havzalariga chiqaradi, bunda global bo‘yoq ishlab chiqarish hajmi yiliga 1,3 million tonnaga yetadi. Ushbu bo‘yoqlar tarkibida naftalin va benzamin kabi aromatik birikmalar mavjud bo‘lib, ular toksik, kanserogen va mutagen xususiyatlarga ega. Natijada siydik pufagi saratoni, markaziy asab tizimi kasalliklari, dermatit, allergik konyunktivit, rinit, kasbiy astma hamda boshqa turli allergik reaksiyalar rivojlanishi mumkin.

Jahon sog‘liqni saqlash tashkiloti (JSST) antimikrob rezistentlikni (AMR) global sog‘liqni saqlash tizimi oldidagi eng muhim o‘nta tahdiddan biri sifatida e’tirof etgan. Mazkur muammo har yili taxminan 1,27 million insonning o‘limiga sabab bo‘lmoqda. Antibiotiklardan ortiqcha va noto‘g‘ri foydalanish oqibatida dunyo bo‘ylab ko‘p dori vositalariga chidamli bakterial shtammlar shakllanib, an’anaviy davolash usullarining samaradorligi keskin pasaygan. So‘nggi o‘n yilliklarda yangi antibiotiklar sinflarini yaratish jarayoni deyarli to‘xtab qolgan bo‘lib, amaliyotga juda kam sonli yangi preparatlar joriy etilgan. Agar zarur choralar ko‘rilmasa, 2050-yilga borib AMR tufayli yuzaga keladigan iqtisodiy zarar 100 milliard AQSh dollariga yetishi prognoz qilinmoqda. Mazkur tadqiqot doirasida ishlab chiqilgan antibakterial nanomateriallar bakterial infeksiyalarga qarshi kurashishda mutlaqo yangi yondashuvni taklif etadi. Muayyan hujayra darajasidagi jarayonlarni nishonga oluvchi antibiotiklardan farqli ravishda (bu bakteriyalarning bitta mutatsiya orqali rezistentlik hosil qilishiga imkon yaratadi), metall oksidli nanozarrachalar bir vaqtning o‘zida bir nechta ta’sir mexanizmlarini amalga oshiradi. Ular bakteriya hujayra membranasini bevosita kontakt orqali fizik-kimyoviy shikastlaydi; hayotiy ahamiyatga ega bo‘lgan tiol guruhli fermentlar bilan o‘zaro ta’sirlashuvchi metall kationlarini (Zn^{2+} , Cu^{2+} , Ag^+ , Ni^{2+} va Fe^{3+}) ajratib chiqaradi; hujayra komponentlarini oksidlovchi zararlanishga olib keluvchi reaktiv kislorod turlarini hosil qiladi; shuningdek, kichik o‘lchamdagi nanozarrachalar bakteriya hujayrasi ichiga kirib, uning ichki tuzilishiga zarar yetkazadi. Tadqiqot natijalariga ko‘ra, rGO–ZSF nanokompoziti *Escherichia coli* (*E. coli*) ga nisbatan 31 mm va

Staphylococcus aureus (*S. aureus*) ga nisbatan 29 mm ingibirlash zonasini hosil qilgan bo'lib, bu standart antibiotik nazoratiga (mos ravishda 21 mm va 20 mm) nisbatan sezilarli darajada yuqori ko'rsatkichdir. Ushbu natijalar mazkur nanokompozitning antibiotiklarga chidamli bakterial shtammlarga qarshi ham yuqori samaradorlikka ega bo'lishi mumkinligini ko'rsatadi.

Oksidlovchi stress – bu reaktiv kislorod va reaktiv azot turlarining ortiqcha hosil bo'lishi hamda ularni zararsizlantiruvchi antioksidant himoya tizimi imkoniyatlari o'rtasidagi nomutanosiblik holati bo'lib, u saraton, yurak-qon tomir kasalliklari, qandli diabet, neyrodegenerativ kasalliklar (Altsgeymer va Parkinson kasalliklari), astma, erta qarish hamda surunkali yallig'lanish jarayonlari kabi ko'plab kasalliklarning rivojlanishida muhim omil hisoblanadi. Reaktiv kislorod turlari (gidroksil radikallari, superoksid anionlari va atomar kislorod) hamda reaktiv azot turlari (peroksinitrit) me'yoridan ortiq hosil bo'lganda, ular DNKni zararlab mutatsiyalar hosil qiladi va saraton rivojlanishiga sabab bo'ladi. Oqsillarni oksidlab fermentlarni faolsizlantiradi hamda hujayra membranalarining yaxlitligi va funksional xususiyatlarini buzadi. Mazkur tadqiqotda sintez qilingan nanomateriallarning antioksidant faolligi juda yuqori bo'lib, GO materiali uchun ABTS radikaliga nisbatan IC_{50} qiymati 11,25 $\mu\text{g/mL}$ va DPPH radikaliga nisbatan 15,98 $\mu\text{g/mL}$ ni tashkil etdi. Ushbu ko'rsatkichlar standart antioksidant hisoblangan askorbin kislotaning IC_{50} qiymati (44,67 $\mu\text{g/mL}$) bilan taqqoslaganda unga yaqin yoki undan ham yuqori samaradorlikni namoyon etadi. Ushbu antioksidant ta'sir mexanizmlari sp^2 -gibridlangan uglerod markazlarida radikal-adduktlarning hosil bo'lishi, elektron almashinuvi hamda funksional guruhlardan vodorod atomining donorligi orqali amalga oshadi. Natijada erkin radikallarni samarali neytrallashning bir nechta parallel yo'llari ta'minlanadi.

Mavzuning zarurati. Ushbu tadqiqotni amalga oshirish zarurati atrof-muhit degradatsiyasining tobora jadallashib borayotgani va uning inson salomatligiga bevosita salbiy ta'siri bilan belgilanadi. So'nggi yuz yil davomida dunyoda suv iste'moli aholi sonining o'sish sur'atiga nisbatan ikki baravar tezroq, ya'ni olti barobar ortgan bo'lsa, suv resurslarining ifloslanishi natijasida ulkan hajmdagi suv manbalari foydalanishga yaroqsiz holga kelgan. Ekologik xavfsizlik choralarisiz amalga oshirilayotgan sanoatlashtirish daryolar, ko'llar va yer osti suvlarining keng ko'lamda ifloslanishiga olib kelmoqda. Rivojlanayotgan mamlakatlarda oqava suvlarning 80 foizdan ortig'i tozalashsiz tabiiy suv havzalariga chiqariladi, bu esa atrof-muhitning ifloslanishi, yuqumli kasalliklarning tarqalishi va qashshoqlikning davom etishiga sabab bo'luvchi uzluksiz salbiy siklni yuzaga keltiradi. Suvning ifloslanishi natijasida yuzaga keladigan iqtisodiy zarar nihoyatda katta bo'lib, u baliqchilik va qishloq xo'jaligi mahsuldorligining pasayishi, sog'liqni saqlash xarajatlarining ortishi, ko'chmas mulk qiymatining kamayishi hamda suvni tozalash infratuzilmasiga katta mablag'lar sarflanishini o'z ichiga oladi. Mavjud an'anaviy suvni tozalash texnologiyalari sanoat chiqindilarining tobora ortib borayotgan hajmi

va murakkab kimyoviy tarkibini samarali bartaraf etishga qodir emas. Jumladan, to‘qimachilik sanoatida 10 000 dan ortiq turdagi sintetik bo‘yoqlar ishlab chiqariladi va ularning aksariyati yorug‘lik ta‘siriga chidamli, yuvilishga bardoshli hamda kimyoviy jihatdan barqaror bo‘lishi uchun ishlab chiqilgan. Aynan ushbu xususiyatlar ularni matolarni bo‘yash uchun samarali qilishi bilan birga, atrof-muhitda uzoq vaqt saqlanib qoluvchi barqaror ifloslantiruvchi moddalarga aylantiradi. Fotokatalizga asoslangan ilg‘or oksidlanish jarayonlari (Advanced Oxidation Processes, AOPs) bunday parchalanishga chidamli organik birikmalarni to‘liq mineralizatsiyalash imkonini beruvchi eng istiqbolli texnologiyalardan biri hisoblanadi. Shu sababli, quyosh nuri ta‘sirida faol ishlaydigan, yuqori samaradorlikka ega va iqtisodiy jihatdan arzon fotokatalizatorlarni yaratish nafaqat ilmiy nuqtai nazardan dolzarb, balki ekologik jihatdan ham muhim zarurat hisoblanadi.

Mazkur tadqiqotning zarurati, shuningdek, AMR keskin ortib borayotgani bilan ham izohlanadi. Bugungi kunda “antibiotiklardan keyingi davr” endi nazariy tushuncha emas, balki global sog‘liqni saqlash tizimi duch kelayotgan real muammoga aylangan. Karbapenemga chidamli *Enterobacteriaceae* (CRE), metitsillinga chidamli *Staphylococcus aureus* (MRSA), vankomitsinga chidamli *Enterococcus* (VRE) hamda ko‘p dori vositalariga chidamli *Pseudomonas aeruginosa* shtammlari dunyoning ko‘plab shifoxonalarida keng tarqalgan. Farmatsevtika kompaniyalari uchun yangi antibiotiklarni ishlab chiqish iqtisodiy jihatdan kam rentabelli bo‘lib qolganligi sababli, so‘nggi 30 yil davomida atigi bir nechta yangi antibiotik sinfi amaliyotga joriy etilgan. Nanomateriallar esa bakteriyalarga qarshi kurashishda mutlaqo yangi konsepsiyani taklif etadi. Ular bakteriyalar vaqt o‘tishi bilan rezistentlik hosil qilishi mumkin bo‘lgan yangi kimyoviy molekulalarni yaratish o‘rniga, hujayra membranasining fizik-kimyoviy buzilishi va oksidlovchi stressni yuzaga keltirish kabi ta‘sir mexanizmlaridan foydalanadi. Ushbu mexanizmlarga nisbatan bakteriyalarning evolyutsion moslashuvi va rezistentlik hosil qilishi ancha murakkab hisoblanadi. Shu sababli, yuqori samaradorlikka ega antibakterial nanomateriallarni yaratish bugungi kunda jamoat salomatligini saqlashning ustuvor yo‘nalishlaridan biri hisoblanadi.

Antioksidantlar bo‘yicha olib borilayotgan tadqiqotlarning zarurati esa surunkali kasalliklarning global miqyosdagi yuklamasi bilan belgilanadi. Yurak-qon tomir kasalliklari har yili 17,9 million kishining hayotiga zomin bo‘lib, bu dunyo bo‘yicha barcha o‘lim holatlarining 32 foizini tashkil etadi. Saraton kasalliklari yiliga 9,6 million, qandli diabet esa 1,6 million insonning o‘limiga sabab bo‘lmoqda. Bundan tashqari, millionlab bemorlar diabetning ko‘rlik, buyrak yetishmovchiligi va pastki oyoq-qo‘llarning amputatsiyasi kabi og‘ir asoratlaridan aziyat chekmoqda. Ushbu kasalliklarning barchasi uchun umumiy patogenetik omillardan biri oksidlovchi stress hisoblanadi. Maqsadli to‘qimalarga xavfsiz yetkazilishi mumkin bo‘lgan samarali antioksidantlar ushbu kasalliklarning tarqalishi va og‘ir oqibatlarini

sezilarli darajada kamaytirish imkoniyatiga ega. Mazkur tadqiqotda sintez qilingan nanomateriallar, xususan IC₅₀ qiymati 11,25 µg/mL gacha past bo'lgan namunalar, terapevtik antioksidant vositalar sifatida qo'llanish uchun katta istiqbolga ega ekanligini ko'rsatadi.

Tadqiqotning xalqaro konteksti. Mazkur tadqiqot atrof-muhitni muhofaza qilish va biotibbiyot sohalarida qo'llaniladigan nanomateriallar bo'yicha olib borilayotgan xalqaro ilmiy izlanishlar doirasida amalga oshirilgan. Web of Science ma'lumotlariga ko'ra, "photocatalytic degradation" yo'nalishidagi ilmiy nashrlar soni 2000-yildagi taxminan 500 tadan 2023-yilda 10 000 tadan ortiq ko'rsatkichga yetgan. Xuddi shuningdek, "nanozarrlarni yashil sintezi" mavzusidagi ilmiy maqolalar soni 2005-yildagi qariyb 100 tadan 2023-yilda 5 000 tadan oshgan, "antibakterial nanomateriallar" yo'nalishidagi nashrlar esa 2005-yildagi 200 ta atrofidan 2023-yilga kelib 8 000 tadan oshganligi aniqlangan. Ushbu ma'lumotlar nanomateriallar sohasidagi ilmiy tadqiqotlarning jadal sur'atlarda rivojlanayotganini yaqqol namoyon etadi.

Mazkur tadqiqot istiqbolli ilmiy yo'nalishlarga bir qator muhim ilmiy bo'shliqlarni to'ldirish orqali o'z hissasini qo'shadi. Jumladan, ko'p qavatli uglerod nanonaychalari (KDUN) bilan modifikatsiyalangan uch metall oksidli nanomateriallar bo'yicha tadqiqotlarning yetarli emasligi, *Diospyros kaki* (*D. kaki*) va *Swertia chirayita* (*S. chirayita*) o'simlik ekstraktleri yordamida yashil sintez usullarining kam o'rganilganligi, to'rt xil metall kationini o'z ichiga olgan qatlamli qo'shgidroksidlar (Layered Double Hydroxides, LDHs) bo'yicha ilmiy ma'lumotlarning cheklanganligi hamda fotokatalitik, antibakterial va antioksidant funksiyalarni bitta nanomaterial tarkibida uyg'unlashtirishga qaratilgan tadqiqotlarning yetarli darajada rivojlanmaganligi mazkur ishda bartaraf etilgan asosiy ilmiy muammolar hisoblanadi.

Mazkur tadqiqot o'zining ilmiy va amaliy natijalari bilan Birlashgan Millatlar Tashkilotining Barqaror rivojlanish maqsadlari (Sustainable Development Goals, SDGs) ning bir nechtasiga bevosita hissa qo'shadi va shu orqali uning xalqaro miqyosdagi ahamiyatini belgilovchi muhim konseptual asosni yaratadi.

Shuningdek, ushbu tadqiqot kelgusidagi xalqaro ilmiy izlanishlar uchun bir qator istiqbolli yo'nalishlarni ochib beradi. Xususan, turli mamlakatlarda haqiqiy sanoat oqava suvlari asosida pilot miqyosdagi sinovlarni o'tkazish orqali nanomateriallarning turli ekologik sharoitlardagi samaradorligini baholash; antibakterial va antisaraton xususiyatiga ega nanomateriallarni AQSh Oziq-ovqat va dori vositalari boshqarmasi (FDA) hamda Yevropa dori vositalari agentligi (EMA) kabi xalqaro me'yoriy talablar asosida klinik sinovlardan o'tkazish; turli hududlar uchun ularning ekologik barqarorligi va iqtisodiy samaradorligini baholash maqsadida hayotiy sikl tahlili (Life Cycle Assessment, LCA) hamda texnik-iqtisodiy tahlillarni (Techno-Economic Analysis, TEA) amalga oshirish; salohiyatni rivojlantirish va ilmiy bilim almashinuvi dasturlari orqali texnologiyalarni

rivojlanayotgan mamlakatlarga transfer qilish; nanomateriallarni sintez qilish, tavsiflash va ularni sinovdan o'tkazish metodologiyalarini xalqaro darajada standartlashtirish orqali ilmiy natijalarni o'zaro taqqoslash va me'yoriy tasdiqlash jarayonlarini soddalashtirish; shuningdek, ushbu ko'p funksiyali nanomateriallarning qo'llanish sohalarini vodorod ishlab chiqarish, CO₂ ni qaytarish, sensor texnologiyalari va boshqa ilg'or yo'nalishlarga kengaytirish imkoniyatlarini o'rganish istiqbolli ilmiy yo'nalishlar sifatida e'tirof etiladi.

Tadqiqotning maqsadi. Ushbu tadqiqotning umumiy maqsadi innovatsion sintez yondashuvlari-yashil sintez, mexanokimyoviy usullar, va modifikatsiyalangan zol-gel jarayonlari-yordamida oqova suvlar tarkibidagi organik ifloslantiruvchi moddalarni bartaraf etish, shuningdek, antibakterial faollik va kimyoviy antioksidant xususiyatlarni baholash uchun samarali, iqtisodiy jihatdan maqbul va ekologik barqaror ko'p funksiyali nanomateriallarni ishlab chiqishdan iborat. Shu bilan birga, nanomateriallarni ilmiy asosda va maqsadli loyihalashga yo'naltiruvchi tuzilish-xossa-samaradorlik o'rtasidagi kompleks o'zaro bog'liqliklarni aniqlash ham tadqiqotning muhim maqsadlaridan biridir.

Tadqiqotning vazifalari. Mazkur tadqiqotning asosiy vazifalari quyidagilardan iborat:

1. **Nanomateriallarni sintez qilish va tayyorlash.** Bir komponentli metall oksidlari (ZnO, Fe₂O₃), ikki komponentli metall oksidlari (CuO–ZrO₂, CuO–Fe₂O₃, CuO–NiO and Zr bilan legirlangan NiO–ZnO), uch komponentli metall oksidlari (Ag₂O–CuO–ZnO, TiO₂ bilan legirlangan SnO₂–ZrO₂, SnO₂–NiO–CuO), Co–Cu–Zn–LHs, qatlamli qo'sh gidroksidlar (Cr/Ni/Mg/Al-LDH) hamda ularning grafen oksidi (GO), qaytarilgan grafen oksidi (rGO) va KDUN asosidagi ilg'or kompozitlarini yashil sintez (*Musa acuminata* - banan po'stlog'i, *Diospyros kaki* (*D. kaki*)- xurmo, *Swertia chirayita* (*S. chirayita*) va *Citrus maxima* (*C. maxima*) ekstraktleri), erituvchisiz mexanokimyoviy maydalash, modifikatsiyalangan Hummers usuli, cho'ktirish hamda modifikatsiyalangan zol-gel usuli yordamida sintez qilish.

2. **Kompleks tavsiflash.** Sintez qilingan nanomateriallarning strukturaviy, morfologik, optik, element tarkibi, termik va tekstura xossalarini rentgen difraksiyasi (XRD), skanerlovchi elektron mikroskopiya (SEM), transmissiyali elektron mikroskopiya (TEM), energiya-dispersiv rentgen spektroskopiyasi (EDX), Furre transformatsiyali infraqizil spektroskopiyasi (FTIR), diffuz aks ettirish spektroskopiyasi (DRS), hamda BET sirt maydoni tahlili usullari yordamida o'rganish va ularning tuzilish-xossa o'rtasidagi bog'liqliklarini aniqlash.

3. **Fotokatalitik degradatsiyani o'rganish.** Quyosh va ultrabinafsha (UV) nurlanishi ostida turli organik bo'yoqlar, jumladan metil oranj (MO), Rodamin-6G (R-6G), Brilliant Yashil (BG), flyuoresein va 4-nitrofenolning fotokatalitik parchalanish samaradorligini baholash, shuningdek, reaksiya kinetikasi va fotokatalitik jarayon mexanizmlarini tadqiq etish.

4. Antibakterial faollikni baholash. Gram-musbat (*Staphylococcus aureus*) va Gram-manfiy (*Escherichia coli*) bakteriyalarga nisbatan bakteritsid faollikni agar quduq diffuziyasi usuli yordamida aniqlash hamda konsentratsiyaga bog‘liq antibakterial faollik profillarini belgilash.

5. Antioksidant faollikni aniqlash. ABTS va DPPH erkin radikallariga nisbatan radikallarni neytrallashtirish (scavenging) qobiliyatini baholash, IC_{50} qiymatlarini hisoblash hamda tuzilish–faollik (structure–activity) o‘zaro bog‘liqliklarini aniqlash.

6. Optimallashtirish tadqiqotlarini amalga oshirish. Nanomateriallarning funksional samaradorligiga kalsinatsiya harorati (kalsinatsiya qilinmagan holatdan 900°C gacha), eritma pH qiymati (2–13), katalizator miqdori (5–60 mg), ifloslantiruvchi moddaning boshlang‘ich konsentratsiyasi (5–30 ppm) hamda qayta foydalanish barqarorligi (4–5 sikl) kabi omillarning ta’sirini tizimli ravishda o‘rganish.

Ilmiy yangilik. Mazkur tadqiqot atrof-muhitni muhofaza qilish va biotibbiyot sohalari uchun mo‘ljallangan nanomateriallar yo‘nalishida bir qator muhim ilmiy yangiliklarni o‘zida mujassam etgan. Birinchidan, ushbu tadqiqot doirasida ilmiy adabiyotlarda ilgari qayd etilmagan bir nechta yangi nanokompozit tizimlar ilk bor sintez qilindi. Xususan, modifikatsiyalangan zol-gel usuli yordamida KDUN bilan modifikatsiyalangan $Ag_2O/CuO/ZnO$ uch komponentli metall nanokompoziti birinchi marta sintez qilinib, uning fotokatalitik, antibakterial va antioksidant xususiyatlarni bir vaqtning o‘zida namoyon etuvchi yuqori samarali ko‘p funktsiyali material ekanligi aniqlandi. Shuningdek, $rGO-ZnO-SnO_2-Fe_2O_3$ komponentli nanokompoziti ham yangi material tizimi bo‘lib, unda qaytarilgan grafen oksidi uch xil metall oksidi bilan integratsiyalangan va biologik qo‘llanmalar uchun yaxshilangan funksional xususiyatlarni namoyish etgan. Bundan tashqari, Zr bilan legirlangan NiO/ZnO nanokompozitlari ilk bor *D. kaki* bargi ekstrakti yordamida yashil sintez usuli orqali tayyorlandi va bu legirlangan ikki komponentli metall oksidlar sintezi uchun yangi ekologik yondashuvni taklif etdi. Xuddi shuningdek, *S. chirayita* o‘simligi ekstrakti yordamida sintez qilingan TiO_2 bilan legirlangan SnO_2-ZrO_2 nanokompozitlari geteroo‘tish hosil qiluvchi yangi material kombinatsiyasi sifatida yaratildi. Tarkibida bir vaqtning o‘zida Cr^{3+} , Ni^{2+} , Mg^{2+} va Al^{3+} metall kationlarini saqlovchi $Cr/Ni/Mg/Al$ LDHs va $Co-Cu-Zn-LHs$ namunasi *C. maxima* barglari ekstrakti yordamida sintez qilinib, ularning MONing fotokatalitik degradatsiyasidagi samaradorligi tadqiq etildi. Bunday ko‘p komponentli LDH tizimlari ilgari ilmiy adabiyotlarda yetarli darajada o‘rganilmagan.

Ikkinchidan, tadqiqot ekologik barqaror nanomateriallar ishlab chiqarishga xizmat qiluvchi yangi sintez metodologiyalarini taklif etadi. Hovoncha va dasta (mortar–pestle) yordamida amalga oshiriladigan erituvchisiz mexanokimyoviy sintez usuli asosida $CuO-ZrO_2$, va $CuO-Fe_2O_3$ bimetall oksidli nanokompozitlari tayyorlandi. Ushbu usul an’anaviy solvotermal sintezga nisbatan ekologik jihatdan

xavfsizroq, sodda, tezkor, energiya tejamkor, sanoat miqyosiga moslashtirish imkoniyatiga ega bo‘lib, zararli organik erituvchilardan foydalanishni to‘liq bartaraf etadi. Shuningdek, *Musa acuminata* po‘stlog‘i, *Diospyros kaki* barglari, *Swertia chirayita* va *Citrus maxima* o‘simlik ekstraktlaridan qaytaruvchi va stabilizator sifatida foydalanilgan yashil sintez usuli zararli kimyoviy reagentlardan foydalanishni cheklash bilan birga, qishloq xo‘jaligi chiqindilarini qayta qiymatga ega resursga aylantirish imkonini yaratadi. Bundan tashqari, o‘simlik ekstraktlari tarkibidagi fitokimyoviy moddalar nanozarrachalar yuzasiga adsorbsiyalanishi natijasida ularning biologik faolligi sezilarli darajada ortishi kuzatildi.

Uchinchidan, mazkur tadqiqot bitta nanomaterialning o‘zida fotokatalitik, antibakterial va antioksidant xususiyatlarni birlashtirgan yangi ko‘p funksiyali platformalarni yaratdi. Bitta nanokompozit tizimda ushbu uch xil biologik va ekologik funktsiyani kompleks ravishda baholash materialshunoslik sohasida kam uchraydigan yaxlit ilmiy yondashuv hisoblanadi. Xususan, grafen oksidi asosidagi rGO–ZSF va GO–SNC nanokompozitlari hamda KDUN asosidagi KDUNs@CuO–NiO va KGUNs@Ag₂O/CuO/ZnO tizimlarida zaryad tashuvchilarning samarali ajralishi, elektronlarning tezroq ko‘chishi va solishtirma sirt maydonining ortishi hisobiga sinergik effekt kuzatildi. Natijada ushbu materiallarning fotokatalitik, antibakterial va antioksidant samaradorligi sezilarli darajada yaxshilandi.

To‘rtinchidan, tadqiqot davomida tuzilish–xossa–funktsional samaradorlik o‘rtasidagi bog‘liqliklar tizimli ravishda tahlil qilinib, nanomateriallar faolligining fundamental mexanizmlari yoritildi. Jumladan, kalsinatsiya harorati oshishi bilan kristallanish darajasi ortishi hamda solishtirma sirt maydonining kamayishi o‘rtasidagi muvozanat bir nechta nanomaterial tizimlarida eksperimental ravishda isbotlandi. Tadqiqot natijalari fotokatalitik faollikni belgilovchi asosiy omil kristallanish darajasi emas, balki materialning solishtirma sirt maydoni ekanligini ko‘rsatdi. Bundan tashqari, legirlash paradoksiga ham oydinlik kiritirildi. Ya’ni, Zr–NiO/ZnO tizimida Zr miqdorini 0,5% dan 1% gacha oshirish fotokatalitik samaradorlikni kutilganidek oshirmasdan, aksincha 86,45% dan 67% gacha kamaytirgani, taqiqlangan zona kengligi esa 3,43 eV dan 3,66 eV gacha oshirgani aniqlandi. Ushbu natijalar “legirlovchi element qancha ko‘p bo‘lsa, material shuncha samarali bo‘ladi” degan keng tarqalgan ilmiy qarashni qayta ko‘rib chiqish zarurligini ko‘rsatadi.

Shuningdek, KDUNning ikki tomonlama ta’siri ham tavsiflandi. KDUN bilan modifikatsiyalash fotokatalitik va antioksidant xususiyatlarni muntazam ravishda yaxshilagan bo‘lsa-da, ayrim hollarda antibakterial faollikning pasayishiga olib kelishi kuzatildi. Bu esa turli amaliy qo‘llanmalar uchun nanomaterial yuzasini modifikatsiyalash strategiyasi alohida tanlanishi lozimligini ko‘rsatadi.

Beshinchidan, mazkur tadqiqot yashil sintez orqali olingan nanozarrachalarning kimyoviy usulda sintez qilingan analoglariga nisbatan ustunligini ko‘rsatuvchi noyob qiyosiy natijalarni taqdim etdi. Olingan ma’lumotlar

o'simlik ekstraktlaridan adsorbsiyalangan fitokimyoviy birikmalar nanozarrachalarning faqat o'lchami va morfologiyasini boshqaribgina qolmay, balki ularning biologik faolligiga ham bevosita hissa qo'shishini ko'rsatdi.

Shuningdek, Cr/Ni/Mg/Al-LDH materiali 30 daqiqa ichida MOning 89,23% degradatsiyasini ta'minlab, $0,07427 \text{ min}^{-1}$ tezlik konstantasini namoyon etdi. Ushbu natijalar ilmiy adabiyotlarda keltirilgan o'xshash LDH tizimlari (odatda 90–180 daqiqa talab qilinadi) bilan taqqoslaganda sezilarli darajada yuqori samaradorlikni ko'rsatib, mazkur tadqiqotning ilmiy yangiligini va amaliy ahamiyatini yana bir bor tasdiqlaydi.

Tadqiqot natijalarining ishonchliligi. Mazkur tadqiqot natijalarining ishonchliligi barcha eksperimental ishlarda bir-birini to'ldiruvchi zamonaviy tavsiflash usullaridan kompleks va izchil foydalanish orqali ta'minlangan. Bu yondashuv olingan ma'lumotlarning aniqligi, takrorlanuvchanligi va ilmiy asoslanganligini kafolatlaydi. XRD yordamida nanomateriallarning faza tarkibi JCPDS (Joint Committee on Powder Diffraction Standards) standart ma'lumotlar asosida identifikatsiya qilindi. Kristallit o'lchamlari Debye–Scherrer tenglamasi ($D = K\lambda/\beta\cos\theta$) yordamida hisoblandi, shuningdek, kristall panjaradagi deformatsiyalar (lattice strain) tahlil qilindi. Difraksion cho'qqilarning barchasi tegishli JCPDS standartlari bilan mos kelgani sintez qilingan materiallarning faza tarkibi to'g'ri aniqlanganligini tasdiqlaydi. SEM va TEM yordamida nanomateriallarning morfologiyasi, zarracha o'lchamlari taqsimoti hamda mikrostrukturasi batafsil o'rganildi. Zarrachalar o'lchamini aniqlash uchun bir nechta mikroskopik tasvirlar ImageJ dasturi yordamida tahlil qilinib, statistik jihatdan ishonchli natijalar olindi. EDX sintez qilingan nanomateriallarning element tarkibi va tozalik darajasini tasdiqladi. Spektrlarda barcha tarkibiy elementlarga xos cho'qqilar kuzatildi hamda begona aralashmalar mavjud emasligi aniqlandi. FTIR yordamida funksional guruhlar identifikatsiya qilinib, metall–kislorod bog'larining hosil bo'lishi tasdiqlandi. Turli namunalarda spektral polosalarning joylashuvi o'zaro mosligi hamda kalsinatsiya haroratining oshishi bilan ularning intensivligidagi muntazam o'zgarishlar sintez jarayonining barqarorligini ko'rsatdi. DRS orqali materiallarning optik xossalari va taqiqlangan zona energiyasi Tauc tenglamasi ($ah\nu = A(h\nu - E_g)^n$) asosida aniqlandi. Bir necha marta o'tkazilgan o'lchovlar natijalarining o'zaro mos kelishi usulning yuqori takrorlanuvchanligini tasdiqladi. BET sirt maydoni tahlili yordamida azotning adsorbsiya–desorbsiya izotermalari asosida materiallarning solishtirma sirt maydoni, g'ovak diametri va g'ovak hajmi IUPAC tasnifi talablariga muvofiq aniqlandi. TGA natijasida nanomateriallarning termik barqarorligi baholandi. Bir necha marotaba qizdirish sikllarida kuzatilgan massaning kamayish profillari o'zaro mos bo'lib, materiallarning termik xususiyatlari yuqori darajada takrorlanuvchan ekanligini ko'rsatdi.

Mazkur tadqiqotda qo'llanilgan sintez usullari batafsil eksperimental metodika asosida amalga oshirildi. Jarayon davomida harorat, pH, eritma

konsentratsiyasi, reaksiya vaqti, aralashtirish tezligi hamda kalsinatsiya sharoitlari kabi barcha asosiy parametrlar qat'iy nazorat qilindi. Har bir sintez jarayoni 3–5 marta takrorlanib, natijalarning o'zaro farqi $\pm 5\%$ dan oshmagani aniqlanib, usullarning yuqori takrorlanuvchanligi tasdiqlandi. Biologik faollik bo'yicha olingan natijalarning ishonchliligi statistik tahlillar yordamida baholandi. Hisob-kitoblarda standart og'ish, dispersiya, IC_{50} qiymatlari hamda korrelyatsiya koeffitsiyentlari aniqlanib, eksperimental ma'lumotlarning ishonchliligi tasdiqlandi. Antibakterial faollikni aniqlashda har bir Petri idishida kamida 3 ta quduq, har bir tajribada esa kamida 3 ta Petri idishi foydalanildi. Olingan natijalarda standart og'ish qiymatlari odatda 1,09–1,83 mm oralig'ida bo'lib, tajribalarning yuqori aniqlik bilan bajarilganligini ko'rsatdi. Antioksidant faollikni baholashda IC_{50} qiymatlari doza–javob egri chiziqlari asosida hisoblandi. Korrelyatsiya koeffitsiyentlari (R^2) odatda 0,98 dan yuqori, standart og'ish qiymatlari esa 1,51–1,75 oralig'ida bo'lib, olingan natijalarning yuqori darajada mosligini tasdiqladi. Tadqiqot natijalari ilmiy adabiyotlarda keltirilgan ma'lumotlar hamda standart nazorat namunalar bilan taqqoslandi. Jumladan, antioksidant faollikni baholashda askorbin kislotasi, antibakterial faollikni baholashda esa siprofloksatsin va boshqa standart antibiotiklar nazorat namunasi sifatida qo'llanildi. Ushbu qiyosiy tahlillar olingan natijalarning ilmiy ahamiyati va ishonchliligini tasdiqladi. Fotokatalitik degradatsiya va dori moddasining ajralib chiqish jarayonlari psevdobirinchi tartibli hamda psevdodikkinchi tartibli kinetik modellar yordamida tavsiflandi. Modellash natijasida $R^2 > 0,98$ bo'lgan yuqori regressiya koeffitsiyentlari kuzatildi, bu esa taklif etilgan reaksiya mexanizmlarining to'g'riligini tasdiqlaydi. Katalizatorlarning amaliy qo'llash imkoniyatlarini baholash maqsadida ularning 4–5 marotaba qayta foydalanish xususiyati o'rganildi. Har bir siklda degradatsiya samaradorligining deyarli o'zgarmasligi materiallarning yuqori barqarorligi va uzoq muddatli foydalanish imkoniyatiga ega ekanligini ko'rsatdi. Shuningdek, nanomateriallarning funksional xossalarga ta'sir etuvchi asosiy omillar, jumladan eritma pH qiymati, katalizator miqdori, ifloslantiruvchi moddaning boshlang'ich konsentratsiyasi, reaksiya harorati hamda kalsinatsiya harorati tizimli ravishda optimallashtirildi. Bu esa materiallarning turli sharoitlardagi ishlash mexanizmini chuqur tushunish imkonini berdi. Fotokatalitik tajribalarda nazorat eksperimentlari ham amalga oshirildi. Xususan, faqat katalizator ishtirokidagi va faqat yorug'lik ta'siridagi tajribalar alohida o'tkazildi. Natijalar organik ifloslantiruvchi moddalarning parchalanishi oddiy adsorbsiya yoki fotoliz natijasida emas, balki aynan fotokatalitik jarayon hisobiga sodir bo'lganligini ishonchli tarzda tasdiqladi.

Tadqiqot natijalarining ahamiyati. Mazkur tadqiqot natijalari atrof-muhitni muhofaza qilish va oqava suvlarni tozalash sohasida yuqori samaradorlikni namoyon etib, muhim amaliy ahamiyatga ega ekanligini ko'rsatadi. O'tkazilgan fotokatalitik tadqiqotlar natijasida $KDUNs@Ag_2O/CuO/ZnO$ nanokompoziti yordamida Rodamin-6G (R-6G) ning 99,61%, yashil sintez orqali olingan temir oksidi

nanozarrachalari yordamida 99,42%, KDUNs@CuO–NiO nanokompoziti yordamida 95,37% hamda SnO₂–ZrO₂ nanokompoziti yordamida 4-nitrofenolning 93,57% fotokatalitik degradatsiyasi ta'minlandi. Ushbu ko'rsatkichlar ilmiy adabiyotlarda keltirilgan o'xshash fotokatalizatorlar natijalari bilan taqqoslaganda yuqori samaradorlikni namoyish etadi. Fotokatalitik jarayonlarning kinetikasi ham yuqori samaradorlikni tasdiqlaydi. Xususan, KDUNs@Ag₂O/CuO/ZnO uchun 0,10012 min⁻¹, Cr/Ni/Mg/Al-LDH materiali uchun esa 0,07427 min⁻¹ tezlik konstantalarining aniqlanishi organik ifloslantiruvchi moddalarni qisqa vaqt ichida samarali parchalanishini ko'rsatadi. Bundan tashqari, fotokatalizatorlarning quyosh nuri ta'sirida faol ishlashi energiya sarfini va ekspluatatsion xarajatlarni sezilarli darajada kamaytiradi. Bu esa mazkur texnologiyani suv resurslari ifloslanishi va energiya taqchilligi bir vaqtda kuzatiladigan rivojlanayotgan mamlakatlarda amaliy qo'llash uchun ayniqsa istiqbolli yechimga aylantiradi. Tadqiqot natijalari biotibbiyot sohasida ham katta amaliy salohiyatga ega ekanligini ko'rsatdi. Olingan nanomateriallar Gram-musbat va Gram-manfiy bakteriyalarga qarshi yuqori antibakterial faollik namoyon etdi. Jumladan, rGO–ZSF nanokompoziti *Escherichia coli* ga nisbatan 31 mm inhibitsiya zonasini hosil qilib, antimikrob rezistentlik muammosini bartaraf etishga xizmat qiluvchi istiqbolli material sifatida namoyon bo'ldi. Shuningdek, kalsinatsiya qilinmagan namunalarning antibakterial faolligi (31 mm) kalsinatsiya qilingan namunalarga (29 mm) nisbatan yuqori ekanligi aniqlandi. Grafen oksidi asosidagi nanokompozitlar (24–31 mm) modifikatsiyalanmagan metall oksidlariga (7–24 mm) hamda standart antibiotiklarga (16–20 mm) nisbatan sezilarli darajada yuqori antibakterial faollikni namoyon etdi. Ushbu natijalar antibiotiklarga chidamli bakterial shtammlarga qarshi kurashish uchun bir nechta samarali strategiyalarni taklif etadi.

Tadqiqot davomida sintez qilingan nanomateriallar yuqori antioksidant faollik ham namoyon etdi. Xususan, grafen oksidi uchun ABTS radikaliga nisbatan IC₅₀ = 11,25 µg/mL, DPPH radikaliga nisbatan esa IC₅₀ = 15,98 µg/mL qiymatlari aniqlandi. Ushbu natijalar materiallarning erkin radikallarni samarali neytrallash qobiliyatiga ega ekanligini va oksidlovchi stress bilan bog'liq kasalliklar, jumladan saraton, yurak-qon tomir kasalliklari, qandli diabet hamda neyrodegenerativ kasalliklarning oldini olish va davolashda istiqbolli terapevtik vosita bo'lishi mumkinligini ko'rsatadi. Ayniqsa, grafen oksidining IC₅₀ = 11,25 µg/mL ko'rsatkichi standart antioksidant bo'lgan askorbin kislotasining (IC₅₀ = 44,67 µg/mL) qiymatiga nisbatan qariyb to'rt baravar yuqori samaradorlikni namoyon etdi. Ushbu natija antioksidant terapiya yo'nalishida yangi nanomateriallar asosidagi dori vositalarini ishlab chiqish uchun keng istiqbollarni ochib beradi. Mazkur tadqiqot materialshunoslik sohasiga ham muhim ilmiy hissa qo'shdi. Xususan, kalsinatsiya haroratining kristallanish darajasi, solishtirma sirt maydoni va taqiqlangan zona energiyasiga ta'siri tizimli ravishda o'rganilib, tuzilish–xossa–funktional samaradorlik o'rtasidagi fundamental bog'liqliklar aniqlandi. Bu natijalar

nanomateriallarni ilmiy asoslangan holda loyihalash uchun muhim nazariy asos yaratadi.

Tadqiqot natijalari shuni ko'rsatdiki, kalsinatsiya qilinmagan Co-Cu-Zn-LHs, nanokompoziti nisbatan past kristallanish darajasiga ega bo'lishiga qaramay, 92 m²/g solishtirma sirt maydoni hisobiga 83,73% fotokatalitik samaradorlikni namoyon etdi. Aksincha, CuO-ZrO₂ tizimida fotokatalitik faollik kalsinatsiya haroratining oshishi bilan ortib, 900°C da 77,27% ga yetdi. Ushbu natijalar turli nanomaterialda fotokatalitik faollikni belgilovchi asosiy omillar bir-biridan farq qilishini va optimallashtirish universal qonuniyatlarga emas, balki har bir materialning o'ziga xos xususiyatlariga asoslanishi zarurligini ko'rsatadi. Shuningdek, CuO-Fe₂O₃ tizimida solishtirma sirt maydonining 152,53 m²/g dan 1,78 m²/g gacha kamayishi fotokatalitik samaradorlikning 88,95% dan 59,19% gacha pasayishi bilan birga kuzatildi. Bu esa fotokatalitik jarayonlarda aynan solishtirma sirt maydoni asosiy kattaliklardan biri ekanligini yana bir bor tasdiqlaydi.

Mazkur tadqiqot yashil sintez usulining ustunliklarini ham yaqqol namoyish etdi. *Musa acuminata* (banan) po'stlog'i ekstrakti yordamida sintez qilingan temir oksidi nanozarrachalari R-6G bo'yog'ining 99,42% parchalanishini ta'minlab, kimyoviy usullar bilan sintez qilingan ko'plab analog nanomateriallarga nisbatan yuqori samaradorlik ko'rsatdi. Organik chiqindilar (banan po'stlog'i) hamda dorivor o'simliklar (*Diospyros kaki*, *Swertia chirayita* va *Citrus maxima*) ekstraktlaridan foydalanish ekologik xavfsiz, iqtisodiy jihatdan arzon va mahalliy sharoitlarga moslashtirilishi mumkin bo'lgan nanomateriallar ishlab chiqarish texnologiyasini taklif etadi. Bundan tashqari, mexanokimyoviy sintez usuli erituvchisiz amalga oshirilishi, energiya tejamkorligi, ekologik xavfsizligi, sanoat miqyosida qo'llash imkoniyati hamda texnologik soddaligi bilan ajralib turadi. Shu sababli, ushbu usul barqaror fotokatalizatorlar ishlab chiqarish uchun istiqbolli va amaliy jihatdan samarali alternativ texnologiya hisoblanadi. Mazkur tadqiqot natijalari Birlashgan Millatlar Tashkilotining Barqaror rivojlanish maqsadlari)ning 3-maqsadi, "Sog'lom turmush va farovonlik" hamda 6-maqsadi, "Toza suv va sanitariya"ga bevosita hissa qo'shadi. Shu jihatdan ushbu tadqiqot global ekologik va sog'liqni saqlash muammolarini hal etishga qaratilgan xalqaro ilmiy tashabbuslarning muhim tarkibiy qismi sifatida e'tirof etilishi mumkin.

Tadqiqot natijalarini amaliyotga joriy etish. Mazkur doktorlik tadqiqoti doirasida olingan ilmiy natijalar yuqori ta'sir ko'rsatkichiga ega xalqaro ilmiy jurnallarda nashr etilgan bo'lib, ular Scopus ma'lumotlar bazasidagi iqtibos ko'rsatkichlari bilan tasdiqlanganidek, jahon ilmiy hamjamiyati tomonidan sezilarli darajada e'tirof etilgan. *Materials Research Express* jurnalida 2024-yilda chop etilgan "Solar light-induced degradation of hazardous organic pollutants using *Diospyros kaki* mediated green synthesized zirconium doped nickel oxide-zinc oxide nanocomposite" nomli maqola 3 ta iqtibos olgan bo'lib, Scopus bazasida 60% va uning Field-Weighted Citation Impact (FWCI) ko'rsatkichi 0,35 ni tashkil etadi. *Arabian Journal of Chemistry* jurnalida 2023-yilda chop etilgan "Antibacterial and

antioxidant screening applications of reduced-graphene oxide modified ternary $\text{SnO}_2\text{-NiO-CuO}$ nanocomposites” nomli maqola 21 ta iqtibos olgan bo‘lib, 89% hamda FWCI 1,40 ko‘rsatkich qayd etgan. Ushbu natija mazkur tadqiqotning tegishli ilmiy yo‘nalish va nashr yili bo‘yicha jahon miqyosidagi o‘rtacha iqtibos ko‘rsatkichidan sezilarli darajada yuqori ekanligini ko‘rsatadi. *RSC Advances* jurnalida 2025-yilda chop etilgan “Fabrication and structural analysis of CuO-NiO and MWCNTs@CuO-NiO hybrid nanostructures: versatile materials for environmental and biomedical remediation” nomli maqola 5 ta iqtibos olgan, 82-% va uning FWCI ko‘rsatkichi 0,71 ni tashkil etadi. Shuningdek, *RSC Advances* jurnalida 2025-yilda chop etilgan “Unveiling the physicochemical, photocatalytic, antibacterial and antioxidant properties of MWCNT-modified $\text{Ag}_2\text{O/CuO/ZnO}$ nanocomposites” nomli maqola 11 ta iqtibos olgan bo‘lib, 95-percentilda qayd etilgan hamda FWCI ko‘rsatkichi 2,38 ga teng. Ushbu maqola mazkur tadqiqot doirasida chop etilgan ishlar orasida eng yuqori iqtibos ta’siriga ega bo‘lib, natijalarning o‘z ilmiy yo‘nalishi bo‘yicha jahon o‘rtacha ko‘rsatkichiga nisbatan ikki martadan ortiq darajada iqtibos olinganligini ko‘rsatadi. *Desalination and Water Treatment* jurnalida 2024-yilda chop etilgan “Enhanced Photocatalytic Performance of Cr/Ni/Mg/Al Layered Double Hydroxides against Methyl Orange in Aqueous Solution” nomli maqola 6 ta iqtibos olgan, 75% va uning FWCI ko‘rsatkichi 0,75 ni tashkil etadi. Shuningdek, *Materials Research Express* jurnalida 2024-yilda chop etilgan “Solvent free fabrication and thermal tuning of copper oxide-zirconium dioxide nanocomposite for enhanced photocatalytic efficacy” nomli maqola 7 ta iqtibos olgan bo‘lib, 75% va FWCI ko‘rsatkichi 0,70 ga teng. Umuman olganda, mazkur nashrlar dunyoning turli mamlakatlaridagi mustaqil tadqiqotchilar tomonidan jami 53 marta iqtibos qilingan, bu esa ushbu doktorlik tadqiqoti doirasida olingan ilmiy natijalarning xalqaro ilmiy hamjamiyat tomonidan e’tirof etilganligi, iqtibos qilinganligi va keyingi ilmiy tadqiqotlarda foydalanilganligini yaqqol ko‘rsatadi. Tadqiqot natijalariga asoslangan ilmiy ishlarga keyingi nashrlarda *Scientific Reports*, *RSC Advances*, *Heliyon*, *Materials Science and Engineering: B*, *Journal of Environmental Chemical Engineering* va *Pharmaceuticals* kabi nufuzli xalqaro jurnallarda, shuningdek, boshqa ilmiy nashrlarda iqtiboslar berilgan. Mazkur iqtibos ko‘rsatkichlari tadqiqot natijalarining yuqori ilmiy sifatini, xalqaro miqyosdagi dolzarbligini va amaliy ahamiyatini tasdiqlaydi. Shu bilan birga, ular ishlab chiqilgan nanomateriallar hamda sintez usullarining atrof-muhitni remediatsiya qilish va biotibbiy davolash yo‘nalishlari rivojiga munosib ilmiy hissa qo‘shganligini ko‘rsatadi.

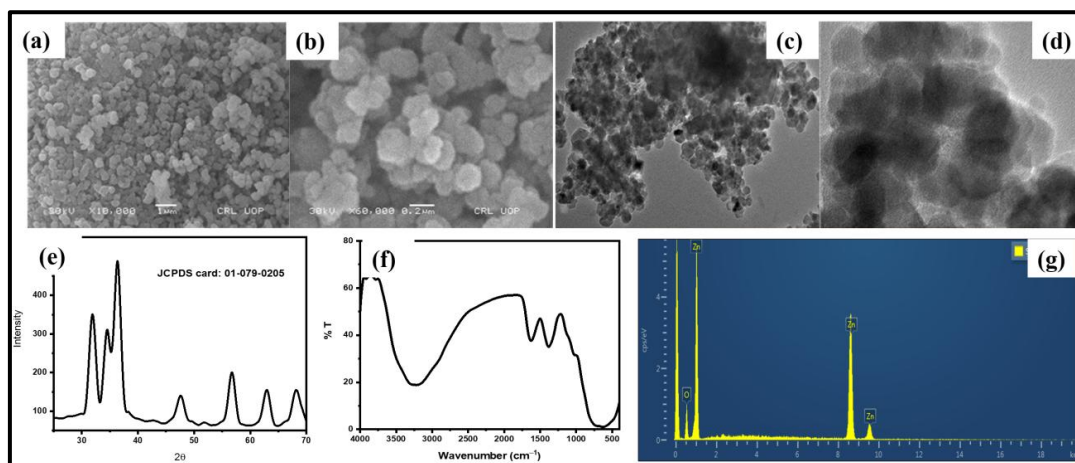
Tadqiqot ishining nashrlari. Mazkur DSc tadqiqoti doirasida olingan natijalar O‘zbekiston Respublikasi Oliy attestatsiya komissiyasi tomonidan D.Sc. dissertatsiyasining asosiy ilmiy natijalarini nashr etish uchun tavsiya etilgan hamda Web of Science ma’lumotlar bazasida indekslangan nufuzli ilmiy jurnallarda chop etilgan 12 ta taqrizdan o‘tgan ilmiy maqolada o‘z aksini topgan.

ASOSIY QISM

1-BOB. YAKKA METALL OKSIDLI NANOMATERIALLAR

1.1 Rux oksidi nanozarrachalari. Rux oksidi nanozarrachalari (ZnO-NZlar) $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ prekursori va KOH cho'ktiruvchi reagent sifatida qo'llanilgan iqtisodiy jihatdan samarali cho'ktirish usuli yordamida sintez qilindi. Sintez jarayonida rux xlorid distillangan suv va etanol aralashmasida eritilib, eritma 60°C haroratda qizdirildi. So'ngra eritmaga pH 10 ga yetguncha KOH tomchilab qo'shildi. Hosil bo'lgan cho'kma iliq distillangan suv bilan bir necha marta yuvildi va 100°C haroratda quritildi. Natijada oq rangli kukunsimon ZnO-NZlar olindi.

Rentgen difraksiyasi (XRD) tahlili sintez qilingan nanomaterialning geksagonal kristall tuzilishga ega ekanligini ko'rsatdi. Difraksion spektrda $31,90^\circ$ (100), $34,45^\circ$ (002), $36,27^\circ$ (101), $47,59^\circ$ (102), $56,63^\circ$ (110), $62,97^\circ$ (103) hamda $68,11^\circ$ (112) burchaklarda kuzatilgan xarakterli cho'qqilar JCPDS №01-079-0205 standart kartasi bilan to'liq mos keldi. Debye–Scherrer tenglamasi yordamida kristallitlarning o'rtacha o'lchami 25,84 nm, kristall panjaradagi deformatsiya esa 0,323% deb aniqlandi. Skanerlovchi elektron mikroskopiya (SEM) tahlili past kattalashtirishda nanozarrachalarning kuchli aglomeratsiyalanib, tekis sirt bo'ylab tartibsiz tarmoqsimon tuzilma hosil qilganini ko'rsatdi. Yuqori kattalashtirishda esa zarrachalar asosan sferik shaklga ega bo'lib, ularning o'lchami 88–121 nm oralig'ida, o'rtacha diametri esa 99,62 nm ekanligi aniqlandi. Transmissiyali elektron mikroskopiya (TEM) tahlili nanomateriallarning morfologiyasini yanada batafsil yoritdi. TEM tasvirlarida zarrachalar o'lchami 25–60 nm oralig'ida bo'lib, ular sferik va ko'pyoqli shakllarda uchrashi kuzatildi. Ayrim hududlarda yuqori sirt energiyasi ta'sirida nanozarrachalar o'zaro qo'shilib, plastinkasimon shakllarni hosil qilgan bo'lsa, boshqa hududlarda zarrachalar zich joylashganiga qaramay, ularning individual chegaralari aniq saqlanib qolgan. EDX tahlili nanomaterialning element tarkibi va yuqori tozalik darajasini tasdiqladi. Spektrda 0,9, 8,70 va 9,60 keV energiyalarda rux (Zn) ga, 0,24 keV da esa kislorod (O) ga xos cho'qqilar kuzatildi. Elementlarning massa ulushi mos ravishda 80,3% Zn va 19,7% O ni tashkil etib, begona elementlarning mavjud emasligi sintez qilingan nanozarrachalarning yuqori darajada toza ekanligini tasdiqladi. Furiye transformatsiyali infraqizil spektroskopiya (FTIR) tahlili natijalariga ko'ra, $3539\text{--}3376\text{ cm}^{-1}$ diapazonda O–H bog'ining valent tebranishlari, $1626,92\text{ cm}^{-1}$ da O–H deformatsion tebranishi, $1379,56\text{ cm}^{-1}$ da M–OH bog'ining tebranishi, $1027,44\text{ cm}^{-1}$ da O–Zn–O bog'ining valent tebranishi hamda $673,71$ va $478,33\text{ cm}^{-1}$ da Zn–O bog'lariga xos valent va deformatsion tebranishlar kuzatildi. Ushbu natijalar rux oksidi nanozarrachalarining muvaffaqiyatli sintez qilinganligini va ularning kristall tuzilmasida Zn–O bog'larining shakllanganligini tasdiqlaydi.



1-rasm. Cho‘ktirish usuli yordamida sintez qilingan ZnO-NZlar ning SEM mikrograflari (a, b), TEM tasvirlari (c, d), XRD difraktogrammasi (e), FTIR spektri (f) va EDX spektri (g) (Azeem va boshq., 2024).

ZnO-NZlarning antibakterial faolligi agar quduq diffuziyasi usuli yordamida Gram-musbat *Staphylococcus aureus* va Gram-manfiy *Escherichia coli* bakteriyalariga nisbatan baholandi. Tajribalarda DMSO da 1 mg/mL konsentratsiyada tayyorlangan nanozarrachalar dispersiyasining 20–100 μ L hajmlari qo‘llanildi. Tadqiqot natijalari shuni ko‘rsatdiki, quduqlardagi ZnO suspenziyasi konsentratsiyasi ortishi bilan bakteriyalar o‘rishini ingibirlash darajasi ham ortib bordi. Bu esa ZnO-NZlarning antibakterial samaradorligi konsentratsiyaga bevosita bog‘liq ekanligini tasdiqlaydi. ZnO-NZlar *E. coli* ga nisbatan *S. aureus* ga qaraganda yuqoriroq antibakterial faollikni namoyon etdi. Xususan, 100 μ L konsentratsiyada *E. coli* uchun 14 mm, *S. aureus* uchun esa 10 mm ingibitsiya zonasi kuzatildi. Ushbu farq ZnO-NZlarning suvli muhitdagi kimyoviy xatti-harakati hamda ikki turdagi bakteriyalarning hujayra devori va tashqi membranasi kimyoviy tarkibidagi farqlar bilan izohlanadi. Zn^{2+} ionlari *E. coli* hujayra yuzasi bilan fosfolipidlar va lipopolisaxaridlar orqali kuchli bog‘lanadi. Aksincha, *S. aureus* ning Gram-musbat hujayra devorida mavjud bo‘lgan teyxoy kislotalari yuzaga qisman manfiy zaryad berganligi sababli, Zn^{2+} ionlari bilan o‘zaro ta’sir nisbatan kuchsizroq kechadi. ZnO-NZlarning antibakterial ta’sir mexanizmi bir nechta jarayonlarni o‘z ichiga oladi. Jumladan, nanozarrachalardan ajralib chiqadigan Zn^{2+} ionlari bakterial hujayra membranasi yaxlitligini buzadi, tiol guruhlarini tutuvchi hayotiy muhim bakterial fermentlar bilan o‘zaro ta’sirlashadi hamda reaktiv kislorod turlarini hosil qiladi. Natijada hujayra komponentlarida oksidlovchi shikastlanish yuzaga kelib, bakteriyalarning nobud bo‘lishiga olib keladi.

ZnO-NZlarining antioksidant faolligi ABTS erkin radikallarini neytrallash usuli yordamida baholandi hamda olingan natijalar standart antioksidant sifatida askorbin kislotasi bilan taqqoslandi. Tadqiqot natijalari shuni ko‘rsatdiki, har ikkala namunada ham konsentratsiya ortishi bilan erkin radikallarni neytrallash faolligi bosqichma-bosqich oshib bordi. ZnO-NZlarning antioksidant faolligi 50 μ g/ μ L konsentratsiyada 40,23% ni tashkil etgan bo‘lsa, 300 μ g/ μ L konsentratsiyada 98,01% gacha yetdi. Ushbu material uchun IC_{50} qiymati 83,89 μ g/ μ L ni tashkil etdi.

Taqqoslash uchun, askorbin kislotasi 300 $\mu\text{g}/\mu\text{L}$ konsentratsiyada 99,56% antioksidant faollikni namoyon etib, uning IC_{50} qiymati 77,35 $\mu\text{g}/\mu\text{L}$ ga teng bo'ldi. Konsentratsiya ortishi bilan antioksidant faollikning kuchayishi yuqori konsentratsiyalarda erkin radikallar bilan o'zaro ta'sirlashuvchi ZnO-NZlar sonining ortishi bilan izohlanadi. Natijada nanozarrachalar erkin radikallarni samarali neytrallab, ularning miqdorini kamaytiradi va hujayralarning oksidlovchi shikastlanishining oldini oladi. IC_{50} qiymati, ya'ni erkin radikallarning 50% ini ingibirlash uchun zarur bo'lgan konsentratsiya, ZnO-NZlarning standart antioksidantga yaqin darajadagi sezilarli antioksidant faollikka ega ekanligini ko'rsatdi. Natijalarning statistik tahlili ZnO-NZlar uchun 2,26 dispersiya va 1,51 standart og'ish qiymatlarini ko'rsatib, tajriba natijalarining yuqori darajada barqaror va takrorlanuvchan ekanligini tasdiqladi. Umuman olganda, mazkur tadqiqot oddiy va iqtisodiy jihatdan samarali usul yordamida sintez qilingan ZnO-NZlarning yuqori kristallik darajaga, notekis zarracha taqsimotiga, yuqori kimyoviy tozalikka, konsentratsiyaga bog'liq antibakterial faollikka hamda *Escherichia coli* ga nisbatan kuchliroq bakteritsid ta'sirga ega ekanligini ko'rsatdi. Shuningdek, ularning sezilarli antioksidant xususiyatlari ham tasdiqlanib, mazkur nanozarrachalar antibiotiklarga chidamli bakterial shtammlarga qarshi kurashish hamda oksidlovchi stress bilan bog'liq kasalliklarni davolashga qaratilgan biotibbiy qo'llanmalar uchun istiqbolli nanomateriallar ekanligi aniqlandi.

1-jadval. Agar quduq diffuziyasi usuli yordamida aniqlangan ZnO-NZlar ning bakteritsid faolligi natijalari (Azeem va boshq., 2024).

Species	Volume of ZnO-NPs in μL					-ve control
	20	40	60	80	100	
<i>S. aureus</i>	0.5	01	04	07	10	00
<i>E. coli</i>	1	02	07	10	14	00

2-jadval. ZnO-NZlar ning ABTS erkin radikallariga nisbatan antioksidant faolligi (Azeem va boshq., 2024).

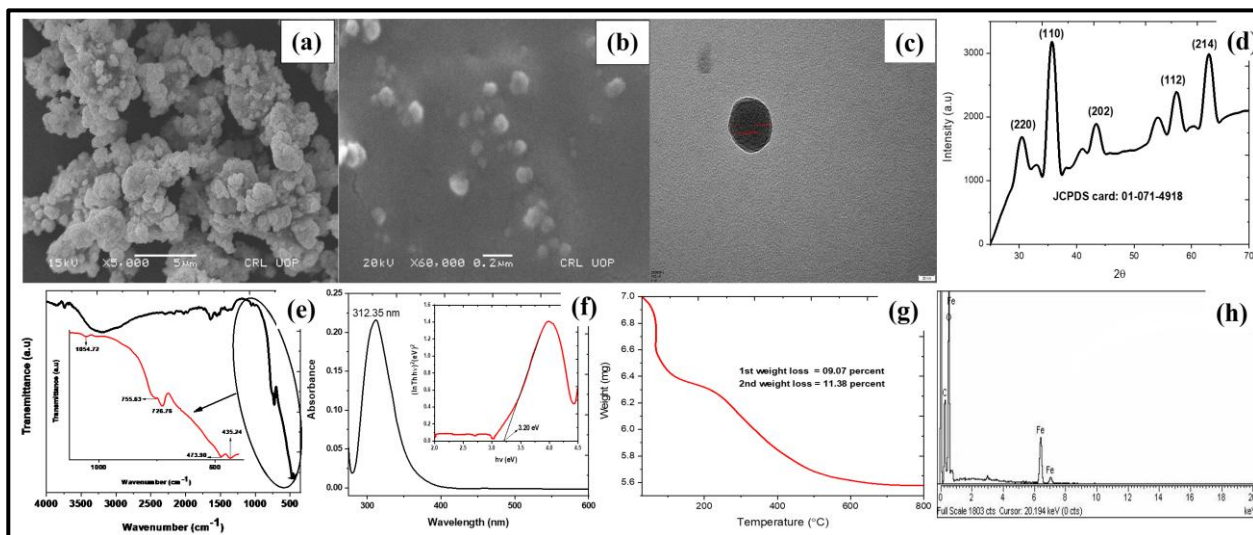
Sample	Concentration ($\mu\text{g}/\mu\text{L}$)	Activity (%)	IC_{50} ($\mu\text{g}/\mu\text{L}$)	Variance (S^2)	STD Dev.
ZnO-NPs	50	40.23	83.89	2.26	1.51
	100	54.02			
	200	81.34			
	300	98.01			
Ascorbic acid	50	41.34	77.35	2.25	1.51
	100	55.78			
	200	83.55			
	300	99.56			

1.2 *Musa acuminata* po'stlog'i ekstrakti yordamida sintez qilingan temir oksidi nanozarrachalari. TO-NZlar ekologik xavfsiz yashil sintez usuli yordamida sintez qilindi. Bunda *Musa acuminata* (banan) po'stlog'i ekstrakti bir vaqtning o'zida qaytaruvchi va stabilizator sifatida qo'llanildi. Ushbu bir idishli va past haroratli sintez usuli zararli kimyoviy reagentlardan foydalanishni bartaraf etishi hamda qishloq xo'jaligi chiqindilarini yuqori qo'shimcha qiymatga ega mahsulotlarga aylantirish imkonini berishi bilan ajralib turadi. O'simlik ekstraktini tayyorlash uchun tozalangan *Musa acuminata* po'stloqlari distillangan suvda 80°C haroratda 2 soat davomida qaynatildi. Natijada och sariq rangli xom ekstrakt hosil bo'lib, u filtrlanib, keyingi foydalanish uchun saqlandi. Nanozarrachalarni sintez qilish jarayonida $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ distillangan suvda eritilib, 15 mM konsentratsiyali eritma tayyorlandi. Ushbu eritma banan po'stlog'i ekstrakti bilan aralashtirilib, 50°C haroratda 250 ayl/min tezlikda 45 daqiqa davomida aralashtirildi. Reaksiya natijasida g'isht-qizil rangli cho'kma hosil bo'ldi. Hosil bo'lgan cho'kma 6 soat davomida saqlangandan so'ng, so'ng filtrlandi, issiq distillangan suv bilan yuvildi va 140°C da quritildi. *Musa acuminata* po'stlog'i qishloq xo'jaligi chiqindilarining keng tarqalgan turi bo'lib, tarkibida antioksidantlar, flavonoidlar va polifenollar kabi biologik faol birikmalarni saqlaydi. Ushbu fitokimyoviy moddalar organik qaytaruvchi va stabilizator sifatida temir ionlariga elektron berib ularni qaytaradi, so'ngra hosil bo'lgan nanozarrachalar yuzasiga adsorbsiyalanib, zarrachalar atrofida himoya qatlami hosil qiladi. Natijada nanozarrachalarning o'lchami va morfologiyasi

XRD tahlili difraktogrammada fitokimyoviy moddalarning mavjudligi bilan bog'liq bo'lgan biroz shovqinli fon kuzatilganligini, ya'ni kristall faza bilan bir qatorda ma'lum miqdorda amorf komponent ham mavjudligini ko'rsatdi. Difraksion cho'qqilar JCPDS №01-071-4918 standart kartasi bilan mos kelib, kubik kristall tuzilishga ega Fe_2O_3 kristallitlari muvaffaqiyatli hosil bo'lganligini tasdiqladi. Debye–Scherrer tenglamasi asosida kristallitlarning o'rtacha o'lchami 38,42 nm, kristall panjaradagi deformatsiya esa 0,149% deb aniqlandi. SEM tasvirlarida past kattalashtirishda zarrachalarning aksariyati yumaloq yoki deyarli yumaloq shaklda bo'lib, notekis taqsimlanganligi kuzatildi. Tasvirning chap pastki qismida ayrim zarrachalarning o'zaro birikib yirikroq agregatlar hosil qilgani, kichik zarrachalar esa yirik zarrachalar yuzasida joylashgani aniqlandi. Yuqori kattalashtirishdagi SEM tasvirlarida chegaralari aniq ko'rinadigan uchta mukammal sferik zarracha hamda bir-biri bilan qisman qo'shilgan, ammo yirik aglomeratlar hosil qilmagan bir nechta deyarli sferik zarrachalar kuzatildi. Ushbu hodisa nanozarrachalarning yuqori sirt energiyasi ta'sirida yuzaga kelgan qisman birikishi bilan izohlanadi. TEM tahlili nanomaterial morfologiyasini yanada batafsil yoritdi. TEM tasvirlarida yuzasi g'ovakli bo'lgan deyarli sferik zarrachalar kuzatildi va ularning o'rtacha o'lchami 56,22 nm ni tashkil etdi. Ushbu qiymat XRD orqali aniqlangan kristallit o'lchamidan deyarli ikki baravar katta bo'lib, bu holat o'simlik ekstraktidagi organik

birikmalarning nanozarrachalar yuzasida hosil qilgan qoplama qatlami bilan izohlanadi.

EDX tahlili temirning 0,6, 6,40 va 7,12 keV energiyalarda, kislorodning esa 0,50 keV da xarakterli cho‘qqilarini qayd etdi. Elementlarning massa ulushi 78,21% Fe va 21,79% O ni tashkil etdi. Bundan tashqari, namunani tayyorlashda ishlatilgan uglerod lentasi sababli uglerod signali ham kuzatildi. TGA natijalari massaning kamayishi ikki bosqichda sodir bo‘lganligini ko‘rsatdi. Birinchi bosqichda 48–130°C oralig‘ida 9,71% massa yo‘qotilishi kuzatildi, bu namlik va fizik adsorbsiyalangan suvning bug‘lanishi bilan bog‘liq. Ikkinchi bosqichda esa 220–535°C oralig‘ida 12,02% massa kamayishi qayd etildi, bu kimyoviy adsorbsiyalangan suvning ajralib chiqishi bilan izohlanadi. FTIR tahlili yuqori tozalikdagi TO-NZlar muvaffaqiyatli sintez qilinganligini tasdiqladi. Spekrda 3742,51 cm^{-1} da bog‘lanmagan suv molekulalariga, 3394,72–3038,59 cm^{-1} oralig‘ida O–H valent tebranishlariga, 1639,28 cm^{-1} da O–H deformatsion tebranishiga, 1054,72, 755,63 va 726,76 cm^{-1} da metall–kislorod bog‘larining valent va deformatsion tebranishlariga, shuningdek 473,90 va 435,24 cm^{-1} da Fe–O bog‘lariga xos kristall panjara tebranishlariga tegishli polosalar kuzatildi. UV–Vis spektroskopiya natijalarida 312,35 nm to‘lqin uzunligida kuchli yutilish zonasi kuzatildi. Ushbu maksimum valent zona va o‘tkazuvchanlik zonasi o‘rtasidagi to‘g‘ridan-to‘g‘ri elektron o‘tishi bilan bog‘liq. Tauc grafigi asosida hisoblangan taqiqlangan zona energiyasi 3,20 eV ni tashkil etdi. Ushbu qiymat elektronlarning valent zonadan o‘tkazuvchanlik zonasiga o‘tishi uchun zarur bo‘lgan minimal energiyani ifodalaydi hamda fotokatalitik jarayonlarda samarali zaryad tashilishi va elektron–teshik juftliklari hosil bo‘lishini ta’minlaydi.



2-rasm. *Musa acuminata* po‘stlog‘i ekstrakti yordamida sintez qilingan TO-NZlarning SEM mikrograflari (a, b), TEM tasviri (c), XRD difraktogrammasi (d), FTIR spektri (e), UV–Visible spektri (f), TGA termogrammasi (g) va EDX spektri (h) (Hedfi va boshq., 2025).

TO-NZlarning fotokatalitik samaradorligi MO va Rodamin-6G (R-6G) organik bo‘yoqlariga nisbatan simulyatsiya qilingan quyosh nuri ostida baholandi.

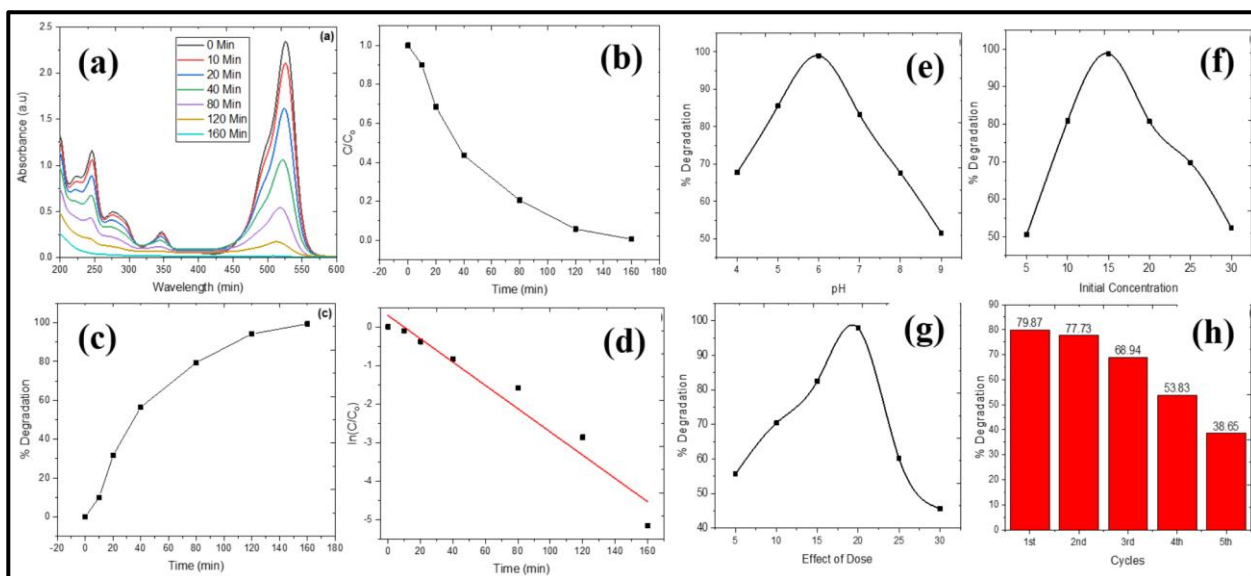
MO ning fotokatalitik degradatsiyasini o'rganishda 15 ppm konsentratsiyali eritmaga 20 mg TO-NZlar qo'shildi. Aralashma avval 30 daqiqa qorong'i sharoitda ushlab turilib, adsorbsiya–desorbsiya muvozanatiga erishildi, so'ngra quyosh nuri ta'siriga qo'yildi. Reaksiya davomida eritmaning yorqin to'q sariq rangi asta-sekin oqarib bordi. Ushbu holat UV–Visible spektroskopiyasi yordamida tasdiqlanib, 464 nm dagi maksimal absorbsiya intensivligining uzluksiz kamayishi kuzatildi. Degradatsiya jarayonining kinetik profili dastlab keskin pasayish, so'ngra esa sekin va barqaror kamayish bosqichidan iborat bo'ldi. Bunday xususiyat fotokatalizator yuzasidagi bo'sh faol markazlarning dastlab bo'yoq molekulalari bilan tez bog'lanishi, keyinchalik esa bog'lanish markazlarining to'yinishi natijasida degradatsiya tezligining pasayishi bilan izohlanadi. 160 daqiqa davom etgan fotokatalitik jarayon yakunida MO ning 79,87% degradatsiyaga uchragani aniqlandi hamda reaksiyaning tezlik konstantasi $0,00873 \text{ min}^{-1}$ ni tashkil etdi. R-6G bo'yog'i uchun ham xuddi shu metodika qo'llanildi. 526 nm to'lqin uzunligida olib borilgan tahlillar natijasida 160 daqiqa ichida 99,42% degradatsiya kuzatildi va jarayonning tezlik konstantasi $0,03012 \text{ min}^{-1}$ ga teng bo'ldi. Ushbu natijalar TO-NZlar ning R-6G bo'yog'iga nisbatan yanada yuqori fotokatalitik faollikka ega ekanligini ko'rsatadi. Fotokatalitik degradatsiya mexanizmi yarimo'tkazgich material tomonidan taqiqlangan zona energiyasidan yuqori energiyaga ega fotonlarning yutilishi bilan boshlanadi. Natijada elektronlar valent zonadan o'tkazuvchanlik zonasiga o'tadi va valent zonada teshiklar (h^+) hosil bo'ladi. Hosil bo'lgan elektron–teshik juftliklari nanozarrachalar yuzasiga ko'chib, adsorbsiyalangan moddalar bilan oksidlanish-qaytarilish reaksiyalarida ishtirok etadi. O'tkazuvchanlik zonasidagi elektronlar adsorbsiyalangan kislorod molekulalari bilan reaksiyaga kirishib superoksid radikallari ($\bullet O_2^-$) ni hosil qiladi, valent zonadagi teshiklar esa suv molekulalari bilan reaksiyaga kirishib gidroksil radikallari ($\bullet OH$) ni hosil qiladi. Ushbu reaktiv kislorod turlari yuqori oksidlovchi xususiyatga ega bo'lib, organik bo'yoq molekulalarini parchalaydi va ularni CO_2 hamda H_2O kabi ekologik xavfsiz mahsulotlarga mineralizatsiyalaydi.

Fotokatalitik jarayonni optimallashtirish bo'yicha olib borilgan tadqiqotlar eritmaning pH qiymati degradatsiya samaradorligiga sezilarli ta'sir ko'rsatishini aniqladi. Eng yuqori fotokatalitik samaradorlik pH 6 da kuzatildi. Bunday sharoitda fotokatalizator yuzasi protonlanish natijasida musbat zaryad hosil qiladi va anion tabiatiga ega MO molekulalari bilan elektrostatik tortishish kuchi yuzaga keladi. Aksincha, yuqori pH qiymatlarida katalizator yuzasi deprotonlanib manfiy zaryadlanadi, bu esa MO molekulalari bilan elektrostatik itarilish hosil qilib, fotokatalitik faollikning pasayishiga olib keladi. Katalizator miqdorini optimallashtirish natijasida eng yuqori degradatsiya 20 mg katalizator ishlatilganda kuzatildi. Kamroq miqdordagi katalizator faol markazlarning yetarli emasligi sababli past samaradorlikni namoyon etdi. Katalizator miqdorining ortishi esa nanozarrachalarning aglomeratsiyasiga olib kelib, faol markazlarning berkilishi

hamda bo'yoq molekulalarining ushbu markazlarga yetib borishini cheklashi natijasida fotokatalitik samaradorlik pasaydi. Boshlang'ich konsentratsiya bo'yicha olib borilgan tadqiqotlar 15 ppm konsentratsiya optimal ekanligini ko'rsatdi. Konsentratsiyaning ortishi eritmada yorug'likning bo'yoq molekulalari tomonidan ko'proq yutilishiga sabab bo'lib, fotokatalizator yuzasiga yetib boradigan fotonlar sonini kamaytiradi. Natijada fotokatalizatorning faollashuvi cheklanadi va degradatsiya samaradorligi pasayadi. Katalizatorning qayta foydalanish imkoniyati ketma-ket besh sikl davomida baholandi. Natijalar degradatsiya samaradorligi 79,87% dan 38,65% gacha bosqichma-bosqich kamayganini ko'rsatdi. Ushbu pasayish katalizator yuzasidagi faol markazlarning to'yinishi, reaksiya mahsulotlarining to'planishi natijasida yorug'likning kirib borish darajasi kamayishi hamda katalizatorning strukturaviy va kimyoviy o'zgarishlari oqibatida faol markazlar sonining qisqarishi bilan izohlanadi. Ilmiy adabiyotlarda keltirilgan TO-NZlar bilan qiyosiy tahlil shuni ko'rsatdiki, yashil sintez orqali olingan temir oksidi nanozarrachalari an'anaviy kimyoviy usullar bilan sintez qilingan analog materiallarga nisbatan kamroq katalizator miqdorida, qisqaroq vaqt ichida va yuqoriroq degradatsiya samaradorligini namoyon etdi. Ushbu natijalar yashil sintez usulining yuqori samaradorligini hamda tabiiy manbalardan olingan prekursorlardan foydalanish ekologik barqaror va yuqori samarali fotokatalitik materiallarni yaratishda istiqbolli yondashuv ekanligini tasdiqlaydi.

Yashil sintez usuli ekologik, iqtisodiy va funksional jihatdan bir qator muhim afzalliklarga ega. Ekologik nuqtai nazardan ushbu usul zararli kimyoviy reagentlardan foydalanishni bartaraf etadi, energiya sarfini kamaytiradi hamda qishloq xo'jaligi va o'simlik chiqindilarini yuqori qo'shimcha qiymatga ega mahsulotlarga aylantirish imkonini beradi. Iqtisodiy jihatdan esa oddiy texnologik jihozlarni talab qilishi, ishlab chiqarish xarajatlarining pastligi va sanoat miqyosida oson kengaytirilishi bilan ajralib turadi. Bundan tashqari, yashil sintez orqali olingan nanomateriallar biologik faolligining yuqoriligi bilan ham tavsiflanadi. O'simlik ekstraktlari tarkibidagi fitokimyoviy birikmalar, jumladan flavonoidlar, polifenollar va terpenoidlar, sintez jarayonida ikki asosiy vazifani bajaradi. Birinchidan, ular qaytaruvchi reagent sifatida metall ionlariga elektron berib, ularni qaytaradi. Masalan, Fe^{3+} ionlari Fe^0 ga qaytariladi, bunda fitokimyoviy moddalarning gidroksil (-OH) guruhlari oksidlanib xinon birikmalariga aylanadi. Ikkinchidan, oksidlangan fitokimyoviy moddalar stabilizator vazifasini bajaradi. Ular nanozarrachalar yuzasiga -OH, -COOH va -C=O funksional guruhlari orqali adsorbsiyalanib, elektrostatik va sterik barqarorlashtirish mexanizmlarini hosil qiladi. Natijada nanozarrachalarning aglomeratsiyasi oldi olinadi hamda ularning o'lchami 15–60 nm diapazonda samarali nazorat qilinadi. Bundan tashqari, nanozarrachalar yuzasida hosil bo'ladigan ushbu organik qoplama ularning biyosligini oshiradi va qo'shimcha biologik faollikni ta'minlaydi. Aynan shu omillar yashil sintez orqali olingan nanozarrachalarning kimyoviy usullar bilan sintez qilingan analoglariga

nisbatan doimiy ravishda yuqoriroq biologik samaradorlikni namoyon etishining asosiy sabablaridan biri hisoblanadi.



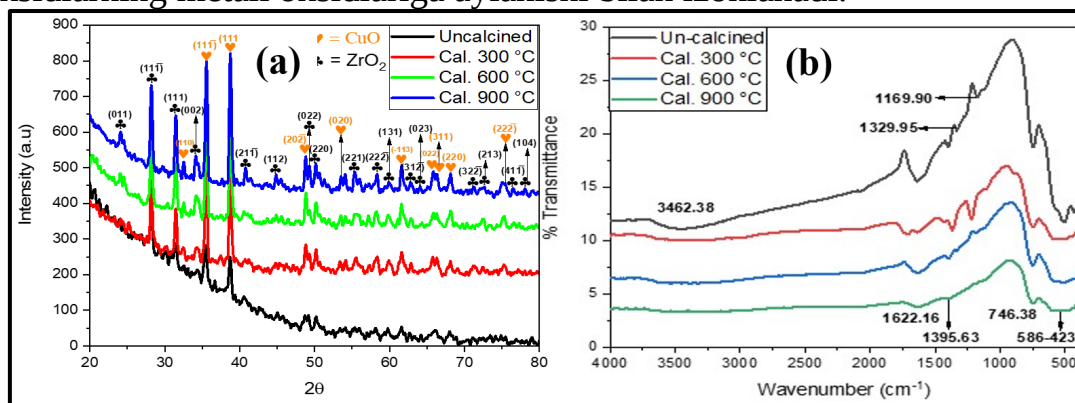
3-rasm. Simulyatsiya qilingan quyosh nuri ostida TO-NZlar ishtirokida Rodamin-6G (R-6G) ning fotokatalitik degradatsiyasiga oid natijalar: degradatsiya profili (a), chiziqli kinetik grafik (b), degradatsiya foizi (c), tezlik konstantasi (d), eritma pH qiymatining ta'siri (e), boshlang'ich konsentratsiyaning ta'siri (f), katalizator miqdorining ta'siri (g) hamda fotokatalitik tajribalar davomida TO-NZlar ning qayta foydalanish samaradorligi (h) (Hedfi va boshq., 2025).

2-BOB. IKKI KOMPONENTLI METALL OKSIDLI NANOKOMPOZITLAR

2.1 Mexanokimyoviy sintez usuli orqali olingan CuO–ZrO₂ nanokompozitlari. Mis oksidi–sirkoniy dioksid (CuO–ZrO₂) nanokompozitlari erituvchisiz innovatsion mexanokimyoviy sintez usuli yordamida, havoncha va dastak orqali maydalash asosida tayyorlandi. Ushbu usul molekulyar darajada mexanik va kimyoviy ta'sirlarni birlashtiruvchi, sodda, ekologik xavfsiz hamda sanoat miqyosida kengaytirish imkoniyatiga ega yondashuv hisoblanadi. Mazkur tadqiqotda ilk bor havoncha–dasta yordamidagi mexanokimyoviy sintez usuli ikki komponentli metall nanochanglarni tayyorlash uchun qo'llanildi. Ushbu usul an'anaviy solvotermal va sol-gel texnologiyalariga nisbatan texnologik soddaligi, sanoat miqyosida qo'llash imkoniyati, ekologik xavfsizligi, erituvchilar bilan bog'liq ifloslanish xavfining yo'qligi hamda mahsulotni tozalash bosqichining soddaligi kabi muhim afzalliklarga ega. Sintez jarayonida mis(II) gidroksid [Cu(OH)₂] va sirkoniy(IV) gidroksid [Zr(OH)₄] prekursorlari teng miqdorda (har biri 1 g) olinib, 6 soat davomida uzluksiz maydalandi. Maydalash jarayonida materialning fizik holatida bir qator o'zgarishlar kuzatildi. Dastlab donador ko'rinishga ega bo'lgan aralashma asta-sekin kukunsimon holatga o'tdi. Taxminan uchinchi soatda gidroksid bog'larining parchalanishi va namlikning hosil bo'lishi natijasida massa yopishqoq holatga keldi. Jarayon davom etishi bilan metall oksidlarning hosil bo'lishi hisobiga namlik yo'qolib, mahsulot yana kukunsimon holatga qaytdi. Hosil qilingan nanokompozitlarning strukturaviy va fotokatalitik xossalari kalsinatsiya haroratining ta'sirini o'rganish maqsadida namunalar 300°C, 600°C va 900°C haroratlarda mufel pechida kalsinatsiya qilindi.

XRD tahlili natijasida CuO fazasiga tegishli 32,61°, 35,58°, 38,72°, 48,78°, 53,44°, 61,61°, 65,86°, 66,24°, 68,15° va 75,35° burchaklardagi difraksion cho'qqilar aniqlandi. Ushbu cho'qqilar mos ravishda (110), (1 $\bar{1}$ 1), (111), (200), (020), (113), (022), (311), (220) va (2 $\bar{2}$ 2) Miller tekisliklariga mos kelib, JCPDS №96-901-6106 standart kartasi bilan to'liq mos tushdi. Natijalar tenorit mineraliga xos monoklinik CuO fazasi (C12/c1 fazoviy guruhi) hosil bo'lganligini tasdiqladi. CuO kristall panjarasining parametrlarini hisoblash natijasida $a = 4,6833 \text{ \AA}$, $b = 3,4208 \text{ \AA}$, $c = 5,1294 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 99,57^\circ$, zichligi $6,51 \text{ g/cm}^3$ hamda elementar yacheyka hajmi $81,00 \times 10^6 \text{ pm}^3$ ekanligi aniqlandi. Kalsinatsiya qilinmagan CuO namunasi uchun kristallitlarning o'rtacha o'lchami 28,3 nm, kristall panjaradagi deformatsiya esa 0,402% ni tashkil etdi. Kalsinatsiya harorati oshishi bilan kristallitlarning o'lchami 42,4 nm gacha ortdi, deformatsiya esa mos ravishda 300°C, 600°C va 900°C da 0,268%, 0,266% va 0,266% gacha kamaydi. ZrO₂ fazasi uchun 24,01°, 28,18°, 31,55°, 34,08°, 40,71°, 44,78°, 49,24°, 50,19°, 55,29°, 58,39°, 59,82°, 62,96°, 64,06°, 71,06°, 72,57°, 76,50° va 78,00° burchaklarda Bragg reflekslari kuzatildi. Ushbu cho'qqilar mos ravishda (011), (1 $\bar{1}$ 1), (111), (002), (2 $\bar{1}$ 1), (112), (022), (220), (221), (2 $\bar{2}$ 2), (131), (311), (023), (322), (213), (4 $\bar{1}$ 1) va (104) kristall tekisliklariga mos kelib, JCPDS №96-230-0297 standart kartasi bilan to'liq mos tushdi. Bu esa P2₁/c fazoviy guruhiga mansub monoklinik ZrO₂ fazasi hosil bo'lganligini tasdiqladi. ZrO₂ ning kristall panjara parametrlari $a = 5,1477 \text{ \AA}$, $b =$

5,2096 Å, $c = 5,3164$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 99,21^\circ$, zichligi $5,82 \text{ g/cm}^3$ va elementar yacheyka hajmi $140,61 \times 10^6 \text{ pm}^3$ deb aniqlandi. ZrO_2 kristallitlarining o'lchami kalsinatsiya harorati ortishi bilan 20,8 nm (kalsinatsiya qilinmagan namuna), 41,6 nm (300°C), 44,9 nm (600°C) va 55,3 nm (900°C) gacha oshdi. Shu bilan birga, kristall panjaradagi deformatsiya 0,680% dan mos ravishda 0,342%, 0,301% va 0,257% gacha kamaydi. FTIR tahlili natijasida $3462,38 \text{ cm}^{-1}$ da O–H valent tebranishlari, $1622,16 \text{ cm}^{-1}$ da H–O–H deformatsion tebranishlari, $1395,63 \text{ cm}^{-1}$ da M–OH tarkibidagi sirt gidroksil guruhlari, $1169,90 \text{ cm}^{-1}$ da tekislikdan tashqari O–H deformatsion tebranishlari, $746,38 \text{ cm}^{-1}$ da M–O–M bog'larining valent tebranishlari, $586\text{--}423 \text{ cm}^{-1}$ oralig'ida M–O bog'lariga tegishli keng polosalar kuzatildi. Kalsinatsiya qilinmagan namunada 530 cm^{-1} da Zr–O bog'iga xos yaqqol cho'qqi qayd etildi, 522 cm^{-1} va 590 cm^{-1} dagi cho'qqilar esa Cu–O bog'larining valent tebranishlariga tegishli ekanligi aniqlandi. Kalsinatsiya harorati oshishi bilan FTIR spektridagi barcha polosalar intensivligining bosqichma-bosqich kamayishi kuzatildi. Ayniqsa $3462,38$, $1622,16$, $1329,95$ va $1169,90 \text{ cm}^{-1}$ dagi polosalarda sezilarli intensivlik pasayishi qayd etildi. Shuningdek, $586\text{--}423 \text{ cm}^{-1}$ oralig'idagi alohida cho'qqilar birlashib keng polosaga aylandi. Ushbu o'zgarishlar kalsinatsiya jarayonida kondensatsiya reaksiyalari sodir bo'lishi, suvning bug'lanishi hamda metall gidroksidlarning metall oksidlariga aylanishi bilan izohlanadi.

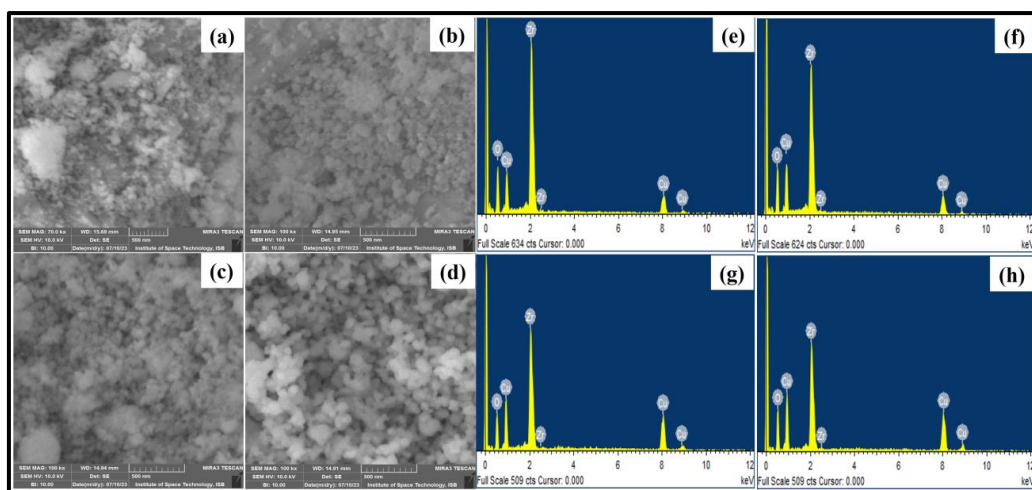


4-rasm. Kalsinatsiya qilinmagan hamda 300 , 600 va 900°C haroratlarda kalsinatsiya qilingan CuO-ZrO_2 nanokompozitlarining XRD difraktogrammalari (a) va FTIR spektrlari (b) (Zain, Yasin, Haq, Shujaat, va boshq., 2024).

SEM tahlili kalsinatsiya jarayonida nanokompozitlarning morfologiyasida sodir bo'ladigan dinamik o'zgarishlarni ko'rsatdi. Kalsinatsiya qilinmagan dastlabki namunada zarrachalar notekis taqsimlangan donador tuzilishga ega bo'lib, ular aniq geometrik shakl hosil qilmagan. Donalar o'lchami $35,47\text{--}52,81 \text{ nm}$ oralig'ida bo'lib, o'rtacha qiymati $44,43 \text{ nm}$ ni tashkil etdi. 300°C haroratda kalsinatsiya qilingan namunada donalar o'lchami $37,60\text{--}53,11 \text{ nm}$ oralig'iga, o'rtacha esa $47,43 \text{ nm}$ gacha oshdi. Yuqori sirt energiyasi ta'sirida kichik donalarning o'zaro qo'shilishi kuzatilib, yirikroq zarrachalar hosil bo'ldi. Ayrim zarrachalar deyarli sferik shaklga ega bo'la boshladi. 600°C da kalsinatsiya qilingan namunada struktura yanada zichlashdi va

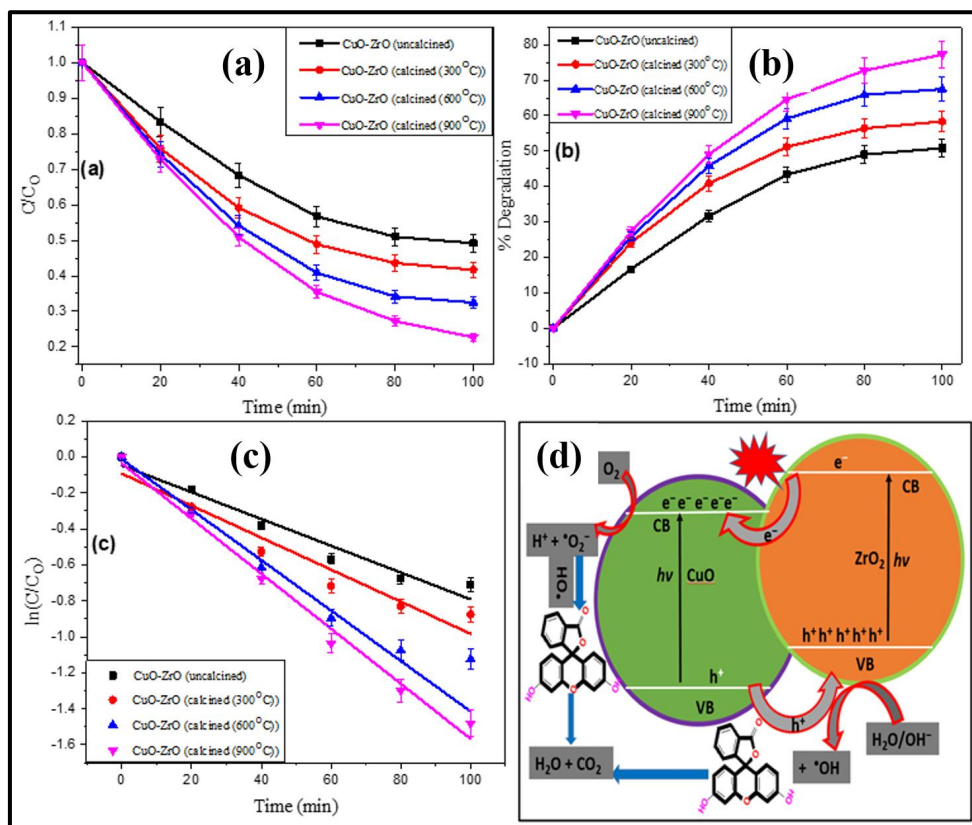
donalar o'lchami 35,50–72,47 nm oralig'iga yetdi (o'rtacha 47,43 nm). Donalar orasidagi bo'shliqlarning kamayishi va ularning o'zaro to'ldirilishi natijasida materialning zichligi ortdi. Morfologiya yanada aniqroq shakllana boshlagan bo'lsa-da, zarrachalar hali ham to'liq bir xil shaklga ega emas edi. 900°C da kalsinatsiya qilingan namunada esa zarrachalarning morfologiyasi yaqqol namoyon bo'ldi. Sferik, deyarli sferik, oval hamda cho'zilgan shakldagi zarrachalar kuzatildi. Donalar o'lchami 55,98–75,30 nm oralig'ida bo'lib, o'rtacha 63,23 nm ni tashkil etdi. Yuqori harorat ta'sirida zarrachalarning o'zaro qo'shilishi natijasida agregatlar hosil bo'lib, bu umumiy donalar o'lchamining sezilarli ortishiga sabab bo'ldi.

EDX tahlili spektrda 0,5 keV da kislorod, 0,9, 8,05 va 8,9 keV da mis, hamda 2,1 va 2,5 keV da sirkoniy elementlariga xos cho'qqilarni qayd etdi. Kalsinatsiya harorati ortishi bilan misning massa ulushi 16,79% (kalsinatsiya qilinmagan namuna) dan 35,79% (900°C) gacha oshgani, sirkoniyning massa ulushi esa 53,27% dan 38,89% gacha kamaygani aniqlandi. Element tarkibidagi ushbu o'zgarishlar yuqori harorat ta'sirida sodir bo'ladigan fazaviy o'zgarishlar, kristallarning o'sishi hamda uchuvchan komponentlarning bug'lanishi bilan izohlanadi. Dastlabki sintezda 0,011 mol $\text{Cu}(\text{OH})_2$ va 0,006 mol $\text{Zr}(\text{OH})_4$ ishlatilgan. Yuqori haroratlarda kondensatsiya reaksiyalari natijasida H_2O molekulari ajralib chiqadi. $\text{Cu}(\text{OH})_2$ tarkibida har bir mol uchun gidroksil guruhlari sonining ko'pligi sababli uning massasi ko'proq kamayadi va natijada tayyor mahsulot tarkibida misning nisbiy massa ulushi yuqoriroq bo'lib qoladi. Bundan tashqari, kristall o'sish kinetikasi ham element tarkibining o'zgarishiga ta'sir ko'rsatadi. CuO kristallari tezroq yadrolanib va o'sib borishi natijasida ZrO_2 kristallarining rivojlanishi qisman cheklanadi. Shu sababli yakuniy nanokompozit tarkibida sirkoniyning nisbiy miqdori kamayganligi kuzatiladi.



5-rasm. Kalsinatsiya qilinmagan hamda 300, 600 va 900°C haroratlarda kalsinatsiya qilingan CuO-ZrO_2 nanokompozitlarining SEM mikroagraflari (a–d) va EDX spektrlari (e–h). Rasmda kalsinatsiya haroratining ortishi bilan nanokompozitlarning strukturaviy o'zgarishlari aks ettirilgan (Zain, Yasin, Haq, Shujaat, va boshq., 2024).

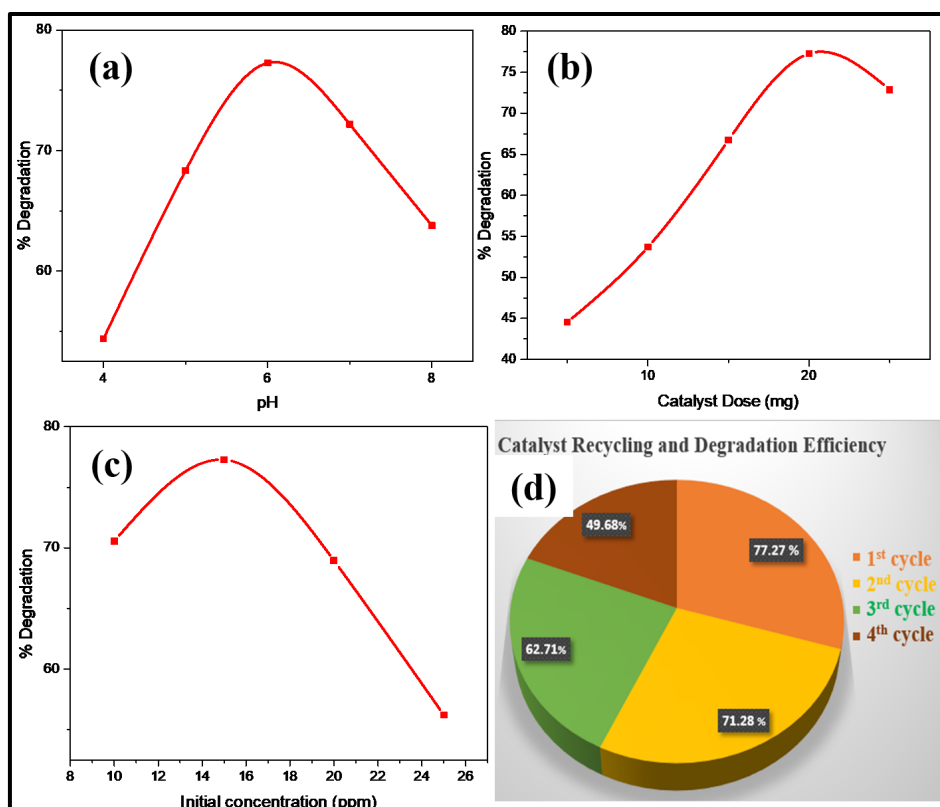
CuO–ZrO₂ nanokompozitlarining fotokatalitik faolligi fluoresein bo‘yog‘iga nisbatan 2023-yil 15–30-iyun kunlari, soat 11:00 dan 15:00 gacha bo‘lgan vaqt oralig‘ida tabiiy quyosh nuri ostida baholandi. Tadqiqot natijalariga ko‘ra, kalsinatsiya qilinmagan namunada bo‘yoqning fotokatalitik degradatsiya darajasi 50,83% ni tashkil etdi. 300°C da kalsinatsiya qilingan namunada ushbu ko‘rsatkich 58,33%, 600°C da 67,50%, 900°C da esa 77,27% gacha oshdi. Fotokatalitik reaksiyaning tezlik konstantalari mos ravishda 0,00744 min⁻¹, 0,00890 min⁻¹, 0,01402 min⁻¹ va 0,01530 min⁻¹ ni tashkil etdi. Natijalar shuni ko‘rsatdiki, 900°C haroratda kalsinatsiya qilingan CuO–ZrO₂ nanokompoziti eng yuqori fotokatalitik faollikni namoyon etdi. Ushbu yuqori samaradorlik zarrachalar o‘lchamining kattalashishi va solishtirma sirt maydonining kamayishiga qaramay, materialning kristallanish darajasi va strukturaviy bir jinsliliigi sezilarli ravishda yaxshilanganligi bilan izohlanadi. Fotokatalitik degradatsiya mexanizmi CuO–ZrO₂ yarimo‘tkazgich nanokompoziti tomonidan quyosh nuri fotonlarining yutilishi bilan boshlanadi. Natijada elektronlar valent zonadan o‘tkazuvchanlik zonasiga o‘tadi va elektron–teshik juftliklari hosil bo‘ladi. Hosil bo‘lgan qo‘zg‘atilgan elektronlar CuO ning o‘tkazuvchanlik zonasida to‘planadi, musbat teshiklar (h⁺) esa ZrO₂ ning valent zonasida yig‘iladi. Fotogeneratsiyalangan teshiklar suv molekulalari bilan reaksiyaga kirishib gidroksil radikallarini (•OH) hosil qiladi. Shu bilan birga, fotogeneratsiyalangan elektronlar kislorod molekulalarini qaytarib, superoksid radikallarini (•O₂⁻) hosil qiladi. Ushbu radikallar keyinchalik vodorod ishtirokida qo‘shimcha gidroksil radikallarini hosil qiladi. Hosil bo‘lgan yuqori reaktiv gidroksil radikallari fotokatalizator yuzasiga adsorbsiyalangan fluoresein molekulalariga hujum qilib, ularning kimyoviy bog‘larini uzadi. Natijada bo‘yoq molekulalari bosqichma-bosqich parchalanib, yakunda CO₂ va H₂O kabi ekologik xavfsiz mahsulotlarga to‘liq mineralizatsiyalanadi.



6-rasm. Quyosh nuri ishtirokida CuO–ZrO₂ nanokompozitlari yordamida fluorescein bo‘yog‘ining fotokatalitik degradatsiyasiga oid natijalar: degradatsiya profili (a), degradatsiya darajasi (%) (b), kinetik tezlik konstantasi (c) va taklif etilgan fotokatalitik degradatsiya mexanizmi (d) (Zain, Yasin, Haq, Shujaat, va boshq., 2024).

900°C da kalsinatsiya qilingan namuna bo‘yicha olib borilgan optimallashtirish tadqiqotlari eng yuqori fotokatalitik degradatsiya samaradorligi pH 6 da kuzatilganini ko‘rsatdi va bu qiymat 77,27% ni tashkil etdi. Kislotali hamda ishqoriy muhitlarda degradatsiya samaradorligining pasayishi katalizator yuzasining zaryad holati bilan izohlanadi. ZrO₂ kislotali muhitda musbat, ishqoriy sharoitda esa manfiy zaryadga ega bo‘ladi. Fluoresein esa pH 4,3–6,4 oralig‘ida monoanion, pH 6,4 dan yuqori qiymatlarda esa dianion shaklida mavjud bo‘ladi. Shu sababli pH 6 da musbat zaryadlangan katalizator yuzasi bilan manfiy zaryadlangan bo‘yoq molekulalari o‘rtasidagi elektrostatik tortishish kuchlari adsorbsiya va keyingi fotokatalitik degradatsiya jarayonlarini kuchaytiradi. Katalizator miqdorini optimallashtirish natijalariga ko‘ra, uning miqdori 5 mg dan 20 mg gacha oshirilganda degradatsiya samaradorligi 44,55% dan 77,27% gacha ortdi. Biroq katalizator miqdori 25 mg ga yetkazilganda ushbu ko‘rsatkich 72,86% gacha kamaydi. Optimal miqdorda katalizatorning umumiy sirt maydoni va faol markazlar soni ortib, fotokatalitik jarayon samaradorligi yaxshilanadi. Katalizator miqdorining bundan keyingi oshirilishi esa zarrachalarning aglomeratsiyasiga, fotonlar bilan o‘zaro ta’sirning kamayishiga va yorug‘likning samarasiz yutilishiga olib keladi. Boshlang‘ich bo‘yoq konsentratsiyasining ta’siri o‘rganilganda, 10, 15, 20 va 25

ppm konsentratsiyalarda degradatsiya samaradorligi mos ravishda 70,56%, 77,27%, 68,95% va 56,21% ni tashkil etdi. Eng yuqori samaradorlik 15 ppm da kuzatildi. Yuqori konsentratsiyalarda degradatsiya darajasining pasayishi katalizator yuzasidagi faol markazlarning to'yinishi hamda bo'yoq molekulalarining yorug'lik bilan katalizator yuzasi o'rtasidagi o'zaro ta'sirga to'sqinlik qilishi bilan izohlanadi. Katalizatorning qayta foydalanish imkoniyati ketma-ket to'rt sikl davomida baholandi. Degradatsiya samaradorligi birinchi, ikkinchi, uchinchi va to'rtinchi sikllarda mos ravishda 77,27%, 71,28%, 62,71% va 49,68% ni tashkil etdi. Birinchi sikldagi yuqori samaradorlik katalizator yuzasining toza va faol holatda bo'lishi bilan bog'liq. Keyingi sikllarda samaradorlikning bosqichma-bosqich kamayishi esa sirtning ifloslanishi, strukturaviy o'zgarishlar, katalizatorning qisman deaktivatsiyasi hamda qayta foydalanish jarayonida bo'yoq molekulalarining fotokatalizator yuzasida adsorbsiyalanib qolishi bilan izohlanadi.



7-rasm. CuO–ZrO₂ nanokompozitlarining fotokatalitik faolligiga ta'sir etuvchi omillar: eritma pH qiymatining ta'siri (a), katalizator miqdorining ta'siri (b), boshlang'ich konsentratsiyaning ta'siri (c) hamda katalizatorning qayta foydalanish samaradorligi (d)(Zain, Yasin, Haq, Shujaat, va boshq., 2024).

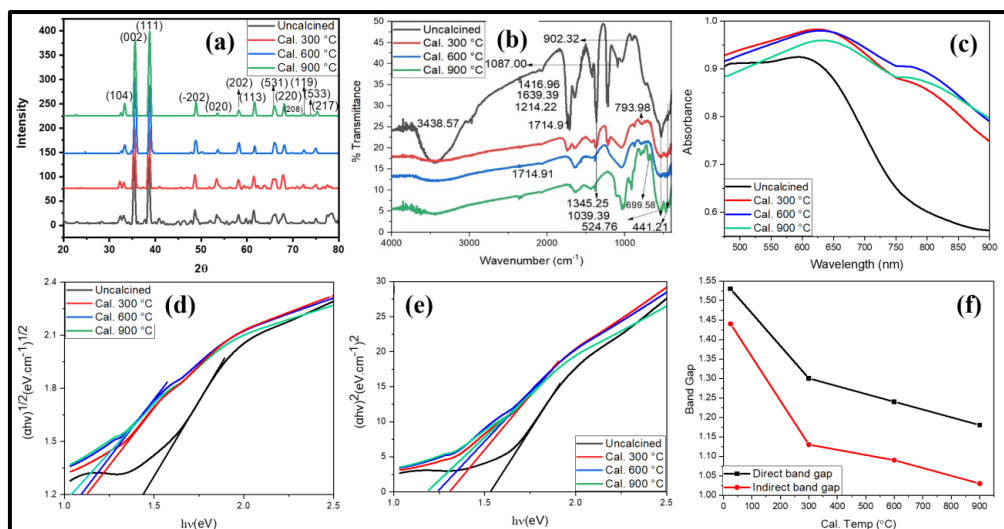
2.2 Mexanokimyoviy sintez usuli orqali olingan CuO–Fe₂O₃ nanokompozitlari. Mazkur tadqiqotda CuO–Fe₂O₃ nanokompozitlarini havoncha va dastak yordamida oddiy, erituvchisiz mexanokimyoviy sintez usuli orqali olish muvaffaqiyatli amalga oshirildi. Sintezdan so'ng namunalar 300°C, 600°C va 900°C haroratlarda kalsinatsiya qilindi. Tadqiqotning asosiy maqsadi kalsinatsiya haroratining bimetall oksid tizimining strukturaviy, morfologik, optik va teksturaviy

xossalariga hamda uning quyosh nuri ostida fluoresein bo'yog'ining fotokatalitik degradatsiyasi samaradorligiga ta'sirini aniqlashdan iborat bo'ldi. Sintez jarayonida mis(II) gidroksid va temir(II) gidroksid prekursorlari teng miqdorda (har biri 1 g) olinib, 6 soat davomida maydalandi. Ushbu jarayon davomida aralashma metall oksidlarning hosil bo'lishi hisobiga donador $\rightarrow$ yopishqoq $\rightarrow$ kukunsimon holatlarga ketma-ket o'tdi. Tayyor mahsulot keyinchalik mufel pechida 300°C, 600°C va 900°C haroratlarda kalsinatsiya qilindi. Fotokatalitik tajribalarda kalsinatsiya qilinmagan hamda 300°C, 600°C va 900°C da kalsinatsiya qilingan har bir nanokompozit namunadan 25 mg olinib, 100 mL hajmdagi 15 ppm konsentratsiyali fluoresein eritmasiga qo'shildi. Aralashma adsorbsiya-desorbsiya muvozanatiga erishish uchun 30 daqiqa davomida qorong'i sharoitda aralashtirildi. Shundan so'ng namunalar 250 W quvvatli simulyatsiya qilingan quyosh nuri ta'siriga qo'yildi va degradatsiya jarayoni 475 nm to'lqin uzunligida ikki nurli UV-Visible spektrofotometr yordamida absorbsiya intensivligining kamayishi orqali kuzatildi.

XRD tahlili natijasida CuO va Fe₂O₃ fazalariga tegishli aniq difraksion cho'qqilar kuzatildi. CuO fazasiga tegishli cho'qqilar 35,49° (002), 38,72° (111), 48,87° (-202), 53,28° (020), 58,16° (202), 61,62° (113) va 68,10° (220) burchaklarda qayd etildi. Ushbu natijalar JCPDS №01-80-1268 standart kartasi bilan mos kelib, C2/c fazoviy guruhiga mansub monoklinik CuO fazasi hosil bo'lganligini tasdiqladi. CuO kristall panjarasi parametrlari $a = 4,6833 \text{ \AA}$, $b = 3,4208 \text{ \AA}$, $c = 5,1294 \text{ \AA}$, $\alpha = \gamma = 90^\circ$ va $\beta = 99,5678^\circ$ deb aniqlandi. Fe₂O₃ (gematit) fazasiga tegishli difraksion cho'qqilar esa 33,13° (104), 65,88° (531), 70,08° (208), 72,40° (119), 73,91° (533) va 75,32° (217) burchaklarda kuzatildi. Ushbu cho'qqilar JCPDS №01-097-1741 standart kartasi bilan mos kelib, R-3c fazoviy guruhiga mansub romboedrik kristall tuzilma hosil bo'lganligini tasdiqladi. Fe₂O₃ kristall panjarasi parametrlari $a = b = 5,0343 \text{ \AA}$ va $c = 13,7460 \text{ \AA}$ ga teng bo'ldi. Tahlillar shuni ko'rsatdiki, kalsinatsiya harorati ortishi bilan difraksion cho'qqilar intensivligi oshdi, bu esa nanokompozitlarning kristallanish darajasi yaxshilanganligini ko'rsatadi. Shu bilan birga, difraksion cho'qqilarning siljishi kuzatilmadi, bu esa kalsinatsiya jarayonida fazaviy o'zgarish sodir bo'lmaganligini tasdiqlaydi. Barcha namunalar ko'rinadigan yorug'lik sohasida sezilarli yutilish xususiyatini namoyon etdi, bu esa ularning quyosh nuri ostida fotokatalizator sifatida qo'llanishi uchun qulay ekanligini ko'rsatadi. Kalsinatsiya harorati ortishi bilan absorbsiya maksimumlarining uzunroq to'lqin uzunliklari tomon siljishi (batoxromik siljish) kuzatildi. Shu bilan birga absorbsiya cho'qqilarining intensivligi ham sezilarli ravishda ortdi. Tauc tahlili natijasida aniqlangan to'g'ridan-to'g'ri elektron o'tishlari uchun band gap qiymatlari kalsinatsiya qilinmagan namunada 1,53 eV, 300°C da 1,30 eV, 600°C da 1,24 eV va 900°C da 1,18 eV ni tashkil etdi. Bilvosita elektron o'tishlari uchun esa band gap qiymatlari mos ravishda 1,44 eV, 1,13 eV, 1,09 eV va 1,03 eV ga teng bo'ldi.

Band gap energiyasining kamayishi yuqori haroratlarda kristallanish darajasining ortishi, kristall panjaradagi nuqsonlar va vakansiyalarning kamayishi hamda begona qo'shimchalarning bug'lanib ketishi bilan izohlanadi. FTIR tahlili natijasida 3438,57 cm⁻¹ da O-H valent tebranishlari, 1712,91 cm⁻¹ da Fe₂O₃ yuzasiga adsorbsiyalangan suv molekullari, 1639,39 cm⁻¹ da H-O-H deformatsion

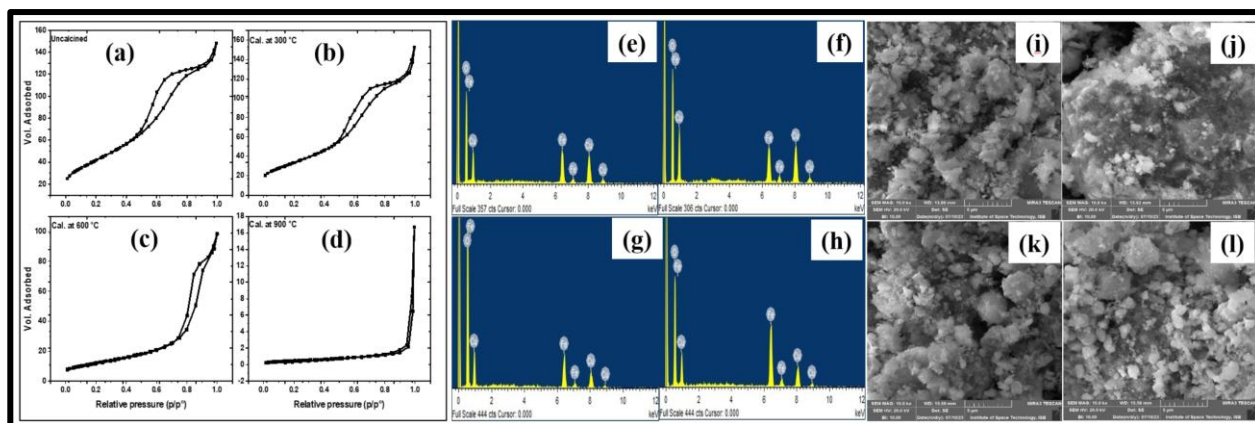
tebranishlari, $1416,96\text{ cm}^{-1}$ da mis bilan bog'liq O–H deformatsion tebranishlari, $1345,25\text{ cm}^{-1}$ da CuO yuzasida adsorbsiyalangan CO_2 va H_2O , $1214,22\text{ cm}^{-1}$ da M–OH tebranishlari, $1087,00\text{ cm}^{-1}$ da terminal M–OH guruhlari, $1039,39\text{ cm}^{-1}$ da Cu–O bog'ining deformatsion tebranishlari, $902,32\text{ cm}^{-1}$ da O–M–O ko'prik bog'lari, $793,98\text{ cm}^{-1}$ da M–O–M bog'larining deformatsion tebranishlari, $699,58\text{ cm}^{-1}$ va $524,76\text{ cm}^{-1}$ da Fe–O bog'lari hamda $441,21\text{ cm}^{-1}$ da Cu–O valent tebranishlari kuzatildi. Kalsinatsiya harorati ortishi bilan FTIR spektridagi barcha polosalar intensivligi asta-sekin kamaydi. Ushbu holat kondensatsiya reaksiyalari natijasida metall gidroksidlarning metall oksidlariga aylanishi sodir bo'lganligini tasdiqlaydi.



8-rasm. Kalsinatsiya qilinmagan hamda 300, 600 va 900°C haroratlarda kalsinatsiya qilingan CuO–Fe₂O₃ nanokompozitlarining XRD difraktogrammalari (a), FTIR spektrlari (b), DRS spektrlari (c), to'g'ridan-to'g'ri elektron o'tishlari uchun Tauc grafigi (d), bilvosita elektron o'tishlari uchun Tauc grafigi (e) hamda taqiqlangan zona energiyasi (band gap) qiymatlarining qiyosiy taqqoslash grafigi (f) (Zain va boshq., 2025).

BET sirt maydoni tahlili natijalari H₂ tipidagi gisterezis halqasiga ega IV turdagi adsorbsiya izotermalarini ko'rsatdi. Bu esa CuO–Fe₂O₃ nanokompozitlarining mezog'ovak tuzilishga hamda murakkab g'ovaklar tarmog'iga ega ekanligini tasdiqlaydi. Kalsinatsiya harorati ortishi bilan nanokompozitlarning solishtirma sirt maydoni keskin kamaydi. Xususan, kalsinatsiya qilinmagan namunada sirt maydoni $152,53\text{ m}^2/\text{g}$ ni tashkil etgan bo'lsa, bu qiymat 300°C da $123,86\text{ m}^2/\text{g}$, 600°C da $43,77\text{ m}^2/\text{g}$ va 900°C da $1,78\text{ m}^2/\text{g}$ gacha kamaydi. G'ovak diametri dastlab 69,53 nm (kalsinatsiya qilinmagan namuna) dan 83,26 nm (300°C) gacha ortdi, keyinchalik esa 600°C da 78 nm va 900°C da 67 nm gacha kamaydi. G'ovak hajmi mos ravishda $0,199\text{ cm}^3/\text{g}$, $0,224\text{ cm}^3/\text{g}$, $0,148\text{ cm}^3/\text{g}$ va $0,025\text{ cm}^3/\text{g}$ ni tashkil etdi. Yuqori kalsinatsiya haroratlari nanostrukturalarning o'sishini va zarrachalarning koalestsensiyasini jadallashtiradi. Natijada sirt maydoni kamayadi hamda issiqlik ta'sirida g'ovaklarning qisman qulashiga yoki yopilib qolishiga olib keladi. tahlili nanokompozit tarkibida kislorod (0,4 keV), temir (0,6,

6,4 va 7,1 keV) hamda mis (0,9, 8,1 va 8,9 keV) elementlari mavjudligini tasdiqladi. Elementlarning atom foizlari kalsinatsiya haroratiga bog‘liq ravishda quyidagicha o‘zgardi: Kalsinatsiya qilinmagan namuna: Cu – 12,83%, Fe – 19,55%, O – 67,62%, Cu:Fe = 0,66; 300°C: Cu – 22,31%, Fe – 24,69%, O – 53,00%, Cu:Fe = 0,90; 600°C: Cu – 21,82%, Fe – 42,45%, O – 35,73%, Cu:Fe = 0,51; 900°C: Cu – 25,60%, Fe – 40,15%, O – 34,25%, Cu:Fe = 0,64. Natijalar shuni ko‘rsatdiki, 300°C da kalsinatsiya qilingan namunaning Cu:Fe nisbati dastlabki 1:1 prekursor nisbatiga eng yaqin bo‘lgan. Yuqori haroratlarda esa ushbu nisbat metall atomlarining diffuziyasi, sirt segregatsiyasi hamda aglomeratsiya jarayonlari sababli sezilarli darajada o‘zgargan. SEM tahlili kalsinatsiya harorati ortishi bilan nanokompozitlarning morfologiyasi sezilarli ravishda o‘zgarishini ko‘rsatdi. Kalsinatsiya qilinmagan namunada cho‘zilgan, yarim sferik, deyarli uchburchak, plastinkasimon va yulduzsimon shakldagi zarrachalar aralashmasi kuzatildi. Shuningdek, yirik aglomeratlar yuzasida ko‘plab mayda zarrachalar joylashgan bo‘lib, zarrachalar notekis taqsimlangan va ko‘plab teshiklar mavjud edi. 300°C da kalsinatsiya qilingan namunada aglomeratsiya darajasi ortdi, teshiklar soni kamaydi hamda turli o‘lchamdagi aglomeratlar bitta yirik struktura ustida tarqalgan holda kuzatildi. 600°C da sinterlanish jarayonlari ta’sirida yirik aglomeratlar parchalanib, nisbatan kichikroq aglomeratlar hosil bo‘ldi. Natijada teshiklar soni ortdi va zarrachalar turli morfologik shakllarni namoyon etdi. 900°C da esa ayrim hududlarda zarrachalarning kuchli aglomeratsiyasi va o‘zaro qo‘shilishi kuzatildi. Buning natijasida teshiklar soni kamaydi va zarrachalar chegaralari noaniq bo‘lib qoldi. Shu bilan birga, ayrim hududlarda nisbatan silliq sirt hamda turli morfologik shakllarning uyg‘unlashuvi kuzatildi. Mayda aglomeratlar yana o‘zaro birikib, yirikroq strukturalarni hosil qilgani aniqlandi.



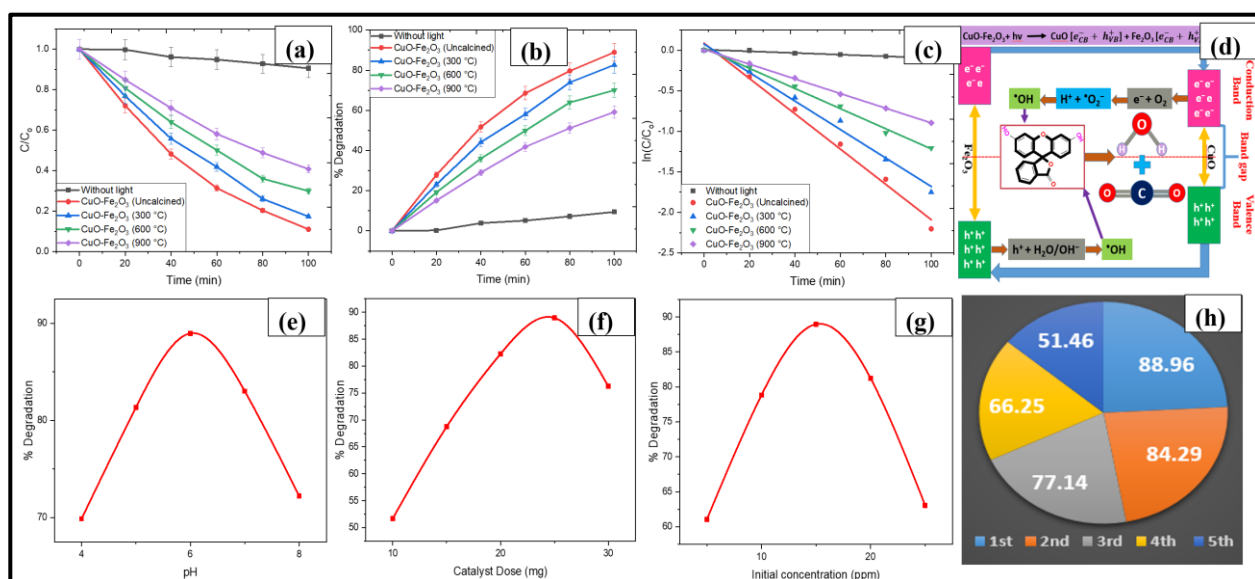
9-rasm. Kalsinatsiya qilinmagan hamda 300, 600 va 900°C haroratlarda kalsinatsiya qilingan CuO–Fe₂O₃ nanokompozitlarining BET izotermalari (a–d), EDX spektrlari (e–h) va SEM mikrograflari (i–l) (Zain va boshq., 2025).

Fotokatalitik degradatsiya profili 475 nm dagi maksimal absorbsiya intensivligining kalsinatsiya harorati ortishi bilan asta-sekin kamayishini ko‘rsatdi. Kalsinatsiya qilinmagan namuna absorbsiya cho‘qqisining eng katta pasayishini

namoyon etib, fluoreseinning 88,95% degradatsiyasiga erishdi. 300°C, 600°C va 900°C haroratlarda kalsinatsiya qilingan namunalar uchun degradatsiya darajalari mos ravishda 82,67%, 70,06% va 59,19% ni tashkil etdi. Reaksiyaning kinetik tezlik konstantalari ham xuddi shu tendensiyani ko'rsatdi: kalsinatsiya qilinmagan namuna uchun 0,02177 min⁻¹, 300°C da 0,01757 min⁻¹, 600°C da 0,01242 min⁻¹ va 900°C da 0,00905 min⁻¹. Chiziqli regressiya koeffitsiyentlari (R²) 0,9859–0,9994 oralig'ida bo'lib, tajriba ma'lumotlarining psevdobirinchi tartibli kinetik modelga yuqori darajada mos kelishini tasdiqladi. CuO–Fe₂O₃ nanokompoziti quyosh nuri fotonlarini yutganda elektronlar valent zonadan (VB) o'tkazuvchanlik zonasiga (CB) o'tadi va elektron–teshik juftliklari (electron–hole pairs) hosil bo'ladi. Qo'zg'atilgan elektronlar CuO ning o'tkazuvchanlik zonasida, musbat teshiklar (h⁺) esa Fe₂O₃ ning valent zonasida to'planadi. CuO va Fe₂O₃ ning o'tkazuvchanlik hamda valent zonalari energiya darajalari turlicha bo'lgani sababli elektronlar energiyasi yuqoriroq bo'lgan o'tkazuvchanlik zonasidan pastroq energiyali zonaga ko'chadi, teshiklar esa qarama-qarshi yo'nalishda harakatlanadi. Natijada zaryad tashuvchilarning samarali ajralishi ta'minlanadi va elektron–teshik juftliklarining rekombinatsiyasi sezilarli darajada sekinlashadi. Fotogeneratsiyalangan teshiklar suv molekullari bilan reaksiyaga kirishib gidroksil radikallarini (•OH) hosil qiladi. Elektronlar esa kislorod molekullarini qaytarib superoksid radikallarini (O₂•⁻) hosil qiladi. Ushbu yuqori reaktiv kislorod turlari fotokatalizator yuzasiga adsorbsiyalangan fluoresein molekullariga hujum qilib, ularning kimyoviy bog'larini parchalaydi va bo'yoqni yakuniy mahsulotlar – CO₂ va H₂O gacha mineralizatsiyalaydi.

pH bo'yicha olib borilgan tadqiqotlar eng yuqori degradatsiya samaradorligi (88,96%) pH 6 da kuzatilganini ko'rsatdi. Kislotali muhitda musbat zaryadlangan fotokatalizator va manfiy zaryadlangan bo'yoq molekullari o'rtasidagi elektrostatik tortishish kuchlari adsorbsiya jarayonini kuchaytiradi. Ishqoriy muhitda esa katalizator yuzasining manfiy zaryadlanishi elektrostatik itarilish kuchlarini yuzaga keltirib, fotokatalitik samaradorlikni pasaytiradi. Katalizator miqdorini optimallashtirish natijasida 25 mg eng maqbul miqdor ekanligi aniqlandi. Katalizator miqdori 10 mg dan 25 mg gacha oshirilganda degradatsiya darajasi 51,69% dan 88,96% gacha ortdi. Biroq miqdor 30 mg ga yetkazilganda samaradorlik 76,25% gacha kamaydi. Bu holat zarrachalarning aglomeratsiyasi hamda yorug'likning tarqalishi (light scattering) kuchayishi bilan izohlanadi. Boshlang'ich bo'yoq konsentratsiyasini optimallashtirish natijalari 15 ppm eng maqbul konsentratsiya ekanligini ko'rsatdi. Konsentratsiya 5 ppm dan 15 ppm gacha oshirilganda degradatsiya samaradorligi 61,07% dan 88,96% gacha ortdi. Konsentratsiyaning bundan yuqori qiymatlarida esa katalizator yuzasidagi faol markazlarning to'yinishi hamda bo'yoq molekullarining yorug'likni yutishi natijasida fotokatalizator yuzasiga yetib boradigan fotonlar sonining kamayishi sababli samaradorlik pasaydi. Qayta foydalanish tajribalari ketma-ket besh sikl davomida amalga oshirildi. Degradatsiya samaradorligi birinchi sikldagi 88,96% dan beshinchi siklda 51,46%

gacha bosqichma-bosqich kamaydi. Ushbu pasayish fotokatalizator yuzasining ifloslanishi, strukturaviy o'zgarishlar hamda faol markazlarning yo'qolishi bilan izohlanadi. Natijalar shuni ko'rsatdiki, kalsinatsiya qilinmagan CuO–Fe₂O₃ nanokompoziti kristallanish darajasi nisbatan past bo'lishiga qaramay, 88,95% fotokatalitik samaradorlikni namoyon etdi. Bu esa mazkur tizimda solishtirma sirt maydoni (152,53 m²/g) fotokatalitik faollikni belgilovchi asosiy omil ekanligini tasdiqlaydi. Kalsinatsiya jarayoni kristallanish darajasini oshirib, taqiqlangan zona energiyasini kamaytirgan bo'lsa-da, solishtirma sirt maydonining keskin kamayishi fotokatalitik faollikka ancha salbiy ta'sir ko'rsatdi. Shuning uchun ushbu tizimda sirt maydonining kamayishi kristallanish darajasining ortishi bilan erishilgan ijobiy ta'sirdan ustun bo'ldi. Taklif etilgan mexanokimyoviy sintez usuli an'anaviy kimyoviy sintez usullariga nisbatan bir qator muhim afzalliklarga ega. Xususan, u erituvchilardan foydalanmasligi, energiya tejamlorligi, ekologik xavfsizligi, sanoat miqyosida kengaytirish imkoniyati hamda texnologik soddaligi bilan ajralib turadi. Kimyoviy usullar bilan olingan ayrim fotokatalizatorlarga nisbatan samaradorligi biroz pastroq bo'lishiga qaramay, ushbu yondashuv barqaror va ekologik xavfsiz fotokatalitik materiallarni ishlab chiqish uchun istiqbolli alternativ texnologiya hisoblanadi.



10-rasm. Simulyatsiya qilingan quyosh nuri ostida CuO–Fe₂O₃ nanokompozitlari ishtirokida Rodamin-6G (R-6G) ning fotokatalitik degradatsiyasiga oid natijalar: chiziqli kinetik grafik (a), degradatsiya darajasi (%) (b), kinetik tezlik konstantasi (c), kalsinatsiya haroratining ta'siri (d), eritma pH qiymatining ta'siri (e), boshlang'ich konsentratsiyaning ta'siri (f), katalizator miqdorining ta'siri (g) hamda fotokatalizatorning qayta foydalanish samaradorligi (h) (Zain va boshq., 2025).

To'rtta paneldan iborat kompleks qiyosiy rasm kalsinatsiya haroratlari (kalsinatsiya qilinmagan, 300°C, 600°C va 900°C) bo'yicha CuO–ZrO₂, hamda

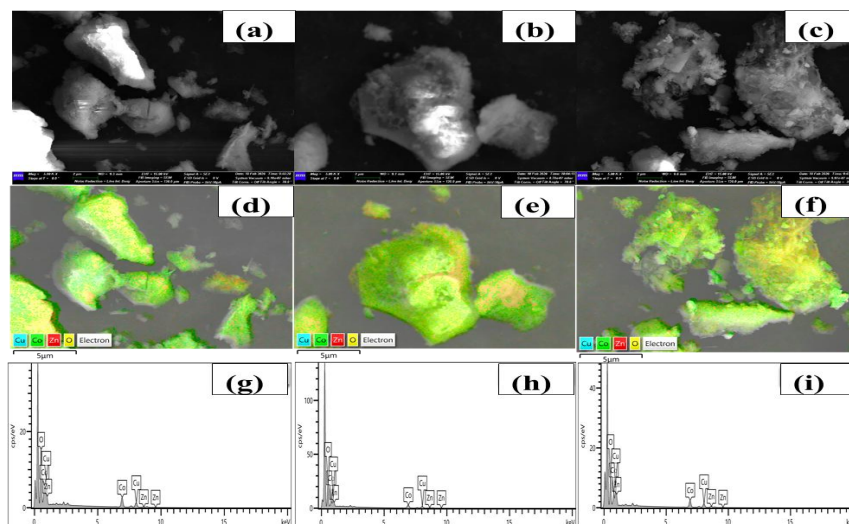
$\text{CuO-Fe}_2\text{O}_3$ bimetall nanokompozitlari uchun solishtirma sirt maydoni, kristallit o'lchami, taqiqlangan zona energiyasi va fotokatalitik degradatsiya samaradorligi o'rtasidagi bog'liqlikni aniq namoyon etadi. Ushbu rasm solishtirma sirt maydoni va kristallanish darajasi o'rtasidagi o'zaro muvozanatni yaqqol ko'rsatadi. A panel (Sirt maydoni – harorat bog'liqligi) barcha tizimlarda kalsinatsiya harorati ortishi bilan solishtirma sirt maydoni keskin kamayishini ko'rsatadi. Xususan, $\text{CuO-Fe}_2\text{O}_3$ nanokompoziti eng katta boshlang'ich sirt maydoniga ($152,53 \text{ m}^2/\text{g}$) ega bo'lib, harorat oshishi bilan eng keskin kamayishni namoyon etadi. B panel (Kristallit o'lchami – harorat bog'liqligi) esa buning teskarisini ko'rsatadi: barcha material tizimlarida kristallit o'lchami kalsinatsiya harorati ortishi bilan muntazam ravishda ortib boradi. C panel (Band gap energiyasi – harorat bog'liqligi) kalsinatsiya harorati oshishi bilan barcha nanokompozitlarda taqiqlangan zona energiyasining bosqichma-bosqich kamayishini aks ettiradi. D panel (Fotokatalitik degradatsiya samaradorligi – harorat bog'liqligi) materiallar orasidagi muhim farqlarni ochib beradi. $\text{CuO-Fe}_2\text{O}_3$ nanokompozitlari kalsinatsiya qilinmagan holatda mos ravishda 88,95% degradatsiya samaradorligini namoyon etib, kristallanish darajasi nisbatan past bo'lishiga qaramay eng yuqori fotokatalitik faollikka ega ekanligini ko'rsatadi. Bunga qarama-qarshi ravishda, CuO-ZrO_2 nanokompoziti 900°C da kalsinatsiya qilinganda 77,27% degradatsiya samaradorligiga erishib, eng yuqori fotokatalitik faollikni namoyon etdi. Bu natija materialning kristallanish darajasi va strukturaviy bir jinsliligining yaxshilanishi bilan izohlanadi. Ushbu qiyosiy tahlil shuni ko'rsatadiki, $\text{CuO-Fe}_2\text{O}_3$ tizimlarida solishtirma sirt maydoni fotokatalitik samaradorlikni belgilovchi asosiy omil bo'lib, uning ta'siri kristallanish darajasidan ustun turadi. Aksincha, CuO-ZrO_2 tizimida esa kristallanish darajasi va strukturaviy bir jinslilik fotokatalitik faollikni belgilovchi asosiy omillar hisoblanadi va ularning ta'siri sirt maydonidan muhimroqdir. Mazkur natijalar har bir material tizimi uchun optimallashtirish alohida yondashuvni talab qilishini va barcha fotokatalitik materiallar uchun yagona umumiy qonuniyat mavjud emasligini ko'rsatadi. Xulosa: ushbu qiyosiy rasm fotokatalitik faollikni belgilovchi dominant omil materialning kimyoviy tarkibi va strukturaviy xususiyatlariga bog'liq holda o'zgarishini isbotlaydi. Ayrim nanokompozitlar uchun solishtirma sirt maydoni asosiy omil bo'lsa, boshqalari uchun kristallanish darajasi va strukturaviy bir jinslilik hal qiluvchi rol o'ynaydi. Shu sababli, yuqori samarali fotokatalizatorlarni yaratishda har bir material tizimi uchun empirik optimallashtirish alohida amalga oshirilishi zarur.

3-BOB. TRIMETALL OKSIDLI NANOKOMPOZITLAR

3.1. Amorf bio-kapsullangan Co–Cu–Zn qatlamli gidroksidlar. *Citrus maxima* bargi ekstraktidan ko‘p funksiyali qaytaruvchi va stabillashtiruvchi (kapping) reagent sifatida foydalangan holda, uch metalli (Co-Cu-Zn) qatlamli gidroksidlarning ekologik toza sintezi amalga oshirildi. Mis(II) nitrat (99.0%), kobalt(II) nitrat (97-98%), rux nitrat (99%), metiloranj va natriy gidroksid olingan holatda, qo‘shimcha ishlov berilmasdan ishlatildi. O‘simlik ekstraktini tayyorlash uchun Pokistonning Muzaffarobod (AJK) hududidan *C. maxima* barglari yig‘ib olindi, jo‘mrak suvi va deionizatsiyalangan suv bilan ikki marta chayqatildi va xona haroratida 4 soat davomida quritildi. So‘ngra 20 g barg maydalanib, germetik yopiq idishda distillangan suvda 12 soat davomida qaynatildi. Ekstrakt dastlab oddiy filtr qog‘ozi, so‘ngra Whatman No. 1 filtr qog‘ozi orqali suzildi va olingan ekstrakt keyinchalik foydalanish uchun saqlab qo‘yildi. Uch metalli qatlamli gidroksidlar sintezi uchun 1 litr deionizatsiyalangan suvda mos ravishda 0.13, 0.29 va 0.40 g miqdordagi moddalarni eritish orqali $Zn(NO_3)_2$ ning uch xil asosiy (stok) eritmasi tayyorlandi; ularga $Co(NO_3)_2$ (0.915 g) va $Cu(NO_3)_2$ (0.938 g) ning 5 mM li asosiy eritmalarining tegishli miqdorlari qo‘shildi. Odatdagi reaksiya uchun alohida reaktorlarda $Co(NO_3)_2$ va $Cu(NO_3)_2$ asosiy eritmalarining har biridan 30 ml dan, shuningdek, $Zn(NO_3)_2$ asosiy eritmasidan 30 ml olinib, 20 ml o‘simlik ekstrakti bilan aralashtirildi va NaOH eritmasi qo‘shilishi orqali pH qiymati 12 ga barqarorlashtirildi. Har bir aralashma tegishli metall ionlarining o‘ziga xos ranglarini namoyon qiluvchi quyuq gel hosil bo‘lguncha alohida qizdirildi va aralashtirildi. 60 daqiqalik qarish (gellanish) jarayonidan so‘ng, barcha uchala gel bitta reaktorga birlashtirildi, qo‘shimcha moddalar qo‘shilmasdan 5 soat davomida qizdirildi va aralashtirildi, so‘ngra atrof-muhit haroratida 24 soat davomida qarishga qoldirildi. Yakuniy mahsulot sentrifugalash orqali ajratib olindi, issiq deionizatsiyalangan suv bilan yaxshilab yuvildi, quritish javonida 120°C haroratda quritildi va S1-LH deb belgilandi. Rux miqdori turlicha bo‘lgan S2-LH va S3-LH namunalari uchun ham xuddi shu muolaja takrorlandi, bunda yagona o‘zgarish faqat $Zn(NO_3)_2$ asosiy eritmasining konsentratsiyasi bo‘ldi.

SEM tahlili morfologik o‘zgarishlarning o‘rish va agregatsiya jarayonlarini tubdan o‘zgartiruvchi tarkibiy modifikator vazifasini o‘tovchi Zn miqdoriga to‘g‘ridan-to‘g‘ri bog‘liqligini ko‘rsatdi. S1-LH namunasi kamroq ko‘rinadigan sirt g‘ovaklariga ega bo‘lgan nisbatan yirik, tartibsiz, bloksimon va monolit agregatlarni namoyon qilgan bo‘lsa, S3-LH namunasi yuqori g‘ovaklikka ega, gubkasimon (g‘ovak-yumshoq) tuzilish va ortib boruvchi sirtlararo faol markazlarni ko‘rsatdi. EDX xaritalash natijalari Co, Cu, Zn va O elementlarining namuna matritsasi bo‘ylab gomogen taqsimlanganini tasdiqladi. Bu esa uchala metall ionining gidroksid karkasiga sezilarli faza ajralishi yoki elementar klasterlanishlarsiz, bir tekisda integratsiyalashganidan dalolat beradi. Ushbu bir tekis taqsimot fotokatalitik jarayonlar uchun juda muhimdir, chunki u ko‘p metalli geterootishlarning (heterojunctions) teng taqsimlanishini ta‘minlaydi, bu esa fazoviy zaryad ajralishini va reaktiv kislorod shakllarining (ROS) hosil bo‘lishini maksimal darajaga yetkazadi. EDX spektri barcha uchta namunada (S1-LH, S2-LH va S3-LH) asosiy

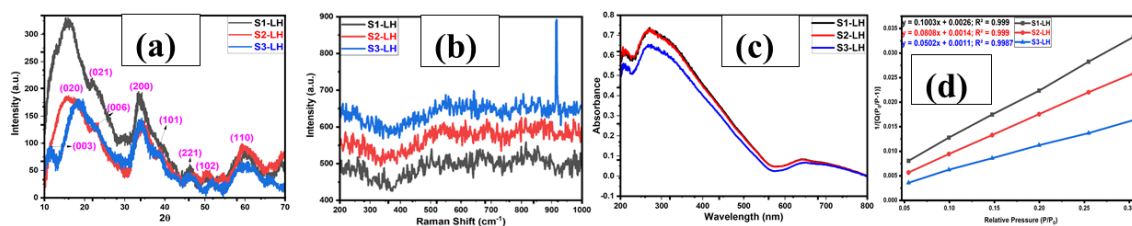
elementar tarkibiy qismlar sifatida kobalt, mis, rux va kislorod mavjudligini tasdiqladi va hech qanday aniqlanadigan aralashmalar kuzatilmadi, bu esa biogen sintez usulining yuqori tozaligini tasdiqlaydi. Elementar tarkib tahlili uchala namunada rux miqdorining tizimli ravishda o'zgarib borishini ko'rsatdi, bu esa maqsadli rejalashtirilgan tarkibiy dizaynga mos keladi: bunda S1-LH eng kam Zn miqdoriga, S2-LH o'rtacha Zn miqdoriga va S3-LH eng yuqori Zn miqdoriga ega bo'ldi.



11-rasm. Amorf bio-kapsullangan Co–Cu–Zn qatlamli gidroksidlarning SEM tasvirlari (a–c), EDX elementlar xaritalari (d–f) va EDX spektrlari (g–i) (Othman et al., 2026).

XRD difraktogrammlarida kristall bo'lmagan yoki yarim amorf strukturaviy xususiyatlarni aks ettiruvchi shovqinli profillar kuzatildi. Bunda $2\theta = 11,42^\circ$ dagi birinchi tartibli bazal refleksiya (003) tekislikka indekslandi va $d_{003} = 7,74 \text{ \AA}$ qatlamlararo masofa aniqlandi. Bu holat hajm jihatdan yirik fitokimyoviy organik birikmalarning birgalikda interkalsiyalangan suv molekullari bilan qatlamlararo sohaga muvaffaqiyatli joylashganligini ko'rsatadi. $2\theta = 23,18^\circ$ dagi keng difraksion cho'qqi (006) tekislikka tegishli deb belgilandi. Past kristallik darajasiga ega boshqa gidroksid fazalar sifatida ortorombik $\text{Cu}(\text{OH})_2$ (JCPDS 00-013-0420) ning $16,55^\circ$ va $21,99^\circ$ dagi, ortorombik $\epsilon\text{-Zn}(\text{OH})_2$ (JCPDS 00-038-0385) ning $34,39^\circ$ va $46,23^\circ$ dagi hamda geksagonal $\beta\text{-Co}(\text{OH})_2$ (JCPDS 00-030-0443) ning $38,99^\circ$, $50,27^\circ$ va $59,37^\circ$ dagi refleksiylari aniqlandi. Keng va noaniq difraksion profillar uch xil metall ionining hamda biologik kelib chiqishga ega sirt turlarining strukturaga kiritilishi uzoq masofali davriylikni sezilarli darajada buzgan holda, lokal metall–gidroksid koordinatsiyasining saqlanib qolishini ko'rsatdi. Raman tahlili S1-LH va S2-LH namunalari uchun shovqinli va aniq ifodalanmagan spektrlarni ko'rsatib, uzoq masofali atom tartibining mavjud emasligi bilan tavsiflanadigan asosan amorf faza shakllanganligini ko'rsatdi. Biroq, S3-LH namunasida 917 cm^{-1} da aniq va keskin cho'qqi kuzatilib, u $\delta\text{-OH}$ egilish tebranishi bilan bog'landi. Bu natija Zn miqdorining ortishi lokal atom tartibining shakllanishini rag'batlantirishi hamda o'simlik ekstraktining fluoressensiyasi bilan bog'liq maskalanish effektini kamaytirgan holda nisbatan qattiq va tartibli tebranish domenlarining hosil bo'lishiga

yordam berishini ko'rsatadi. DRS tahlili 200–800 nm oralig'ida keng va intensiv yorug'likni yutish qobiliyatini namoyon etib, taxminan 230, 540 va 800 nm da uchta xarakterli yutilish chegarasini aniqladi. Ular mos ravishda taxminan 5,4, 2,3 va 1,6 eV o'tish energiyalariga to'g'ri keladi. Yuqori energiyali ultrabinafsha (UV) sohadagi yutilish taxminan 5,4 eV ga teng fundamental taqiqlangan zona energiyasi (band gap) bilan tavsiflanib, metall–ligand zaryad ko'chishi polosalari hamda fitokimyoviy stabillashtiruvchi (capping) agentlar tarkibidagi aromatik halqalarning $\pi \rightarrow \pi^*$ o'tishlariga tegishli deb baholandi. Ko'rinadigan sohadagi taxminan 2,3 eV li o'tish $O^{2-} \rightarrow M^{2+}$ ligand–metall zaryad ko'chishi bilan belgilanadi. Past energiyali, taxminan 1,6 eV dagi yutilish esa oktaedrik koordinatsiyalangan Co^{2+} ionlarining spin bo'yicha ruxsat etilgan d–d elektron o'tishlari hamda kristall panjarada chegaralangan Cu^{2+} ionlarining ajralgan Yahn–Teller (Jahn–Teller) holatlariga indekslandi. BET tahlili natijasida solishtirma sirt maydoni S1-LH uchun 42,31 m²/g dan S2-LH uchun 52,97 m²/g gacha izchil ortgani va S3-LH namunasida 84,87 m²/g bilan maksimal qiymatga yetgani aniqlandi. Shu bilan birga, g'ovak hajmi 0,26 dan 0,78 cm³/g gacha oshdi. Mazkur tizimli o'zgarishlar SEM tahlili orqali tasdiqlangan strukturaviy o'zgarishlar bilan yaxshi muvofiqlashdi. Ya'ni, Zn miqdorining ortishi ultra-kichik, yarim amorf Zn(OH)₂ sirt nanoklasterlarining nazorat ostida shakllanishini rag'batlantirdi. Ushbu nanoklasterlar donalar chegaralarini mustahkamlab, uzoq masofali zich kristallikning rivojlanishini chekladi va natijada morfologik jihatdan parchalanib, juda ochiq hamda katta solishtirma sirt maydoniga ega agregat tarmoqlarning shakllanishiga olib keldi.

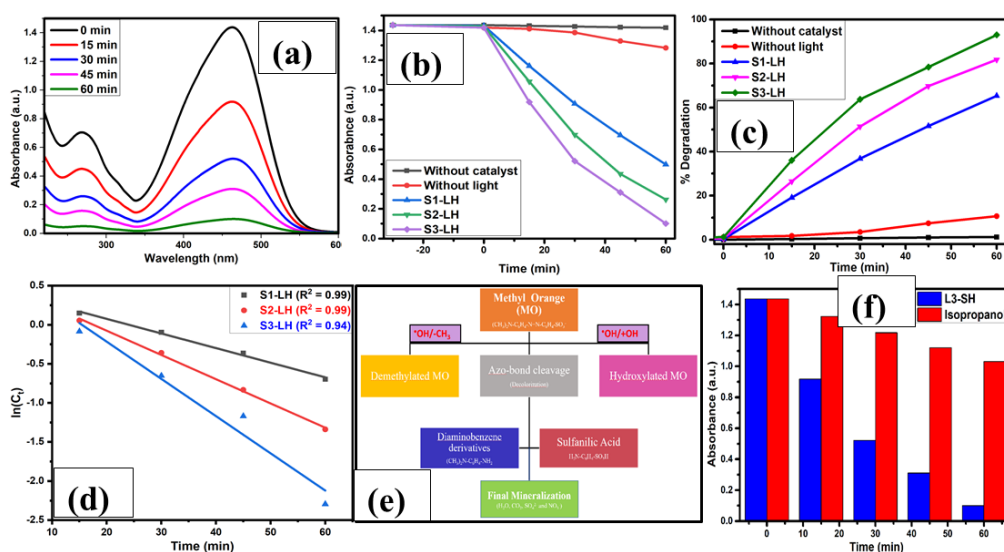


12-rasm. Amorf bio-kapsullangan Co–Cu–Zn qatlamli gidroksidlarning XRD difraktogrammalari (a), Raman spektrlari (b), DRS spektrlari (c) va N₂ adsorbsiya tahlili (d) (Othman et al., 2026).

Fotokatalitik tahlil natijalariga ko'ra, 60 daqiqalik UV nurlanishdan so'ng MO degradatsiyasi S1-LH uchun 65,31%, S2-LH uchun 81,74% va S3-LH uchun 92,98% ni tashkil etdi. S3-LH ning yuqori fotokatalitik samaradorligi optik taqiqlangan zona energiyasining tizimli ravishda kengayishi va absolyut zona chegaralarining optimal qayta moslashuvi bilan bog'liq bo'lib, bu gidroksil radikallari ($\bullet OH$) hosil bo'lishi uchun kuchli termodinamik ortiqcha potensialni yuzaga keltiradi. Nazorat tajribalari degradatsiya jarayoni yorug'lik bilan faollashadigan o'ziga xos sinergik katalitik hodisa ekanligini tasdiqladi: faqat yorug'lik ta'sirida o'z-o'zidan fotoliz juda kam darajada kuzatildi; S3-LH ishtirokidagi qorong'i sharoitdagi nazorat tajribasida fizik adsorbsiya hisobiga atigi 10,68% kamayish qayd etildi; fotokatalizator va yorug'lik birgalikda qo'llanganda esa degradatsiya keskin tezlashib, 92,98% ga yetdi. Taklif etilgan mexanizmga ko'ra, dastlab anion tabiatli MO molekullari manfiy zaryadlangan sulfonat guruhlari bilan protonlangan, musbat zaryadlangan metall

gidroksid qatlamlari o'rtasidagi elektrostatik tortishish natijasida katalizator sirtiga birikadi. Yoritish jarayonida katalizator fotonlarni yutib, fotoqo'zg'aladi va elektronlar o'tkazuvchanlik zonasiga (CB) o'tadi, kovaklar esa valent zonada (VB) qoladi. Ko'p metallik tarkib zaryad tashuvchilarni tutib qoluvchi oraliq energetik holatlarni hosil qilish orqali zaryadlarning samarali ajralishini ta'minlaydi. h^+ sirt gidroksil guruhlari yoki sirtga adsorbsiyalangan suv molekulalari bilan reaksiyaga kirishib, $\bullet OH$ hosil qiladi, qo'zg'algan elektronlar esa erigan kislorodni qaytarib, superoksid radikal anionlari ($O_2^{\bullet-}$) ni hosil qiladi. Hosil bo'lgan reaktiv kislorod turlari (ROS) MO molekulalarining strukturasi bilan reaksiyaga kirishadi. Degradatsiya jarayoni aromatik halqadagi N-demetillanish va gidroksillanish bosqichlaridan boshlanadi. Rangning yo'qolishi markaziy azo bog'ining ($-N=N-$) uzilishi natijasida sodir bo'lib, natijada sulfon kislota va N,N-dimetil-p-fenilendiamin hosilalariga parchalanish yuz beradi. Uzoq davom etgan nurlanish natijasida aromatik halqalarning oksidlovchi ochilishi sodir bo'lib, quyi molekulyar massali organik kislotalar hosil bo'ladi va jarayon oxir-oqibat H_2O , CO_2 , SO_4^{2-} va NO_3^- gacha to'liq mineralizatsiyalanish bilan yakunlanadi. Radikallarni tutib qolish tajribasi IPA ishtirokida degradatsiya jarayoni asosan $\bullet OH$ radikallari orqali kechishini tasdiqladi. Xususan, IPA qo'shilganda degradatsiya samaradorligi keskin pasayib, 28,11% ni tashkil etdi. Ekspluatatsion parametrlarni o'rganish natijasida boshlang'ich konsentratsiya 0,02 dan 0,06 mM gacha oshirilganda degradatsiya darajasi 79,64% dan 92,8% gacha ortgani aniqlandi. Katalizator miqdori bo'yicha 100 mg/L optimal chegara sifatida belgilandi. Maksimal degradatsiya samaradorligi $pH = 4$ da 92,98% ni tashkil etgan bo'lsa, $pH = 6$ da bu ko'rsatkich 78,04% gacha kamaydi. Bunday pasayish OH^- ionlari va MO molekulalari o'rtasidagi raqobatli adsorbsiya bilan izohlanadi. Qayta foydalanish tajribalarida samaradorlikning bosqichma-bosqich pasayishi degradatsiya jarayonida hosil bo'lgan qiyin parchalanadigan oraliq mahsulotlarning to'planib, faol bog'lanish markazlarini to'sib qo'yishi bilan bog'liq bo'ldi. Kinetik tahlil natijalari tajriba ma'lumotlarining ham psevdonol tartibli, ham psevdobirinchi tartibli kinetik modellarga yaxshi mos kelishini ko'rsatdi. Psevdonol tartibli model uchun yuqori $R^2 = 0,996$ qiymatining S1-LH namunasida kuzatilishi g'ovak va tartibsiz amorf tuzilmaning ortiqcha miqdordagi ochiq faol markazlarni ta'minlashi bilan izohlandi. Biroq, degradatsiyaning umumiy kinetik trayektoriyasi Langmyur–Xinshilvud (Langmuir–Hinshelwood) mexanizmi doirasidagi psevdobirinchi tartibli model bilan eng yaxshi tavsiflandi. Eng yuqori samaradorlikka ega S3-LH namunasi uchun 92,98% degradatsiya va $k_1 = 0,04763 \text{ min}^{-1}$ qiymatlarining olinishi uning yuqori g'ovakli morfologiyasi sababli kinetik jarayonning sirt reaksiyasi bilan chegaralangan rejimdan diffuziya bilan chegaralangan rejimga o'tganligini ko'rsatdi. Qiyosiy baholash natijalari S3-LH katalizatori murakkab sharoitlarda ham raqobatbardosh yuqori samaradorlik ko'rsatkichlariga ega ekanligini ko'rsatdi. An'anaviy ko'p metallik tuzilmalar, masalan, $MgAlCu$ -LDH (96,5%) va $CuAl$ -LDH (93%), o'xshash degradatsiya samaradorligini namoyon qilgan bo'lsa-da, ularni olishda yuqori energiya sarfini va agressiv prekursorlarni talab qiluvchi an'anaviy gidrotermal

usullar qo'llaniladi. S3-LH katalizatori esa ekologik xavfsiz biologik sintez jarayoni yordamida atigi 60 daqiqa ichida MO ning 92,98% degradatsiyasini ta'minladi.



13-rasm. UV nurlanishi ostida amorf bio-kapsullangan Co–Cu–Zn qatlamli gidroksid ishtirokida MO ning fotokatalitik degradatsiyasi natijalari: degradatsiya profili (a), chiziqli grafiklar (b), degradatsiya darajasi (%) (c), tezlik konstantasi (d), degradatsiya mexanizmi (e) va radikallarni tutib qolish tajribasi natijalari (f) (Othman et al., 2026).

3.2 Sirkoniy bilan legirlangan NiO–ZnO nanokompozitlari (yashil sintez usuli). Sirkoniy bilan legirlangan nikel oksidi/rux oksidi (Zr–NiO/ZnO) nanokompozitlari qaytaruvchi va stabillashtiruvchi agent sifatida D. kaki barglari ekstrakti qo'llanilgan ekologik xavfsiz yashil sintez usuli orqali tayyorlandi. Mazkur tadqiqot fotokatalitik qo'llanmalar uchun ushbu material kombinatsiyasining ilk bor sintez qilinishi haqida xabar beradi. D. kaki barglari yig'ilib, yuvildi, soyada quritildi va ekstrakt tayyorlash maqsadida uch soat davomida distillangan suvda qaynatildi. NiO–ZnO nanokompozitlarini sintez qilish uchun avval $Zn(OH)_2$ va $Ni(OH)_2$ gellari alohida tayyorlandi. Buning uchun rux sulfat geksagidrati va nikel sulfat geksagidrati distillangan suvda eritilib, barg ekstrakti qo'shildi hamda aralashma $60^\circ C$ da 30 daqiqa davomida qizdirildi. So'ng hosil qilingan gellar o'zaro aralashtirilib, kuchli aralashtirish ostida $70^\circ C$ da 4 soat davomida qizdirildi va komponentlarning bir jinsli taqsimlanishi ta'minlandi. Olingan mahsulot filtrlandi, etanol va distillangan suv bilan yuvildi hamda $150^\circ C$ da 24 soat davomida quritildi. Zr bilan legirlash uchun tayyorlangan 0,95 g NiO–ZnO nanokompoziti distillangan suvda eritilib, kuchli aralashtirildi. So'ng legirlovchi modda sifatida 0,05 g (0,5%) yoki 0,10 g (1%) sirkoniy xlorid qo'shildi va aralashma $60^\circ C$ da 5 soat davomida aralashtirildi. Eritmaning pH qiymati NaOH yordamida 10 ga yetkazildi. Yakuniy mahsulot filtrlandi, yuvildi, $150^\circ C$ da quritildi, maydalandi va $500^\circ C$ da 2 soat davomida kalsinatsiya qilindi.

XRD tahlili difraktogrammada asosan geksagonal ZnO fazasiga tegishli kuchli difraksion cho'qqilar va difraksion cho'qqilar o'zaro ustma-ust tushgani sababli nisbatan past intensivlikdagi NiO cho'qqilari mavjudligini ko'rsatdi. Sirkoniy legirlovchi elementiga tegishli alohida difraksion cho'qqilar kuzatilmadi,

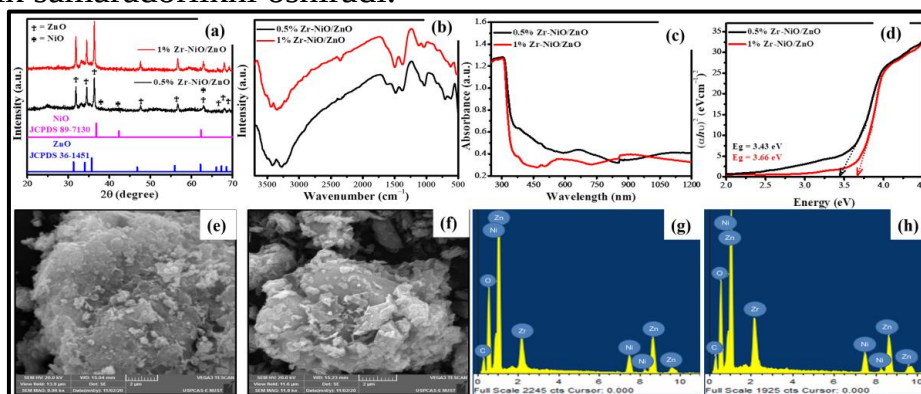
bu esa legirlovchi atomlarning ZnO ning geksagonal kristall panjarasiga muvaffaqiyatli integratsiyalashganini hamda kristall tuzilmani buzmasdan yoki ikkilamchi fazalarni hosil qilmasdan joylashganini ko'rsatadi. Ushbu holat legirlovchi elementning kam miqdorda qo'llanilishi tufayli Zr atomlarining kristall panjaradagi interstitsial bo'shliqlarni egallashi yoki Zn^{2+} hamda Ni^{2+} ionlari o'rnini qisman bosishi bilan izohlanadi. Difraksion cho'qqilar ZnO ning NiO yuzasida to'planishi natijasida biroz katta difraksiya burchaklari tomon siljidi. Legirlovchi modda miqdori 0,5% dan 1% gacha oshirilganda difraksion cho'qqilar intensivligi ortdi, bu esa kristallit o'lchamining kattalashishi bilan bog'liq. Debye-Scherrer formulasi asosida hisoblangan o'rtacha kristallit o'lchami 0,5% Zr-NiO/ZnO uchun 35,5 nm, 1% Zr-NiO/ZnO uchun esa 49,4 nm ni tashkil etdi.

FTIR tahlili 3700–3000 cm^{-1} oralig'ida adsorbsiyalangan suv molekulalarining O–H valent tebranishlariga tegishli keng yutilish polosalarini, 1500 cm^{-1} atrofida O–H deformatsion tebranishlariga tegishli polosalarni, 1370 cm^{-1} da o'simlik ekstrakti tarkibidagi aromatik C–C bog'lariga tegishli polosalarni hamda 1030–1070 cm^{-1} oralig'ida C–O bog'larining tebranishlariga mos keluvchi polosalarni namoyon etdi. 0,5% Zr-NiO/ZnO namunasi uchun 713, 590 va 500 cm^{-1} dagi polosalar mos ravishda Ni–O, Zn–O va Zr–O bog'larining valent tebranishlariga tegishli bo'ldi. 1% Zr-NiO/ZnO namunasi uchun esa 598, 561 va 517 cm^{-1} dagi polosalar metall–kislorod bog'larining valent tebranishlariga mos kelib, metall–kislorod bog'lari muvaffaqiyatli hosil bo'lganini hamda fitokimyoviy moddalarning capping agent sifatidagi samarali rolini tasdiqladi. DRS tahlili ultrabinafsha (UV) sohada yuqori absorbsiya kuzatilganini ko'rsatdi, bu esa sintez qilingan nanokompozitlarda elektronlarni qo'zg'atish uchun yuqori energiyali fotonlar talab qilinishini bildiradi. 0,5% Zr-NiO/ZnO namunasining spektrida 580 nm va 900 nm atrofida o'simlik ekstraktidan qolgan adsorbsiyalangan organik birikmalarga tegishli absorbsiya polosalari kuzatildi. Tauc usuli yordamida aniqlangan taqiqlangan zona energiyasi (band gap) 0,5% Zr-NiO/ZnO uchun 3,43 eV, 1% Zr-NiO/ZnO uchun esa 3,66 eV ni tashkil etdi, bu esa legirlovchi modda konsentratsiyasi ortishi bilan band gap kengayishini ko'rsatadi.

SEM tahlili 0,5% Zr-NiO/ZnO namunasida zarrachalar 1% Zr-NiO/ZnO ga nisbatan kamroq aglomeratsiyalanganini ko'rsatdi, har ikkala holatda ham mikrostrukturalar tartibsiz morfologiyaga ega bo'lib, notekis taqsimlangan. Kamroq aglomeratsiyalangan nanozarrachalar katta solishtirma sirt maydonini ta'minlaganligi sababli fotokatalitik samaradorlikka ijobiy ta'sir ko'rsatadi. EDX natijalariga ko'ra, 0,5% legirlangan mahsulot tarkibida uglerod 16,30%, nikel 7,24%, rux 32,56%, kislorod 42,70% va sirkoniy 1,20% ni tashkil etdi. 1% legirlangan mahsulot tarkibida esa uglerod 12,21%, nikel 6,32%, rux 41,15%, kislorod 38,13% va sirkoniy 2,19% ni tashkil etdi. Har ikkala nanokompozitda ham Zn ning yuqori ulushi XRD natijalarini tasdiqlaydi va sintez jarayonida $Zn(OH)_2$ ning $Ni(OH)_2$ ga nisbatan ko'proq hosil bo'lganligi sababli yakuniy mahsulotda rux miqdori yuqori bo'lganini ko'rsatadi. TEM tahlili 0,5% Zr-NiO/ZnO namunasida zarrachalar kamroq aglomeratsiyalanganini, ularning chegaralari aniqroq va o'zaro ustma-ust tushishi kamroq ekanligini ko'rsatdi. Aksincha, 1% Zr-NiO/ZnO namunasi kuchliroq aglomeratsiyalangan bo'lib, yirik va zich joylashgan zarracha klasterlarini

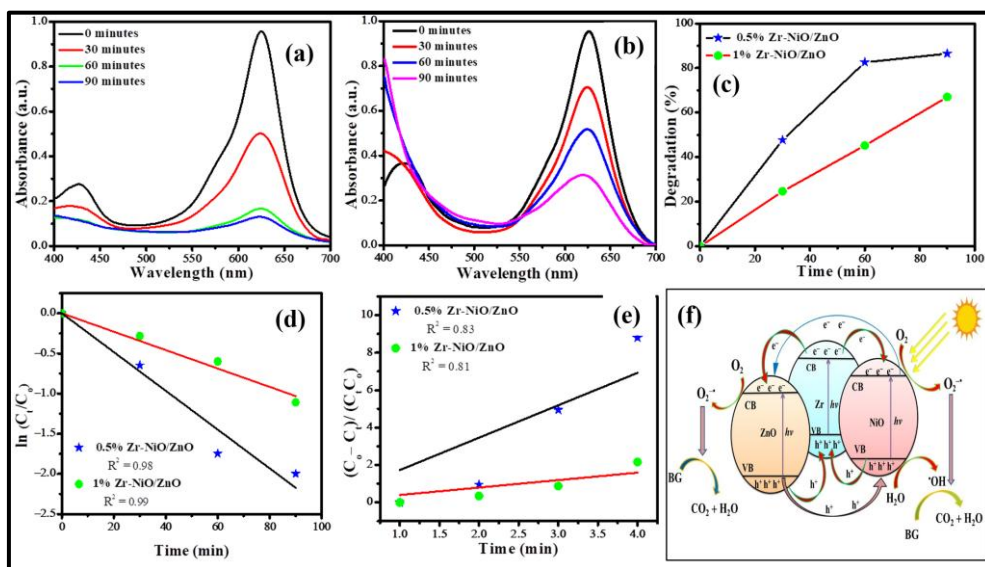
hosil qilgan. O‘rtacha zarracha o‘lchami 0,5% Zr–NiO/ZnO uchun 14,67 nm, 1% Zr–NiO/ZnO uchun esa 17,40 nm ni tashkil etdi.

Brilliant Green bo‘yog‘iga nisbatan olib borilgan fotokatalitik tadqiqotlar natijasida 0,5% Zr–NiO/ZnO nanokompoziti 90 daqiqa ichida 86,45% degradatsiyani ta‘minladi va reaksiyaning kinetik tezlik konstantasi $0,024 \text{ min}^{-1}$ ni tashkil etdi. Bunga nisbatan 1% Zr–NiO/ZnO namunasi 67% degradatsiyaga erishib, uning kinetik tezlik konstantasi $0,011 \text{ min}^{-1}$ bo‘ldi. 4-nitrofenol uchun esa 0,5% Zr–NiO/ZnO 60 daqiqa davomida 89% degradatsiyani amalga oshirdi va $0,044 \text{ min}^{-1}$ tezlik konstantasini namoyon etdi. Aksincha, 1% Zr–NiO/ZnO faqat 51% degradatsiyani ta‘minlab, uning kinetik tezlik konstantasi $0,015 \text{ min}^{-1}$ ni tashkil etdi. 0,5% Zr–NiO/ZnO nanokompozitining yuqori fotokatalitik samaradorligi uning taqiqlangan zona energiyasining nisbatan kichik (3,43 eV) bo‘lishi tufayli elektron–teshik juftliklari hosil bo‘lish tezligining yuqoriligi hamda nanozarrachalarning kamroq aglomeratsiyalanganligi sababli solishtirma sirt maydonining kattaligi bilan izohlanadi. Fotokatalitik mexanizmga ko‘ra, quyosh nuri Zr–NiO/ZnO nanokompoziti yuzasiga tushganda elektronlar valent zonadan (VB) o‘tkazuvchanlik zonasiga (CB) qo‘zg‘atiladi. Sirkoniy ning o‘tkazuvchanlik zonasi ZnO va NiO nikiga nisbatan yuqoriroq (yanada manfiy potensialga ega), NiO ning o‘tkazuvchanlik zonasi esa ZnO nikiga nisbatan manfiyroq bo‘lganligi sababli elektronlar Zr ning o‘tkazuvchanlik zonasidan ZnO va NiO ning o‘tkazuvchanlik zonalariga, shuningdek NiO ning o‘tkazuvchanlik zonasidan ZnO ning o‘tkazuvchanlik zonasiga ko‘chadi. ZnO va NiO ning o‘tkazuvchanlik zonalarida kislorod molekullari qaytarilib superoksid radikallari ($\text{O}_2^{\bullet-}$) hosil qiladi va ular ifloslantiruvchi moddalar bilan reaksiyaga kirishib degradatsiyani amalga oshiradi. Shu bilan bir vaqtda, ZnO va NiO ning valent zonasidagi teshiklar Zr ning valent zonasiga, shuningdek ZnO ning valent zonasidan NiO ning valent zonasiga ko‘chadi va OH^- ionlarini oksidlab gidroksil radikallari ($\bullet\text{OH}$) ni hosil qiladi. Ushbu radikallar ham ifloslantiruvchi moddalar bilan reaksiyaga kirishib ularning parchalanishini ta‘minlaydi. Elektronlar va teshiklarning bunday bir vaqtning o‘zida ko‘chishi ularning rekombinatsiyalanish ehtimolini sezilarli darajada kamaytiradi va natijada fotokatalitik samaradorlikni oshiradi.



14-rasm. Sof va Zr bilan legirlangan NiO/ZnO nanokompozitlarining XRD difraktogrammalari (a), FTIR spektrlari (b), DRS spektrlari (c), Tauc grafiklari (d), SEM mikrograflari (e, f) hamda EDX spektrlari (g, h) (Haq va boshq., 2024).

Zr legirlovchi moddasining miqdorini 0,5% dan 1% gacha oshirish fotokatalitik faollikning pasayishiga olib keladi. Bu holat to‘rtta asosiy mexanizm bilan izohlanadi: (1) taqiqlangan zona energiyasining kengayishi ($3,43 \text{ eV} \rightarrow 3,66 \text{ eV}$), buning natijasida elektronlarni qo‘zg‘atish uchun yuqoriroq energiyali fotonlar talab qilinadi va hosil bo‘ladigan elektron–teshik juftliklari soni kamayadi; (2) nuqsonlarning hosil bo‘lishi, bunda ortiqcha Zr^{4+} ionlari kristall panjarada deformatsiyalar hamda taqiqlangan zona ichidagi energetik holatlar ni yuzaga keltirib, rekombinatsiya markazlari sifatida faoliyat ko‘rsatadi; (3) sirt segregatsiyasi, bunda ortiqcha Zr^{4+} ionlari fotokataliz uchun muhim bo‘lgan Zn^{2+} va Ni^{2+} faol markazlarini qoplaydi; (4) kristallik darajasining pasayishi, bunda kristallit o‘lchami 35,5 nm dan 49,4 nm gacha ortgan bo‘lsa-da, difraksion cho‘qqilarning kengayishi nuqsonlar zichligining ortganligini ko‘rsatadi. Ushbu natijalar legirlash jarayoni juda nozik optimallashtirishni talab qilishini va “ko‘proq miqdor har doim ham yaxshiroq natija bermaydi” degan tamoyilni tasdiqlaydi. Mazkur tizim uchun eng maqbul legirlash konsentratsiyasi 0,5% ekanligi aniqlandi.



15-rasm. Simulyatsiya qilingan quyosh nuri ostida sof va Zr bilan legirlangan NiO/ZnO nanokompozitlari ishtirokida Brilliant Green bo‘yog‘ining fotokatalitik degradatsiyasiga oid natijalar: degradatsiya profili (a, b), degradatsiya darajasi (%) (c), kinetik tezlik konstantasi (d, e) hamda taklif etilgan fotokatalitik mexanizm (f) (Haq va boshq., 2024).

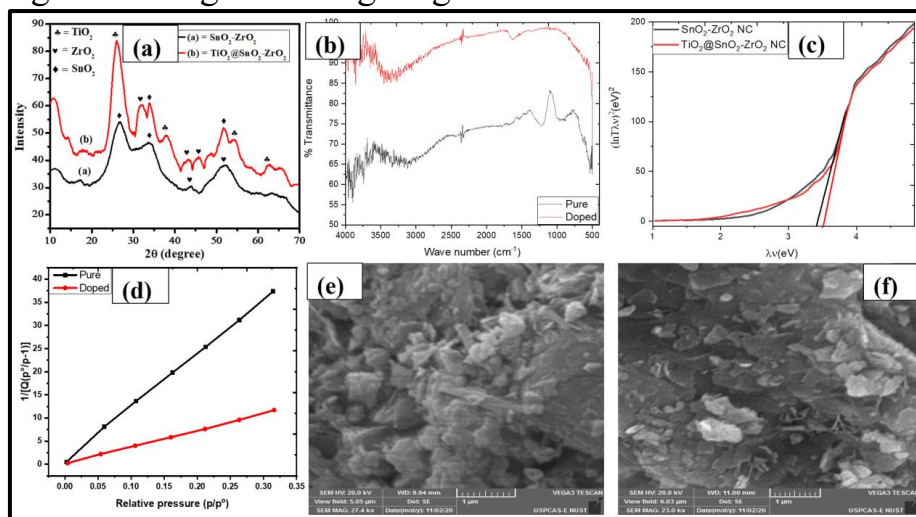
3.3 TiO_2 bilan legirlangan $\text{SnO}_2\text{--ZrO}_2$ nanokompozitlari (yashil sintez usuli). Titan dioksid bilan legirlangan qalay dioksid–sirkoniy dioksid nanokompozitlari *S. chirayita* barg ekstrakti stabillashtiruvchi agent sifatida qo‘llanilgan ekologik toza yashil sintez usuli orqali tayyorlandi. Mazkur tadqiqot *S. chirayita* o‘simlik ekstraktining nanokompozitlar sintezida ilk bor qo‘llanilganligini ifodalaydi. Gentianaceae oilasiga mansub bir yillik dorivor o‘simlik hisoblangan *S. chirayita* tarkibida terpenoidlar, iridoidlar, flavonoidlar, ksantonlar hamda sekoyiridoid glikozidlar kabi tabiiy birikmalar mavjud bo‘lib, ular samarali

qaytaruvchi va stabillashtiruvchi agentlar vazifasini bajaradi. O‘simlik ekstrakti yuvilgan *S. chirayita* barglarini 60 °C da 3 soat davomida distillangan suvda qaynatish, sovitish va filtrlash orqali tayyorlandi. $\text{Sn}(\text{OH})_2$ sintezi uchun SnCl_2 distillangan suvda eritildi, stabillashtiruvchi sifatida o‘simlik ekstrakti qo‘shildi va aralashma 45 daqiqa davomida qizdirilib aralashtirildi. So‘ngra NaOH eritmasi qo‘shilib pH qiymati moslashtirildi, natijada hosil bo‘lgan cho‘kma nanozarrachalar filtrlanib, distillangan suv va etanol bilan yuvildi hamda 90 °C da quritildi. Xuddi shu usul ZrCl_2 dan $\text{Zr}(\text{OH})_2$ sintezi uchun ham qo‘llanildi. $\text{SnO}_2\text{--ZrO}_2$ nanokompozitini sintez qilishda tayyorlangan $\text{Sn}(\text{OH})_2$ va $\text{Zr}(\text{OH})_2$ (har biri 0,5 g) distillangan suvda gidroliz qilindi, 0,1 M NaOH eritmasi qo‘shilib pH 10 ga yetkazildi, aralashma 4 soat davomida qizdirilib aralashtirildi, so‘ng 12 soat xona haroratida saqlandi, yuvildi va 100 °C da quritildi. $\text{TiO}_2@\text{SnO}_2\text{--ZrO}_2$ nanokompozitini tayyorlash uchun 1 g $\text{SnO}_2\text{--ZrO}_2$ nanokompoziti distillangan suvda gidroliz qilinib, 0,5% legirlash uchun titan izopropoksid qo‘shildi. Aralashma 4 soat davomida qizdirilib aralashtirildi, 12 soat davomida saqlandi, yuvildi, pechda quritildi va keyingi tahlillar uchun saqlandi.

XRD tahlili natijalari SnO_2 ga tegishli 26,5° (110), 33,86° (101) va 51,8° (211) difraksion cho‘qqilarni namoyon qilib, JCPDS 01-077-0448 kartasiga mos ravishda tetragonal kristall tuzilmani tasdiqladi. ZrO_2 uchun 31,9° (012), 34,1° (111), 43,1° (022), 45,1° (121) va 52,1° (113) burchaklarda kuzatilgan Bragg reflekslari JCPDS 00-033-1483 ma’lumotlariga mos kelib, romboedrik kristall tuzilishga ega ekanligini ko‘rsatdi. TiO_2 bilan legirlangan namunada esa 25,9° (101), 37,86° (004), 54,3° (211) va 62,5° (204) burchaklardagi qo‘shimcha difraksion cho‘qqilar JCPDS 01-071-1167 kartasiga mos keluvchi anatase fazasining hosil bo‘lganligini tasdiqladi. ZrO_2 , SnO_2 va TiO_2 ga xos alohida difraksion cho‘qqilar majmuasining kuzatilishi tizimda geteroo‘tish (heterojunction) hosil bo‘lganligini ko‘rsatdi. FTIR tahlili 3500–3000 cm^{-1} oralig‘idagi keng yutilish polosi O–H valent tebranishlariga, 2335 cm^{-1} dagi polosaning sirtga adsorbsiyalangan CO_2 ga, 1628 cm^{-1} dagi cho‘qqining O–H deformatsion tebranishlariga, 895 cm^{-1} dagi polosaning Sn–O–Zr bog‘iga, 626 cm^{-1} dagi yutilishning qalay oksidiga xos tebranishlarga hamda 532 cm^{-1} dagi polosaning SnO_2 ning terminal kislorod tebranishlariga tegishli ekanligini ko‘rsatdi. TiO_2 bilan legirlangan kompozitda 1622 cm^{-1} dagi polosa Ti–OH deformatsion tebranishlarini, 1346 va 586 cm^{-1} dagi polosalar esa Zr–O bog‘larini ifodaladi. DRS natijalari $\text{SnO}_2\text{--ZrO}_2$ uchun 300,78 nm, TiO_2 bilan legirlangan namuna uchun esa 294,14 nm da optik o‘tish chegaralarini ko‘rsatdi. Legirlashdan so‘ng kuzatilgan spektral siljish kvant o‘lcham effekti hamda kislorod vakantlari hosil bo‘lishi bilan izohlandi. Tauc grafiklari asosida aniqlangan to‘g‘ridan-to‘g‘ri taqiqlangan zona energiyasi $\text{SnO}_2\text{--ZrO}_2$ uchun 3,41 eV, TiO_2 bilan legirlangan kompozit uchun esa 3,47 eV ni tashkil etdi. TiO_2 legirlanishi natijasida band gap qiymatining ortishi fazalararo nomuvofiqlik yuzaga kelganligini ko‘rsatadi. Bunda TiO_2 alohida va yetarli darajada integratsiyalanmagan faza hosil qilishi yoki kristall panjarada deformatsiyalarni

yuzaga keltirishi natijasida fazalar chegaralarida energiya to'siqlari hosil bo'ladi. Ushbu to'siqlar fotohosil bo'lgan zaryad tashuvchilarning erkin ko'chishini cheklaydi va ularning rekombinatsiyasini kuchaytiradi.

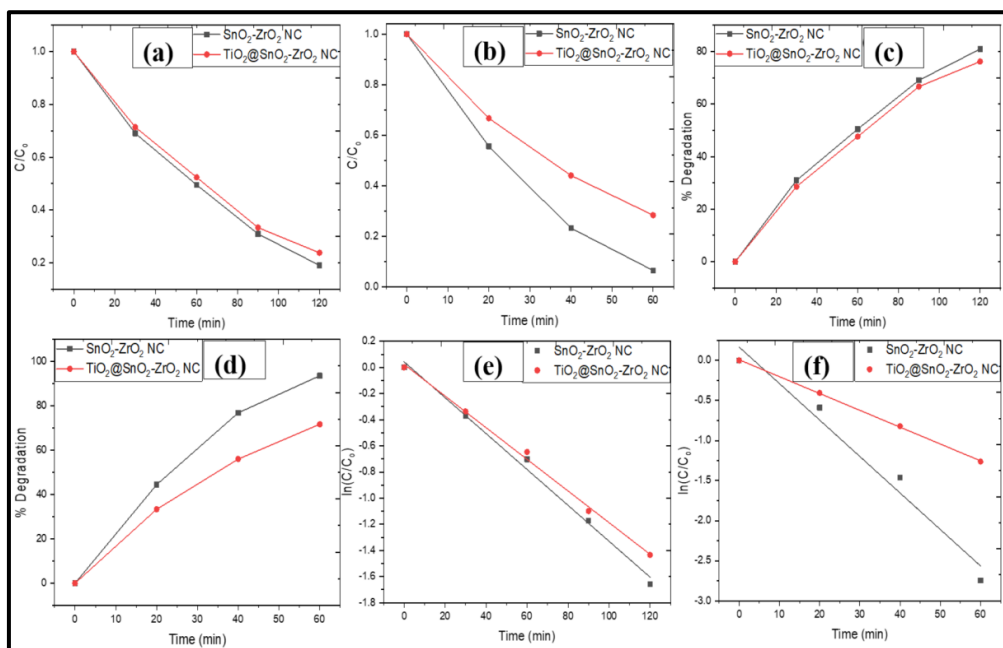
BET usuli bo'yicha N_2 adsorbsiyasi yordamida o'tkazilgan solishtirma sirt maydoni tahlili SnO_2-ZrO_2 nanokompoziti uchun $96,04 \text{ m}^2/\text{g}$, TiO_2 bilan legirlangan SnO_2-ZrO_2 nanokompoziti uchun esa $29,75 \text{ m}^2/\text{g}$ qiymatni ko'rsatdi. Legirlashdan keyin sirt maydonining kamayishi TiO_2 ning SnO_2-ZrO_2 yuzasini qoplashi natijasida sirt faol markazlari va g'ovaklarning band bo'lishi, adsorbsiya uchun mavjud faol sirtning kamayishi hamda TiO_2 ning kiritilishi kristall o'sish jarayoniga ta'sir qilib, yirikroq kristallitlarning hosil bo'lishiga sabab bo'lishi bilan izohlanadi. Natijada sirt maydoni/hajm nisbati kamayadi. SEM tahlili sof SnO_2-ZrO_2 nanokompozitining asosan yirik va zich tuzilmalardan tashkil topganligini, ularning yuzasida esa mayda aglomeratlar notekis taqsimlanganligini ko'rsatdi. Morfologiyada cho'zilgan shakllar ustun bo'lib, mayda aglomeratlar deyarli sferik, cho'zilgan yoki ko'p qirrali shakllarda uchradi. Ularning notekis joylashuvi sirt bo'shliqlarining hosil bo'lishiga olib kelgan bo'lsa-da, umumiy sirt nisbatan silliq va g'ovaksiz xususiyatga ega ekanligi kuzatildi. Zarracha o'lchamlari $51,68-64,38 \text{ nm}$ oralig'ida bo'lib, o'rtacha qiymati $56,09 \text{ nm}$ ni tashkil etdi. $TiO_2@SnO_2-ZrO_2$ nanokompozitida esa morfologiya biroz o'zgarib, ko'plab zich tuzilmalar, sirt bo'shliqlarining kamayishi hamda zich strukturalar yuzasida joylashgan mayda aglomeratlar kuzatildi. Aglomeratlar ko'p qirrali va aniq chegaralarga ega bo'ldi. Zarracha o'lchamlari $56,85-61,68 \text{ nm}$ oralig'ida bo'lib, o'rtacha qiymati $59,48 \text{ nm}$ ni tashkil etdi. TiO_2 bilan legirlash natijasida sirt bo'shliqlarining kamayishi, zichroq strukturaning shakllanishi va zarrachalarning o'rtacha o'lchami ortishi TiO_2 prekursorlari bir tekis legirlovchi qatlam hosil qilmaganligini, aksincha qisman aglomeratsiyaga hamda g'ovaklarning berkilishiga olib kelganligini ko'rsatadi.



16-rasm. Sof va TiO_2 bilan legirlangan ZrO_2-SnO_2 nanokompozitlarining XRD difraktogrammalari (a), FTIR spektrlari (b), Tauc grafiklari (c), BET tahlili natijalari (d) hamda SEM mikrograflari (e, f) (Haq, Mushtaq, va boshq., 2026).

2024-yil 18-iyun kuni soat 11:00 dan 14:00 gacha bo'lgan vaqt oralig'ida quyosh nuri ostida Brilliant Green va 4-nitrofenol ning fotokatalitik degradatsiyasi o'rganildi. Tadqiqot natijalari har ikkala ifloslantiruvchi modda uchun maksimal yutilish (absorbsiya) cho'qqilarining bosqichma-bosqich kamayishini ko'rsatdi. Biroq, 4-nitrofenol uchun absorbsiya intensivligining ancha keskin pasayishi ushbu moddaning fotokatalitik parchalanishga nisbatan yuqoriroq moyillikka ega ekanligini tasdiqladi. Brilliant Green bo'yog'i uchun 120 daqiqa davomida $\text{SnO}_2\text{--ZrO}_2$ nanokompoziti 80,9% degradatsiyani ta'minlab, $1,373 \times 10^{-2} \text{ min}^{-1}$ kinetik tezlik konstantasini namoyon etdi. $\text{TiO}_2@\text{SnO}_2\text{--ZrO}_2$ nanokompoziti esa 77% degradatsiyaga erishib, uning kinetik tezlik konstantasi $1,211 \times 10^{-2} \text{ min}^{-1}$ ni tashkil etdi. 4-nitrofenol uchun 60 daqiqa ichida $\text{SnO}_2\text{--ZrO}_2$ nanokompoziti 93,57% degradatsiyani amalga oshirdi va $4,56 \times 10^{-2} \text{ min}^{-1}$ kinetik tezlik konstantasiga ega bo'ldi. Shu bilan birga, $\text{TiO}_2@\text{SnO}_2\text{--ZrO}_2$ nanokompoziti 71,70% degradatsiyani ta'minlab, uning kinetik tezlik konstantasi $2,78 \times 10^{-2} \text{ min}^{-1}$ ni tashkil etdi. Legirlanmagan $\text{SnO}_2\text{--ZrO}_2$ nanokompozitining yuqori fotokatalitik faolligi uning kattaroq solishtirma sirt maydoni va pastroq taqiqlangan zona energiyasi (band gap) bilan izohlanadi. Ikkala ifloslantiruvchi modda orasidagi fotokatalitik faollikdagi farq ularning molekulyar tuzilishi va reaksiya qobiliyati bilan bog'liq. 4-nitrofenol nisbatan sodda molekulyar tuzilishga ega bo'lib, tarkibidagi elektron tortuvchi nitro guruhi uni gidroksil radikallari ($\bullet\text{OH}$) hujumiga yanada sezgir qiladi. Aksincha, Brilliant Green bir nechta substitutsiyalangan benzol halqalaridan tashkil topgan murakkab molekulyar tuzilishga ega bo'lgani sababli fotokatalitik parchalanishga nisbatan barqarorroq hisoblanadi.

Fotokatalitik mexanizmga ko'ra, $\text{SnO}_2\text{--TiO}_2\text{--ZrO}_2$ nanokompoziti taqiqlangan zona energiyasidan yuqori energiyaga ega bo'lgan quyosh nuri fotonlari ta'sirida nurlantirilganda, tizimning uchala komponenti (SnO_2 , TiO_2 va ZrO_2) da elektron-teshik juftliklari hosil bo'ladi. Fotonlar ta'sirida qo'zg'atilgan elektronlar valent zonadan (VB) o'tkazuvchanlik zonasiga (CB) o'tadi va valent zonada musbat zaryadlangan teshiklar hosil bo'ladi. Qo'zg'atilgan elektronlar asosan TiO_2 ning o'tkazuvchanlik zonasida to'planadi, hosil bo'lgan teshiklar esa ZrO_2 ning valent zonasiga ko'chadi. Valent zonadagi teshiklar katalizator yuzasiga adsorbsiyalangan organik bo'yoq molekulalarini oksidlab radikal kationlar hosil qiladi. Shu bilan bir vaqtda, o'tkazuvchanlik zonasidagi elektronlar kislorod molekulalarini qaytarib superoksid radikallarini ($\text{O}_2\bullet^-$) hosil qiladi. Yuqori reaktivlikka ega bo'lgan radikal kationlar va superoksid radikallari katalizator yuzasida adsorbsiyalangan organik ifloslantiruvchi molekulalarga hujum qilib, ularning kimyoviy tuzilishini bosqichma-bosqich parchalaydi va natijada CO_2 hamda H_2O kabi nisbatan zararsiz mahsulotlarga aylantiradi. ZrO_2 va SnO_2 kabi komponentlarning mavjudligi fotohosil bo'lgan elektronlar va teshiklarni vaqtinchalik tutib qolish orqali ularning rekombinatsiyalanish tezligini kamaytiradi, zaryad tashuvchilarning yashash vaqtini uzaytiradi va natijada fotokatalitik samaradorlikni oshiradi.

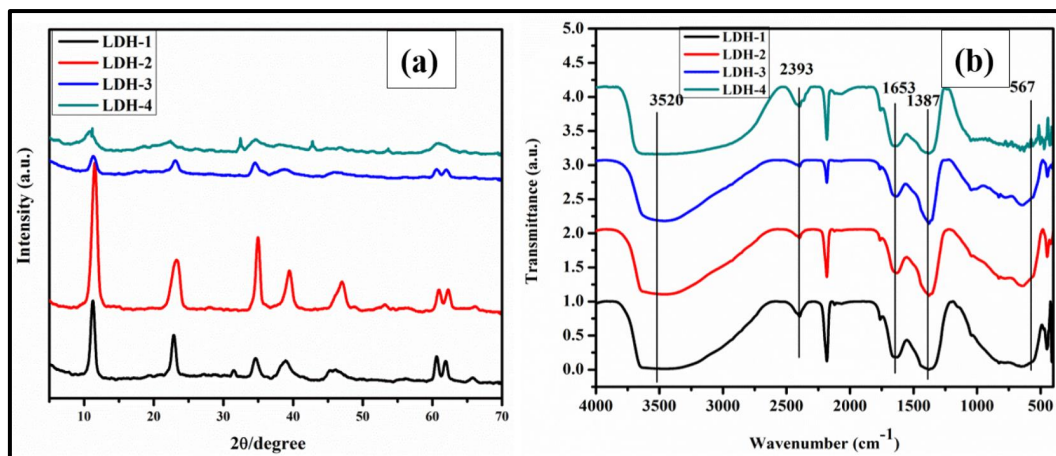


17-rasm. Simulyatsiya qilingan quyosh nuri ostida sof va TiO_2 bilan legirlangan $\text{ZrO}_2\text{--SnO}_2$ nanokompozitlari ishtirokida Brilliant Green va 4-nitrofenol ning fotokatalitik degradatsiyasiga oid natijalar: chiziqli kinetik grafiklar (a, b), degradatsiya darajasi (%) (c, d) hamda kinetik tezlik konstantalari (e, f) (Haq, Mushtaq, va boshq., 2026).

3.4 Cr/Ni/Mg/Al qatlamli qo'sh gidroksidlari. Ushbu bo'limda Cr/Ni/Mg/Al qatlamli qo'sh gidroksidlari LDHs ning sintezi hamda ularning to'qimachilik, kosmetika va sog'liqni saqlash mahsulotlarida keng qo'llaniladigan anionli bo'yoq –MO ni fotokatalitik degradatsiyalashdagi yuqori samaradorligi bayon etilgan. Tadqiqotda Mg/Al-LDH tarkibiga Ni va Cr metallari kiritilib, LDH materiallarining katta solishtirma sirt maydoni, yuqori anion almashinish sig'imi va tarkibining moslashtirilishi mumkin bo'lgan xususiyatlaridan foydalanish orqali ularning fotokatalitik faolligini oshirish maqsad qilingan. LDH namunalari gidrotermal ko'chirish (co-precipitation) usuli yordamida sintez qilinib, to'rtta turdagi material tayyorlandi: LDH-1 (Mg/Al-LDH), LDH-2 (Ni/Mg/Al-LDH), LDH-3 (Cr/Mg/Al-LDH) va LDH-4 (Ni/Cr/Mg/Al-LDH). LDH-1 ni tayyorlash uchun 0,01 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ va 0,01 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 20 mL deionizatsiyalangan suvda eritilib, 0,04 M $\text{CO}(\text{NH}_2)_2$ (mochevina) cho'ktiruvchi reagent sifatida qo'shildi va hosil bo'lgan mahsulot 400 °C da 2 soat davomida kalsinatsiya qilindi. LDH-2 va LDH-3 namunalari Mg/Al-LDO tarkibiga mos ravishda 0,01 M $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ va 0,01 M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ qo'shib, 120 °C da 24 soat davomida gidrotermal ishlov berish orqali olindi. LDH-4 namunasi esa LDH-2 va LDH-3 dan 0,5 g dan olinib, 50 mL deionizatsiyalangan suv va mochevina ishtirokida dispersiyalanib, so'ngra 120 °C da 24 soat davomida gidrotermal ishlov berish orqali sintez qilindi. Fotokatalitik tajribalar davomida har bir LDH namunasidan 20 mg miqdorda olinib, 100 mL hajmdagi 15 ppm MO eritmasiga qo'shildi. Aralashma adsorbsiya–desorbsiya muvozanatiga erishish uchun qorong'i sharoitda 30 daqiqa davomida aralashtirildi. Shundan so'ng namunalari iyun oyida

soat 12:00 dan 13:00 gacha bo'lgan tabiiy quyosh nuri ta'siriga qo'yildi va 464 nm to'lqin uzunligidagi absorbsiya intensivligining kamayishi ikki nurli UV–Vis spektrofotometri yordamida har 15 daqiqada qayd etib borildi.

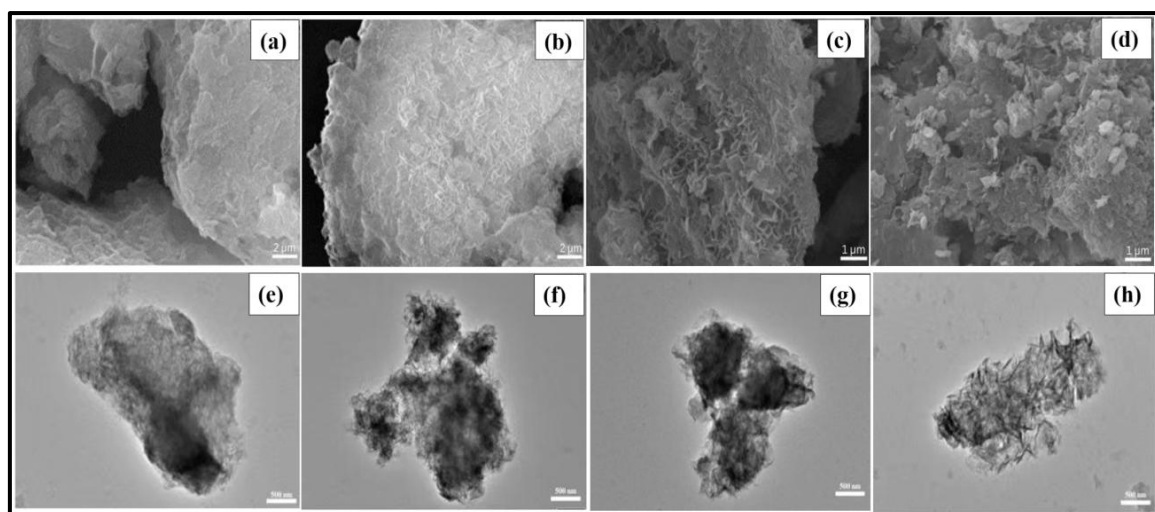
To'rtta LDH namunasining XRD difraktogrammlarida (003), (006), (012) va (015) kristall tekisliklariga mos keluvchi yaqqol difraksion cho'qqilar kuzatildi. Ushbu cho'qqilar JCPDS 35-0965 ma'lumotlariga mos ravishda Mg/Al gidrotalsitga o'xshash materiallarning shakllanganligini tasdiqladi va kerakli LDH tuzilmasining muvaffaqiyatli hosil bo'lganligini ko'rsatdi. Bundan tashqari, yuqori difraksiya burchaklarida ($2\theta \approx 60^\circ$) kuzatilgan (018), (110) va (113) tekisliklariga mos qo'shimcha cho'qqilar Ni^{2+} va Al^{3+} metall kationlarining LDH mezbon qatlamiga muvaffaqiyatli kiritilganligini ko'rsatdi (JCPDS 15-0087). (003) tekisligi uchun hisoblangan d-oraliq (d-spacing) qiymatlari mos ravishda LDH-1 uchun 0,779 nm, LDH-2 uchun 0,762 nm, LDH-3 uchun 0,779 nm va LDH-4 uchun 0,789 nm ni tashkil etdi. LDH-4 namunasida qatlamlararo masofaning ortishi Cr^{3+} va Ni^{2+} ionlarining Mg^{2+} va Al^{3+} ionlariga nisbatan kattaroq ion radiusiga ega ekanligi bilan izohlanadi. Bu holat LDH tuzilmasidagi tarkib va qatlamlarning joylashishida yuz bergan o'zgarishlarni aks ettiradi. FTIR spektrlari 3100–3600 cm^{-1} oralig'ida keng yutilish polosalarini namoyon etdi. Ushbu polosalar bazal gidroksil guruhlari va qatlamlararo suv molekullari bilan bog'liq O–H valent tebranishlariga tegishlidir. Taxminan 1653 cm^{-1} da kuzatilgan keng polosa qatlamlararo H_2O molekullarining deformatsion tebranishlarini ifodalaydi. 1363–1507 cm^{-1} oralig'idagi yutilish polosalari O–C–O guruhining asimmetrik valent tebranishlariga mos keladi. Past to'lqin sonlarida (taxminan 567 cm^{-1}) kuzatilgan polosalar esa M–O–H va O–M–O bog'larining tebranishlariga tegishli bo'lib, qatlamli qo'sh gidroksidlar (LDHs) ning muvaffaqiyatli shakllanganligini tasdiqlaydi.



18-rasm. Tayyorlangan LDH-1, LDH-2, LDH-3 va LDH-4 namunalarining XRD difraktogrammlari (a) hamda FTIR spektrlari (b) (Waheed va boshq., 2024).

SEM mikrograflari har bir LDH namunasi uchun o'ziga xos morfologik xususiyatlarni namoyon etdi. LDH-1 kichik individual zarrachalarning aglomeratsiyasi natijasida hosil bo'lgan zich va kompakt tuzilishga ega bo'lib, ular bir-biriga yaqin joylashgan qatlamlarni hosil qilgan. Aglomeratsiya darajasining yuqoriligi sababli zarrachalarning aniq morfologik shaklini ajratish qiyin bo'ldi.

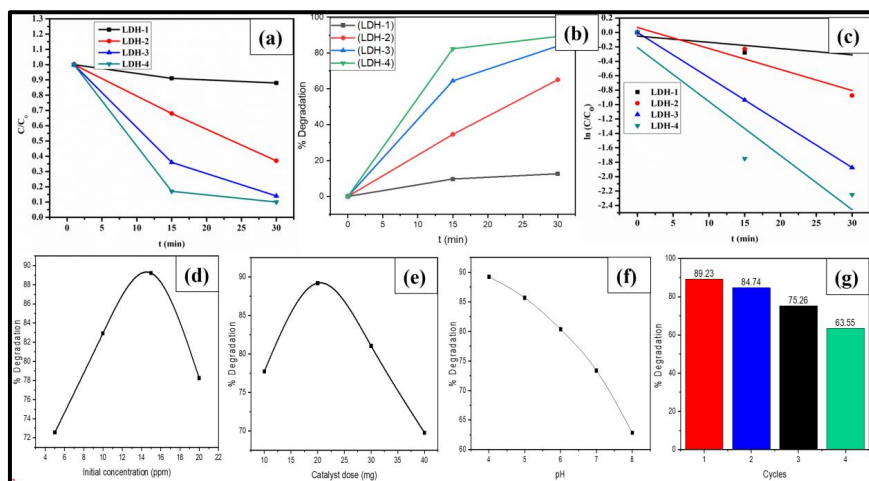
LDH-2 tarkibiga $\text{Ni}(\text{OH})_2$ kiritilgandan so'ng morfologiya sezilarli darajada o'zgarib, zich qattiq struktura yuzasida tartibsiz joylashgan ingichka tolalardan iborat aralash tuzilma kuzatildi. $\text{Cr}(\text{OH})_3$ ning LDH-1 matritsasiga kiritilishi natijasida hosil bo'lgan LDH-3 da bir-biriga yaqin joylashgan tolasimon tuzilmalar murakkab va g'ovakli, asalari uyasi (honeycomb) ga o'xshash morfologiyani hosil qildi. LDH-2 va LDH-3 ni birlashtirish orqali olingan LDH-4 namunasi esa aralash morfologik tuzilishga ega bo'lib, fon qismida qatlamli asalari uyasi ko'rinishidagi struktura kuzatildi. Ushbu struktura yuzasida turli shakl va o'lchamdagi agregatlar hamda yirik zarrachalar tasodifiy tarzda taqsimlanganligi aniqlandi. Umuman olganda, barcha namunalarda bir-biriga zich joylashgan qatlamsimon tuzilmalar kuzatilib, ular murakkab morfologik arxitekturani hosil qilgan. TEM tasvirlari barcha namunalarning ichki tuzilishi gelga o'xshash matritsadan hamda uning ichiga joylashgan tolasimon tuzilmalardan iborat ekanligini ko'rsatdi. LDH-1 tor tolasimon strukturalardan tashkil topgan bo'lib, ular o'zaro tutashib murakkab tarmoq hosil qilgan va natijada yirik, aniq shaklga ega bo'lmagan tuzilmalar yuzaga kelgan. Ayrim hududlarda tolalar monodispers, boshqa qismlarda esa zich joylashgan polidispers tolalar kuzatildi. LDH-2 namunasi tasodifiy joylashgan tolalar va yupqa plastinkasimon qatlamlardan iborat bo'lib, ular zich strukturalarni hosil qilgan. Namunaning quyi qismi yuqori qismiga nisbatan ko'proq g'ovakli ekanligi kuzatildi. LDH-3 da tor tolalar notekis taqsimlangan bo'lib, ular aniq geometrik shaklga ega bo'lmagan ko'p qatlamli tuzilmani hosil qilgan va LDH-2 ga nisbatan g'ovakliligi yuqoriroq ekanligi aniqlandi. LDH-4 namunasi esa yanada ravshan va deyarli monodispers tolasimon tuzilmalarni namoyon etdi. Tolalarning kengligi LDH-1 dan LDH-4 gacha bosqichma-bosqich ortib borgan bo'lsa-da, ularning o'lchami va shakli barcha namunalar bo'ylab to'liq bir xil bo'lmaganligi kuzatildi.



19-rasm. LDH-1 (a), LDH-2 (b), LDH-3 (c) va LDH-4 (d) namunalarining SEM tasvirlari (a–d) hamda TEM tasvirlari (e–h) (Waheed va boshq., 2024).

Sintez qilingan LDH namunalarining quyosh nuri ta'siridagi fotokatalitik faolligi iyun oyida soat 12:00–13:00 oralig'ida tabiiy quyosh nuri ostida Metil

Orange (MO) bo'yog'iga nisbatan baholandi. Reaksiya davomida eritmaning yorqin to'q sariq rangi vaqt o'tishi bilan asta-sekin yo'qolib bordi, bu esa bo'yoqning mineralizatsiyalanishi sodir bo'lganligini ko'rsatdi. Ushbu holat UV-Vis tahlili orqali ham tasdiqlanib, 464 nm dagi maksimal absorbsiya qiymatining uzluksiz kamayishi kuzatildi. Degradatsiya profili dastlab keskin pasayish, keyinchalik esa nisbatan sekin va barqaror kamayish bilan tavsiflandi. Bu holat LDH yuzasidagi faol markazlarning bosqichma-bosqich band bo'lishi bilan izohlanadi. Dastlab har bir LDH yuzasidagi barcha bog'lanish markazlari erkin bo'lgani sababli bo'yoq molekulalarining adsorbsiyasi maksimal darajada amalga oshdi. 15 daqiqadan so'ng esa faol markazlarning katta qismi band bo'lib, keyingi vaqt oralig'ida degradatsiya tezligi cheklangan. To'rtta LDH namunasi fotokatalitik samaradorlik bo'yicha sezilarli farqlarni namoyon etdi. LDH-1 faqat 12,63%, LDH-2 65,10%, LDH-3 83,92%, LDH-4 esa 89,23% MO degradatsiyasini ta'minladi. Natijalar quyidagi tartibda kuzatildi: LDH-4 > LDH-3 > LDH-2 > LDH-1. LDH-4 ning yuqori fotokatalitik samaradorligi uning yuqori g'ovakli tuzilishi tufayli katta solishtirma sirt maydoni hosil qilishi hamda Ni, Cr, Mg va Al metall kationlarining sinergik ta'siri natijasida zaryad tashuvchilarning samarali ajralishi va ko'plab faol markazlarning hosil bo'lishi bilan izohlanadi. Psevdobirinchi tartibli kinetik model asosida hisoblangan reaksiya tezlik konstantalari mos ravishda LDH-1 uchun 0,0045 min⁻¹, LDH-2 uchun 0,03509 min⁻¹, LDH-3 uchun 0,06090 min⁻¹ va LDH-4 uchun 0,07427 min⁻¹ ni tashkil etdi. LDH-4 ning kinetik tezlik konstantasi LDH-1 ga nisbatan taxminan 16,5 baravar yuqori bo'lib, bu uning degradatsiya jarayoni ancha tez kechishini ko'rsatadi. Yuqori regressiya koeffitsiyentlari (R²) esa eksperimental natijalarning tanlangan kinetik modelga yaxshi mos kelishini tasdiqladi. Fotokatalitik mexanizmga ko'ra, LDH materiali quyosh nuri fotonlarini yutganda elektronlar valent zonadan (VB) o'tkazuvchanlik zonasiga (CB) o'tadi va natijada elektron-teshik juftliklari hosil bo'ladi. O'tkazuvchanlik zonasidagi qo'zg'atilgan elektronlar O₂ molekulalari bilan reaksiyaga kirishib superoksid radikallari (O₂•⁻) ni hosil qiladi. Shu bilan bir vaqtda, valent zonadagi teshiklar H₂O yoki OH⁻ ionlarini oksidlab gidroksil radikallari (•OH) ni hosil qiladi. Hosil bo'lgan ushbu yuqori reaktiv zarrachalar MO molekulalariga hujum qilib, ularni bosqichma-bosqich parchalaydi va yakunda CO₂ hamda H₂O kabi nisbatan zararsiz mahsulotlarga aylantiradi. Cr³⁺, Ni²⁺, Mg²⁺ va Al³⁺ kabi bir nechta metall kationlarining birgalikda mavjudligi ko'plab faol markazlarni hosil qilish hamda zaryad tashuvchilarning ajralishini yaxshilash orqali fotokatalitik samaradorlikni oshiradi. Xususan, Cr ning kiritilishi taqiqlangan zona ichida yangi energetik sathlarning hosil bo'lishiga olib keladi.



20-rasm. Simulyatsiya qilingan quyosh nuri ostida tayyorlangan LDH namunalari ishtirokida Metil Orange (MO) ning fotokatalitik degradatsiyasiga oid natijalar: chiziqli kinetik grafik (a), degradatsiya darajasi (%) (b), kinetik tezlik konstantasi (c), boshlang'ich konsentratsiyaning ta'siri (d), katalizator miqdorining ta'siri (e), pH qiymatining ta'siri (f) hamda fotokatalizatorning qayta foydalanish samaradorligi (g) (Waheed va boshq., 2024).

MO ning boshlang'ich konsentratsiyasi 15 ppm gacha oshirilganda degradatsiya foizi ortib bordi. Bu eritmada oksidlanish-qaytarilish reaksiyalarida ishtirok etuvchi MO molekulalari sonining ko'payishi bilan bog'liq. Biroq, konsentratsiyaning bundan ortiq oshirilishi yorug'likni to'sish effektini yuzaga keltirdi. Bunda tushayotgan yorug'likning katta qismi bo'yoq molekulalari tomonidan yutilib, fotonlarning katalizator yuzasiga yetib borishi cheklanadi. Fotokatalitik faollikning eng yuqori qiymati 20 mg katalizator miqdorida kuzatildi. 10 mg katalizator qo'llanilganda faol markazlar sonining yetarli emasligi degradatsiya samaradorligini chekladi. 20 mg miqdorda esa faol markazlar soni MO molekulalari bilan samarali o'zaro ta'sirlashish uchun optimal bo'ldi. Katalizator miqdorining bundan ortiq oshirilishi zarrachalarning aglomeratsiyasi ga olib kelib, faol markazlarning berkilishiga va MO molekulalarining ushbu markazlarga yetib borishini qiyinlashtirdi. Eng yuqori fotokatalitik faollik pH 4 da kuzatildi va pH qiymati ortishi bilan degradatsiya samaradorligi muntazam ravishda kamaydi. Kislotali muhitda LDH-4 yuzasi protonlanish natijasida musbat zaryadlanadi va bu anionli MO molekulalari bilan kuchli elektrostatik tortishishni yuzaga keltiradi. Neytral muhitda (pH = 7) sirt zaryadi izoelektrik nuqta ga yaqinlashgani sababli o'zaro ta'sir o'rtacha darajada bo'ladi. Ishqoriy muhitda esa sirt deprotonlanish natijasida manfiy zaryadlanadi, bu esa anionli MO bilan elektrostatik itarilish kuchlarini yuzaga keltirib, fotokatalitik faollikning pasayishiga sabab bo'ladi. LDH-4 fotokatalizatori ketma-ket to'rt marotaba qayta qo'llanganda degradatsiya samaradorligi asta-sekin kamaydi. Bu holat katalizator yuzasining reaksiya mahsulotlari bilan to'yinishi, hosil bo'lgan yon mahsulotlar tufayli yorug'likning kirib borish darajasining pasayishi hamda katalizatorning tuzilishi va kimyoviy tarkibida yuz beradigan o'zgarishlar bilan izohlanadi. Mazkur omillar katalizator yuzasidagi faol bog'lanish markazlarining soni va samaradorligini kamaytirib, fotokatalitik faollikning pasayishiga olib keladi.

4-BOB. GRAFEN OKSIDI–METALL OKSIDLI NANOKOMPOZITLAR

4.1 rGO–ZnO–SnO₂–Fe₂O₃ (rGO–ZSF) nanokompoziti. Qaytarilgan grafen oksidi–rux oksidi–qalay oksidi–temir oksidi (rGO–ZnO–SnO₂–Fe₂O₃) to‘rt komponentli nanokompoziti biologik qo‘llanmalarda samaradorlikni oshirish maqsadida grafen oksidi va uch xil metall oksidini birlashtirish orqali sintez qilindi. Mualliflarning mavjud ilmiy ma’lumotlariga ko‘ra, ushbu tarkibdagi to‘rt komponentli nanokompozit ilk bor tayyorlangan. Grafen oksidi (GO) modifikatsiyalangan Hummers usuli yordamida grafit parchalari, H₂SO₄, H₃PO₄ va KMnO₄ dan foydalanib sintez qilindi. Dastlab reaksiya aralashmasi 10 °C haroratdagi muz hammomida 10 daqiqa davomida aralashtirildi. So‘ngra grafit va KMnO₄ qo‘shilib, qoramtir-yashil rang hosil bo‘lguncha 6 soat davomida aralashtirildi. Keyinchalik ortiqcha KMnO₄ ni yo‘qotish uchun, reaksiyaning kuchli ekzotermik xususiyatini hisobga olgan holda ehtiyotkorlik bilan H₂O₂ qo‘shildi. Aralashma sovutilgandan so‘ng HCl va deionizatsiyalangan suv qo‘shildi, so‘ngra sentrifugalandi, bir necha marta yuvildi va quritildi. ZnO–SnO₂–Fe₂O₃ (ZSF) nanokompoziti sintezi uchun SnCl₂·2H₂O, FeSO₄·7H₂O va ZnSO₄·7H₂O alohida-alohida deionizatsiyalangan suv va metanol aralashmasida eritildi. Eritmalarning pH qiymati 2 M NaOH yordamida 10 ga yetkazildi. Hosil bo‘lgan aralashmalar 50 °C da 30 daqiqa davomida aralashtirilib, barqaror gidroksid suspenziyalari hosil qilindi. Keyinchalik uchala suspenziya bitta idishda birlashtirilib, 50 °C haroratda 300 rpm tezlikda 4 soat davomida aralashtirildi. Olingan mahsulot filtrlandi, deionizatsiyalangan suv bilan yuvildi, 100 °C da quritildi va 450 °C da 2 soat davomida kalsinatsiya qilindi. rGO–ZSF nanokompoziti sintezida ham xuddi shu metall tuzlari eritmaları tayyorlandi. Shundan so‘ng 1 g GO deionizatsiyalangan suvda ultratovush yordamida dispersiyalanib, 2 soat davomida aralashtirildi va qaytarilgan grafen oksidi (rGO) hosil qilindi. Metall gidroksid suspenziyalari kuchli aralashtirish sharoitida 6 soat davomida asta-sekin GO suspenziyasiga qo‘shildi. Hosil bo‘lgan aralashma 24 soat davomida saqlandi, filtrlandi, deionizatsiyalangan suv bilan yuvildi va 100 °C da quritildi. Tayyor mahsulotning yarmi 450 °C da 2 soat davomida kalsinatsiya qilindi.

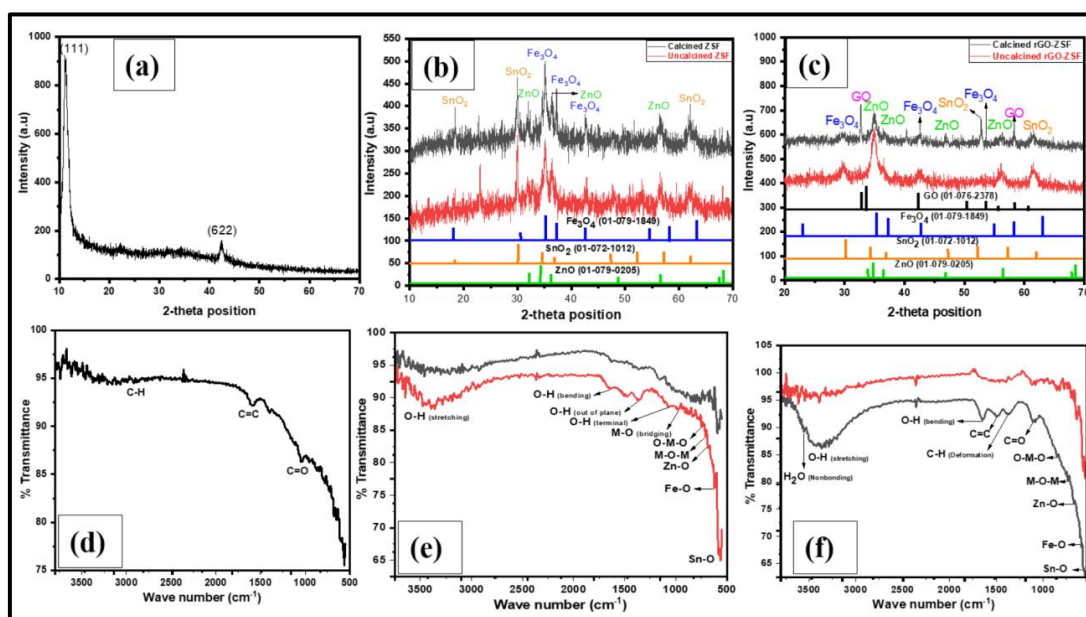
XRD tahliliga ko‘ra, rGO namunasi 11,01° da joylashgan difraksiya cho‘qqisini namoyon etdi. Ushbu cho‘qqi (111) kristall tekisligiga mos kelib, 8,18 Å qatlamlararo masofani (d-spacing) ifodalaydi va JCPDS №01-082-2261 kartasi bilan mos tushadi. Mazkur faza 2,12 g/cm³ zichlikka va 2834,35 × 10⁶ pm³ birlik hujayra hajmiga ega. Bundan tashqari, 42,43° dagi (622) tekislikka tegishli difraksiya cho‘qqisi namuna tarkibida oz miqdorda qoldiq grafit mavjudligini ko‘rsatadi. ZSF nanokompoziti tarkibida Fe₃O₄ fazasiga tegishli 35,06° (311), 37,09° (222) va 42,57° (400) difraksiya cho‘qqilari kuzatildi. Ushbu cho‘qqilar Fd3m fazoviy guruhiga mansub kubik magnetit tuzilmasini ifodalovchi JCPDS №01-079-1849 kartasi bilan mos keladi. Fe₃O₄ ning kristallit o‘lchami 57,93 nm, kristall panjara deformatsiyasi 0,419%, mikrodeformatsiyasi 2,2 × 10⁻³ va dislokatsiya zichligi 2,98 × 10⁻⁴ nm⁻² ni tashkil etdi. SnO₂ fazasi 18,40° (001), 29,92° (101) va 61,99° (202) difraksiya cho‘qqilarini namoyon etdi. Bu cho‘qqilar P4/nmm fazoviy guruhiga mansub kvadrat asosli kristall tuzilmani ifodalovchi JCPDS №01-072-1012 kartasiga mos

keladi. Mazkur fazaning kristallit o'lchami 35,33 nm, kristall panjara deformatsiyasi 0,256%, mikrodeformatsiyasi $6,6 \times 10^{-3}$ va dislokatsiya zichligi $8,02 \times 10^{-4} \text{ nm}^{-2}$ ni tashkil etdi. ZnO fazasi uchun $31,96^\circ$, $36,38^\circ$ va $56,40^\circ$ da kuzatilgan difraksiya cho'qqilari mos ravishda (100), (101) va (110) tekisliklarga tegishli bo'lib, $P6_3mc$ fazoviy guruhiga mansub geksagonal kristall tuzilmani ifodalovchi JCPDS №01-079-0205 kartasi bilan mos tushadi. ZnO ning kristallit o'lchami 29,56 nm, kristall panjara deformatsiyasi 0,419%, mikrodeformatsiyasi $4,9 \times 10^{-3}$ va dislokatsiya zichligi $1,1458 \times 10^{-3} \text{ nm}^{-2}$ ni tashkil etdi. rGO-ZSF nanokompoziti ning XRD difraktogrammasida GO ga tegishli $32,67^\circ$ (101) va $58,18^\circ$ (200) difraksiya cho'qqilari kuzatildi. Ular geksagonal uglerod oksidi fazasini ifodalovchi JCPDS №01-076-2378 kartasi bilan mos keladi. GO ning kristallit o'lchami 24,10 nm, dislokatsiya zichligi $1,722 \times 10^{-3} \text{ nm}^{-2}$ va mikrodeformatsiyasi $6,11 \times 10^{-3}$ ni tashkil etdi. Nanokompozit tarkibidagi Fe_3O_4 fazasi uchun $29,50^\circ$ (220), $42,66^\circ$ (400) va $53,70^\circ$ (422) difraksiya cho'qqilari qayd etildi. Ushbu fazaning kristallit o'lchami 21,15 nm, mikrodeformatsiyasi $7,35 \times 10^{-3}$ va dislokatsiya zichligi $2,237 \times 10^{-4} \text{ nm}^{-2}$ bo'ldi.

ZnO fazasi $34,91^\circ$ (002), $36,46^\circ$ (101), $46,83^\circ$ (102) va $56,25^\circ$ (110) difraksiya cho'qqilarini namoyon etdi. Ushbu fazaning kristallit o'lchami 17,31 nm, mikrodeformatsiyasi 7×10^{-3} va dislokatsiya zichligi $3,341 \times 10^{-3} \text{ nm}^{-2}$ ni tashkil etdi. SnO_2 fazasi uchun $52,75^\circ$ (101) va $61,48^\circ$ (222) difraksiya cho'qqilari kuzatildi. Ular JCPDS №00-029-1484 kartasi bilan mos keluvchi ortorombik kristall tuzilmaning shakllanganligini tasdiqladi. Ushbu fazaning kristallit o'lchami 15,25 nm, mikrodeformatsiyasi 35,42 va dislokatsiya zichligi $4,303 \times 10^{-3} \text{ nm}^{-2}$ ni tashkil etdi. FTIR tahlilida rGO namunasi uchun $2918,19$ va $2873,80 \text{ cm}^{-1}$ da C–H valent tebranishlari, 1587 cm^{-1} da aromatik halqalarga xos C=C bog'lari, $1043,22 \text{ cm}^{-1}$ da C–O guruhi hamda $946,92$ va $1402,36 \text{ cm}^{-1}$ da C–O va O–H deformatsion tebranishlari kuzatildi.

ZSF nanokompoziti ning FTIR spektrida $3383,94 \text{ cm}^{-1}$ da O–H valent tebranishlari, $1631,49 \text{ cm}^{-1}$ da O–H deformatsion tebranishlari, $1366,96 \text{ cm}^{-1}$ da tekislikdan tashqari O–H tebranishlari, $1115,69 \text{ cm}^{-1}$ da terminal OH guruhi, $1069,08$ va $974,97 \text{ cm}^{-1}$ da metall–kislorod (M–O) ko'prik bog'lari, $740,22 \text{ cm}^{-1}$ da O–M–O, $706,73 \text{ cm}^{-1}$ da M–O–M, $685,24 \text{ cm}^{-1}$ da Zn–O, $621,52 \text{ cm}^{-1}$ da Fe–O hamda $557,05 \text{ cm}^{-1}$ da Sn–O tebranishlari aniqlandi. Kalsinatsiya jarayonidan so'ng suv va gidroksil guruhlariga tegishli tebranishlarning intensivligi sezilarli darajada kamaydi. Bu esa adsorbsiyalangan suvning yo'qolishi hamda metall gidroksidlarning mos metall oksidlariga aylanganligini tasdiqlaydi. rGO-ZSF nanokompoziti ning FTIR spektrida $3555,45 \text{ cm}^{-1}$ hamda $3491\text{--}3195 \text{ cm}^{-1}$ oralig'ida keng O–H valent tebranishlari, $1643,11 \text{ cm}^{-1}$ da O–H deformatsion tebranishi, $1478,1 \text{ cm}^{-1}$ da sirt faol modda qoldiqlariga tegishli CH_2/CH_3 deformatsion tebranishlari, $1367,4 \text{ cm}^{-1}$ da aromatik halqa tebranishlari, $1080,94 \text{ cm}^{-1}$ da karbonil guruhlariga, $724,58 \text{ cm}^{-1}$ da M–O–M, $660,47 \text{ cm}^{-1}$ da Zn–O, $589,40 \text{ cm}^{-1}$ da Fe–O hamda $562,05 \text{ cm}^{-1}$ da Sn–O bog'larga xos tebranishlar kuzatildi. Kalsinatsiya natijasida gidroksil guruhlariga tegishli tebranishlar intensivligi kamaydi va ayrim cho'qqilarning siljishi kuzatildi.

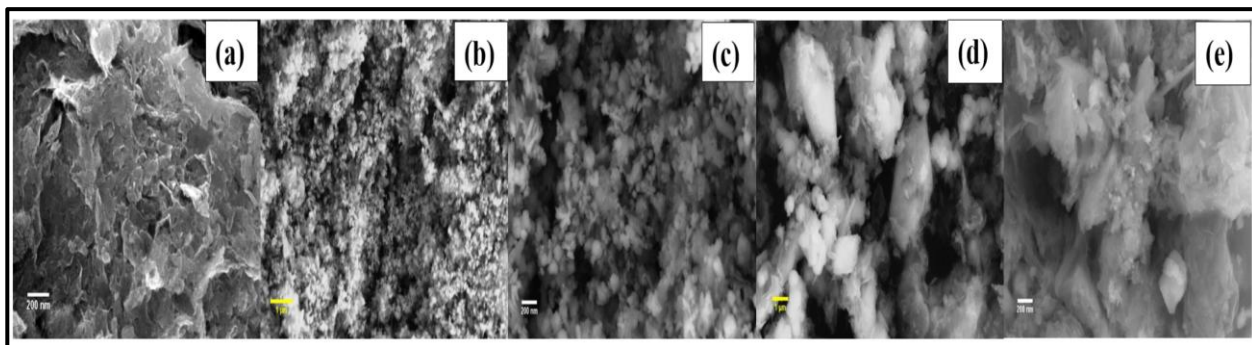
Bu holat zarracha o'lchamining o'zgarishi hamda nanokompozitning kristallanish darajasi ortishi bilan izohlanadi.



21-rasm. GO (a), kalsinatsiya qilinmagan va kalsinatsiya qilingan ZSF (b) hamda kalsinatsiya qilinmagan va kalsinatsiya qilingan rGO–ZSF (c) namunalarining XRD difraktogrammalari; GO (d), kalsinatsiya qilinmagan va kalsinatsiya qilingan ZSF (e) hamda kalsinatsiya qilinmagan va kalsinatsiya qilingan rGO–ZSF (f) namunalarining FTIR spektrlari (Haq, Ashravi, va boshq., 2026).

SEM tahlili rGO namunasining mayda o'lchamli qatlamlardan tashkil topgan qatlamsimon tuzilishga ega ekanligini tasdiqladi. Namuna yuzasi notekis morfologiyani namoyon etib, mikrometr o'lchamidagi qatlamlar yaqqol kuzatildi. Qatlamlarning notekis taqsimlanishi sirtning g'adir-budirligi va bo'shliqlar (teshiklar) hosil bo'lishiga sabab bo'lgan. Shuningdek, namuna yuzasida aniq ifodalangan o'tkir qirralar kuzatilmadi. ZSF nanokompoziti ning past kattalashtirishdagi SEM tasvirlarida yorqin va xira kontrastli zarrachalardan tashkil topgan tartibsiz tarmoqsimon tuzilma kuzatildi. Zarrachalarning notekis taqsimlanishi morfologiyaning bir jinsli emasligini ko'rsatdi. Yuqori kattalashtirishda esa zarrachalarning o'rtacha darajadagi aglomeratsiyasi kuzatildi. Kichik zarrachalar o'zaro birikib yirik agregatlarni hosil qilgan bo'lib, ular orasidagi chegaralar aniq ajralmagan. Agregatlar keng o'lcham diapazoniga hamda turli morfologik shakllarga ega ekanligi aniqlandi. Ayrim agregatlar yuzasida turli o'lcham va shakldagi alohida zarrachalar ham kuzatildi. Bundan tashqari, zarrachalarning nomukammal joylashuvi natijasida bo'shliqlar hosil bo'lgan. Agregatlar o'lchami 6,31–44,29 nm oralig'ida bo'lib, ularning o'rtacha o'lchami 16,02 nm ni tashkil etdi. rGO–ZSF nanokompoziti ning SEM tasvirlarida grafen oksidiga xos alohida bloksimon yoki yirik bulutsimon agregatlar kuzatildi. Ushbu strukturalar ichiga trimetall oksidli nanokompozit zarrachalari muvaffaqiyatli joylashtirilganligi aniqlandi. Grafen oksidi qatlamlari yuzasida mayda nuqtasimon hamda cho'zilgan shakldagi zarrachalar joylashgan bo'lib, turli o'lcham va shakldagi

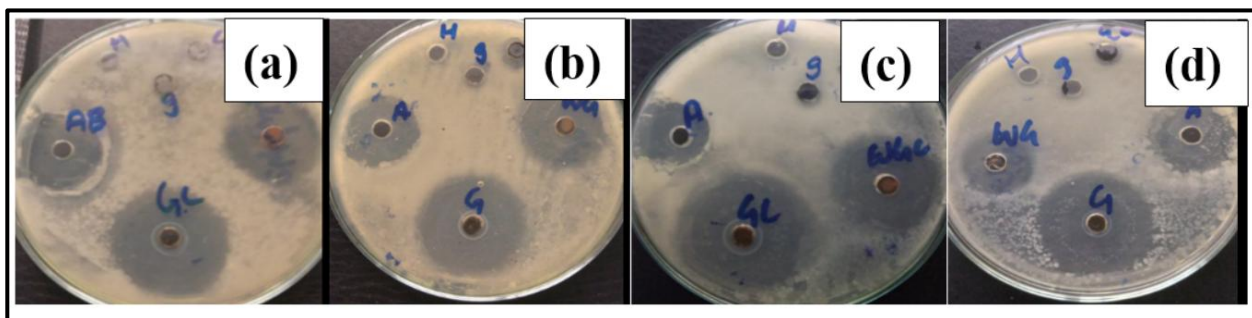
bulutsimon strukturalarning tasodifiy taqsimlanishi natijasida bo'shliqlar hosil bo'lgan. Yuqori aniqlikdagi SEM tasvirlari qattiq zarrachalarning grafen oksidi matritsasi ichiga muvaffaqiyatli singdirilganligini ko'rsatdi. Sintez jarayonida uzoq vaqt davomida aralashtirilganligi sababli zarrachalar bir-biridan nisbatan uzoq masofada joylashgan. Zarrachalar shakli va o'lchami bir xil bo'lmay, matritsa bo'ylab notekis tarqalgan. Nanokompozit tarkibidagi zarrachalar o'lchami 4,29–49,89 nm oralig'ida bo'lib, ularning o'rtacha o'lchami 22,5 nm ni tashkil etdi.



22-rasm. GO (a), sintez qilingan ZSF (b) va kalsinatsiya qilingan ZSF (c) namunalarining, shuningdek sintez qilingan rGO–ZSF (d) hamda kalsinatsiya qilingan rGO–ZSF (e) nanokompozitlarining SEM tasvirlari (Haq, Ashravi, va boshq., 2026).

S. aureus va *E. coli* bakteriyalariga qarshi antibakterial faollik agar quduq diffuziyasi (agar well diffusion) usuli yordamida 10–60 µg/mL konsentratsiyalar oralig'ida baholandi. Natijalar shuni ko'rsatdiki, namunalar konsentratsiyasi ortishi bilan antibakterial faollik ham sezilarli darajada oshdi. Bu holat yuqori konsentratsiyada namuna miqdorining ko'payishi natijasida ko'proq reaktiv zarrachalar (metall kationlari va erkin radikallar) hosil bo'lishi bilan izohlanadi. Ushbu faol zarrachalar bakteriya hujayrasi yuzasi hamda tarkibida tiol (-SH) guruhlarini saqlovchi hayotiy fermentlar bilan o'zaro ta'sirlashib, hujayraning metabolik faoliyatini izdan chiqaradi va natijada bakteriya hujayrasining nobud bo'lishiga olib keladi. rGO–ZSF nanokompozitlari har ikkala bakterial shtammga nisbatan ZSF nanokompozitlari ga qaraganda yuqori antibakterial faollikni namoyon etdi. Xususan, kalsinatsiya qilinmagan rGO–ZSF namunasi *E. coli* va *S. aureus* ga nisbatan mos ravishda 31 mm va 29 mm inhibisiya zonalarini hosil qildi. Kalsinatsiya qilingan rGO–ZSF namunasi uchun ushbu qiymatlar mos ravishda 29 mm va 27 mm ni tashkil etdi. Kalsinatsiya qilinmagan ZSF namunasi *E. coli* va *S. aureus* ga qarshi mos ravishda 24 mm va 23 mm, kalsinatsiya qilingan ZSF esa 23 mm va 22 mm inhibisiya zonalarini hosil qildi. Taqqoslash uchun qo'llanilgan antibiotik mos ravishda 21 mm va 20 mm inhibisiya zonasini ko'rsatdi. Grafen oksidi esa nisbatan past antibakterial faollikka ega bo'lib, *E. coli* uchun 7 mm, *S. aureus* uchun esa 6 mm inhibisiya zonasini hosil qildi. Grafit namunasi esa antibakterial faollik namoyon etmadi. Grafen metall oksidli nanokompozitlar uchun tayanch (substrat) vazifasini bajarib, grafensiz metall oksidli nanokompozitlarga nisbatan yuqori antibakterial samaradorlikni ta'minlaydi. Buning asosiy sababi grafen qatlamlarining o'tkir qirralari bakteriya hujayrasi bilan bevosita kontaktda uning hujayra devoriga kirib

borib, membranada teshiklar hosil qilishi hamda sitoplazmatik tarkibning tashqariga sizib chiqishiga sabab bo'lishidir. Bundan tashqari, bakteriya hujayralari grafen qatlamlari orasida ushlanib qolishi natijasida ularning biologik faolligi susayadi va hujayralar inaktivatsiyaga uchraydi. Kalsinatsiya qilinmagan namunalarda kalsinatsiya qilingan namunalarga nisbatan yuqoriroq antibakterial faollikni namoyon etdi. Bu holat ularning zarracha o'lchami kichikroq hamda solishtirma sirt maydoni kattaroq bo'lishi natijasida bakteriya hujayrasi yuzasi bilan yanada samarali o'zaro ta'sirlashishi bilan izohlanadi. *E. coli* ga nisbatan kuzatilgan inhibitsiya zonalarining kattaroq bo'lishi ushbu Gram-manfiy bakteriya hujayra devoridagi peptidoglikan qatlamlarining yupqaligi bilan bog'liq. Yupqa peptidoglikan qatlami nanokompozit zarrachalarining hujayra ichiga kirib borishini osonlashtiradi. Aksincha, Gram-musbat *S. aureus* bakteriyasida peptidoglikan qatlami qalin bo'lgani sababli nanokompozitlarning hujayraga kirishi cheklanadi va antibakterial samaradorlik nisbatan pasayadi. Bundan tashqari, *E. coli* hujayra yuzasi tarkibidagi lipopolisaxaridlar va fosfolipidlar tufayli kuchli manfiy zaryadga ega bo'lib, metall kationlarining bog'lanishi uchun ko'plab faol markazlarni ta'minlaydi. *S. aureus* hujayra yuzasida esa teyxoy kislotalari mavjudligi sababli manfiy zaryad faqat qisman namoyon bo'ladi. Shu bois metall kationlari bilan elektrostatik o'zaro ta'sir kuchsizroq bo'lib, antibakterial faollik *E. coli* ga nisbatan biroz past kuzatiladi.



23-rasm. Kalsinatsiya qilinmagan va kalsinatsiya qilingan ZSF hamda rGO-ZSF nanokompozitlarining antibakterial faolligi. Bu yerda H – manfiy nazorat (erituvchi), AB – musbat nazorat (antibiotik), GO – grafen oksidi, G – rGO-ZSF, WG – ZSF, GC – kalsinatsiya qilingan rGO-ZSF, WGC – kalsinatsiya qilingan ZSF (Haq, Ashravi, va boshq., 2026).

Antioksidant faollik DPPH va ABTS erkin radikallarini tutib qolish (free radical scavenging) usullari yordamida baholandi. Tadqiqot natijalari shuni ko'rsatdiki, namuna suspenziyasi miqdori ortishi bilan absorbsiya qiymati bosqichma-bosqich kamaydi. Bu holat namuna miqdori ortgan sari ko'proq reaktiv kislorod turlarini (RKT) neytrallashtirish imkoniyati ortishi va natijada antioksidant faollikning kuchayishi bilan izohlanadi. DPPH usuli bo'yicha GO namunasi 88,91–98,25% radikallarni tutib qolish faolligini (RSA) namoyon etdi hamda uning IC_{50} qiymati 21,55 $\mu\text{g/mL}$ ni tashkil qildi. Kalsinatsiya qilinmagan rGO-ZSF nanokompoziti 77,04–94,16% RSA va 36,92 $\mu\text{g/mL}$ IC_{50} qiymatini ko'rsatdi. Kalsinatsiya qilinmagan ZSF namunasi uchun RSA 56,03–75,87%, IC_{50} esa 42,65

$\mu\text{g/mL}$ ni tashkil etdi. Kalsinatsiya qilingan rGO–ZSF namunasi 58,36–80,73% RSA va 43,56 $\mu\text{g/mL}$ IC_{50} , kalsinatsiya qilingan ZSF esa 50,19–90,66% RSA hamda 46,76 $\mu\text{g/mL}$ IC_{50} qiymatlarini namoyon etdi. Taqqoslash uchun qo‘llanilgan askorbin kislotasi 68,87–76,84% RSA va 25,25 $\mu\text{g/mL}$ IC_{50} qiymatini ko‘rsatdi. ABTS usuli bo‘yicha GO namunasi 83,92–94,73% RSA va 27,51 $\mu\text{g/mL}$ IC_{50} qiymatini namoyon etdi. Kalsinatsiya qilinmagan rGO–ZSF nanokompoziti 51,46–93,86% RSA hamda 46,92 $\mu\text{g/mL}$ IC_{50} ga ega bo‘ldi.

3-jadval. Kalsinatsiya qilinmagan va kalsinatsiya qilingan rGO–ZSF hamda ZSF nanokompozitlarining DPPH va ABTS erkin radikallarini tutib qolish tahlillari bo‘yicha %RSA va IC_{50} qiymatlari (Haq, Ashravi, va boshq., 2026).

Sample	Concentration mg/mL	%RSA	IC_{50}	Sample	Concentration mg/ml	%RSA	IC_{50}
GO	0.005	88.91	21.55	GO	0.005	83.92	27.51
	0.010	94.16			0.010	88.59	
	0.015	96.69			0.015	92.10	
	0.020	98.25			0.020	94.73	
rGO-ZSF (Uncalcined)	0.005	77.04	36.92	rGO-ZSF (Uncalcined)	0.005	51.46	46.92
	0.010	85.60			0.010	77.19	
	0.015	89.88			0.015	90.35	
	0.020	94.16			0.020	93.86	
ZSF (Uncalcined)	0.005	56.03	42.65	ZSF (Uncalcined)	0.005	33.91	47.37
	0.010	61.28			0.010	56.14	
	0.015	68.09			0.015	72.80	
	0.020	75.87			0.020	81.87	
rGO-ZSF (calcined)	0.005	58.36	43.56	rGO-ZSF (calcined)	0.005	28.65	48.94
	0.010	62.64			0.010	39.76	
	0.015	72.17			0.015	61.11	
	0.020	80.73			0.020	67.83	
ZSF (calcined)	0.005	50.19	46.76	ZSF (calcined)	0.005	26.90	49.97
	0.010	74.51			0.010	41.23	
	0.015	83.46			0.015	64.91	
	0.020	90.66			0.020	76.60	
Ascorbic acid	0.005	68.87	25.25	Ascorbic acid	0.005	42.39	43.75
	0.010	71.01			0.010	50.87	
	0.015	73.73			0.015	55.55	
	0.020	76.84			0.020	60.82	

Kalsinatsiya qilinmagan ZSF namunasi 33,91–81,87% RSA va 47,37 $\mu\text{g/mL}$ IC_{50} ni ko‘rsatdi. Kalsinatsiya qilingan rGO–ZSF uchun RSA 28,65–67,83%, IC_{50} esa 48,94 $\mu\text{g/mL}$ ni tashkil etdi. Kalsinatsiya qilingan ZSF namunasi 26,90–76,60% RSA va 49,97 $\mu\text{g/mL}$ IC_{50} qiymatlarini namoyon etdi. Askorbin kislotasi esa 42,39–

60,82% RSA hamda 43,75 $\mu\text{g/mL}$ IC_{50} qiymatini qayd etdi. rGO–ZSF nanokompozitining ZSF ga nisbatan yuqoriroq antioksidant faolligi grafenning sp^2 -gibridlangan uglerod markazlari bilan bog‘liq xususiyatlari orqali izohlanadi. Erkin radikallar ushbu markazlarda adduktlar hosil qiladi va buning natijasida juftlanmagan elektronlarning spin delokalizatsiyasi grafenning kon‘yugirlangan tuzilmasi bo‘ylab tarqaladi. Ushbu jarayon elektron uzatilishi hamda grafen yuzasidagi funksional guruhlardan vodorod atomlarining donorligi hisobiga erkin radikallarning neytrallanishiga olib keladi. Bundan tashqari, metall oksid komponentlari bilan grafen oksidi o‘rtasidagi o‘zaro ta’sir elektron almashinuvini kuchaytirib, RKTning hosil bo‘lishi va ularning zararsizlantirilishini yanada samarali amalga oshiradi. Shuningdek, kalsinatsiya qilinmagan namunalar kalsinatsiya qilingan namunalarga nisbatan yuqoriroq radikal tutib qolish faolligini namoyon etdi. Bu ularning zarracha o‘lchami kichikroq, solishtirma sirt maydoni kattaroq va erkin radikallarni adsorbsiya qilish hamda barqarorlashtirish uchun ko‘proq faol markazlar mavjudligi bilan izohlanadi.

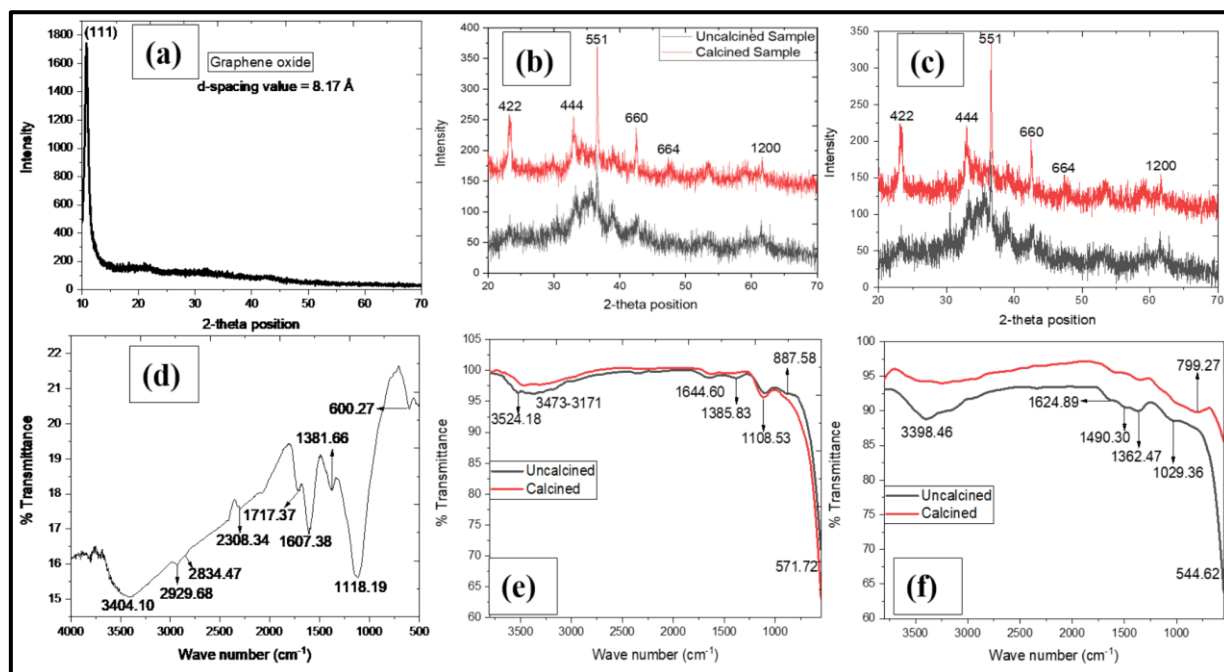
4.2 rGO bilan modifikatsiyalangan uch komponentli SnO_2 – NiO – CuO nanokompozitlari (GO–SNC). Ushbu bo‘limda qaytarilgan grafen oksidi (rGO) bilan modifikatsiyalangan uch komponentli SnO_2 – NiO – CuO nanokompozitlari (GO–SNC) hamda ularning modifikatsiyalanmagan analoglari (SNC) ning sintezi, tavsiflanishi va biologik qo‘llanilishi bayon etilgan. Grafen oksidi (GO) grafit parchalari, H_2SO_4 , H_3PO_4 va KMnO_4 ishtirokida modifikatsiyalangan Hummers usuli yordamida, ekzotermik reaksiya sharoitlari qat’iy nazorat qilingan holda sintez qilindi. Keyinchalik termik qaytarish orqali qaytarilgan grafen oksidi olindi. SnO_2 – NiO – CuO (SNC) uch komponentli nanokompoziti 3,78 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 4,48 g $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ va 3,93 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ni 50 mL deionizatsiyalangan suv hamda 10 mL metanolda eritish orqali tayyorlandi. Eritmaning pH qiymati 2 M NaOH yordamida 10 ga yetkazildi va aralashma 50 °C da 30 daqiqa davomida aralashtirildi. Shundan so‘ng uchala eritma birlashtirilib, 50 °C haroratda 3 soat davomida aralashtirildi. Hosil bo‘lgan mahsulot filtrlandi va 100 °C da quritildi. GO–SNC nanokompoziti ex-situ gibridizatsiya usuli orqali tayyorlandi. Bunda 1,0 g GO 100 mL deionizatsiyalangan suvda ultratovush ta’sirida 100 °C da 2 soat davomida termik qaytarilib rGO hosil qilindi. Olingan rGO suspenziyasi oldindan tayyorlangan metall nanokompozit eritmasiga asta-sekin qo‘shilib, 4 soat davomida uzluksiz aralashtirildi. Tayyorlangan SNC va GO–SNC namunalarining har ikkalasi ham 450 °C da 2 soat davomida mufel pechida kalsinatsiya qilindi. Antibakterial faollik Gram-manfiy *Escherichia coli* (*E. coli*) va Gram-musbat *Staphylococcus aureus* (*S. aureus*) bakteriyalariga nisbatan agar quduq diffuziyasi usuli yordamida baholandi. Tajribalarda namunalar 10–60 mg/3 mL konsentratsiyalar oralig‘ida sinovdan o‘tkazildi. Siprofloksatsin musbat nazorat, deionizatsiyalangan suv esa manfiy nazorat sifatida qo‘llanildi. Antioksidant faollik ABTS va DPPH erkin radikallarini tutib qolish usullari yordamida baholandi. Tajribalar 5, 10, 15 va 20 μg namunalar 5

mL deionizatsiyalangan suvda tayyorlangan eritmalar yordamida amalga oshirildi. Askorbin kislotasi standart modda sifatida ishlatildi. Absorbsiya qiymatlari ABTS uchun 734 nm, DPPH uchun esa 517 nm to'liq uzunliklarida o'lchandi. Sintez qilingan GO namunasining XRD difraktogrammasida $10,78^\circ$ da joylashgan difraksiya cho'qqisi kuzatildi. Ushbu cho'qqi 01-082-2261 ma'lumot kartasiga muvofiq (111) kristall tekisligiga tegishli bo'lib, $8,17 \text{ \AA}$ qatlamlararo masofani (d-spacing) ifodalaydi. Hisob-kitob natijasida materialning zichligi $2,12 \text{ g/cm}^3$, elementar hujayra hajmi esa $2834,35 \times 10^6 \text{ pm}^3$ ekanligi aniqlandi. Difraktogrammada grafitga xos cho'qqilarning kuzatilmaligi grafitning GO ga to'liq aylanganligini tasdiqlaydi. Kalsinatsiya qilinmagan SNC namunasining XRD difraktogrammasida $36,55^\circ$ da joylashgan aniq difraksiya cho'qqisi (551) kristall tekisligiga tegishli bo'ldi. Boshqa sohalarda esa difraktogrammaning shovqinli ko'rinishi namunaning asosan amorf tabiatga ega ekanligini ko'rsatdi. Kalsinatsiya jarayonidan so'ng $23,26^\circ$, $33,06^\circ$, $36,55^\circ$, $42,46^\circ$, $47,41^\circ$ va $61,76^\circ$ qiymatlarida yangi difraksiya cho'qqilari paydo bo'ldi. Ushbu cho'qqilar mos ravishda (422), (444), (551), (660), (664) va (1200) Miller tekisliklariga tegishli bo'lib, 00-030-0496 ma'lumot kartasi bilan mos tushadi. Bu natijalar kubik kristall tuzilishga ega Cu_9NiSn_3 nanokompozitining muvaffaqiyatli sintez qilinganligini tasdiqlaydi (fazoviy guruhi F-43m, $a = 1,801 \text{ nm}$, $\alpha = \beta = \gamma = 90^\circ$). Debye-Scherrer tenglamasi asosida hisoblangan o'rtacha kristallit o'lchami 14 nm , kristall panjaradagi nuqsonlar darajasi esa $0,75\%$ ni tashkil etdi.

GO-SNC nanokompozitining XRD difraktogrammasida difraksiya cho'qqilarining joylashuvida sezilarli siljish kuzatilmadi. Bu Cu_9NiSn_3 zarrachalarining grafen oksidi qatlamlari yuzasiga kimyoviy bog' hosil qilmasdan muvaffaqiyatli joylashtirilganligini ko'rsatadi. Shu bilan birga, (551) tekisligi uchun d-spacing qiymati sof SNC dagi $2,523 \text{ \AA}$ dan GO-SNC da $2,458 \text{ \AA}$ gacha kamaygani kuzatildi. Bu holat grafen oksidining nanokompozit tarkibiga muvaffaqiyatli kiritilganligini tasdiqlaydi. Mazkur kamayish grafen oksidi bilan aralashtirish jarayonida kristall panjaraning qayta tashkil topishi bilan izohlanadi. Bunda ion radiusi kichik bo'lgan uglerod atomlari yirikroq Cu^{2+} , Ni^{2+} va Sn^{4+} ionlari orasidagi bo'shliqlarga joylashib, panjara parametrlarining o'zgarishiga sabab bo'ladi. Natijada o'rtacha kristallit o'lchami 14 nm dan $57,45 \text{ nm}$ gacha ortdi, kristall panjara deformatsiyasi esa $0,59\%$ gacha kamaydi. Bu esa GO ning kiritilishi nanokompozitning strukturaviy barqarorligini oshirganligini ko'rsatadi. FTIR tahlilida GO namunasi uchun $3404,10 \text{ cm}^{-1}$ da O-H valent tebranishlari, $2929,68$ va $2834,47 \text{ cm}^{-1}$ da C-H bog'larining simmetrik va assimmetrik valent tebranishlari, $2308,34 \text{ cm}^{-1}$ da C=O yoki O=C=O guruhlari, $1717,37 \text{ cm}^{-1}$ da C=C bog'lari tebranishlari, $1607,38 \text{ cm}^{-1}$ da aromatik C=C bog'lari, $1381,66$ va $1118,19 \text{ cm}^{-1}$ da C=C hamda C-O funksional guruhlari, shuningdek $600,27 \text{ cm}^{-1}$ da tekislikdan tashqari C-H deformatsion tebranishlari kuzatildi. SNC namunasi uchun $3524,18 \text{ cm}^{-1}$ da bog'lanmagan suv molekulalariga, 3473 cm^{-1} da OH guruhlarning valent

tebranishlariga xos cho‘qqilar qayd etildi. Kalsinatsiyadan so‘ng ushbu cho‘qqining intensivligi suvning bug‘lanishi tufayli kamaydi. Bundan tashqari, $1385,83\text{ cm}^{-1}$ da C=O valent tebranishlari, $1044,60\text{ cm}^{-1}$ da Cu–O–Cu, $571,72\text{ cm}^{-1}$ da Ni–O hamda $887,58\text{ cm}^{-1}$ da C–C bog‘lariga tegishli tebranishlar kuzatildi. GO–SNC nanokompozitining FTIR spektrida $3398,46\text{ cm}^{-1}$ da keng O–H valent tebranishlari qayd etildi. Ushbu cho‘qqining intensivligi kalsinatsiyadan so‘ng kamaydi. Shuningdek, $1624,89\text{ cm}^{-1}$ da C=O, $1490,30\text{ cm}^{-1}$ da C–O–C, $1362,47\text{ cm}^{-1}$ da O–C=O, $1028,36\text{ cm}^{-1}$ da Cu–O–Cu, $544,63\text{ cm}^{-1}$ da Ni–O hamda $799,27\text{ cm}^{-1}$ da Sn–O bog‘lariga xos tebranishlar kuzatildi.

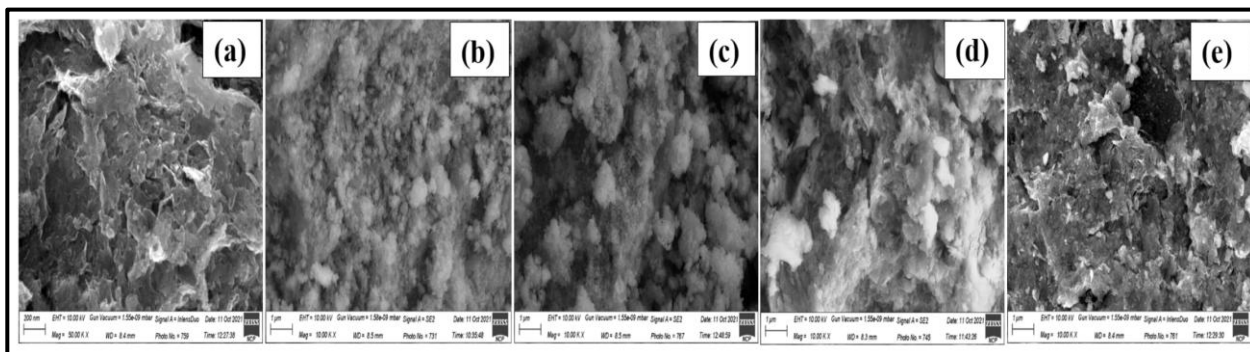
SEM tasvirlari GO namunasining ko‘p qatlamli qatlamsimon tuzilishga ega ekanligini ko‘rsatdi. Namuna yuzasida yuqori darajadagi g‘adir-budurlik hamda ko‘plab bo‘shliqlar va yoriqlar kuzatildi. Ushbu yoriqlar va bo‘shliqlar, ehtimol, suvsizlantirish jarayonidan so‘ng namunani maydalash natijasida hosil bo‘lgan. Sintez qilingan SNC nanokompozitining SEM tasvirlarida qor sharchasiga o‘xshash donador tuzilma kuzatildi. Bunday morfologiya sintez jarayonida hosil bo‘lgan mayda zarrachalarning o‘zaro agregatsiyalanishi natijasida shakllangan. Zarrachalar notekis taqsimlangan bo‘lib, bir-biriga yopishishi natijasida yirikroq agregatlar hosil qilgan. Fon qismida zarrachalarning kuchli aglomeratsiyasi kuzatildi, bu esa ularning yuqori sirt energiyasi ta‘sirida o‘zaro tortilishi bilan izohlanadi. Sintez qilingan SNC namunasi donalarining o‘lchami $40,75\text{--}98,93\text{ nm}$ oralig‘ida bo‘lib, o‘rtacha qiymati $84,55\text{ nm}$ ni tashkil etdi. Namunalar $450\text{ }^{\circ}\text{C}$ da kalsinatsiya qilingandan so‘ng qor sharchasi ko‘rinishidagi alohida donalar diffuziya bilan boshqariladigan jarayonlar, jumladan donalar chegaralarining migratsiyasi va qayta kristallanish hisobiga yanada yiriklashdi. Natijada donalarning o‘rtacha o‘lchami 101 nm gacha ortdi, ularning o‘lchamlari esa $68\text{--}123\text{ nm}$ oralig‘ida qayd etildi. Shuningdek, donalarning notekis joylashuvi tufayli turli o‘lchamdagi bo‘shliqlar hosil bo‘lgani kuzatildi. GO–SNC nanokompozitida metall komponentlar GO bilan birlashtirilgandan so‘ng morfologiyada sezilarli o‘zgarishlar yuz berdi. Metall nanokompozit zarrachalari grafen oksidi qatlamlari orasiga chuqur joylashganligi aniqlandi. Sintez qilingan GO–SNC namunasida donalar GO qatlamlariga singdirilgan holda joylashgan bo‘lib, SNC namunasida kuzatilgan bo‘shliqlarning aksariyati GO ning cho‘kishi natijasida to‘ldirilgan. Kalsinatsiya jarayonidan so‘ng GO qatlamlari yanada aniq namoyon bo‘lib, yarim g‘ovak varaqsimon tuzilma hosil qildi. Shu bilan birga, Cu_9NiSn_3 donalari orasidagi chegaralar deyarli yo‘qolib, nanokompozitning yanada yaxlit va uzluksiz morfologik tuzilishga ega bo‘lganligi kuzatildi.



24-rasm. GO (a), kalsinatsiya qilinmagan va kalsinatsiya qilingan SNC (b) hamda kalsinatsiya qilinmagan va kalsinatsiya qilingan GO-SNC (c) namunalarining XRD difraktogrammalari, shuningdek GO (d), kalsinatsiya qilinmagan va kalsinatsiya qilingan SNC (e) hamda kalsinatsiya qilinmagan va kalsinatsiya qilingan GO-SNC (f) namunalarining FTIR spektrlari (Haq va boshq., 2023).

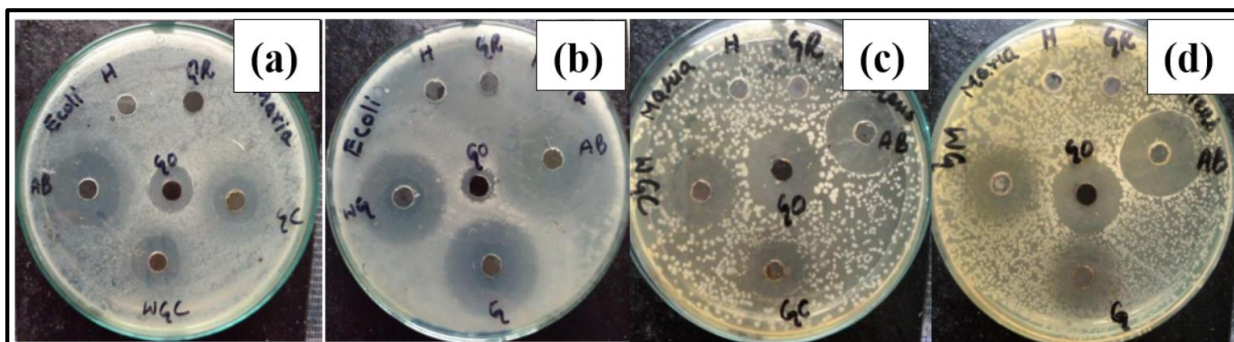
Kalsinatsiya qilinmagan va kalsinatsiya qilingan SNC hamda GO-SNC nanokompozitlarining antibakterial faolligi Gram-manfiy *E. coli* va Gram-musbat *S. aureus* bakteriyalariga nisbatan agar quduq diffuziyasi usuli yordamida baholandi. Tajribalar 10, 20, 30, 40, 50 va 60 $\mu\text{g/mL}$ konsentratsiyalarda amalga oshirildi. Natijalar bakteriyalarga qarshi faollik namuna konsentratsiyasi bilan bevosita bog'liqligini ko'rsatdi. Konsentratsiya ortishi bilan suvli muhitda metall kationlari, gidroksil radikallari ($\bullet\text{OH}$) va superoksid radikal anionlari ($\text{O}_2^{\bullet-}$) kabi reaktiv turlar ko'proq hosil bo'ldi. Metall kationlari bakteriya hujayralaridagi muhim fermentlarning tiol ($-\text{SH}$) guruhlarini bilan reaksiyaga kirishib, ularning biologik faolligini susaytiradi va hujayra metabolizmini izdan chiqaradi, natijada hujayra nobud bo'ladi. Shu bilan birga, hosil bo'lgan radikallar bakteriya hujayra devorining manfiy zaryadlangan yuzasi bilan o'zaro ta'sirlashib, hujayra devorining shikastlanishi, membrana yaxlitligining buzilishi va hujayra ichki tarkibining tashqariga chiqib ketishiga sabab bo'ladi. Tadqiqotda qo'llanilgan eng yuqori konsentratsiyada (60 mg/3 mL) GO-SNC nanokompoziti *E. coli* ga nisbatan 24 mm, *S. aureus* ga nisbatan esa 21 mm ingibitsiya zonasini hosil qildi. Kalsinatsiya qilingan GO-SNC namunasi mos ravishda 9 mm va 12 mm ingibitsiya zonalarini namoyon etdi. SNC namunasi *E. coli* uchun 21 mm, *S. aureus* uchun 7 mm, kalsinatsiya qilingan SNC esa mos ravishda 11 mm va 15 mm ingibitsiya zonalarini hosil qildi. Musbat nazorat sifatida qo'llanilgan siprofloksatsin antibiotigi *E. coli* ga

qarshi 16 mm, *S. aureus* ga qarshi esa 20 mm ingibitsiya zonasini ko'rsatdi. GO namunasi esa mos ravishda *E. coli* va *S. aureus* ga qarshi 6 mm va 11 mm ingibitsiya zonalarini hosil qildi.



25-rasm. GO (a), SNC ning sintezlangan (b) va kalsinatsiyalangan (c); GO-SNC ning sintezlangan (d) va kalsinatsiyalangan (e) SEM tasvirlari (Haq va boshq., 2023).

GO-SNC nanokompoziti har ikkala bakterial shtammga nisbatan SNC ga qaraganda yuqoriroq antibakterial faollik namoyon etdi. Bu holat grafen oksidi bilan modifikatsiyalangan metall nanokompozitlarning kuchaytirilgan antibakterial xususiyatlari bilan izohlanadi. Xususan, GO yuzasidagi kislorod vakant o'rinlari suv molekulalari uchun adsorbsiya markazlari vazifasini bajaradi va ularning ishtirokida gidroksil radikallari ($\bullet\text{OH}$) hosil bo'lishini jadallashtiradi. Bundan tashqari, grafen qatlamlarining o'tkir qirralari bakteriya hujayralari bilan bevosita kontaktda bo'lganda hujayra membranasiga kirib borib, unda teshiklar hosil qiladi va sitoplazmatik tarkibning tashqariga sizib chiqishiga sabab bo'ladi. Shuningdek, bakteriya hujayralari grafen qatlamlari orasida qamalib qolishi natijasida ularning fiziologik faolligi izdan chiqadi va ko'payishi to'xtaydi. Tadqiqot natijalari kalsinatsiya qilinmagan namunalarning kalsinatsiya qilingan namunalarga nisbatan yuqoriroq antibakterial faollikka ega ekanligini ham ko'rsatdi. Buning asosiy sababi kalsinatsiya jarayonida zarracha o'lchamining ortishi natijasida sirt hajmga nisbatining kamayishi hamda bakteriya hujayralari bilan o'zaro ta'sirlashuvchi faol bog'lanish markazlari sonining qisqarishidir. Shuningdek, barcha namunalarda *E. coli* ga nisbatan kuzatilgan antibakterial faollik *S. aureus* ga qaraganda yuqoriroq bo'ldi. Bu farq ikki bakteriyaning hujayra devori tuzilishidagi tafovutlar bilan bog'liq. Gram-manfiy *E. coli* ning hujayra devori yupqa peptidoglikan qatlamidan tashkil topgan bo'lib, tashqi membranasida mavjud lipopolisaxaridlar va fosfolipidlar unga kuchli manfiy zaryad beradi. Natijada metall kationlari bakteriya yuzasiga osonroq birikadi va antibakterial ta'sir kuchayadi. Aksincha, Gram-musbat *S. aureus* qalin peptidoglikan qatlamiga ega bo'lib, tarkibidagi teixoyk kislotalar faqat qisman manfiy zaryad hosil qiladi. Shu sababli metall ionlari bilan o'zaro ta'sir nisbatan sust kechadi va bakteriyaning antibakterial omillarga chidamliligi yuqoriroq bo'ladi.



26-rasm. Kalsinatsiya qilinmagan va kalsinatsiya qilingan SNC hamda GO–SNC nanokompozitlarining antibakterial faolligi. Bunda H – manfiy nazorat (erituvchi), AB – musbat nazorat (antibiotik), GO – grafen oksidi, G – GO–SNC, WG – SNC, GC – kalsinatsiya qilingan GO–SNC, WGC – kalsinatsiya qilingan SNC (Haq va boshq., 2023).

Kalsinatsiya qilingan va kalsinatsiya qilinmagan SNC hamda GO–SNC nanokompozitlarining antioksidant faolligi ABTS va DPPH erkin radikallarini tutib qolish usullari yordamida baholandi. Tajribalar 5, 10, 15 va 20 μg namunalar 5 mL deionizatsiyalangan suvda tayyorlangan eritmalarda amalga oshirildi. Askorbin kislotasi standart modda sifatida qo‘llanildi. ABTS radikalini tutib qolish tahlili natijalariga ko‘ra, GO namunasi 5 μg konsentratsiyada 74,46%, 20 μg konsentratsiyada esa 96,11% radikallarni tutib qolish faolligini (RSA) namoyon etdi va uning IC_{50} qiymati 11,25 $\mu\text{g/mL}$ ni tashkil etdi. Kalsinatsiya qilinmagan SNC namunasi 44,78–86,33% RSA va 36,84 $\mu\text{g/mL}$ IC_{50} qiymatini ko‘rsatdi. Kalsinatsiya qilingan SNC uchun RSA 38,68–77,65%, IC_{50} esa 41,03 $\mu\text{g/mL}$ ni tashkil etdi. Kalsinatsiya qilinmagan GO–SNC nanokompoziti 56,65–91,69% RSA va 28,95 $\mu\text{g/mL}$ IC_{50} , kalsinatsiya qilingan GO–SNC esa 31,73–67,82% RSA hamda 48,56 $\mu\text{g/mL}$ IC_{50} qiymatlarini namoyon etdi. Taqqoslash uchun qo‘llanilgan askorbin kislotasi 34,60–58,67% RSA va 44,67 $\mu\text{g/mL}$ IC_{50} qiymatini ko‘rsatdi. DPPH radikalini tutib qolish tahlilida GO namunasi 89,68–99,02% RSA va 15,98 $\mu\text{g/mL}$ IC_{50} qiymatini namoyon etdi. Kalsinatsiya qilinmagan SNC namunasi 73,93–88,91% RSA va 36,55 $\mu\text{g/mL}$ IC_{50} , kalsinatsiya qilingan SNC esa 53,51–65,17% RSA hamda 36,98 $\mu\text{g/mL}$ IC_{50} qiymatlariga ega bo‘ldi. Kalsinatsiya qilinmagan GO–SNC nanokompoziti 76,85–90,86% RSA va 33,68 $\mu\text{g/mL}$ IC_{50} , kalsinatsiya qilingan GO–SNC esa 42,02–68,09% RSA hamda 46,18 $\mu\text{g/mL}$ IC_{50} qiymatlarini ko‘rsatdi. Askorbin kislotasi esa 69,26–76,45% RSA va 22,33 $\mu\text{g/mL}$ IC_{50} qiymatini namoyon etdi.

Har ikkala tahlil natijalari kalsinatsiya qilinmagan namunalarning kalsinatsiya qilingan namunalarga nisbatan yuqoriroq radikallarni tutib qolish faolligiga ega ekanligini ko‘rsatdi. Shuningdek, ularning IC_{50} qiymatlarining pastroq bo‘lishi yuqori antioksidant salohiyatni tasdiqlaydi. Buning asosiy sababi kalsinatsiya jarayonida zarracha o‘lchamining ortishi natijasida eritmadagi nanopartikulalar

sonining kamayishi va erkin radikallarni adsorbsiya qilish hamda barqarorlashtirish uchun mavjud faol markazlar sonining qisqarishidir.

4-jadval. GO, SNC va GO–SNC nanokompozitlarining ABTS va DPPH erkin radikallariga nisbatan antioksidant faolligi (Haq va boshq., 2023).

Samples	Concentration mg/mL	%RSA	IC ₅₀	Samples	Concentration mg/mL	%RSA	IC ₅₀
GO	0.005	90.35	14.82	GO	0.005	89.68	15.98
	0.010	92.39			0.010	94.94	
	0.015	93.57			0.015	97.08	
	0.020	98.25			0.020	99.02	
SNC	0.005	83.04	32.43	SNC	0.005	73.93	36.55
	0.010	89.18			0.010	76.07	
	0.015	93.86			0.015	81.32	
	0.020	96.78			0.020	88.91	
SNC calcined	0.005	41.52	42.33	SNC calcined	0.005	53.51	36.98
	0.010	67.25			0.010	57.97	
	0.015	75.73			0.015	61.28	
	0.020	81.58			0.020	65.17	
GO-SNC	0.005	83.92	24.56	GO-SNC	0.005	76.85	33.68
	0.010	86.84			0.010	79.96	
	0.015	88.59			0.015	81.71	
	0.020	93.86			0.020	90.86	
GO-SNC calcined	0.005	52.22	45.43	GO-SNC calcined	0.005	42.02	46.18
	0.010	59.35			0.010	50.39	
	0.015	62.86			0.015	59.14	
	0.020	82.46			0.020	68.09	
Ascorbic acid	0.005	33.04	41.81	Ascorbic acid	0.005	69.26	22.33
	0.010	37.42			0.010	71.40	
	0.015	40.35			0.015	73.92	
	0.020	44.15			0.020	76.45	

Barcha namunalar orasida GO eng yuqori antioksidant faollikni namoyon etdi. Bu holat erkin radikallarning sp^2 -gibridlangan uglerod markazlari bilan adduktlar hosil qilishi, juftlanmagan elektronlarning grafenning kon'yugirlangan skeleti bo'ylab spin delokalizatsiyasi sodir bo'lishi, elektronlarning samarali uzatilishi hamda gidroksil funksional guruhlari tomonidan vodorod atomlarining donorligi bilan izohlanadi. GO–SNC nanokompoziti SNC ga nisbatan yuqoriroq antioksidant faollikni namoyon etdi. Bu GO va SNC o'rtasidagi sinergik ta'sir bilan bog'liq bo'lib, ularning o'zaro ta'siri natijasida hosil bo'ladigan RKT erkin radikallarga elektron berish orqali ularni barqaror holatga keltiradi va radikal faolligini kamaytiradi. Bundan tashqari, barcha namunalarda radikallarni tutib qolish faolligi (%) namuna konsentratsiyasi ortishi bilan muntazam ravishda oshib bordi. Bu yuqori konsentratsiyalarda eritmada ko'proq nanopartikulalar mavjud bo'lishi, ularning erkin radikallar bilan o'zaro ta'sirlashish ehtimolini oshirishi hamda radikallarni samaraliroq neytrallashtirishini ko'rsatadi.

5-BOB. KDUN–METALL OKSIDLI NANOKOMPOZITLAR

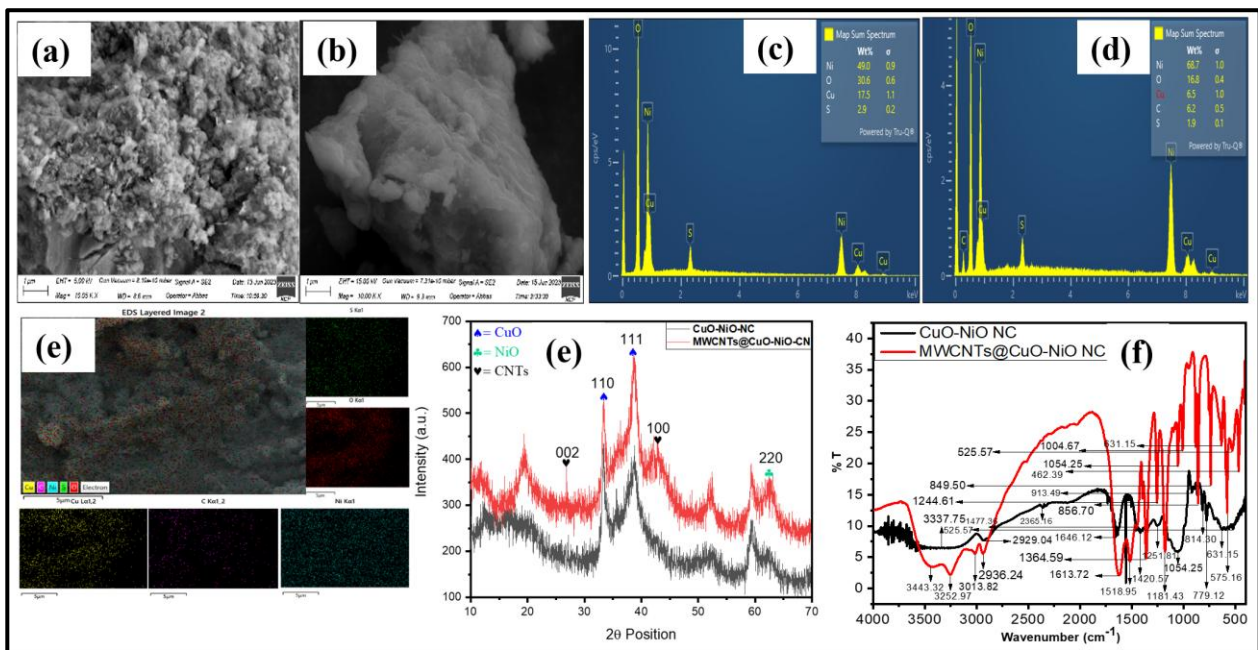
5.1 CuO–NiO va KQUs@CuO–NiO nanokompozitlari. CuO–NiO nanokompoziti hamda uning ko'p devorli uglerod nanonaychalari (KDUNlar) bilan modifikatsiyalangan analogi an'anaviy zol-gel usulining takomillashtirilgan varianti hisoblangan modifikatsiyalangan sol-gel usuli yordamida sintez qilindi. CuO–NiO nanokompozitini sintez qilishda nikel(II) nitrat geksagidrat va mis(II) nitrat pentagemigidrat alohida-alohida deionizatsiyalangan suvda 30 daqiqa davomida uzluksiz aralashtirildi. So'ngra ikkala eritma birlashtirilib, 60 °C da 30 daqiqa davomida kuchli aralashtirish sharoitida qizdirildi. Eritmaning pH qiymati 10 ga yetguncha natriy gidroksid (NaOH) eritmasi qo'shildi va aralashma 60 °C da 3 soat davomida uzluksiz aralashtirilib qizdirildi. Aralashma sovutilgach, 24 soat davomida yetiltirildi, keyin filtrlandi, deionizatsiyalangan suv bilan uch marta yuvildi va hosil bo'lgan qattiq qoldiq mufel pechida 350 °C da 4 soat davomida kalsinatsiya qilindi. KQUs@CuO–NiO nanokompozitini sintez qilishda karboksil kislota funksional guruhlari bilan modifikatsiyalangan KDUNlar avval deionizatsiyalangan suvda ultratovush yordamida dispersiyalandi va pH ni sozlashdan oldin metall nitratlar eritmasiga qo'shildi. Reaksiya aralashmasi 80 °C da 5 soat davomida uzluksiz aralashtirish sharoitida olib borildi. Keyinchalik aralashma 24 soat davomida yetiltirildi, filtrlandi, issiq distillangan suv bilan to'rt marta yuvildi, 100 °C da quritildi va 350 °C da 4 soat davomida kalsinatsiya qilindi. Mazkur modifikatsiyalangan zol-gel usuli bimetall oksidli nanopartikulalar hamda KDUN bilan modifikatsiyalangan nanokompozitlarni sintez qilishning samarali, tezkor va soddalashtirilgan usuli hisoblanadi.

SEM tahlili CuO–NiO nanokompozitining zarrachalar aglomeratsiyasi tufayli bulutsimon ko'rinishga ega ekanligini va sirtning aniq ajralmaganligini ko'rsatdi. Namuna yuzasida ko'plab bo'shliqlar kuzatildi. Ushbu bo'shliqlar zol-gel sintezi davomida erituvchining bug'lanishi yoki quritish jarayonida hajmning qisqarishi

natijasida hosil bo'lgan. Metall oksidli nanopartikulalar uchun xos bo'lgan kuchli o'zaro tortilish tufayli zarrachalar sezilarli darajada aglomeratsiyalangan bo'lib, bir-birining ustiga joylashishi natijasida zich morfologiya shakllangan. Ayrim cho'zilgan yoki ignasimon strukturalar anizotropik o'sish jarayonini ko'rsatsa, notekis shakldagi zarrachalar sol-gel sintezi davomida nukleatsiya va o'sish jarayonlarining bir xil kechmaganligini bildiradi. Shuningdek, ayrim tangachasimon tuzilmalar erituvchining bug'lanishi natijasida hosil bo'lgan. KDUNlar nanokompozit tarkibiga kiritilgandan so'ng morfologiyada sezilarli o'zgarishlar kuzatildi. KDUNlar katta solishtirma sirt maydoni ga ega tayanch vazifasini bajarib, CuO va NiO nanopartikulalari bilan kuchli o'zaro ta'sirlashdi hamda ularni silliq sirtli, zich va ixcham struktura hosil qiladigan tarzda birlashtirdi. Shu bilan birga, bo'shliqlar soni sezilarli darajada kamaydi. KDUNlar va metall oksid nanopartikulalari orasidagi kuchli van-der-Vaals tortishish kuchlari natijasida aglomeratsiya yanada kuchaydi va yagona yaxlit struktura shakllandi. Bunda alohida zarrachalar orasidagi chegaralar deyarli yo'qolib, uzluksiz faza hosil bo'ldi. Nanopartikulalarning to'planishi natijasida yuzada bo'rtmalar hosil bo'lgan bo'lsa, KDUNlar bo'shliqlarni to'ldirishi hisobiga g'ovaksiz va ixcham morfologiya yuzaga keldi. EDX tahlili nanokompozit tarkibidagi elementlarni tasdiqladi. Spektrlarda uglerod uchun 0,14 keV, kislorod uchun 0,50 keV, mis uchun 0,93, 8,10 va 8,90 keV, nikel uchun 0,81 va 7,50 keV, shuningdek SDS sirt-faol moddasi tarkibidagi oltingugurt uchun 2,30 keV energiyalarda xarakterli cho'qqilar kuzatildi. KDUNlar ning qo'shilishi CuO va NiO nanopartikulalarining dispersiyalanishini yaxshilab, ularning sirt ekspozitsiyasini oshirdi va natijada kislorod signalining intensivligi kuchaydi. Mis signallari ham ortdi, chunki KDUNlar nanopartikulalarning aglomeratsiyasini kamaytirib, ularning bir tekis taqsimlanishini ta'minladi. Uglerod miqdori KDUNlar ning yuqori sirt maydoni va elektr o'tkazuvchanligi tufayli sezilarli darajada oshdi. Aksincha, nikel signalining intensivligi biroz kamaydi, bu esa KDUNlar ning CuO bilan nisbatan kuchliroq bog'lanishi va kompozit morfologiyasining o'zgarishi bilan izohlanadi. EDX xaritalash tahlili nanokompozit tarkibidagi elementlarning mavjudligi va taqsimlanishini tasdiqladi. Xaritalarda Cu, Ni va O elementlarining ayrim hududlarda yengil aglomeratsiyalanganligi kuzatilgan bo'lsa, KDUNlar namunada monodispers holatda va bir tekis taqsimlanganligi aniqlandi. Ushbu natijalar CuO–NiO nanopartikulalarining muvaffaqiyatli sintez qilinganini hamda KDUNlar ning nanokompozit tarkibiga samarali inkorporatsiya qilinganini tasdiqlaydi.

XRD tahlili har ikkala namuna difraktogrammasida ma'lum darajada shovqin mavjudligini ko'rsatdi, bu esa kristall fazalar bilan bir qatorda sezilarli miqdorda amorf faza ham mavjudligini bildiradi. Bunday holat Scherrer effekti bilan izohlanadi, ya'ni kristallit o'lchamining kichik bo'lishi difraksiya cho'qqilarining kengayishiga va intensivligining pasayishiga olib keladi. Bundan tashqari, KDUN, CuO va NiO fazalariga tegishli difraksiya cho'qqilarining ustma-ust tushishi difraktogrammaning murakkablashishiga sabab bo'lgan. $26,81^\circ$ va $42,10^\circ$ dagi difraksiya cho'qqilari JCPDS 00-041-1487 ma'lumot kartasiga muvofiq KDUNlar ning mos ravishda (002) va (100) kristall tekisliklariga tegishli bo'lib, ular grafit

qatlamlari orasidagi masofa hamda geksagonal panjaradagi uglerod atomlarining tekislik ichidagi joylashuvini ifodalaydi. $33,38^\circ$ va $38,67^\circ$ dagi Bragg reflekslari monoklinik kristall tizimiga mansub CuO ning mos ravishda (110) va (111) kristall tekisliklariga to'g'ri keladi. Ushbu faza Cc fazoviy guruhiga mansub bo'lib, panjara parametrlari $a = 4,6927 \text{ \AA}$, $b = 3,4283 \text{ \AA}$, $c = 5,1370 \text{ \AA}$, panjara burchaklari esa $\alpha = \gamma = 90^\circ$ va $\beta = 99,5460^\circ$ ni tashkil etadi. $62,29^\circ$ dagi difraktsiya cho'qqisi kubik kristall tizimiga mansub NiO ning (220) kristall tekisligiga tegishli bo'lib, u Fm3m fazoviy guruhiga ega. Ushbu fazada panjara parametrlari $a = b = c = 3,1700 \text{ \AA}$ bo'lib, barcha panjara burchaklari 90° ga teng. FTIR tahlilida $3337,57 \text{ cm}^{-1}$ markazida keng yutilish zonasi hamda $3443,32$ va $3252,97 \text{ cm}^{-1}$ dagi yutilish cho'qqilari H–O–H bog'lari tebranishlari va gidroksil guruhlarining mavjudligi bilan bog'landi. $3013,82 \text{ cm}^{-1}$ dagi kuchsiz cho'qqi C–H bog'ining assimetrik valent tebranishlariga, $2936,24 \text{ cm}^{-1}$ dagi cho'qqi esa KDUNlar dagi C–H bog'larining valent tebranishlariga tegishli bo'ldi. $2929,04 \text{ cm}^{-1}$ dagi cho'qqi vodorod bog'lanishlarida ishtirok etuvchi ko'priksimon gidroksil guruhlarining 2D tebranish rejimi bilan bog'landi. $2365,16 \text{ cm}^{-1}$ dagi kuchsiz cho'qqi nanokompozit yuzasiga adsorbsiyalangan atmosfera CO₂ si mavjudligini ko'rsatdi. $1646,12 \text{ cm}^{-1}$ dagi o'rta intensivlikdagi cho'qqi koordinatsiyalangan suv molekularidagi H–O–H bog'ining egilish tebranishlari bilan bog'liq bo'ldi. $1613,72$ va $1518,95 \text{ cm}^{-1}$ dagi cho'qqilar KDUNlar tarkibidagi C=C bog'larining valent tebranishlari natijasida hosil bo'lgan bo'lsa, $1477,36 \text{ cm}^{-1}$ dagi kuchsiz cho'qqi C–H bog'larining deformatsion tebranishlariga tegishli bo'ldi. $1420,57 \text{ cm}^{-1}$ dagi cho'qqi panjaradagi M–OH tebranishlari bilan, $1364,95 \text{ cm}^{-1}$ dagi intensiv cho'qqi esa O–C–O guruhlarining assimetrik tebranishlari bilan bog'landi. $1251,81$ va $1244,61 \text{ cm}^{-1}$ dagi cho'qqilar O–M–O (M = Cu) bog'lari tebranishlariga, $1181,43 \text{ cm}^{-1}$ dagi kuchli cho'qqi C–O bog'i tebranishlariga, $1054,25 \text{ cm}^{-1}$ dagi turli intensivlikdagi cho'qqilar esa M–O–M bog'lari tebranishlariga tegishli bo'ldi. $1004,67 \text{ cm}^{-1}$ dagi cho'qqi Cu–O bog'ining deformatsion tebranishlari bilan, $913,49 \text{ cm}^{-1}$ dagi kuchsiz cho'qqi esa M–O bog'lari tebranishlari bilan bog'landi. $856,70 \text{ cm}^{-1}$ dagi cho'qqi tekislikdan tashqari C–H deformatsion tebranishlariga, $849,50 \text{ cm}^{-1}$ dagi cho'qqi esa M–O–C bog'lari tebranishlariga tegishli bo'ldi. $779,12 \text{ cm}^{-1}$ dagi cho'qqi monoklinik panjaradagi Cu–O bog'ining valent tebranishlari bilan bog'liq bo'lsa, $631,15$ va $575,16 \text{ cm}^{-1}$ dagi cho'qqilar Ni–O bog'lari tebranishlari natijasida yuzaga kelgan. $525,57$ va $462,39 \text{ cm}^{-1}$ dagi cho'qqilar esa Cu–O valent tebranishlariga tegishli bo'ldi. KDUNlar ning nanokompozit tarkibiga kiritilishi natijasida ayrim yutilish cho'qqilarining intensivligi o'zgardi, ayrimlari yo'qolib, yangi cho'qqilar paydo bo'ldi hamda fingerprint sohasidagi spektral xususiyatlar yanada yaqqol namoyon bo'ldi. Bu holat KDUNlar va metall oksidlar o'rtasidagi yangi o'zaro ta'sirlarning yuzaga kelishi, bog'lanish muhitining o'zgarishi, nanopartikulalarning yaxshiroq dispersiyalanishi, yangi tebranish rejimlarining paydo bo'lishi hamda tebranishlarning o'zaro bog'lanish darajasining ortishi bilan izohlanad.



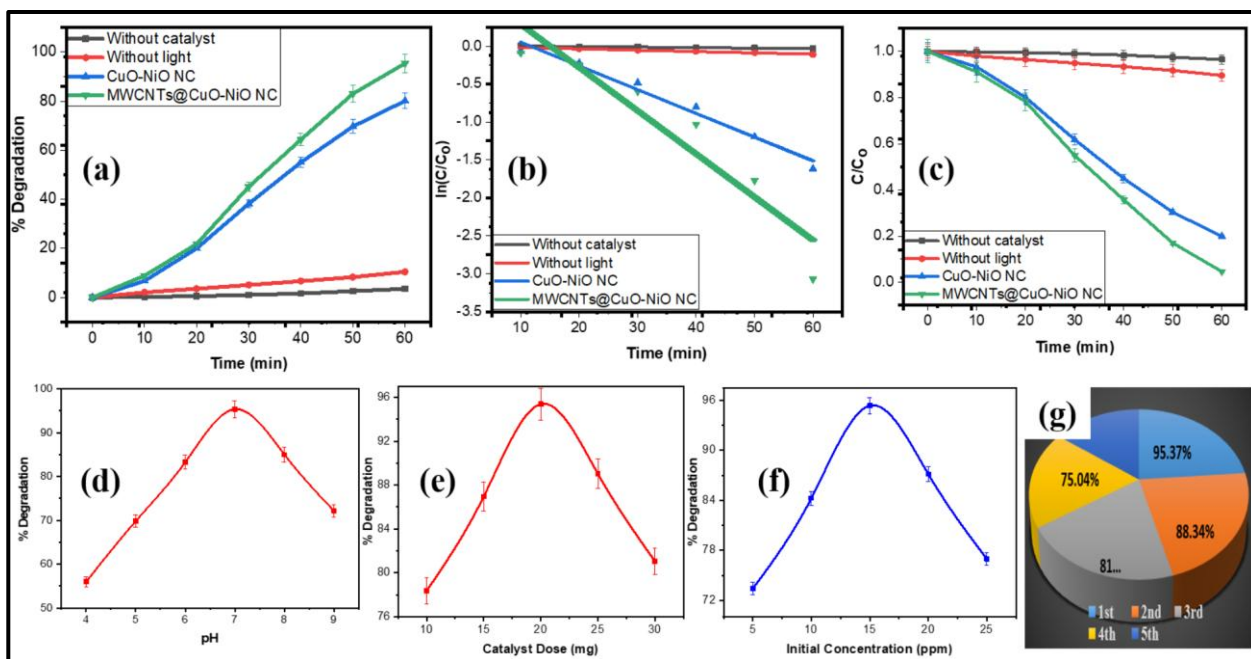
27-rasm. CuO–NiO va KDUNs@CuO–NiO nanokompozitlarining SEM tasvirlari (a, b), EDX spektrlari (c, d), EDX elementlar xaritalari (e), XRD difraktogrammalari (g) hamda FTIR spektrlari (Lone, Rehman, Haq, Shahzad, va boshq., 2025).

Fotokatalitik faollik R-6G bo‘yog‘iga nisbatan 2024-yil 3–14-iyun kunlari soat 11:00 dan 15:00 gacha bo‘lgan vaqt oralig‘ida tabiiy quyosh nuri ostida baholandi. Fotokatalitik degradatsiya jarayonida reaksiya aralashmasining yorqin jigarrang rangi bosqichma-bosqich oqarib bordi. 526 nm dagi maksimal absorbsiya qiymatining keskin kamayishi bo‘yoq molekulasidagi xromofor guruhlarining parchalanishi sodir bo‘lganligini ko‘rsatdi. Katalizatorsiz nazorat namunasida absorbsiya qiymatining juda kam o‘zgarishi kuzatilgan bo‘lsa, fotokatalizator ishtirokidagi barcha namunalarda sezilarli kamayish qayd etildi. Ayniqsa, KDUN bilan modifikatsiyalangan nanokompozit eng yuqori fotokatalitik faollikni namoyon etdi. Degradatsiya profili barcha namunalarda dastlabki 20 daqiqa davomida maksimal absorbsiya qiymatining keskin pasayishini, keyingi bosqichlarda esa degradatsiya tezligining asta-sekin kamayishini ko‘rsatdi. CuO–NiO nanokompoziti 80,09%, KDUNs@CuO–NiO nanokompoziti esa 95,37% fotodegradatsiya samaradorligini namoyon etdi. Nazorat tajribalarida faqat yorug‘lik (katalizatorsiz) sharoitida 3,52%, faqat katalizator (yorug‘liksiz) ishtirokida esa 10,45% degradatsiya kuzatildi. Ushbu natijalar fotokatalitik jarayonda yorug‘lik va fotokatalizator ning o‘zaro sinergik ta’siri hal qiluvchi ahamiyatga ega ekanligini tasdiqlaydi. Hisoblangan tezlik konstantalari (k) CuO–NiO uchun $0,02737 \text{ min}^{-1}$, KDUNs@CuO–NiO uchun esa $0,0477 \text{ min}^{-1}$ ni tashkil etdi. Katalizatorsiz nazorat namunasi uchun hisoblangan qiymat $5,99312 \text{ min}^{-1}$ sifatida qayd etildi. Shuningdek, Fotokatalitik Faollik Indeksi (Photocatalytic Activity Index, PAI) mos ravishda CuO–NiO va KDUNs@CuO–NiO nanokompozitlari uchun $0,13 \times 10^{-4}$ hamda $0,22 \times 10^{-4}$ ga teng bo‘ldi. Ushbu natijalar KDUN ning nanokompozit tarkibiga kiritilishi fotokatalitik faollikni sezilarli darajada oshirishini yaqqol ko‘rsatadi.

Fotokatalitik degradatsiya mexanizmi R-6G molekulalarining hosil bo'lgan gidroksil radikallari ($\bullet\text{OH}$) va boshqa RKT ta'sirida bosqichma-bosqich parchalanishiga asoslanadi. Fotokatalizator quyosh nurini yutganda valent zonadagi (VB) elektronlar o'tkazuvchanlik zonasiga (CB) qo'zg'atiladi va natijada valent zonada musbat teshiklar (h^+) hosil bo'ladi. Ushbu teshiklar OH^- ionlari yoki H_2O molekulalari bilan reaksiyaga kirishib gidroksil radikallari ni hosil qiladi. Mazkur radikallar bo'yoq molekulasining etil guruhlariga va ksanten halqasi ga hujum qiladi. Shu bilan bir vaqtda, qo'zg'atilgan elektronlar kislorod molekulalari bilan reaksiyaga kirishib RKTni hosil qiladi. Ushbu faol zarrachalar kon'yugirlangan bog'larning uzilishiga sabab bo'ladi. Fotodegradatsiyaning dastlabki va eng muhim bosqichi N-deetillanish (N-de-ethylation) hisoblanadi. Bunda yuqori reaktiv gidroksil radikallari ksanten yadrosidagi azot atomlariga birikkan etil guruhlariga hujum qilib, N-deetillangan oraliq mahsulotlar ni hosil qiladi. Aynan shu bosqich eritmaning dastlabki rangsizlanishiga sabab bo'ladi. Keyingi bosqichlarda RKT ksanten halqasi tuzilishiga hujum qilib, kon'yugirlangan qo'sh bog'larning uzilishiga olib keladi. Bundan tashqari, gidroksil radikallari ning aromatik halqalarga elektrofil hujumi natijasida kichik aromatik fragmentlar hosil bo'ladi. Oksidlanish jarayonining davom etishi C-C, C-N va C-O bog'larining uzilishiga sabab bo'lib, oxir-oqibat H_2O , CO_2 , NH_4^+ va NO_3^- kabi oddiy mahsulotlar hosil bo'ladi.

pH ning ta'siri o'rganilganda fotodegradatsiya darajasi pH 4 da 56,02%, pH 5 da 69,83%, pH 6 da 83,29%, pH 7 da 95,37%, pH 8 da 85,02% va pH 9 da 72,17% ni tashkil etdi. Eng yuqori fotokatalitik samaradorlik neytral muhit (pH 7) da kuzatildi. R-6G eritmada ionli (R6G^+) va ionlanmagan shakllarda mavjud bo'ladi. Eritmaning pH qiymati ortishi bilan kationli bo'yoq molekulalari asta-sekin neytral shaklga o'tadi. Natijada ular manfiy zaryadlangan nanokompozit yuzasi bilan samarali elektrostatik o'zaro ta'sirlasha olmaydi va pH 7 dan yuqori qiymatlarda degradatsiya samaradorligi kamayadi. Aksincha, pH 7 dan past sharoitlarda ikkilamchi amin guruhidagi azot atomining protonlanishi natijasida bo'yoq molekulalari gidrofillashadi va neytral muhitga nisbatan kamroq reaktiv radikallar hosil bo'ladi, bu esa fotodegradatsiya samaradorligining pasayishiga olib keladi. Fotokatalizator miqdorini optimallashtirish natijalariga ko'ra, fotodegradatsiya darajasi katalizator miqdori 10 mg dan 20 mg gacha oshirilganda 78,36% dan 95,37% gacha ortdi. Biroq katalizator miqdori 25 mg va 30 mg gacha ko'paytirilganda degradatsiya mos ravishda 89,01% va 81,03% gacha kamaydi. Optimal miqdorda fotokatalizatorning umumiy sirt maydoni ortishi hisobiga faol markazlar soni ko'payadi va bo'yoq molekulalari bilan o'zaro ta'sir kuchayadi. Ammo yuqori dozada nanopartikulalar aglomeratsiyalanib, fotonlarning fotokatalizator yuzasiga yetib borishi va yutilishi cheklanadi, natijada fotokatalitik samaradorlik pasayadi. Bo'yoqning boshlang'ich konsentratsiyasi ta'sirini o'rganish natijasida 5, 10, 15, 20 va 25 ppm konsentratsiyalarda degradatsiya darajalari mos ravishda 73,42%, 84,26%, 95,37%, 87,16% va 76,97% ni tashkil etdi. Eng yuqori fotodegradatsiya 15 ppm da kuzatildi. Konsentratsiyaning bundan yuqori qiymatlarida fotokatalizator yuzasidagi faol markazlarning to'yinishi hamda bo'yoq eritmasining yorug'likni kuchli yutishi natijasida fotonlarning fotokatalizator

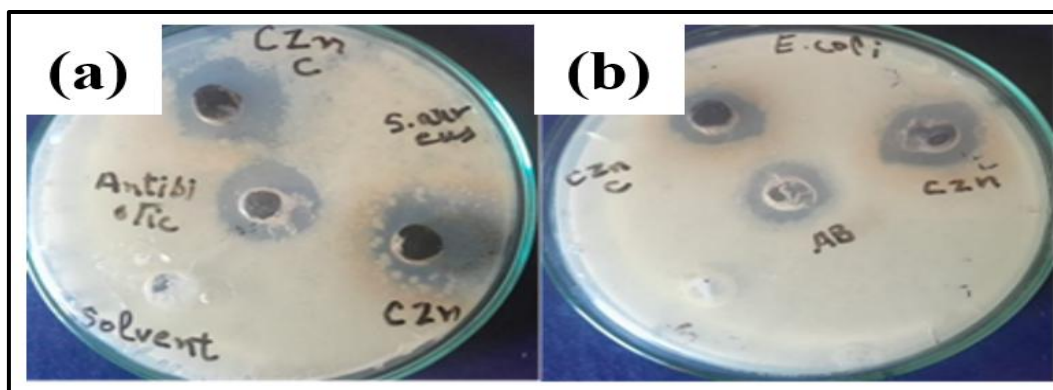
yuzasiga yetib borishi cheklanib, degradatsiya samaradorligi pasaydi. Fotokatalizatorning qayta foydalanish imkoniyati ketma-ket besh sikl davomida baholandi. Fotodegradatsiya samaradorligi mos ravishda 1–5-sikllarda 95,37%, 88,34%, 81,69%, 75,04% va 61,21% ni tashkil etdi. Birinchi siklda yuqori samaradorlik fotokatalizator yuzasining yangi va faol holatda bo‘lishi bilan izohlanadi. Keyingi sikllarda esa fotokatalizator yuzasida ifloslantiruvchi moddalar va bo‘yoq qoldiqlarining to‘planishi, strukturaviy o‘zgarishlar, faol markazlarning deaktivatsiyasi hamda bo‘yoq molekulalarining fotokatalizator yuzasiga adsorbsiyalanishi natijasida fotokatalitik samaradorlik bosqichma-bosqich kamaygan.



28-rasm. Simulyatsiya qilingan quyosh nuri ostida CuO–NiO va KDUNs@CuO–NiO nanokompozitlari ishtirokida R-6G ning fotokatalitik degradatsiyasiga oid natijalar: degradatsiya darajasi (%) (a), tezlik konstantasi (b), chiziqli kinetik grafik (c), pH ning ta’siri (d), fotokatalizator miqdorining ta’siri (e), boshlang‘ich konsentratsiyaning ta’siri (f) hamda KDUNs@CuO–NiO nanokompozitining fotokatalitik jarayondagi qayta foydalanish samaradorligi (g) (Lone, Rehman, Haq, Shahzad, va boshq., 2025).

Antibakterial faollik *S. aureus* va *E. coli* bakteriyalariga nisbatan agar quduq diffuziyasi usuli yordamida baholandi. Tadqiqot natijalari CuO–NiO nanokompozitining har ikkala bakteriya turiga nisbatan yuqori antibakterial faollik namoyon etganligini ko‘rsatdi. Biroq, *E. coli* ning tashqi membranasi yaxshi rivojlangan himoya tuzilishiga ega bo‘lgani sababli u *S. aureus* ga nisbatan nisbatan yuqori chidamlilik ko‘rsatdi. CuO–NiO nanokompozitining antibakterial samaradorligi standart antibiotik bilan taqqoslaganda yuqoriroq bo‘lib, ushbu nanokompozitni istiqbolli antibakterial material sifatida qo‘llash mumkinligini ko‘rsatadi. Nazorat tajribalarida ishlatilgan erituvchi antibakterial faollikka hech

qanday ta'sir ko'rsatmaganligi aniqlanib, kuzatilgan antibakterial samaradorlik faqat nanokompozitlarning o'ziga xos xususiyatlari bilan bog'liqligi tasdiqlandi. KDUNs@CuO–NiO nanokompoziti ham sezilarli antibakterial faollik namoyon etgan bo'lsa-da, uning samaradorligi sof CuO–NiO nanokompozitiga nisbatan pastroq bo'ldi. Bu holat KDUNlar ning kiritilishi natijasida CuO–NiO nanopartikulalarining faol markazlari qisman berkilishi yoki ekranlanishi bilan izohlanadi, buning natijasida ularning bakteriya hujayralari bilan bevosita o'zaro ta'sirlashish imkoniyati kamayadi. Shuningdek, KDUNlar ning mavjudligi nanopartikulalarning aglomeratsiyasini kuchaytirishi, natijada samarali solishtirma sirt maydoni ning kamayishiga olib kelishi mumkin. Bundan tashqari, metall ionlarining KDUNlar yuzasidagi funksional guruhlar bilan bog'lanishi nanokompozitning sirt kimyosini o'zgartiradi va metall oksidlarning bakteriya hujayra devori bilan o'zaro ta'sirlashish qobiliyatini pasaytiradi.



29-rasm. CuO–NiO va KDUNs@CuO–NiO nanokompozitlarining antibakterial faolligini aks ettiruvchi tajriba suratlari (Lone, Rehman, Haq, Shahzad, va boshq., 2025).

Antioksidant faollik ABTS⁺ radikal kation eritmasiga nisbatan baholandi hamda vitamin C (askorbin kislotasi) standart (nazorat) modda sifatida qo'llanildi. Olingan natijalar har ikkala nanokompozitning ham konsentratsiya ortishi bilan antioksidant faolligi izchil oshib borishini ko'rsatdi. 5–400 µg/mL konsentratsiya oralig'ida CuO–NiO nanokompoziti erkin radikallarni neytrallash (RSA) samaradorligini 22,076% dan 82,336% gacha namoyon etib, IC₅₀ = 116,52 µg/mL qiymatini qayd etdi. Shu bilan birga, KDUNs@CuO–NiO nanokompoziti 24,14% dan 90,924% gacha bo'lgan radikalni so'ndirish faolligini namoyish etib, IC₅₀ = 84,61 µg/mL qiymatiga ega bo'ldi. Taqqoslash uchun, askorbin kislotasi ning IC₅₀ qiymati 92,74 µg/mL ni tashkil etdi. Nanokompozitlarning yuqori antioksidant faolligi ularning manfiy zaryadlangan yuzasi elektron donor sifatida ABTS erkin radikal kationlarini samarali tutib qolish qobiliyatiga ega ekanligi bilan izohlanadi. Natijada ko'proq RKTneytrallanib, antioksidant samaradorlik ortadi. Statistik tahlil natijalariga ko'ra, CuO–NiO, KDUNs@CuO–NiO va askorbin kislotasi uchun standart og'ish (SD) qiymatlari mos ravishda 1,68, 1,69 va 1,75 ni tashkil etdi. Ushbu natijalar CuO–NiO nanokompoziti eng yuqori aniqlik va takrorlanuvchanlikka ega eksperimental natijalarni berganligini ko'rsatadi. Dispersiya (variance) qiymatlari

mos ravishda 2,82, 2,84 va 3,09 bo'lib, CuO–NiO nanokompozitida natijalar orasidagi o'zgaruvchanlik eng past darajada ekanligi aniqlandi. Doza bilan RSA (%) o'rtasidagi korrelyatsiya koeffitsiyentlari CuO–NiO, KDUNs@CuO–NiO va askorbin kislotasi uchun mos ravishda 0,098, 0,108 va 0,102 ni tashkil etdi. Ushbu natijalar konsentratsiya ortishi bilan RSA (%) ning oshishi barcha namunalarda kuzatilganligini, ayniqsa KDUNs@CuO–NiO nanokompozitida bu bog'liqlik kuchliroq namoyon bo'lganligini ko'rsatadi. KDUNlar ning nanokompozit tarkibiga kiritilishi elektronlarning samarali ko'chishini ta'minlaydi, faol markazlar sonini ko'paytiradi hamda reaktiv zarrachalarni barqarorlashtiradi. Natijada sirt plazmon rezonansi (SPR) ta'siri, redoks sikllanishi va metall–ligand o'zaro ta'sirlari hisobiga nanokompozitning umumiy antioksidant samaradorligi sezilarli darajada ortadi.

5-jadval. Sintez qilingan nanokompozitlarning ABTS erkin radikallariga nisbatan antioksidant faolligi (Lone, Rehman, Haq, Shahzad, va boshq., 2025).

Samples	Concentration ($\mu\text{g/mL}$)	%RSA	IC ₅₀ ($\mu\text{g/mL}$)	Variance (S ²)	Standard deviation (S)	Correlation between dose and %RSA
CuO–NiO NC	5	22.076	116.52	2.82	1.68	0.098
	25	30.188				
	50	43.228				
	100	59.916				
	200	74.004				
	400	82.336				
MWCNT@ CuO–NiO NC	5	24.144	84.61	2.84	1.69	0.108
	25	33.432				
	50	49.796				
	100	65.124				
	200	79.612				
	400	90.924				
Ascorbic acid	5	21.92	92.74	3.09	1.75	0.102
	25	33.58				
	50	47.956				
	100	57.396				
	200	83.976				
	400	94.068				

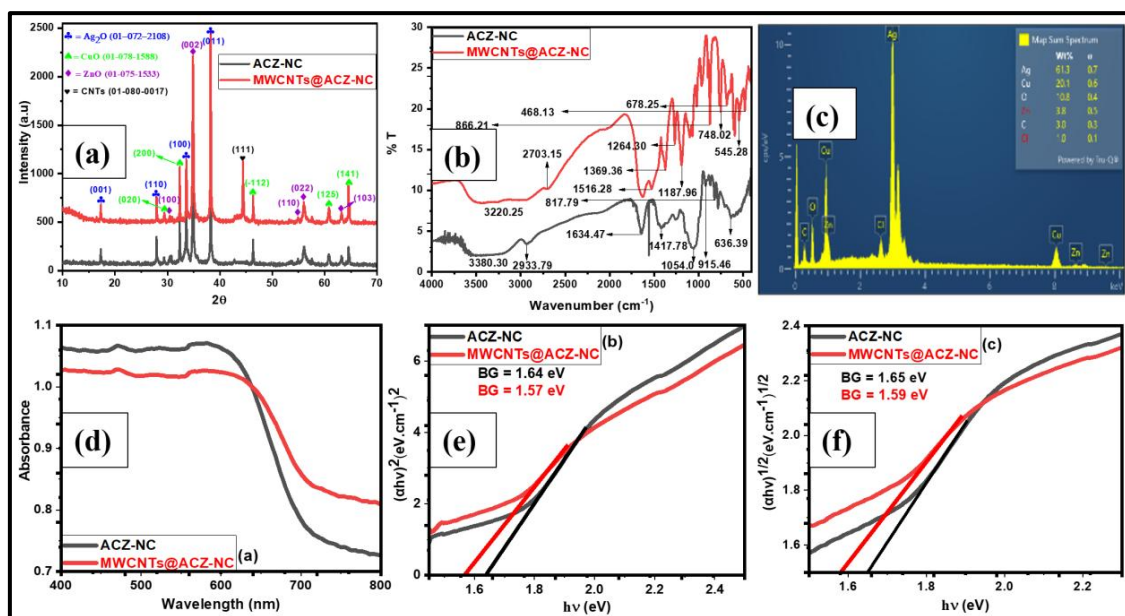
5.2 Ag₂O/CuO/ZnO va KDUNs@Ag₂O/CuO/ZnO nanokompozitlari.

Kumush oksidi/mis oksidi/rux oksidi (Ag₂O/CuO/ZnO) asosidagi uch komponentli nanokompozit hamda uning KDUN bilan modifikatsiyalangan analogi modifikatsiyalangan sol-gel usuli yordamida sintez qilindi. Mazkur tadqiqot fotokatalizator, antibakterial material va antioksidant agent sifatida ko'p funktsiyali qo'llanish imkoniyatiga ega bo'lgan KDUN bilan modifikatsiyalangan Ag₂O/CuO/ZnO nanokompozitlari haqida ilk ilmiy hisobot hisoblanadi. ACZ-NC nanokompozitini sintez qilish uchun Zn(NO₃)₂·5H₂O, AgNO₃ va Cu(NO₃)₂·5H₂O tuzlari alohida-alohida deionizatsiyalangan suvda doimiy aralashtirish ostida 30

daqiqa davomida eritildi. Soʻngra tayyorlangan eritmalar kuchli aralashtirish orqali birlashtirilib, 60 °C da 30 daqiqa qizdirildi. Keyinchalik eritmaning pH qiymatini 10 ga yetkazish uchun 1 M NaOH eritmasi qoʻshildi va aralashma uzluksiz qizdirish hamda aralashtirish sharoitida 3 soat davomida reaksiyaga kiritildi. Reaksiya aralashmasi xona haroratida 24 soat sovutilgandan soʻng filtrlandi, deionizatsiyalangan suv bilan yuvildi, 100 °C da 8 soat quritildi va yakunda 350 °C da 4 soat davomida kalsinatsiya qilindi. KDUNs@ACZ-NC nanokompozitini sintez qilishda esa karboksil guruhi bilan funkcionallashtirilgan KDUNlar ultratovush yordamida bir tekis dispersiyalandi va pH ni sozlashdan oldin metall nitratlari aralashmasiga qoʻshildi. Reaksiya 80 °C da 5 soat davom ettirildi, soʻng hosil boʻlgan choʻkma 24 soat yetiltirildi (aging). Keyinchalik mahsulot filtrlanib, toʻrt marta issiq distillangan suv bilan yuvildi, 100 °C da quritildi hamda 350 °C da 4 soat davomida kalsinatsiya qilindi.

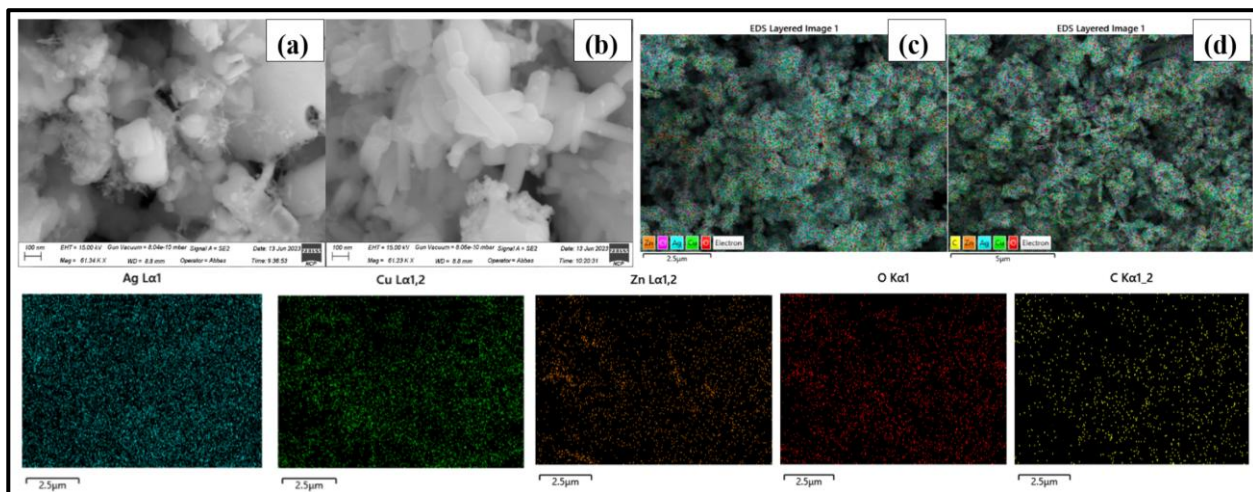
XRD tahlili natijalari Ag₂O, CuO, ZnO va CNT fazalariga xos Bragg reflekslari mavjudligini tasdiqladi. 44,39° da kuzatilgan va (111) kristall tekisligiga mos keluvchi difraksiya choʻqqisi CNT lar mavjudligini koʻrsatdi hamda JCPDS № 01-080-0017 kartasi bilan mos keldi. Ag₂O fazasi uchun 17,31° (001), 27,93° (110), 33,59° (100) va 38,24° (011) burchaklardagi difraksiya choʻqqilari P3m1 fazoviy guruhiga mansub geksagonal kristall tuzilma mavjudligini tasdiqladi. Kristall panjara parametrlari $a = b = 3,0720 \text{ \AA}$, $c = 4,9410 \text{ \AA}$, $\alpha = \beta = 90^\circ$ va $\gamma = 120^\circ$ ni tashkil etdi. Kristallit oʻlchami 14,25 nm, kristall panjara deformatsiyasi esa 0,074% ga teng boʻldi. CuO fazasi uchun 29,43° (020), 32,35° (200), 46,25° (−112), 60,83° (125) va 64,54° (141) burchaklardagi choʻqqilar Bmm2 fazoviy guruhiga mansub ortorombik kristall tuzilma ni tasdiqladi. Elementar katak parametrlari $a = 5,3510 \text{ \AA}$, $b = 6,0200 \text{ \AA}$, $c = 9,3400 \text{ \AA}$ boʻlib, barcha burchaklar 90° ga teng ekanligi aniqlandi. Mazkur fazaning kristallit oʻlchami 14,02 nm, panjara deformatsiyasi esa 0,089% ni tashkil etdi. ZnO fazasi uchun 30,38° (100), 34,87° (002), 54,93° (110), 55,59° (022) va 63,20° (103) burchaklarda kuzatilgan difraksiya choʻqqilari P6₃mc fazoviy guruhiga mansub geksagonal kristall tuzilma mavjudligini tasdiqladi. Uning elementar katak parametrlari $a = b = 3,3520 \text{ \AA}$, $c = 5,2260 \text{ \AA}$, $\alpha = \beta = 90^\circ$ va $\gamma = 120^\circ$ ga teng boʻldi. Kristallit oʻlchami 60,3 nm, panjara deformatsiyasi esa 0,192% ni tashkil etdi. FTIR tahlili 3380,30 va 3220,25 cm^{−1} da joylashgan keng yutilish polosalari O–H valent tebranishlariga tegishli ekanligini koʻrsatdi. 2933,79 cm^{−1} dagi polosalar KDUN lardagi C–H valent tebranishlariga, 2703,15 cm^{−1} dagi signal esa C–H valent tebranishiga mos keldi. 1634,47 cm^{−1} dagi kuchli yutilish polosasi H–O–H deformatsion tebranishlariga tegishli boʻlsa, 1516,28 cm^{−1} dagi kuchsiz polosalar KDUN larning C=C valent tebranishlarini ifodaladi. 1417,78 cm^{−1} va 1054,10 cm^{−1} dagi polosalar M–OH tebranishlariga, 1369,36 cm^{−1} dagi keskin choʻqqi esa tekislikdan tashqari O–H deformatsion tebranishiga mos keldi. 1264,30 cm^{−1} dagi signal C–O valent tebranishiga, 1187,96 cm^{−1} dagi polosalar esa C–H bukilish tebranishlariga tegishli ekanligi aniqlandi. Shuningdek, 915,46 cm^{−1} dagi polosalar O–M–O, 866,21 va 817,79 cm^{−1} dagilari M–O–M, 748,02 cm^{−1} dagi signal C–O–M, 678,25 cm^{−1} dagi choʻqqi Cu–O, 636,39 cm^{−1} dagi choʻqqi Ag–O, 545,28 va 468,13 cm^{−1} dagi polosalar esa ZnO ga xos deformatsion va valent tebranishlarni ifodaladi.

KDUN larni nanokompozit tarkibiga kiritish natijasida yangi yutilish polosalari paydo bo'ldi, mavjud polosalarning joylashuvi siljidi, intensivligi va kengligi o'zgardi hamda ayrim yangi funksional guruhlarning shakllanishi kuzatildi. Ushbu o'zgarishlar KDUN lar bilan metall oksidlar o'rtasidagi o'zaro ta'sirlarning kuchayishi, mahalliy elektron muhitining o'zgarishi, zarrachalarning yaxshiroq dispersiyalanishi, fazalararo bog'lanishning mustahkamlanishi hamda π -elektronlar hisobiga qutblanuvchanlikning ortishi bilan izohlanadi. EDX mapping natijalari nanokompozit tarkibida KDUN lardan kelib chiqqan uglerod, shuningdek Ag_2O , CuO va ZnO fazalariga mos ravishda kumush, mis, rux va kislorod elementlari bir tekis taqsimlanganligini tasdiqladi. Tahlil davomida sezilarli miqdorda begona aralashmalar aniqlanmadi. EDX spektrlari 0,5 keV da kislorod signalini, 3,08 keV da kumush, 0,9 va 8,05 keV da mis, 1,05, 8,7 va 9,6 keV da rux, 2,62 keV da xlor hamda 0,21 keV da uglerod signalini qayd etdi. Uglerod signalining mavjudligi KDUN larning nanokompozit tarkibiga muvaffaqiyatli kiritilganligini tasdiqlaydi. Diffuz qaytarish spektroskopiyasi (DRS) natijalari ACZ-NC uchun yutilish chegarasi 720,56 nm, KDUNs@ACZ-NC uchun esa 765,70 nm ekanligini ko'rsatdi. KDUN lar kiritilgandan so'ng yutilish chegarasining uzun to'lqinlar tomon siljishi (red shift) nanokompozitning ko'rinadigan yorug'lik sohasidagi yutilish qobiliyati kengayganligini ko'rsatadi. Tauc grafigi asosida hisoblangan taqiqlangan zona energiyasi (band gap) qiymatlari KQUN lar kiritilgandan so'ng biroz kamaygani aniqlandi. Bu holat metall oksidlarning elektron tuzilishi bilan KDUN larning yuqori elektr o'tkazuvchan π -elektron tarmog'i o'rtasidagi o'zaro ta'sir natijasida elektronlarning samarali ko'chishi va zaryad tashuvchilarning ajralish jarayoni yaxshilanishi bilan izohlanadi.



30-rasm. ACZ-NC va KDUNs@ACZ-NC nanokompozitlarining XRD difraktogrammalari (a), FTIR spektrlari (b), EDX spektrlari (c), DRS spektrlari (d) hamda to'g'ridan-to'g'ri (direct) (e) va bilvosita (indirect) (f) o'tishlar uchun Tauc grafiqlari (Lone, Rehman, Haq, Alkhuriji, va boshq., 2025).

Maydon emissiyali skanerlovchi elektron mikroskopiya (FESEM) tahlili ACZ-NC nanokompozitining zarracha o'lchami va morfologiyasi bir xil emasligini ko'rsatdi. Namunada alohida joylashgan nanopartikulalar bilan bir qatorda yirik aglomeratlar ham kuzatildi. Alohida zarrachalar sharsimon, deyarli sharsimon, biroz cho'zilgan tolasimon hamda ko'p qirrali (poliedrik) morfologiyaga ega bo'ldi. Zarralar shakli va o'lchamining notekisligi natijasida nanokompozit tuzilmasida turli xil strukturaviy nuqsonlar hosil bo'lganligi aniqlandi. Quritish jarayonida erituvchining bug'lanishi va uchuvchan yon mahsulotlarning ajralib chiqishi natijasida material yuzasida teshiklar (bo'shliqlar) hosil bo'ldi. Alohida nanopartikulalarning o'lchami keng diapazonda, ya'ni 15–110 nm oralig'ida o'zgarishi kuzatildi, yirik aglomeratlarning o'lchami esa 160 nm dan oshgani aniqlandi. KDUNs@ACZ-NC nanokompoziti esa aniq ifodalangan cho'zilgan naychasimon morfologiya bilan tavsiflandi. KDUN larning naychasimon tuzilmalari yaqqol kuzatilib, ACZ-NC nanopartikulalari ushbu naychasimon strukturalar yuzasida joylashgani aniqlandi. Biroq, ularning taqsimlanishi to'liq bir xil emasligi qayd etildi. KDUN lar dastlabki nanokompozitdagi bo'shliqlarni to'ldirgani sababli teshiklar soni sezilarli darajada kamaydi. Shuningdek, naychasimon strukturalarning nisbatan muntazam taqsimlangani hamda ularning yuzasi silliq va g'ovaksiz ekanligi kuzatildi. Elementlar xaritalash (EDX mapping) natijalari barcha elementlarning CNT matritsasi bo'ylab bir tekis taqsimlanganligini ko'rsatdi. Bu esa KDUN lar bilan metall oksid nanopartikulalari o'rtasida yaxshi fazalararo o'zaro ta'sir mavjudligini hamda yaxlit va barqaror nanokompozit tuzilma muvaffaqiyatli shakllanganligini tasdiqlaydi.



31-rasm. ACZ-NC va KDUNs@ACZ-NC nanokompozitlarining SEM tasvirlari (a, b) hamda EDX elementlar xaritalari (c, d) (Lone, Rehman, Haq, Alkhuriji, va boshq., 2025).

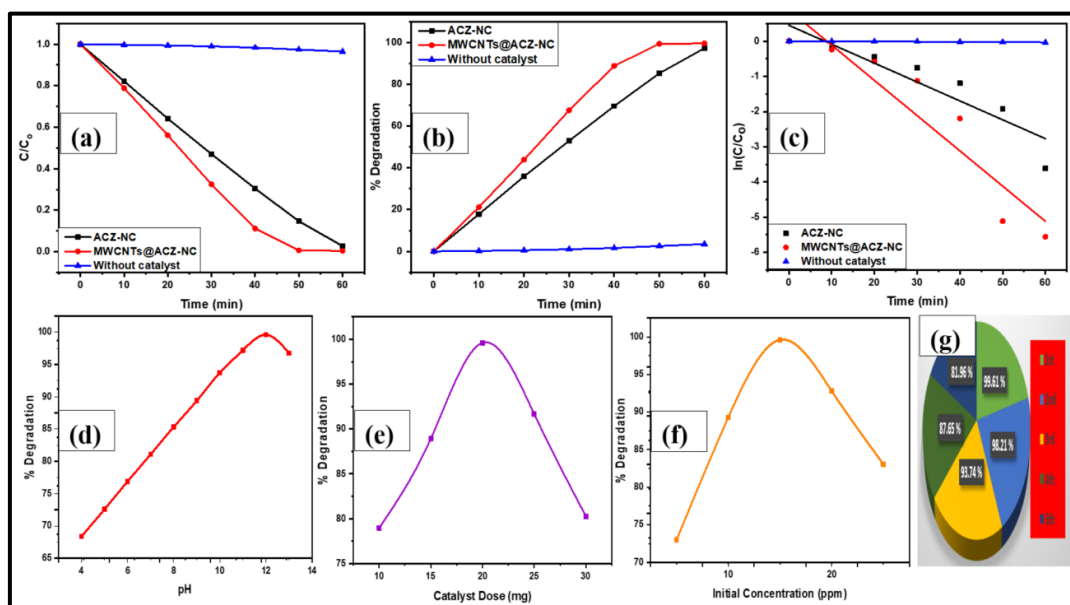
Fotokatalitik faollik R-6G bo'yog'iga nisbatan 2024-yil 3–14-iyun kunlari tabiiy quyosh nuri ostida baholandi. Olingan natijalarga ko'ra, ACZ-NC nanokompoziti 97,31%, KDUNs@ACZ-NC nanokompoziti esa 99,61% fotodegradatsiya samaradorligini namoyon etdi. Taqqoslash uchun, katalizatorsiz nazorat namunasi da degradatsiya darajasi atigi 3,52% ni tashkil etdi. Hisoblangan tezlik konstantalari (k) ACZ-NC uchun $0,05368 \text{ min}^{-1}$, KDUNs@ACZ-NC uchun

0,10012 min⁻¹ ni tashkil etdi. Nazorat namunasi uchun hisoblangan qiymat 5,90528 min⁻¹ sifatida qayd etildi. KDUN bilan modifikatsiyalangan nanokompozitning yuqori fotokatalitik samaradorligi uning elektr o'tkazuvchanligi oshgani hamda elektron-teshik juftliklarining samarali ajralishi bilan izohlanadi. KDUNs@ACZ-NC nanokompozitida pH ning ta'siri o'rganilganda fotodegradatsiya darajalari pH 4 da 68,38%, pH 5 da 72,59%, pH 6 da 76,91%, pH 7 da 81,10%, pH 8 da 85,334%, pH 9 da 89,40%, pH 10 da 93,74%, pH 11 da 97,21%, pH 12 da 99,61% va pH 13 da 96,76% ni tashkil etdi. Natijalar pH ortishi bilan fotodegradatsiya samaradorligi ham ortishini ko'rsatdi. Bu holat R-6G molekulasining eritmada ionli (R6G⁺) va ionlanmagan shakllarda mavjud bo'lishi bilan izohlanadi. Ishqoriy muhitda ionlanmagan shaklning ulushi ortib, uning reaktivligi kuchayadi hamda bo'yoq molekulalarining fotokatalizator yuzasidagi faol markazlarga yetib borishi osonlashadi. Bundan tashqari, kavitatsion bo'shliqlarning qisqarishi va kuchli kavitatsiya hodisalari bo'yoq molekulalarining parchalanishini tezlashtiradi. Biroq pH 13 da degradatsiya samaradorligining optimal pH 12 ga nisbatan biroz pasayishi juda kuchli ishqoriy muhitda gidroksil radikallari (•OH) ning tez neytrallanishi natijasida selektiv oksidlanish uchun mavjud faol radikallar miqdorining kamayishi bilan bog'liq. Fotokatalizator miqdorini optimallashtirish natijalariga ko'ra, fotodegradatsiya darajasi katalizator miqdori 10 mg dan 20 mg gacha oshirilganda 78,96% dan 99,61% gacha ortdi. Biroq katalizator miqdori 25 mg va 30 mg ga yetkazilganda degradatsiya darajasi mos ravishda 91,67% va 80,25% gacha kamaydi. Optimal miqdorda fotokatalizatorning solishtirma sirt maydoni ortishi hisobiga faol markazlar soni ko'payadi va bo'yoq molekulalari bilan o'zaro ta'sir kuchayadi. Aksincha, yuqori dozada nanopartikulalarning aglomeratsiyalanishi, fotonlarning fotokatalizator yuzasi bilan o'zaro ta'sirining kamayishi hamda yorug'likning samarasiz yutilishi fotokatalitik samaradorlikning pasayishiga olib keladi. Bo'yoqning boshlang'ich konsentratsiyasi ta'sirini o'rganish natijasida 5, 10, 15, 20 va 25 ppm konsentratsiyalarda fotodegradatsiya darajalari mos ravishda 72,97%, 89,26%, 99,61%, 92,79% va 83,05% ni tashkil etdi. Eng yuqori samaradorlik 15 ppm konsentratsiyada kuzatildi. Konsentratsiyaning yanada ortishi fotokatalizator yuzasidagi faol markazlarning to'yinishi hamda yorug'likning fotokatalizator yuzasiga yetib borishiga to'sqinlik qilishi natijasida degradatsiya samaradorligining pasayishiga olib keldi. Fotokatalizatorning qayta foydalanish imkoniyati ketma-ket besh sikl davomida baholandi. Fotodegradatsiya samaradorligi mos ravishda 1–5-sikllarda 99,61%, 98,21%, 93,74%, 87,65% va 81,96% ni tashkil etdi. Dastlabki siklda yuqori samaradorlik fotokatalizatorning yangi va faol holatda bo'lishi bilan bog'liq bo'lsa, keyingi sikllarda fotokatalizatorning deaktivatsiyasi, strukturaviy o'zgarishlar, sirt ifloslanishi hamda bo'yoq molekulalarining fotokatalizator yuzasiga adsorbsiyalanishi natijasida samaradorlik bosqichma-bosqich kamaydi.

Fotokatalizatorning 4–5 ta qayta foydalanish siklidan so'ng faolligining pasayishiga bir nechta asosiy omillar sabab bo'ladi. Birinchidan, fotokatalizator yuzasida bo'yoq molekulalari va oraliq parchalanish mahsulotlarining adsorbsiyalanishi natijasida faol markazlar to'yinadi va yuzaning ifloslanishi yuz beradi. Ikkinchidan, reaksiya davomida hosil bo'lgan yon mahsulotlarning

g'ovaklarda to'planishi ularning berkilishiga olib keladi. Bu holat BET tahlili natijasida g'ovak hajmining kamayishi orqali ham tasdiqlangan. Uchinchidan, fotokatalizator tarkibidagi faol metall ionlarining (Zn^{2+} , Cu^{2+} va Ni^{2+}) qisman eritmaga o'tishi (leaching) hamda strukturaviy o'zgarishlar katalitik faollikni pasaytiradi. Bundan tashqari, nanopartikulalarning aglomeratsiyalanishi hamda rangli oraliq mahsulotlarning hosil bo'lishi natijasida yorug'likning fotokatalizator qatlamiga kirib borishi cheklanadi.

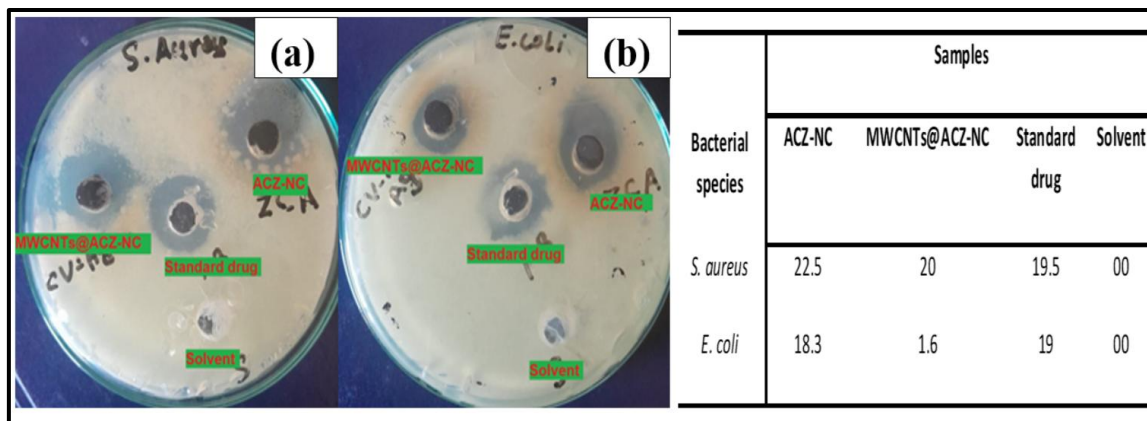
Fotokatalizatorning uzoq muddatli barqarorligini oshirish uchun bir qator usullar tavsiya etiladi. Jumladan, 300–400 °C da issiqlik bilan ishlav berish orqali organik qoldiqlarni yo'qotish, suyultirilgan kislotaga yoki ishqor eritmalariga yordamida kimyoviy yuvish, fotokatalizatorni grafen yoki biochar kabi tayanch materiallarga immobilizatsiya qilish, sirtini PEG yoki silika qatlami bilan qoplash, etanol–suv aralashmasida optimallashtirilgan yuvish usullaridan foydalanish hamda jarayon parametrlarini optimallashtirish (masalan, pH 6–7, reaksiya vaqtini qisqartirish va fotokatalizator miqdorini kamaytirish) fotokatalizatorning xizmat muddatini sezilarli darajada uzaytirishi mumkin.



32-rasm. Simulyatsiya qilingan quyosh nuri ostida ACZ-NC va KDUNs@ACZ-NC nanokompozitlari ishtirokida R-6G ning fotokatalitik degradatsiyasiga oid natijalar: degradatsiya darajasi (%) (a), tezlik konstantasi (b), chiziqli kinetik grafik (c), pH ning ta'siri (d), fotokatalizator miqdorining ta'siri (e), boshlang'ich konsentratsiyaning ta'siri (f) hamda KDUNs@ACZ-NC nanokompozitining fotokatalitik tajribadagi qayta foydalanish samaradorligi (g) (Lone, Rehman, Haq, Alkhuriji, va boshq., 2025).

Antibakterial faollik *S. aureus* va *E. coli* bakteriyalariga nisbatan baholandi. Tadqiqot natijalari ACZ-NC nanokompozitining antibakterial samaradorligi KDUNs@ACZ-NC nanokompozitiga nisbatan yuqoriroq ekanligini ko'rsatdi. ACZ-NC uchun ingibitsiya zonalar *S. aureus* ga nisbatan 22,5 mm, *E. coli* ga nisbatan esa 18,3 mm ni tashkil etdi. KDUNs@ACZ-NC nanokompozitida ushbu ko'rsatkichlar

mos ravishda 20 mm va 16 mm ga teng bo'ldi. Taqqoslash uchun, standart antibiotik *S. aureus* va *E. coli* ga nisbatan mos ravishda 19,5 mm va 19 mm ingibitsiya zonalarini hosil qildi. KDUN larni nanokompozit tarkibiga kiritish antibakterial faollikning ma'lum darajada pasayishiga olib keldi. Bu holat KDUN larning bakteriya hujayralari bilan bevosita o'zaro ta'sir qilishda ishtirok etuvchi faol bog'lanish markazlarini qisman egallashi yoki berkitishi bilan izohlanadi. Bundan tashqari, KDUN lar nanokompozitning sirt morfologiyasi, sirt zaryadi va kimyoviy funksional guruhlarini o'zgartiradi. Shuningdek, zarracha o'lchamining ortishi nanopartikulalarning bakteriya hujayralariga samarali kirib borish qobiliyatini cheklaydi, natijada umumiy antibakterial samaradorlik pasayadi.



33-rasm. Sintez qilingan nanokompozitlarning *S. aureus* (a) va *E. coli* (b) bakteriyalariga nisbatan antibakterial faolligi (Lone, Rehman, Haq, Alkhuriji, va boshq., 2025).

6-jadval. ACZ-NC va KDUNs@ACZ-NC nanokompozitlarining ABTS erkin radikallariga nisbatan antioksidant faolligi (Lone, Rehman, Haq, Alkhuriji, va boshq., 2025).

Samples	Concentration (µg/mL)	%RSA	IC ₅₀ (µg/mL)	Variance (S ²)	Standard deviation (S)	Correlation between dose and %RSA
ACZ-NC	5	26.076	80.65	2.65	1.63	0.110
	25	34.188				
	50	48.228				
	100	65.916				
	200	81.004				
	400	91.336				
MWCNT@ACZ-NC	5	27.144	59.22	2.71	1.64	0.119
	25	36.432				
	50	53.796				
	100	71.124				
	200	84.612				
	400	95.924				
Ascorbic acid	5	21.92	92.74	3.09	1.75	0.102
	25	33.58				
	50	47.956				
	100	57.396				
	200	83.976				
	400	94.068				

Antioksidant faollik ABTS⁺ radikal kation eritmasiga nisbatan baholandi. Tadqiqot natijalariga ko'ra, ACZ-NC nanokompoziti 5–400 µg/mL konsentratsiya oralig'ida 26,076% dan 91,336% gacha erkin radikallarni so'ndirish (RSA) faolligini namoyon etdi va uning IC₅₀ qiymati 80,65 µg/mL ni tashkil etdi. KDUNs@ACZ-NC nanokompoziti esa xuddi shu konsentratsiya oralig'ida 27,144% dan 95,924% gacha antioksidant faollik ko'rsatib, IC₅₀ = 59,22 µg/mL qiymatiga ega bo'ldi. Taqqoslash uchun, askorbin kislotasi ning IC₅₀ qiymati 49,79 µg/mL ni tashkil etdi. KDUN bilan modifikatsiyalangan nanokompozitning yuqori antioksidant faolligi elektronlarning yanada samarali ko'chishi, faol markazlar sonining ortishi hamda reaktiv zarrachalarning barqarorlashishi bilan izohlanadi. Ushbu omillar nanokompozitning erkin radikallarni neytrallash qobiliyatini sezilarli darajada kuchaytiradi. Statistik tahlil natijalariga ko'ra, ACZ-NC, KDUNs@ACZ-NC va askorbin kislotasi uchun standart og'ish (SD) qiymatlari mos ravishda 1,63, 1,64 va 1,75 ni tashkil etdi. Dispersiya qiymatlari esa mos ravishda 2,65, 2,71 va 3,09 ga teng bo'ldi. Ushbu natijalar ACZ-NC nanokompoziti tajriba natijalarining eng yuqori aniqligi va takrorlanuvchanligi bilan tavsiflanganligini ko'rsatadi. Doza bilan RSA (%) o'rtasidagi korrelyatsiya koeffitsiyentlari ACZ-NC, KDUNs@ACZ-NC va askorbin kislotasi uchun mos ravishda 0,110, 0,119 va 0,102 ni tashkil etdi. Bu natijalar barcha namunalarda konsentratsiya ortishi bilan RSA (%) ning ham oshishini ko'rsatsa-da, KDUNs@ACZ-NC nanokompozitida ushbu bog'liqlik eng kuchli ekanligini namoyon etdi.

KDUN larning metall oksidli nanokompozitlar tarkibiga kiritilishi fotokatalitik va antioksidant xususiyatlarni izchil ravishda yaxshilagan bo'lsa-da, antibakterial faollikka turlicha ta'sir ko'rsatdi. Fotokatalitik va antioksidant samaradorlikning ortishi bir necha omillar bilan izohlanadi. Jumladan, KDUN lar elektron tashuvchi "kanallar" sifatida faoliyat yuritib, zaryad tashuvchilarning samarali ajralishini tezlashtiradi va ularning yashash vaqtini uzaytiradi. Bundan tashqari, ular elektronlarning samarali ko'chishi uchun yuqori elektr o'tkazuvchan yo'llarni hosil qiladi, nanopartikulalar orasidagi bo'shliqlarni to'ldirib, yanada zich va kompakt tuzilma shakllanishiga yordam beradi. FTIR spektrlarida yangi tebranish polosalarining paydo bo'lishi hamda fingerprint sohasining yanada aniq ifodalanishi ham KDUN lar bilan metall oksidlar o'rtasidagi kuchli o'zaro ta'sirni tasdiqlaydi. Shuningdek, KDUN lar reaktiv zarrachalarni barqarorlashtirib, nanokompozitlarning antioksidant samaradorligini sezilarli darajada oshiradi. Ayrim hollarda kuzatilgan antibakterial faollikning pasayishi esa KDUN larning metall oksid nanopartikulalarining faol markazlarini qisman berkitishi natijasida bakteriya hujayralari bilan bevosita o'zaro ta'sirning cheklanishi bilan izohlanadi. Bundan tashqari, KDUN lar nanokompozitning sirt kimyosi va sirt zaryadini o'zgartiradi, bu esa bakteriya hujayra membranasi bilan o'zaro ta'sir samaradorligini kamaytiradi. Shuningdek, zarracha o'lchamining ortishi bakteriya hujayralariga kirib borish qobiliyatini cheklaydi, nanopartikulalarning aglomeratsiyalanishi esa ularning

solishtirma sirt maydoni ni kamaytiradi. Ushbu natijalar KDUN bilan modifikatsiyalash metall oksidli nanokompozitlarning ma'lum funksional xususiyatlarini yaxshilash uchun samarali strategiya ekanligini, biroq uning afzalligi nanokompozitning qo'llanilish sohasiga bevosita bog'liq ekanligini ko'rsatadi.

KDUN lar fotokatalitik jarayonda "elektron kanallari" (electron highways) yoki "elektron tutqichlari" (electron sinks) sifatida faoliyat yuritadi va fotogeneratsiyalangan elektronlarning metall oksid yuzasidan tezkor uzatilishini ta'minlaydi. Yarimo'tkazgich ($h\nu \geq E_g$) energiyaga ega fotonlarni yutganda, elektronlar valent zonadan (VB) o'tkazuvchanlik zonasiga (CB) qo'zg'aladi va natijada elektron-teshik juftliklari hosil bo'ladi. KDUN larning yuqori elektr o'tkazuvchanligi hamda metall oksid bilan hosil qilgan geteroo'tish tufayli hosil bo'lgan elektronlar tezda KDUN tarmog'iga ko'chadi. Natijada elektron-teshik rekombinatsiyasi ehtimoli keskin kamayadi va zaryad tashuvchilarning yashash vaqti uzayadi. Ushbu yo'naltirilgan elektron transporti fotokatalitik jarayonning samaradorligini sezilarli darajada oshiradi. Olingan eksperimental natijalar ushbu mexanizmni tasdiqlaydi. Jumladan, KDUNs@CuO-NiO nanokompoziti 95,37% fotodegradatsiya samaradorligini namoyon etib, CuO-NiO nanokompozitining 80,09% ko'rsatkichidan ancha yuqori natija berdi. Shu bilan birga, uning tezlik konstantasi 74,3% ga oshgani kuzatildi. Xuddi shuningdek, KDUNs@Ag₂O/CuO/ZnO nanokompoziti 99,61% fotodegradatsiya samaradorligiga erishgan bo'lsa, Ag₂O/CuO/ZnO nanokompozitida bu ko'rsatkich 97,31% ni tashkil etdi. Mazkur tizimda tezlik konstantasi 86,5% ga ortgani aniqlandi. Ushbu natijalar KDUN larning zaryad tashuvchilarni samarali ajratishi va elektron transportini jadallashtirishi hisobiga metall oksidli nanokompozitlarning fotokatalitik samaradorligini sezilarli darajada yaxshilashini yaqqol tasdiqlaydi.

XULOSALAR

1. Ushbu tadqiqotda atrof-muhitni muhofaza qilish va biotibbiyot sohalarida qo'llash uchun mo'ljallangan turli xil ko'p funksiyali nanomateriallar innovatsion sintez usullari yordamida muvaffaqiyatli ishlab chiqildi. Qo'llanilgan yondashuvlar qatoriga qishloq xo'jaligi chiqindilaridan (*Musa acuminata* po'stlog'i) hamda dorivor o'simlik ekstraktlaridan (*Diospyros kaki*, *Swertia chirayita* va *Citrus maxima*) foydalangan holda yashil sintez, erituvchisiz mexanokimyoviy maydalash, modifikatsiyalangan Hummers usuli, gidrotermal kopretsipitatsiya hamda modifikatsiyalangan sol-gel usuli kiradi. Ushbu sintez strategiyalari yuqori funksional xususiyatlarga ega nanomateriallarni ekologik jihatdan maqbul va samarali usulda olish imkonini berdi.

2. Bir komponentli metall oksidlari (ZnO va Fe₂O₃) yuqori antibakterial (masalan, *E. coli* ga nisbatan 14 mm ingibitsiya zonasi) hamda fotokatalitik (R-6G ning 99,42% degradatsiyasi) faollikni namoyon etdi. Ushbu natijalar qishloq

xo'jaligi chiqindilaridan foydalanish asosida nanomateriallarni sintez qilish usuli yuqori samaradorlikka ega funksional nanomateriallar olish uchun istiqbolli va samarali yondashuv ekanligini tasdiqlaydi.

3. Ikki komponentli metall oksidlari, jumladan CuO–NiO, CuO–ZrO₂, CuO–Fe₂O₃, hamda Zr–NiO/ZnO nanokompozitlari yuqori fotokatalitik xususiyatlarni namoyon etdi. Tadqiqot natijalari ushbu nanomateriallarning fotokatalitik samaradorligi kalsinatsiya harorati, dopant konsentratsiyasi hamda sintez usuli kabi omillarga sezilarli darajada bog'liq ekanligini ko'rsatdi.

4. Solishtirma sirt maydoni va kristallik darajasi o'rtasidagi muhim muvozanat aniq namoyon bo'ldi. Xususan, kalsinatsiya qilinmagan Co–Cu–Zn–LH namunalari kristallik darajasi nisbatan past bo'lishiga qaramay, eng yuqori solishtirma sirt maydoni (84,87 m²/g) hisobiga maksimal faollikni (92,98%) namoyon etdi. Aksincha, CuO–ZrO₂ nanokompozitida kalsinatsiya haroratining oshishi kristallik darajasi va strukturaviy bir jinslilikning yaxshilanishiga olib kelib, fotokatalitik faollikning ortishini ta'minladi va 900 °C da 77,27% ga yetdi.

5. Uch komponentli metall oksidlari, Co–Cu–Zn–LHs, jumladan Ag₂O–CuO–ZnO, TiO₂ bilan legirlangan SnO₂–ZrO₂ hamda SnO₂–NiO–CuO nanokompozitlari ko'p funksiyali xususiyatlarni namoyon etdi. Ushbu nanomateriallar 99,61% gacha yetgan yuqori fotokatalitik faollik hamda kuchli antioksidant xususiyatlari bilan ajralib turdi. Olingan natijalar uch komponentli metall oksid tizimlari turli funksional xossalarni birlashtirish orqali atrof-muhitni tozalash va biotibbiyot sohalarida istiqbolli materiallar sifatida xizmat qilishi mumkinligini ko'rsatdi.

6. Qatlamli qo'sh gidroksidlar (LDH) yuqori samaradorlikni namoyon etdi. Xususan, Cr/Ni/Mg/Al-LDH (LDH-4) namunasi MO ning 89,23% fotodegradatsiyasiga erishib, 0,07427 min⁻¹ tezlik konstantasini qayd etdi. Ushbu ko'rsatkich legirlanmagan LDH-1 ga nisbatan taxminan 16,5 baravar yuqori ekanligi aniqlandi. Bunday yuqori fotokatalitik samaradorlik yuqori g'ovakli tuzilma, katta solishtirma sirt maydoni, bir nechta metall kationlari o'rtasidagi sinergik ta'sir hamda Cr ning kiritilishi natijasida taqiqlangan zona energiyasi (band gap) ichida yangi energetik sathlarning hosil bo'lishi hisobiga elektron–teshik juftliklarining samarali ajralishi bilan izohlanadi.

7. Grafen oksidi–metall oksid nanokompozitlari (rGO–ZSF va GO–SNC) yuqori antibakterial faollikni namoyon etib, 31 mm gacha bo'lgan ingibitsiya zonasi ni hosil qildi. Bunday yuqori samaradorlik grafen oksidi qatlamlari va metall oksid nanopartikulalari o'rtasidagi sinergik ta'sir bilan izohlanadi. Xususan, grafen oksidi qatlamlari bakteriya hujayralariga kirib borish hamda ularni o'z yuzasida tutib qolishga xizmat qilsa, metall oksid nanopartikulalari esa metall kationlarining ajralishi va RKTning hosil bo'lishi orqali bakteriyalarga qarshi ta'sirni kuchaytiradi.

Ushbu omillarning birgalikdagi ta'siri nanokompozitlarning antibakterial samaradorligini sezilarli darajada oshiradi.

8. Antioksidant faollik bo'yicha grafen oksidi (GO) eng yuqori erkin radikallarni so'ndirish qobiliyatini namoyon etdi. Xususan, ABTS radikallariga nisbatan $IC_{50} = 11,25 \mu\text{g/mL}$, DPPH radikallariga nisbatan esa $IC_{50} = 15,98 \mu\text{g/mL}$ qiymatlari qayd etildi. Ushbu natijalar GO ning SNC, GO–SNC hamda hatto askorbin kislotasi standartiga ($IC_{50} = 44,67 \mu\text{g/mL}$) nisbatan yuqori antioksidant samaradorlikka ega ekanligini ko'rsatd.

9. KDUN–metall oksid nanokompozitlari, jumladan KDUNs@CuO–NiO va KDUNs@Ag₂O/CuO/ZnO, zaryad tashuvchilarining samarali ajralishi hamda elektronlarning tezkor ko'chishi hisobiga fotokatalitik va antioksidant xususiyatlarni izchil ravishda yaxshiladi. Natijada tezlik konstantasi $0,02737 \text{ min}^{-1}$ dan $0,0477 \text{ min}^{-1}$ gacha ortgan bo'lsa, IC_{50} qiymati $116,52 \mu\text{g/mL}$ dan $84,61 \mu\text{g/mL}$ gacha kamaydi, bu esa nanokompozitlarning antioksidant samaradorligi sezilarli darajada oshganligini ko'rsatadi. Biroq, antibakterial faollik sirt modifikatsiyasining xususiyatiga bog'liq ravishda turlicha o'zgarishi kuzatildi.

10. Mexanokimyoviy sintez usuli bir qator muhim afzalliklarga ega bo'lib, ular qatoriga erituvchisiz amalga oshirilishi, yuqori energiya samaradorligi, ekologik xavfsizligi, sanoat miqyosida oson qo'llash imkoniyati (masshtablanuvchanligi) hamda jarayonning soddaligi kiradi. Ushbu afzalliklar mexanokimyoviy sintezni funksional nanomateriallarni ekologik jihatdan barqaror va iqtisodiy samarali usulda olish uchun istiqbolli yondashuv sifatida tavsiflaydi.

11. O'simlik ekstraktlari asosidagi yashil sintez usullari an'anaviy kimyoviy sintez usullariga nisbatan ekologik xavfsiz muqobil yondashuvni taqdim etadi. Ushbu usullar atrof-muhitga salbiy ta'sirni kamaytirish bilan birga, barqaror rivojlanish tamoyillarini qo'llab-quvvatlaydi. Bundan tashqari, nanomateriallar yuzasiga adsorbsiyalangan fitokimyoviy birikmalar ularning biologik faolligi, jumladan antibakterial va antioksidant xususiyatlarini bevosita kuchaytirishga hissa qo'shadi.

12. Bir vaqtning o'zida fotokatalitik degradatsiya, antibakterial faollik va antioksidant himoya xususiyatlarini namoyon etuvchi ko'p funksiyali nanomateriallarning muvaffaqiyatli ishlab chiqilishi atrof-muhitni muhofaza qilish va biotibbiyot sohalarida integratsiyalashgan yechimlarni yaratish uchun yangi imkoniyatlarni ochib berdi. Ushbu natijalar global ekologik va sog'liqni saqlash muammolarini hal etishga qaratilgan yuqori samarali funksional nanomateriallarni ishlab chiqish hamda ularni amaliyotga joriy etish uchun mustahkam ilmiy asos yaratad.

13. Ushbu tadqiqot tuzilish–xossa–samaradorlik o‘rtasidagi aniq o‘zaro bog‘liqliklarni yoritib berib, funksional nanomateriallarni ilmiy asosda maqsadli loyihalash uchun muhim yo‘riqnomalarni taqdim etadi. Shuningdek, tadqiqot natijalari masshtablanuvchi, iqtisodiy jihatdan samarali ishlab chiqarish usullarini belgilab berdi hamda qayta foydalanish imkoniyatlarini o‘rganish va amaliy qo‘llash parametrlarini optimallashtirish orqali ushbu nanomateriallarning real sharoitlarda qo‘llash imkoniyatlarini muvaffaqiyatli namoyish etdi.

14. Ishlab chiqilgan ushbu nanomateriallar sanoat oqova suvlarini tozalash, ichimlik suvini tozalash, antibakterial hamda antioksidant qo‘llanmalar sohalarida qo‘llash uchun yuqori salohiyatga ega ekanligini namoyon etdi. Mazkur natijalar Birlashgan Millatlar Tashkilotining Barqaror rivojlanish maqsadlari doirasidagi 6-maqsad – Toza suv va sanitariya (SDG 6) hamda 3-maqsad – Sog‘liq va farovonlik (SDG 3) ga erishishga munosib hissa qo‘shadigan innovatsion funksional nanomateriallarni yaratish imkoniyatini tasdiqlaydi.

**НАУЧНЫЙ СОВЕТ ПО ПРИСУЖДЕНИЮ УЧЕНЫХ СТЕПЕНЕЙ ПОД
НОМЕРОМ DSc.03/06.11.2025.K/FM.10.09 ПРИ ИНСТИТУТЕ
ФУНДАМЕНТАЛЬНЫХ И ПРИКЛАДНЫХ ИССЛЕДОВАНИЙ ПРИ
НИУ «ТИИИМСХ»**

**ИНСТИТУТ ФУНДАМЕНТАЛЬНЫХ И ПРИКЛАДНЫХ
ИССЛЕДОВАНИЙ**

СИРАДЖУЛ ХАК

**МНОГОКОМПОНЕНТНАЯ НАНОМАТЕРИАЛЬНАЯ ПЛАТФОРМА,
ФУНКЦИОНАЛИЗИРОВАННАЯ НА ОСНОВЕ
ОДНОКОМПОНЕНТНЫХ ОКСИДОВ МЕТАЛЛОВ ДЛЯ
ЭКОЛОГИЧЕСКИХ ПРИМЕНЕНИЙ**

**02.00.04 - ФИЗИЧЕСКАЯ ХИМИЯ
(Химические Науки)**

**ПРЕДСТАВЛЕНИЕ НА СОИСКАНИЕ УЧЕНОЙ СТЕПЕНИ ДОКТОРА
ХИМИЧЕСКИХ НАУК (DSc) БЕЗ ДИССЕРТАЦИИ НА ОСНОВЕ
ОПУБЛИКОВАННЫХ НАУЧНЫХ ТРУДОВ**

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Тема представления на соискание ученой степени доктора химических наук (DSc) зарегистрирована Высшей аттестационной комиссией при Кабинете Министров Республики Узбекистан под номером B2026.3.DSc/K274.

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С представлением можно ознакомиться в Информационно-ресурсном центре Института фундаментальных и прикладных исследований при Национальном исследовательском университете «ТИИИМСХ» (зарегистрировано под №____). (Адрес: 100000, город Ташкент, улица Кори Ниязи, 39А, ИФПИ, кабинет 105, Тел.: 71 237-09-61).

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ВВЕДЕНИЕ (Аннотация к представлению)

Актуальность темы. Исследования, представленные в данном отчете, направлены на решение одной из наиболее критических экологических проблем современности: загрязнения водных ресурсов органическими красителями. Согласно докладу ЮНЕСКО, представленному на Водной конференции ООН 2023 года в Нью-Йорке, около 2 миллиардов человек во всем мире (что составляет 26% мирового населения) не имеют доступа к безопасной питьевой воде. Это не просто статистические данные, а повседневная реальность, влияющая на здоровье, экономическую продуктивность и человеческое достоинство миллиардов людей.

Загрязнение воды обуславливает 70% смертности от диарейных заболеваний, а также значительный процент случаев брюшного тифа (8%), паратифа (20%) и инфекций нижних дыхательных путей (2%). Только текстильная промышленность ежегодно сбрасывает около 10–25% текстильных красителей в пресноводные водоемы, при этом мировое производство красителей достигает 1,3 миллиона тонн в год. Эти красители содержат ароматические соединения, такие как нафталин и бензамин, которые являются токсичными, канцерогенными и мутагенными, вызывая рак мочевого пузыря, расстройства центральной нервной системы, дерматиты, аллергический конъюнктивит, ринит, профессиональную астму и различные другие аллергические реакции.

Всемирная организация здравоохранения включила антимикробную резистентность (АМР) в число десяти главных глобальных угроз общественному здравоохранению, приводящую примерно к 1,27 миллиона смертей ежегодно. Штаммы бактерий с множественной лекарственной устойчивостью появились во всем мире из-за чрезмерного и неправильного использования антибиотиков, что делает традиционные методы лечения неэффективными. Разработка новых антибиотиков зашла в тупик: в последние десятилетия на рынок выходят лишь единичные новые классы. Согласно оценкам, экономическое бремя АМР достигнет 100 миллионов долларов к 2050 году, если не будут приняты меры.

Разработанные в данном исследовании антибактериальные наноматериалы предлагают принципиально иной подход к борьбе с бактериальными инфекциями. В отличие от антибиотиков, которые обычно нацелены на конкретные клеточные процессы (что позволяет бактериям развивать устойчивость за счет одиночных мутаций), наночастицы оксидов металлов используют несколько одновременных механизмов действия:

- физическое разрушение клеточных мембран бактерий при прямом контакте;
- высвобождение катионов металлов (Zn^{2+} , Cu^{2+} , Ag^{+} , Ni^{2+} , Fe^{3+}), которые взаимодействуют с жизненно важными ферментами бактерий, содержащими тиоловые группы;

- генерация активных форм кислорода (АФК), вызывающих окислительное повреждение клеточных компонентов;
- проникновение мелких наночастиц внутрь бактериальных клеток, вызывающее внутренние структурные повреждения.

Наноккомпозит GO-ZSF обеспечил зоны ингибирования 31 мм против *E. coli* и 29 мм против *S. aureus*, что значительно превышает показатели стандартного контроля антибиотиками (21 мм и 20 мм соответственно), демонстрируя потенциал для борьбы даже с устойчивыми штаммами бактерий.

Окислительный стресс - дисбаланс между избыточным образованием активных форм кислорода/азота и способностью антиоксидантных защитных механизмов нейтрализовать их — лежит в основе многочисленных хронических заболеваний, включая рак, сердечно-сосудистые заболевания, диабет, нейродегенеративные расстройства (болезни Альцгеймера, Паркинсона), астму, преждевременное старение и воспалительные процессы. Когда активные формы кислорода (гидроксильные радикалы, супероксид-анионы, атомарный кислород) и активные формы азота (пероксинитрит) производятся в избытке, они повреждают ДНК (вызывая мутации и рак), белки (инактивируя ферменты) и клеточные мембраны (нарушая их целостность и функцию). Антиоксидантная активность, продемонстрированная данными наноматериалами, со значениями IC₅₀ всего 11,25 мкг/мл для оксида графена (ОГ) против ABTS и 15,98 мкг/мл против DPPH, приближается к показателям стандартных антиоксидантов, таких как аскорбиновая кислота IC₅₀ 44,67 мкг/мл), или превосходит их. Механизмы включают образование радикальных аддуктов на sp²-гибридизированных углеродных центрах, перенос электрона и донирование водорода от функциональных групп, обеспечивая множественные пути нейтрализации радикалов.

Необходимость темы. Необходимость данного исследования продиктована ускоряющимися темпами деградации окружающей среды и ее прямым воздействием на здоровье человека. За последний век мировое потребление воды увеличилось в шесть раз, что в два раза превышает темпы роста населения, в то время как загрязнение сделало непригодными огромные водные ресурсы. Индустриализация без надлежащих мер экологической безопасности привела к повсеместному загрязнению рек, озер и подземных вод. В развивающихся странах более 80% сточных вод сбрасывается в водоемы без очистки, создавая порочный круг загрязнения и болезней, который укореняет бедность. Экономический ущерб от загрязнения воды колоссален: снижение продуктивности рыболовства и сельского хозяйства, рост расходов на здравоохранение, обесценивание недвижимости и дороговизна инфраструктуры для очистки воды.

Традиционные технологии очистки не успевают справляться с объемами и сложностью промышленных загрязнителей. Только текстильная промышленность производит более 10 000 различных синтетических красителей, многие из которых разработаны с учетом устойчивости к деградации (светостойкие, устойчивые к стирке, химически стабильные). Те же

свойства, которые делают их полезными для окрашивания тканей, превращают их в стойкие загрязнители окружающей среды. Перспективные процессы окисления (ПОО) с использованием фотокатализа представляют собой единственный жизнеспособный путь к полной минерализации этих трудноразлагаемых соединений. Поэтому разработка эффективных, экономически выгодных фотокатализаторов, активируемых солнечным светом, является не просто академическим интересом, а экологической необходимостью.

Необходимость этого исследования также обусловлена тревожным ростом антимикробной резистентности. «Эра пост-антибиотиков» - это уже не теоретическая угроза, а настоящая реальность. Энтеробактерии, устойчивые к карбапенемам (CRE), метициллин-резистентный золотистый стафилококк (MRSA), ванкомицин-резистентный энтерококк (VRE) и синегнойная палочка с множественной лекарственной устойчивостью (*P. aeruginosa*) сейчас часто встречаются в больницах по всему миру. Разработка новых антибиотиков оказалась экономически непривлекательной для фармацевтических компаний: за последние 30 лет было разработано всего несколько новых класса антибиотиков. Наноматериалы предлагают принципиально иную парадигму: вместо создания новых молекулярных агентов, к которым бактерии со временем могут развить устойчивость, наноматериалы используют физические механизмы действия (разрушение мембран, окислительный стресс), к которым бактериям гораздо труднее выработать адаптивную резистентность. Таким образом, разработка эффективных антибактериальных наноматериалов является необходимостью для системы общественного здравоохранения.

Необходимость антиоксидантных исследований продиктована глобальным бременем хронических заболеваний. Сердечно-сосудистые заболевания уносят 17,9 миллиона жизней ежегодно (32% от всех смертей в мире). Рак уносит 9,6 миллиона жизней ежегодно. Диабет является причиной 1,6 миллиона смертей в год, при этом еще миллионы людей страдают от осложнений, включая слепоту, почечную недостаточность и ампутацию нижних конечностей. Все эти заболевания имеют окислительный стресс в качестве общего патогенетического механизма. Эффективные антиоксиданты, которые можно безопасно доставить в ткани-мишени, могли бы существенно снизить бремя этих болезней. Наноматериалы, разработанные в ходе данного исследования, со значениями IC_{50} всего 11,25 мкг/мл, открывают потенциал для терапевтического применения в качестве антиоксидантов.

Международный контекст исследования. Данное исследование позиционирует себя в международном научном пространстве в области наноматериалов для экологического и биомедицинского применения. Согласно данным Web of Science, число публикаций по теме «фотокаталитическая деградация» выросло с примерно 500 в 2000 году до более чем 10 000 в 2023 году. Публикации по теме «наночастицы зеленого синтеза» выросли со 100 в 2005 году до более чем 5 000 в 2023 году. Число

публикаций по «антибактериальным наноматериалам» увеличилось с ~200 в 2005 году до более чем 8 000 в 2023 году.

Данная работа вносит вклад в эти быстроразвивающиеся области, устраняя конкретные пробелы: ограниченность исследований триметаллических оксидов, модифицированных МУНТ; нехватку работ по зеленому синтезу с использованием *D. kaki* и *S. chirayita*; недостаточную изученность СДГ с четырьмя катионами металлов, а также редкую интеграцию фотокаталитической, антибактериальной и антиоксидантной функций в одном наноматериале.

Данное исследование напрямую способствует достижению нескольких Целей устойчивого развития Организации Объединенных Наций, что обеспечивает международную значимость его результатов. Работа открывает ряд международных направлений исследований:

- пилотные исследования с реальными промышленными сточными водами в нескольких странах для подтверждения эффективности в различных экологических условиях;
- клинические испытания антибактериальных и противоопухолевых наноматериалов в соответствии с международными регуляторными стандартами (FDA, EMA);
- оценка жизненного цикла (LCA) и технико-экономический анализ для демонстрации устойчивости и экономической жизнеспособности для различных регионов;
- трансфер технологий в развивающиеся страны посредством программ по наращиванию потенциала и обмену знаниями;
- стандартизация протоколов синтеза, характеристики и тестирования для обеспечения возможности международного сравнения и получения одобрения регулирующих органов;
- изучение дополнительных областей применения (например, производство водорода, восстановление CO₂, сенсорики) для расширения сферы внедрения этих multifunctional наноматериалов.

Цель исследования. Общая цель данного исследования заключается в разработке эффективных, экономически доступных и экологически устойчивых multifunctional наноматериалов с использованием инновационных подходов к синтезу, включая зелёный синтез, механохимические методы, и модифицированные золь-гель процессы, для удаления органических загрязнителей из сточных вод, а также для оценки антибактериальной активности и химических антиоксидантных свойств. Одновременно исследование направлено на установление комплексных взаимосвязей «структура–свойства–эффективность», необходимых для научно обоснованного и рационального проектирования функциональных наноматериалов.

Задачи исследования. Основными задачами данного исследования являются:

1. Синтез и изготовление: Разработать различные наноматериалы, включая простые оксиды металлов (ZnO , Fe_2O_3), биметаллические оксиды (CuO-ZrO_2), ($\text{CuO-Fe}_2\text{O}_3$), (CuO-NiO), легированный цирконием (NiO-ZnO), триметаллические оксиды ($\text{Ag}_2\text{O-CuO-ZnO}$), легированный ($\text{TiO}_2@\text{SnO}_2\text{-ZrO}_2$), ($\text{SnO}_2\text{-NiO-CuO}$), Co-Cu-Zn-LHs , слоистые двойные гидроксиды (Cr/Ni/Mg/Al-LDH), а также их перспективные композиты с оксидом графена, восстановленным оксидом графена и многостенными углеродными нанотрубками, используя «зеленый» синтез (кожура *M. acuminata*, экстракты *D. kaki*, *S. Chirayita*, *C. maxima*), безрастворительное механохимическое измельчение, модифицированный метод Хаммерса, соосаждение и модифицированные золь-гель методы.

2. Комплексная характеристика: Исследовать структурные, морфологические, оптические, композиционные, термические и текстурные свойства с использованием РД, СЭМ, ПЭМ, ЭДС, ИК-Фурье, СДО, и анализа удельной площади поверхности по БЭТ для установления подробных корреляций «структура - свойства».

3. Фотокаталитическая деградация: Оценить фотокаталитическую эффективность в отношении различных органических красителей (МО, R-6G, бриллиантовый зеленый (BG), флуоресцеин, 4-нитрофенол) под воздействием солнечного/УФ-излучения, включая кинетический анализ и изучение механизмов реакций.

4. Антибактериальная активность: Оценить бактерицидный потенциал против грамположительных (*S. aureus*) и грамотрицательных (*E. coli*) бактерий методом диффузии в агар (в лунки), установив профили активности в зависимости от концентрации.

5. Антиоксидантная активность: Оценить способность связывать свободные радикалы в отношении радикалов ABTS и DPPH, рассчитывая значения IC_{50} и устанавливая взаимосвязь «структура - активность».

6. Оптимизационные исследования: Систематически изучить влияние температуры прокаливания (от непрокаленного состояния до $900\text{ }^\circ\text{C}$), pH (2–12), дозы катализатора (5–30 мг), исходной концентрации (5–30 ppm) и стабильности при циклическом повторном использовании (4–5 циклов) на эффективность материалов.

НАУЧНАЯ НОВИЗНА. Данное исследование представляет несколько значимых элементов научной новизны, которые продвигают вперед область наноматериалов для экологического и биомедицинского применения.

Во-первых, в работе впервые сообщается о синтезе нескольких новых нанокompозитных систем, которые ранее не были описаны в литературе. Модифицированные МУНТ триметаллические нанокompозиты ($\text{Ag}_2\text{O/CuO/ZnO}$) были впервые синтезированы модифицированным золь-гель методом, продемонстрировав исключительные многофункциональные

свойства в качестве фотокатализатора, антибактериального и антиоксидантного агента. Аналогичным образом, четверной наноккомпозит (GO-ZnO-SnO₂-Fe₂O₃) представляет собой новую комбинацию, в которой восстановленный оксид графена интегрирован с тремя различными оксидами металлов для расширения биологического применения. Наноккомпозиты (NiO/ZnO), легированные цирконием, были впервые изготовлены с использованием экстракта листьев *D. kaki*, что представляет собой новый подход «зеленого» синтеза для легированных биметаллических оксидов. Наноккомпозиты (SnO₂-ZrO₂), легированные (TiO₂), с использованием экстракта растения *S. chirayita*, представляют собой новую комбинацию материалов с формированием гетероперехода. Слоистые двойные гидроксиды (Cr/Ni/Mg/Al) с несколькими катионами металлов (Cr³⁺, Ni²⁺, Mg²⁺, Al³⁺) и Co-Cu-Zn-LHs был получен с использованием экстракта листьев С были синтезированы и исследованы для деградации МО, что ранее было недостаточно изучено в литературе.

Во-вторых, в работе внедрены инновационные методологии синтеза, продвигающие экологически устойчивое производство наноматериалов. Механохимический безрастворительный синтез с помощью ступки и пестика для биметаллических оксидных наноккомпозитов (CuO-ZrO₂, CuO-Fe₂O₃) представляет собой более «зеленую» альтернативу традиционным сольвотермическим методам, являясь более эффективным, быстрым, простым, масштабируемым и экологически безопасным благодаря исключению опасных растворителей. «Зеленый» синтез с использованием различных растительных экстрактов (кожуры *M. acuminata*, листьев *D. kaki*, *S. chirayita*, *C. maxima*) в качестве восстанавливающих и стабилизирующих (капсулирующих) агентов устраняет вредные химикаты, способствует утилизации побочных продуктов сельского хозяйства и позволяет получать наночастицы с более высокой биологической активностью за счет адсорбированных фитохимических соединений.

В-третьих, исследование предлагает новые многофункциональные платформы, где единый наноматериал демонстрирует одновременные фотокаталитические, антибактериальные и антиоксидантные способности. Интеграция комплексной биологической оценки (фотокаталитической, антибактериальной и антиоксидантной) в рамках единых наноккомпозитных систем представляет собой холистический подход к разработке материалов, о котором редко сообщается. Co-Cu-Zn-LHs, Синергетическое сочетание оксида графена с триметаллическими оксидами (GO-ZSF, GO-SNC) и МУНТ с биметаллическими/триметаллическими оксидами (МУНТ@CuO-NiO, МУНТ@Ag₂O/CuO/ZnO) продемонстрировало улучшенные свойства за счет более эффективного разделения зарядов, переноса электронов и увеличения площади поверхности.

В-четвертых, исследование дает фундаментальное понимание механизмов благодаря систематической корреляции взаимосвязей «структура - свойства - эффективность». Был наглядно продемонстрирован компромисс между

площадью поверхности и кристалличностью при повышении температуры прокаливания в различных системах, что показало: площадь поверхности является доминирующим фактором, определяющим фотокаталитическую активность, несмотря на более низкую кристалличность. Была разъяснена «дилемма легирования»: показано, что увеличение концентрации легирующей примеси с 0,5% до 1% в Zr-NiO/ZnO неожиданно снизило фотокаталитическую активность (86,45% $\rightarrow$ 67%) и увеличило ширину запрещенной зоны (3,43 - 3,66 эВ), что ставит под сомнение предположение о том, что «большее легирование всегда означает лучшую эффективность». Был охарактеризован «обоюдоострый меч МУНТ», когда введение МУНТ стабильно повышало фотокаталитические и антиоксидантные свойства, но иногда снижало антибактериальную активность, показывая, что разные применения требуют различных модификаций поверхности.

В-пятых, исследование предоставляет беспрецедентные сравнительные данные об эффективности, где наночастицы «зеленого» синтеза последовательно превосходят свои аналоги, полученные химическим путем. Это указывает на то, что адсорбированные фитохимические вещества вносят прямой вклад в биологическую активность, а не просто контролируют размер и морфологию. Превосходная эффективность Cr/Ni/Mg/Al-LDH (89,23% деградации МО за 30 мин с константой скорости 0,07427 мин⁻¹ по сравнению с описанными в литературе СДГ (требующими 90–180 мин) демонстрирует значительный шаг вперед.

ДОСТОВЕРНОСТЬ РЕЗУЛЬТАТОВ ИССЛЕДОВАНИЯ.

Достоверность результатов данного исследования обеспечивается использованием множества взаимодополняющих методов характеристики, последовательно применявшихся во всех экспериментах, что гарантирует точность и воспроизводимость данных.

- **Рентгеновская дифракция** обеспечила идентификацию фаз с использованием стандартных эталонных карт JCPDS, расчет размера кристаллитов по уравнению Дебая-Шеррера ($D = K\lambda/\beta\cos\theta$) и анализ микронапряжений решетки; совпадение всех пиков с эталонными картами гарантирует правильность фазовой идентификации.

- **Сканирующая и просвечивающая электронная микроскопия** позволили определить морфологию, распределение частиц по размерам и микроструктуру; для оценки размеров по нескольким изображениям использовалось программное обеспечение ImageJ для обеспечения статистической значимости.

- **Энергодисперсионная рентгеновская спектроскопия** подтвердила элементный состав и чистоту: спектры показали ожидаемые пики для всех составляющих элементов при отсутствии непредусмотренных примесей.

- **ИК-фурье-спектроскопия** определила функциональные группы и подтвердила образование связей металл-кислород, продемонстрировав стабильные положения полос для множества образцов и систематические изменения интенсивности в зависимости от температуры прокаливания.

- **Спектроскопия диффузного отражения** определила оптические свойства и энергию запрещенной зоны с помощью графиков Тауца ($\alpha h\nu = A(h\nu - E_g)^n$), при этом множественные измерения подтвердили воспроизводимость.
- **Анализ удельной площади поверхности по БЭТ** позволил количественно определить площадь поверхности, размер и объем пор на основе изотерм адсорбции-десорбции N_2 в соответствии со стандартами классификации IUPAC.
- **Термогравиметрический анализ** предоставил профили термической стабильности со стабильными паттернами потери веса в нескольких циклах нагрева.

Воспроизводимые методы синтеза с подробными экспериментальными процедурами, включая контролируемые параметры (температура, pH, концентрация, время, скорость перемешивания, условия прокаливания), гарантируют, что результаты могут быть повторены независимыми исследователями. Все синтезы повторялись многократно (3–5 раз) для проверки воспроизводимости, при этом стабильные результаты укладывались в пределы $\pm 5\%$ отклонения.

Статистический анализ биологической активности включает стандартное отклонение, дисперсию, значения IC_{50} и коэффициенты корреляции, что доказывает надежность данных. Для антибактериальной активности использовалось несколько лунок на планшеты (минимум 3) и несколько планшетов на эксперимент (минимум 3), при этом значения стандартного отклонения обычно составляли от 1,09 до 1,83 мм, что указывает на хорошую прецизионность. Для антиоксидантной активности значения IC_{50} рассчитывались по кривым «доза-эффект» со значениями R^2 обычно $>0,98$, а стандартное отклонение варьировалось от 1,51 до 1,75, что указывает на высокую сходимость результатов.

Сравнительный анализ с литературными данными и стандартными контролями (аскорбиновая кислота для антиоксидантного теста, ципрофлоксацин/антибиотики для антибактериального теста) подтверждает значимость полученных результатов. Кинетическое моделирование данных фотокатализа и высвобождения лекарственных веществ, аппроксимированное моделями псевдопервого и псевдовторого порядка с высокими коэффициентами регрессии ($R^2 > 0,98$), подтверждает адекватность предложенных механизмов.

Исследования стабильности при повторном использовании в течение 4–5 циклов демонстрируют устойчивость катализатора и практическую применимость со стабильными показателями деградации от цикла к циклу. Систематическая оптимизация влияющих факторов (pH, доза, концентрация, температура, температура прокаливания) обеспечивает всестороннее понимание работы материала в различных условиях. Для фотокаталитических исследований проводились контрольные эксперименты (только катализатор, только свет), чтобы подтвердить, что деградация происходила именно за счет фотокатализа, а не в результате исключительно адсорбции или фотолиза.

ЗНАЧИМОСТЬ РЕЗУЛЬТАТОВ ИССЛЕДОВАНИЯ. Исследование демонстрирует исключительные возможности очистки окружающей среды со значительными практическими последствиями. Эффективность фотокаталитической деградации достигает 99,61% для R-6G с использованием МУНТ@Ag₂O/CuO/ZnO, 99,42% для R-6G с использованием наночастиц оксида железа «зеленого» синтеза, 95,37% с использованием МУНТ@CuO-NiO и 93,57% для 4-нитрофенола с использованием SnO₂-ZrO₂, что представляет собой превосходные показатели по сравнению со значениями, известными в литературе. Такие высокие константы скорости, как 0,10012 мин⁻¹ (МУНТ@Ag₂O/CuO/ZnO) и 0,07427 мин⁻¹ (Cr/Ni/Mg/Al-LDH), указывают на быструю кинетику деградации, подходящую для практической очистки сточных вод. Активация солнечным светом снижает энергозатраты и эксплуатационные расходы, делая технологию доступной для развивающихся регионов, где загрязнение воды соседствует с энергетической бедностью.

Биомедицинские применения показывают многообещающие результаты с существенным терапевтическим потенциалом. Антибактериальная активность с зонами ингибирования до 31 мм GO-ZSF против *E. coli*) доказывает эффективность против как грамположительных, так и грамотрицательных бактерий, отвечая на глобальный вызов антимикробной резистентности. Более высокая активность непрокаленных образцов (31 мм против 29 мм для прокаленных) и нанокомпозитов на подложке из ОГ (24–31 мм) по сравнению с чистыми оксидами металлов (7–24 мм) и стандартными антибиотиками (16–20 мм) предлагает множественные стратегии борьбы с устойчивыми к лекарствам бактериями. Повышенная антиоксидантная активность со значениями IC₅₀ всего 11,25 мкг/мл (ОГ против ABTS) и 15,98 мкг/мл (ОГ против DPPH) указывает на сильную способность улавливать свободные радикалы для борьбы с болезнями, связанными с окислительным стрессом, включая рак, сердечно-сосудистые заболевания, диабет и нейродегенеративные расстройства. Исключительные показатели ОГ (IC₅₀ 11,25 мкг/мл) по сравнению с аскорбиновой кислотой (IC₅₀ 44,67 мкг/мл) представляют собой 4-кратное улучшение, открывая новые пути для антиоксидантной терапии.

Достижения в области материаловедения включают фундаментальное понимание влияния температуры прокаливании на кристалличность, площадь поверхности и ширину запрещенной зоны, устанавливая корреляции «структура - свойства - эффективность», необходимые для рационального проектирования материалов. Четкая демонстрация того, что непрокаленный Co-Cu-Zn-LNs (площадь поверхности 84,87 м²/г) показал самую высокую активность (92,98 %), несмотря на более низкую кристалличность, в то время как CuO-ZrO₂ показал рост активности при прокаливании (77,27% при 900 °C), обнаруживает, что различные материалы имеют разные доминирующие факторы, и оптимизация должна быть специфичной для каждого материала, а не следовать универсальным трендам. Корреляция между уменьшением площади поверхности (152,53 к 1,78 м²/г) и снижением

фотокаталитической активности (88,95% - 59,19%) для $\text{CuO-Fe}_2\text{O}_3$ дополнительно подтверждает, что площадь поверхности выступает ключевым фактором.

Преимущество «зеленого» синтеза наглядно доказано: наночастицы оксида железа, полученные с помощью экстракта *M. acuminata*, обеспечили 99,42% деградации R-6G, превзойдя многие химически синтезированные аналоги. Использование сельскохозяйственных отходов (банановой кожуры) и лекарственных растений (*D. kaki*, *S. chirayita*, *C. maxima*) обеспечивает устойчивые, недорогие и локально адаптируемые пути производства. Механохимический подход предлагает такие преимущества, как отсутствие растворителей, энергоэффективность, экологичность, масштабируемость и простота, что делает его перспективной альтернативой для экологически устойчивой разработки фотокатализаторов. Соответствие Целям устойчивого развития ООН₃ (хорошее здоровье) и 6 (чистая вода) позиционирует это исследование в рамках глобальной структуры по решению насущных гуманитарных проблем.

ВНЕДРЕНИЕ РЕЗУЛЬТАТОВ ИССЛЕДОВАНИЯ. Научные результаты, полученные в ходе данного DSc-исследования, опубликованы в международных научных журналах с высоким импакт-фактором и получили значительное признание мирового научного сообщества, что подтверждается показателями цитирования, полученными из базы данных Scopus. Статья под названием «Solar light-induced degradation of hazardous organic pollutants using Diospyros kaki mediated green synthesized zirconium doped nickel oxide-zinc oxide nanocomposite», опубликованная в журнале Materials Research Express (2024), получила 3 цитирования и занимает 60-й перцентиль при Field-Weighted Citation Impact (FWCI), равном 0,35. Статья «Antibacterial and antioxidant screening applications of reduced-graphene oxide modified ternary $\text{SnO}_2\text{-NiO-CuO}$ nanocomposites», опубликованная в Arabian Journal of Chemistry (2023), получила 21 цитирование и занимает 89-й перцентиль с показателем FWCI 1,40, что свидетельствует о значительно более высоком цитатном влиянии по сравнению со среднемировым уровнем для соответствующей научной области и года публикации. Статья «Fabrication and structural analysis of CuO-NiO and MWCNTs@CuO-NiO hybrid nanostructures: versatile materials for environmental and biomedical remediation», опубликованная в RSC Advances (2025), получила 5 цитирований и занимает 82-й перцентиль с FWCI 0,71. Статья «Unveiling the physicochemical, photocatalytic, antibacterial and antioxidant properties of MWCNT-modified $\text{Ag}_2\text{O/CuO/ZnO}$ nanocomposites», опубликованная в RSC Advances (2025), получила 11 цитирований и занимает 95-й перцентиль с FWCI 2,38, что представляет собой наивысшее цитатное влияние среди опубликованных работ и свидетельствует о том, что данное исследование цитируется более чем в два раза чаще среднемирового уровня в соответствующей научной области. Статья «Enhanced Photocatalytic Performance of Cr/Ni/Mg/Al Layered Double Hydroxides against Methyl Orange in Aqueous Solution», опубликованная в Desalination and Water Treatment (2024),

получила 6 цитирований и занимает 75-й процентиль с FWCI 0,75. Статья «Solvent free fabrication and thermal tuning of copper oxide-zirconium dioxide nanocomposite for enhanced photocatalytic efficacy», опубликованная в Materials Research Express (2024), получила 7 цитирований и занимает 75-й процентиль с FWCI 0,70. В совокупности данные публикации получили в общей сложности 53 цитирования от независимых исследователей со всего мира, что демонстрирует признание, цитирование и использование научных результатов данного DSc-исследования международным научным сообществом в публикациях, представленных в высокорейтинговых журналах. Результаты исследования были процитированы в последующих публикациях в таких журналах, как Scientific Reports, RSC Advances, Heliyon, Materials Science and Engineering: B, Journal of Environmental Chemical Engineering и Pharmaceuticals, а также в ряде других научных изданий. Данный показатель цитируемости подтверждает научное качество, международную значимость и практическую ценность полученных результатов, а также демонстрирует, что разработанные наноматериалы и подходы к их синтезу внесли существенный вклад в развитие областей экологической ремедиации и биомедицинской терапии.

Публикации по результатам исследовательской работы. Результаты, полученные в рамках данной DSc-диссертации, представлены в 12 рецензируемых научных статьях, опубликованных в престижных научных журналах, рекомендованных Высшей аттестационной комиссией Республики Узбекистан для публикации основных научных результатов диссертаций на соискание ученой степени DSc и индексируемых в базе данных Web of Science.

ВЫВОДЫ

1. Данное исследование успешно демонстрирует разработку различных многофункциональных наноматериалов для экологического и биомедицинского применения с помощью инновационных подходов к синтезу, включая «зеленый» синтез с использованием сельскохозяйственных отходов (кожуры *M. acuminata*) и экстрактов лекарственных растений (*D. kaki*, *S. chirayita*, *C. maxima*), безрастворительное механохимическое измельчение, модифицированный метод Хаммерса, гидротермальное соосаждение и модифицированные золь-гель методы.

2. Простые оксиды металлов (ZnO , Fe_2O_3) проявили многообещающую антибактериальную (зоны ингибирования 14 мм для *E. coli*) и фотокаталитическую (деградация R-6G на 99,42%) активность, что доказывает эффективность использования сельскохозяйственных отходов для синтеза наноматериалов.

3. Биметаллические оксиды, включая CuO-NiO , CuO-ZrO_2 , $\text{CuO-Fe}_2\text{O}_3$ и Zr-NiO/ZnO , продемонстрировали улучшенные фотокаталитические свойства, на которые сильное влияние оказывали температура прокаливания, концентрация легирующей примеси и метод синтеза.

4. Критический баланс между удельной площадью поверхности и степенью кристалличности был чётко продемонстрирован. В частности, некальцинированные Co–Cu–Zn-LH образцы, несмотря на относительно низкую степень кристалличности, проявили максимальную активность (92,98%) благодаря наибольшей удельной площади поверхности (84,87 м²/г). Напротив, для нанокompозита CuO–ZrO₂ повышение температуры кальцинации способствовало увеличению степени кристалличности и структурной однородности, что привело к повышению фотокаталитической активности до 77,27% при 900 °С.

5. Триметаллические оксиды, включая Ag₂O–CuO–ZnO, легированный TiO₂@SnO₂–ZrO₂ и SnO₂–NiO–CuO, продемонстрировали многофункциональные возможности с исключительной фотокаталитической активностью (до 99,61%) и сильными антиоксидантными свойствами.

6. Слоистые двойные гидроксиды доказали свою высокую эффективность: Cr/Ni/Mg/Al-LDH (СДГ-4) обеспечил 89,23% деградации МО с константой скорости 0,07427 мин⁻¹ (что примерно в 16,5 раз выше, чем у нелегированного СДГ-1). Это обусловлено высокопористой структурой, увеличенной площадью поверхности, синергетическим эффектом нескольких катионов металлов и улучшенным разделением зарядов за счет введения Cr, приводящего к появлению новых энергетических уровней внутри запрещенной зоны.

7. Композиты «оксид графена - оксид металла» (GO-ZSF, GO-SNC) продемонстрировали исключительную антибактериальную активность с зонами ингибирования до 31 мм благодаря синергетическому эффекту между графеновыми листами (обеспечивающими проникновение в бактериальные клетки и их захват) и наночастицами оксидов металлов (обеспечивающими высвобождение катионов металлов и генерацию активных форм кислорода).

8. В тесте на антиоксидантную активность оксид графена (ОГ) показал исключительное связывание радикалов (IC₅₀ 11,25 мкг/мл для ABTS, 15,98 мкг/мл для DPPH), превзойдя SNC, GO-SNC и даже стандартный контроль - аскорбиновую кислоту (IC₅₀ 44,67 мкг/мл).

9. Композиты «МУНТ - оксид металла» (МУНТ@CuO–NiO, МУНТ@Ag₂O/CuO/ZnO) последовательно улучшали фотокаталитические и антиоксидантные свойства за счет более эффективного разделения зарядов и переноса электронов: константы скорости увеличились с 0,02737 до 0,0477 мин⁻¹, а значения IC₅₀ снизились со 116,52 до 84,61 мкг/мл, в то время как антибактериальные эффекты варьировались в зависимости от модификации поверхности.

10. Механохимический подход к синтезу предлагает очевидные преимущества, включая проведение процесса без растворителей, энергоэффективность, экологичность, масштабируемость и простоту.

11. Методы «зеленого» синтеза с использованием растительных экстрактов представляют собой экологически безопасную альтернативу химическим методам, снижая воздействие на окружающую среду и

способствуя устойчивому развитию, с дополнительным преимуществом в виде прямого вклада адсорбированных фитохимических соединений в биологическую активность.

12. Успешная демонстрация многофункциональных наноматериалов, способных к одновременной фотокаталитической деградации, антибактериальной активности и антиоксидантной защите, открывает новые пути для интегрированных экологических и биомедицинских решений, направленных на борьбу с глобальными угрозами для здоровья.

13. Исследование устанавливает четкие корреляции «структура - свойства - эффективность», которые служат руководством для направленного дизайна материалов, определяет масштабируемые и экономически выгодные пути производства, а также доказывает применимость материалов в реальных условиях посредством исследований стабильности при повторном использовании и оптимизации практических параметров.

14. Разработанные наноматериалы демонстрируют превосходный потенциал для очистки промышленных сточных вод, обеззараживания питьевой воды, антибактериального и антиоксидантного применения, внося значительный вклад в достижение Целей устойчивого развития ООН в области чистой воды (ЦУР 6) и хорошего здоровья (ЦУР 3).

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Part 1

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