Journal for Re-Attach Therapy and Developmental Diversities
eISSN: 2589-7799
2023 Sepetember; 6 (9s): 1944-1950

Green Synthesis And Characterization of Copper Oxide And Cobalt Oxides Nanoparticles Using Moringa Oleifera Fruit Extract

Shital Shivaji Bankar[1], Anita Kashinath Kshirsagar[2], Priyanka Ganesh Bhutekar[3], Shivaji Baburao Munde[4*]
Corresponding author email- principalsbmunde@gmail.com

[1,2,3]P.G. Department of Chemistry, Jalna Education Society's, R. G. Bagdia Arts, S. B. Lakhotia Commerce, and R. Bezonji Science College, Jalna-431203 (M.S.), [4*]Department of Chemistry, Shri Muktanand College Gangapur, Aurangabad -431001 (M.S.)

Abstract

Currently, researchers widely use natural resources as reducing and stabilizing agents to synthesize copper oxide nanoparticles (CuO-NPs) and cobalt oxide nanoparticles (CoO NPs) due to their eco-friendly, easy, affordable, and viable characteristics. Non-toxic and cost-effective CuO nanoparticles were produced utilizing an eco-friendly method involving *moringa oleifera* fruit extract. The UV-visible spectroscopy technique was used to uncover the optical characteristics of copper oxide and cobalt oxide nanoparticles synthesized using green methods. The study used Fourier transform infrared spectroscopy (FTIR) to analyze the active biomolecules and functional groups involved in the biological reduction of metal ions into nano-scale CuO and CoO particles. X-ray diffraction experiments were conducted to examine the structure, phase, and crystalline planes of nanoparticles. The experimental findings demonstrate that *moringa oleifera* fruit can be used as a cost-effective and advantageous bio-resource for producing metal oxide nanoparticles. These standard nanoparticles have potential applications in various domains such as medicinal, industrial, and environmental. The bioactivity and potential uses of an environmentally friendly metal oxide nanoparticle were established.

Keywords: Moringa Oleifera Fruit, Copper oxide nanoparticles, Cobalt oxide nanoparticles UV-visible spectroscopy, XRD-EDX

1. Introduction:

Nanotechnology involves creating, characterizing, speeding up, and using materials that are nano-sized (1-100 nm) to alter material properties by regulating their size. Nanotechnology is being explored for various applications in electronics, industry, imaging, and medicine [1-5]. Nanoparticles have attracted considerable interest because of their large surface area, high reactivity, and distinctive particle shape. Metal oxide nanoparticles have garnered attention in recent years because of their exceptional characteristics and diverse uses. Nanotechnology research has focused on the synthesis of nanomaterials due to growing demand in the industrial and medical sectors for applications such as fillers, disinfectants, optics, antibacterial agents, medication delivery, and catalytic products [6]. Metal oxide nanoparticles like CoO_2, CuO_2, ZnO, and Fe_2O_3 are being studied for potential uses in environmental and biomedical fields. Copper oxide nanoparticles (CuO-NPs) and Cobalt oxide nanoparticles (CoO-NPs) are highly stable and biocompatible, attracting significant interest from researchers for their applications in catalysis, water purification through photocatalysis, cells, batteries, sensor fabrication, therapeutic agents, and drug delivery [7-10]. Various techniques, including co-precipitation [11], solvothermal [12], template-assisted precipitation [13], spray drying [14], microwave [15], hydrothermal [16], and sol-gel [17] procedures, are extensively employed for synthesizing nanoparticles. Many of these treatments are intricate, time-consuming, costly, and use harmful chemicals that pose multiple risks to the ecosystem. Researchers have lately used a technology called green synthesis, which is simple, safe, less harmful, and eco-friendly. Nanoparticles prepared by a green approach are a novel technique in the field of nanotechnology, made possible by using plant extracts [18-19], microbes [20-21], vitamins, carbohydrates, and other derivatives [22-23]. The biological extracts contain phytochemicals such as carbohydrates, saponins, amino acids, flavonoids, terpenoids, and proteins. These compounds are thought to play a role in reducing and stabilizing bulk salts into nanoparticles. A literature review shows that the biosynthesis of CuO-NPs and CoO-NPs has been reported using fruit extracts from various. This method is considered a straightforward and feasible alternative to chemical and physical synthesis methods.

This paper discusses the green manufacture of CuO and CoO nanoparticles using *moringa oleifera* fruit extract and examines their characteristics. No literature exists on the green synthesis of CuO and CoO nanoparticles using *moringa oleifera* fruit extract. *Moringa oleifera* fruit, a medicinal herb, is classified under the genus *Moringa* in the family *Moringaceae*. The leaves of this plant are typically greenish or reddish on the underside and darker on the upper surface. They are arranged in an opposing pattern and are lanceolate in shape. The stem is thin, adorned with yellowish bristly hairs, and frequently crimson in hue. When cut or wounded, aerial components generate a milky fluid. The plant is recognized for its effectiveness in treating cough, coryza, asthma, intestinal issues, worm infestations, and kidney stones in traditional medicine. *Moringa oleifera* fruit includes a variety of bioactive components including alkaloids, flavonoids, saponins, carbohydrates, terpenoids, amino acids, and polyphenols, which are mostly used for inhibiting corrosion. *Moringa oleifera* possesses beneficial antibacterial, antioxidant, antifungal, and anti-inflammatory activities. This work aims to produce CuO and CoO nanoparticles by using a cost-effective, straightforward, time-efficient, and environmentally friendly technique including the fruit extract of *moringa oleifera*. The CuO and CoO nanoparticles were analyzed using standard techniques including XRD, UV-Vis, FTIR, and FE-SEM.

2. Experimental:

2.1. Materials:

Copper chloride pentahydrate and cobalt chloride hexahydrate of analytical reagent grade was used as the precursor for preparing metal oxide nanoparticles. *Moringa oleifera* fruit were freshly gathered from the college. All solutions were produced using water that had been distilled three times.

2.2. Preparation of Moringa oleifera fruit extract:

The gathered fruit of the chosen weed plant was cleaned to eliminate dust particles and then dried in the shade at room temperature for a specific timeframe. Dried fruit was crushed and ground into a fine powder. The powdered fruit of *moringa oleifera* was utilized to prepare an extract using a Soxhlet extractor and triple distilled water as the solvent. The colloidal solution extracted is centrifuged and filtered through Whatman paper to eliminate plant residues, then kept in a refrigerator at 4°C for future use.

2.3. Synthesis of Copper Oxide Nanoparticles (CuO-NPs):

Copper oxide nanoparticles (CuO-NPs) were prepared using an environmentally friendly method. A 0.01M solution of $[Cu(Cl)_2 \cdot 5H_2O]$ was produced in triply distilled water. The *moringa oleifera* fruit extract was gradually added in a specific ratio while continuously swirling with a magnetic stirrer until a brown colloidal solution was formed. The colloidal solution was centrifuged at 10,000 rpm for a specific period. The centrifuged particles were rinsed 2-3 times with distilled water. The centrifuged particles were separated and then dried in a hot air oven at 60°C. The CuO-NPs were kept in a plastic tube vial at room temperature.

2.4. Synthesis of Cobalt Oxide Nanoparticles (CoO-NPs):

CoO-NPs, or cobalt oxide nanoparticles, were prepared in an eco-friendly manner. In triply distilled water, a 0.01M solution of $[Co(Cl)_2 \cdot 7H_2O]$ was obtained. Until a brown colloidal solution formed, the *moringa oleifera* fruit extract was added gradually in a predetermined ratio while being constantly swirled with a magnetic stirrer. For a predetermined amount of time, the colloidal solution was centrifuged at 10,000 rpm. Two or three times, distilled water was used to rinse the centrifuged particles. After being separated, the centrifuged particles were dried at 60°C in a hot air oven. The CuO-NPs were stored at room temperature in a plastic tube vial.

2.5. Characterization of Synthesized Nanoparticles:

The nanoparticles were analyzed using standard analytical procedures.

2.5.1. UV visible spectrum:

UV visible absorption spectra were measured using a JASCO V650 UV-spectrometer.

2.5.2. FT-IR spectroscopy:

An IR Brucker instrument was used to capture the FT-IR spectra of synthesized metal oxide nanoparticles. The spectra were obtained by scanning the material within the 500-4000 cm^{-1} range.

2.5.3: X-ray diffraction spectra:

The powdered raw material was utilized to conduct the X-ray diffraction spectra. The X-PERT PRO diffractometer was utilized to capture the X-ray diffraction spectra of the produced nanoparticles. X-ray diffraction (XRD) was conducted in the 2θ range of 10-90 degrees using Cu Kα radiation with a wavelength of 1.5406 Å. An operating voltage of 40 kV was applied with a current of 40 mA at room temperature.

2.5.4 FE-SEM and EDS analysis:

The SEM pictures of the produced nanoparticles were obtained using the Nova Nano FEI Nova Nano-SEM 450 device. The nanoparticle's elemental composition was determined using Energy Dispersive X-ray Spectroscopy with FE-SEM equipment.

eISSN: 2589-7799
2023 Sepetember; 6 (9s): 1944-1950

2.6: Antimicrobial activities:

The developed Cu and Co oxide nanoparticles were tested for their antimicrobial properties against *B. subtilis, P. aeruginosa, E. coli* and *S. aureus*, four types of bacteria. The antibacterial activity was measured using a modified Kirby-Bauer disc diffusion method [24]. The negative control was a solvent blank. A positive control was conducted using the antibiotic *streptomycin*.

We used an antifungal susceptibility test to determine the extent to which fruit extract of *moringa oleifera* encapsulated CuO and CoO nanoparticles worked against fungus. To test the nanoparticles' antifungal efficacy, samples of the fungus *A. niger* and *S. cerevisiae* were used.

3. Result and Discussion:

The CuO and CoO nanoparticles synthesis product was evaluated and analyzed using standard equipment and methodologies in a more environmentally friendly manner. The initial observation was a colour change in the reaction mixture indicating the development of metal oxide nanoparticles. Metal oxide nanoparticles were produced by examining UV-Vis and FTIR spectrum data.

3.1. UV-visible spectroscopy:

UV-visible spectroscopy was used to confirm the production of nanoparticles. **Figure-1** displays the UV-Vis absorption spectra of the extract and CuO and CoO nanoparticles.

CuO and CoO nanoparticles showed an absorption peak at 325 and 345 nm respectively, in the spectra (**Figure 1**). The direct band gap energy of produced by nanoparticles is determined by fitting the absorption data to a specific equation
$\alpha h\nu = K (h\nu - E^{g})^2$.

α represents the optical absorption coefficient, hν stands for the photon energy, E_g is the direct bandgap, and K is a constant. By plotting $(\alpha h\nu)^2$ against photon energy (hν) and extending the linear section of the curve to where absorption reaches zero, the direct band gap energy value can be determined. The direct band gap energy of the produced CuO and CoO nanoparticles were determined to be 3.6 and 3.7 eV respectively. The band gap value is within the range reported in literature.

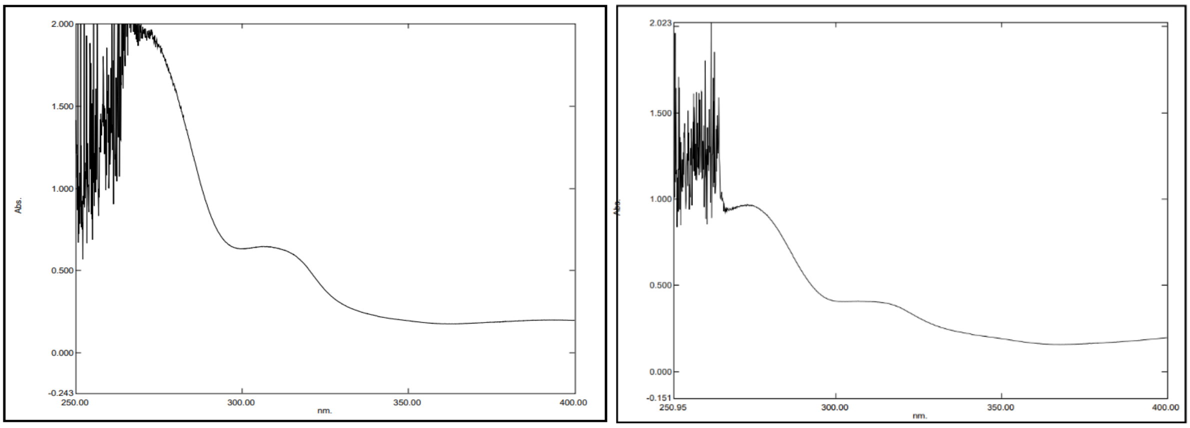


Figure 1. UV-Vis spectra of *moringa oleifera* mediated CuONPs and CoONPs

3.2: FTIR analysis:

Infrared spectroscopy is a valuable method for identifying chemical functional groups in a molecule and determining the potential involvement of phyto-constituents in the capping and stability of nanoparticles. **Figure-2** displays the FTIR spectra of CuO and CoO nanoparticles synthesized using *moringa oleifera*. Several notable peaks were detected in the spectra (**Figure-2**). The band at 3534-3555 cm^{-1} is attributed to the stretching vibration of hydroxyl (O–H) molecules. The peak at 1618-1634 cm^{-1} corresponds to the bending vibrations of the adsorbed –OH groups. The peaks at 981-989 cm^{-1} and 540-556 cm^{-1} in the spectra correspond to the vibration modes of O-M-O and M-O, respectively (where M = Cu, Co). The identification of M-O vibrational absorption bands indicates the production of nanoparticles as MO.

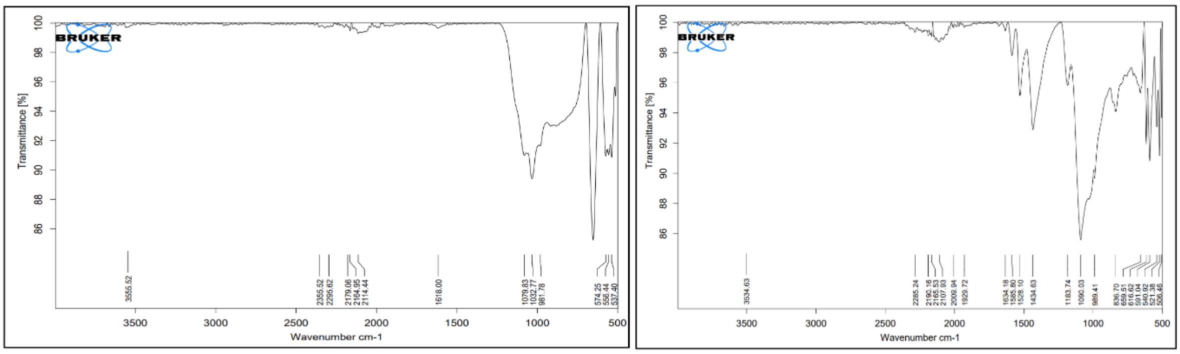


Figure 2. FTIR spectra of *moringa oleifera* mediated CuONPs and CoONPs

3.3. XRD Analyses:

The X-ray diffraction (XRD) pattern of cerium oxide nanoparticles was obtained in the 20° to 80° range of 2θ values, as shown in **Figure 3**. The diffraction peak occurs at several 2θ values: 28.1-28.3°, 47.30-47.36°, 56.25-56.28°, and 76.83-76.85°, corresponding to the crystallographic planes (111), (022), (113), and (133) correspondingly [25-26]. The indices of these planes align with the FCC cubic fluorite structure of CuO and CoO. The XRD patterns were analyzed using Rietveld refinement using PANalytical HighScore software and compared to the JCPDS reference code 98-062-1704.The crystal structure of CuO and CoO is cubic with Fm-3m as the space group and a lattice constant of 5.411 Å. The volume of CuO and CoO produced using *moringa oleifera* is determined to be 156.92 cubic angstroms. The size of the crystallites in the nanoparticles was determined using Debye-Scherrer's formula
Average crystallite size (D) = 0.9λ/βcosθ.
The formula involves λ as the X-ray source's wavelength for analysis, β as the angular peak width at half maxima in radians, and θ as Bragg's angle of diffraction. The average size of the crystallites, calculated using the Scherrer formula provided above, was determined to be 16 nm.

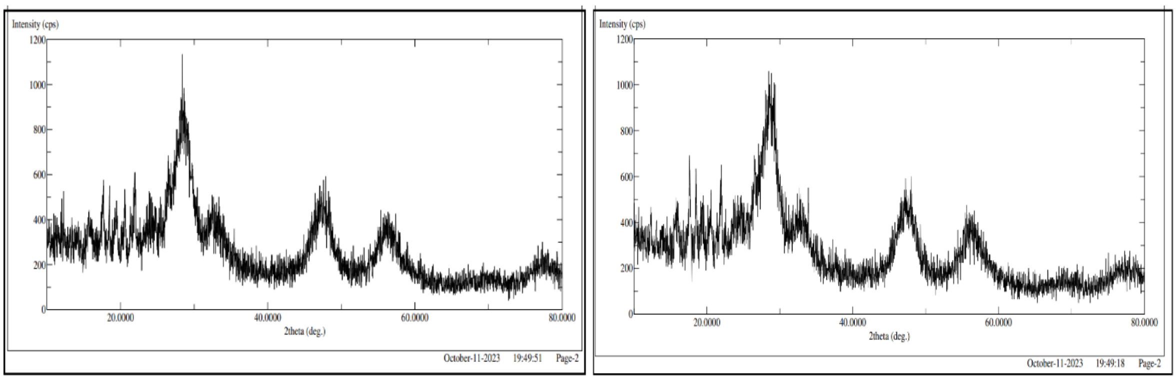


Figure 3: XRD spectra of *moringa oleifera* mediated CuONPs and CoONPs

3.4 FE-SEM and EDS analysis:

The structure of the produced cobalt and copper oxide nanoparticles was analyzed by FE-SEM, and the results are shown in **Figure-4** to **7**. The photos clearly show the non-uniform morphology of the cerium oxide nanoparticles, with some spherical particles. The CuONPs and CoONPs nanoparticles were observed at magnifications of 10μm and 1μm. **Figure 7** displays the EDS spectrum of CuONPs and CoONPs produced with *moringa oleifera* fruit extract, revealing the presence of copper, cobalt, and oxygen components in the sample composition. The spectrum peak indicates the existence of copper (Cu) and oxygen (O) at energy levels of 8.052 and 0.534 kilo electronvolts (keV) respectively. The presence of cobalt (Co) and oxygen (O) is shown by the spectra peak at 5.396 and 0.509 keV, respectively.

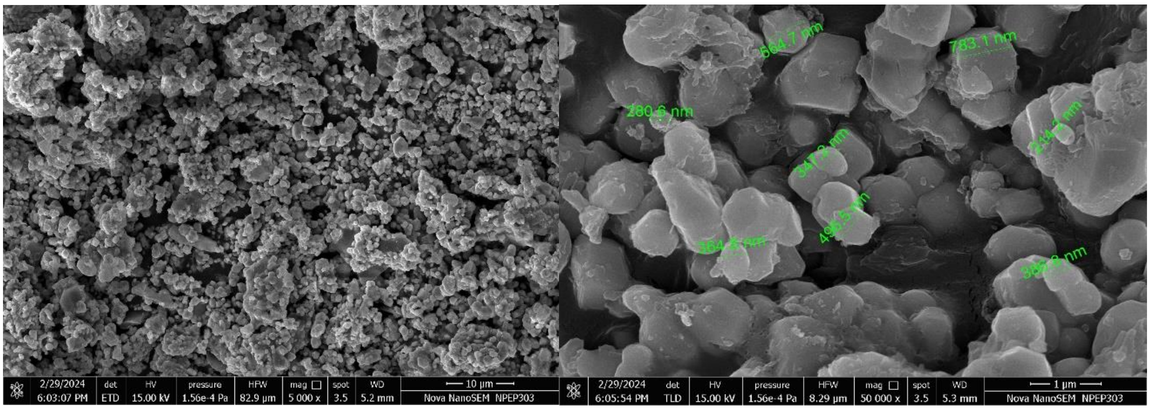
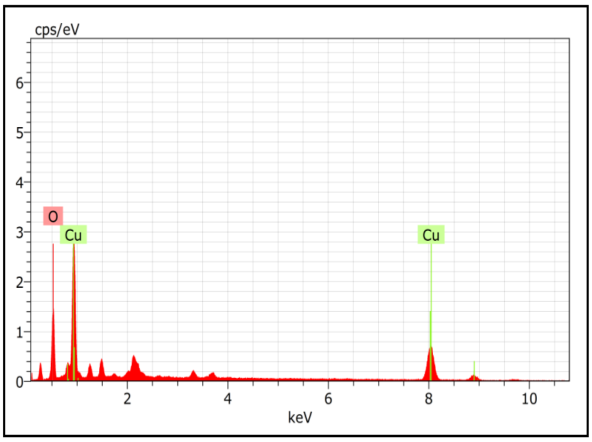


Figure 4: FE-SEM images of *moringa oleifera* mediated CuO-NPs with a magnification (10µm and 1µm).



EDS Report

Spectrum: OBJECT1 727

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Cu	29	K-series	52.31	86.17	61.07	1.74
O	8	K-series	8.40	13.83	38.93	1.20
		Total:	60.70	100.00	100.00	

Figure 5: EDAX spectrum for *moringa oleifera* mediated CuO-NPs.

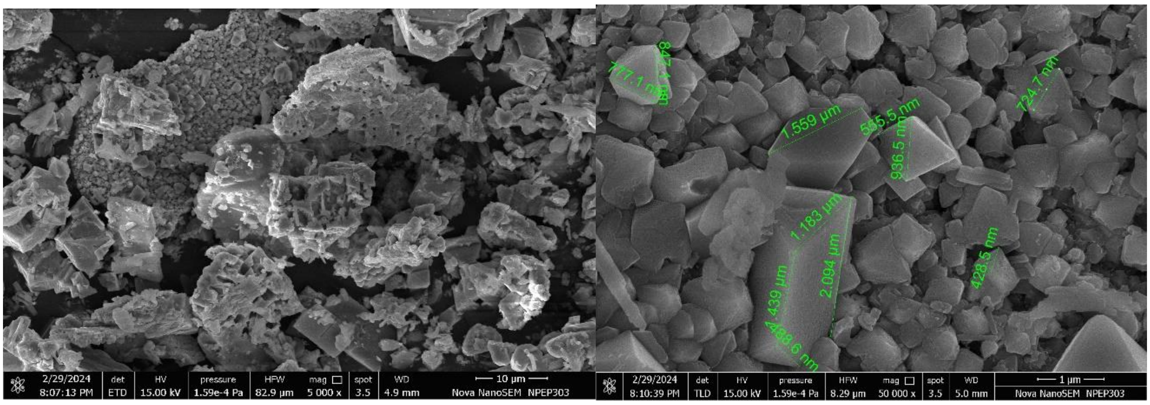
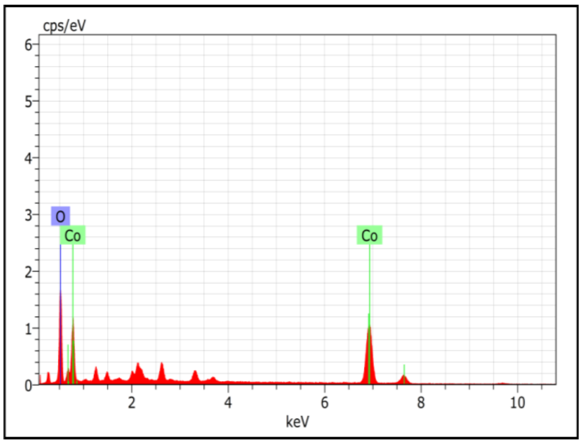


Figure 5: FE-SEM images of *moringa oleifera* mediated CoO-NPs with a magnification (10µm and 1µm)



EDS Report

Spectrum: OBJECT1 735

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Co	27	K-series	57.62	82.86	56.75	1.78
O	8	K-series	11.92	17.14	43.25	1.60
		Total:	69.54	100.00	100.00	

Figure 7: EDAX spectrum for *moringa oleifera* mediated CoO-NPs.

3.5: Antimicrobial activities:

The inhibitory effect of 25 µg, 50 µg, and 75 µg doses of CuO and CoO nanoparticles on bacterial growth on agar plates is illustrated in **Table 1**. An enhancement in the antibacterial action was observed with an increase in the concentration of CuO and CoO nanoparticles. The respiration mechanism that takes place at the bacterial cell membrane causes nanoparticles to dehydrogenate once they adsorb on the bacterial cell. The bacteria had already deactivated their enzymes before reacting with the nanoparticles, which led to the production of hydrogen peroxide, which kills the bacteria [27].

4. Conclusions:

Copper and cobalt oxide nanoparticles were fabricated using *moringa oleifera* fruit extracts through an environmentally friendly method that minimally used chemicals. Initial findings supporting the creation of CuO-NPs and CoO-NPs were conducted using FTIR spectra. The peaks in the FTIR spectra support the existence of M-O bond and indicate the involvement of *moringa oleifera* fruit extract in the nanoparticle formation. Analyzed the morphological, compositional, and optical characteristics of synthesized CuO-NPs and CoO-NPs nanoparticles using FE-SEM, EDAX, and UV-visible spectroscopy. The XRD analysis reveals the presence of a face-centered cubic phase of CuO-NPs and CoO-NPs with an average crystallographic size of 16 nm. The band gap of CuO-NPs and CoO-NPs nanoparticles was determined using a Tauc plot method and found to be 3.8eV. This rapid, uncomplicated, and environmentally friendly synthetic method is highly appealing and efficient for producing nano-scale metal oxide particles that are used in various industrial fields.

References:

1. J. Jeevanandam, A. Barhoum, Y. S. Chan, A. Dufresne and M. K. Danquah, Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations, Beilstein J Nanotechnol, 9 (2018), 1050-1074.
2. H. Hou, G. Shao, W. Yang and Wai-Yeung Wong, One-dimensional, mesoporous inorganic nanostructures and their applications in energy, sensor, catalysis and adsorption, Prog mater Sci, 113 (2020) 100671. http://doi.org/10.1016/j.pmatsci. 2020.100671.
3. N. Baig, I. Kammakakam and W. Falath, Nanomaterials: A Review of Synthesis Methods, Properties, Recent Progress, and Challenges, Mater Adv, 2(6) (2021)1821- 1871. http://doi.org/10.1039/D0MA00807A.
4. K. Banerjee and H. Madhyastha, Immunology and Nanotechnology: Effects and Affects. In: V. K. Arivarasan, K. Loganathan, P. Janarthanan(eds), Nanotechnology in the Life Science. Springer, 2021. http://doi.org/10.1007/978-3-030-61021-02.
5. Z. Shamasi, A. Es-haghi, M. F. Taghavizadeh Yazdi, M. S. Amiri and M. Homayouni-Tabrizi, Role of Rubia tinctorum in the synthesis of Zinc oxide nanoparticles and apoptosis induction in breast cancer cell line, Nanomed J, 8(1) (2021), 65-72. http://doi.org/10.22038/nmj.2021.08.07.
6. A. Muthuvel, M. Jothibas and C. Manoharan, Synthesis of copper oxide nanoparticles by chemical and biogenic methods: photocatalytic degradation and in vitro antioxidant activity, Nanotechnol Environ Eng, 5(2) (2020). http://doi.org/10. 1007/s41204-020-00078-w
7. S. Rajesh kumar and P. Naik, Synthesis and biomedical applications of Cerium oxide nanoparticles–A Review, Biotechnol Rep, 17 (2018) 1-5. http://doi.org/10.1016/ j.btre.2017.11.008.
8. G. Song, N. Cheng, J. Zhang, H. Huang, Y. Yuan, X. He, Y. Luo and K. Huang, Nanoscale Cerium Oxide: Synthesis, Biocatalytic, Mechanism and Applications, Catalysts, 11(9) (2021), 1-15. http://doi.org/10.3390/catal11091123.
9. F. Charbgoo, M. Ramezani and M. Darroudi, Bio-sensing Applications of Cerium Oxide Nanoparticles: Advantages and Disadvantages, Biosens & Bioelectron, 96 (2017), 33-43. http://doi.org/10.1016/j.bios.2017.04.037.

10. C. Walkey, S. Das and S. Seal, Catalytic properties and biomedical applications of cerium oxide nanoparticles, Environ Sci, 2(1) (2015), 33-53. http://doi.org/10.1039/ C4EN00138A.
11. Ayman A. Ali, Sahar R. EL-Sayed, Sayed A. Shama, Talaat Y. Mohamed and Alaa S. Amin, Fabrication and characterization of cerium oxide nanoparticles for the removal of naphthol green B dye, DesalinWater Treat, 204 (2020), 124-135. http://doi.org/10. 5004/dwt.202026245.
12. M. Shaterian, A. Rezvani and A.R. Abbasian, Controlled synthesis and self-assembly of ZnFe2O4 nanoparticles into microsphere by solvothermal method, Mater Res Express, 6(12) (2020), 1250. http://doi.org/10.1088/2053-1591/ab65e0.
13. H. Balavi, S. Samadanian, M. Mehrabani-Zeinabad and M. Edrissi, Preparation and optimization of CeO2 nanoparticles and its application in photocatalytic degradation of Reactive Orange 16 dye, Powder Technol, 249 (2013), 549-555. http://doi.org/10. 1016/j.potec.2013.09.021.
14. M. Malamatari, A. Charisi, S. Malammataris, K. Kachrimanis and I. Nikolakais, Spray drying for the preparation of nanoparticles-based drug formulation as dry powders for inhalation, Processes, 8(7) 788 (2020), 1-27. http://doi.org/10.33390/ pr8070788.
15. S. Harini, A. Aswini, S. C. Kale, J. Narawane, J. Patel, S. Masurkar and S.s Ruikar, Microwave-assisted solvothermal Synthesis of Tungstan oxide Nanoparticles for microbial inhibition, Int J Curr Res Rev, 13(02) (2010), 76-69. http://doi.org/10/ 31782/ IJCRR.2021.13226.
16. D. B. Bharti and A. V. Bharati, Synthesis of ZnO nanoparticles using a hydrothermal method and a study its optical activity, Luminescence, 32(3) (2017), 317-320. http://doi.org/10.1002/bio.3180.
17. S. Tambat, S. Umale and S. Sontakke, Photocatalytic degradation of Milling Yellow dye using Sol-gel synthesized CeO2, Mater Res Bull.,76 (2016), 466-472. http://doi. morg /10.1016/J.MATERRESBULL.2016.01.010.
18. S. Pirtarighat, M. Ghannadnia and S. Baghshahi, Green synthesis of silver nanoparticles using the plant extract of Salvia spinosa grown in vitro and their antibacterial activity assessment, J Nanostruct Chem, 9 (2019), 1-9. http://doi.org/10 .1007/s40097-018-0291-4.
19. G. A. Naikoo, M. Mustaqeem, I. U. Hassan,T. Awan, F. Arshad, H. Salim and A. Qurashi, Bioinspired and green synthesis of nanoparticles from plant extracts with antiviral and antimicrobial properties: A critical review, J Saudi Chem Soc, 25(9) (2021), 101304. http://doi.org/10.1016/j.jscs.2021.101304.
20. Y. Kato and M. Suzuki, Synthesis of metal nanoparticles by Microorganisms, crystals, 10(7) (2020), 1-20. http://doi.org/10.3390/cryst10070589.
21. I. Ghiuta, C. Croitoru, J. Kost, R. Wenkert and D. Munteanu, Becteria mediated synthesis of silver and silver chloride nanoparticles and their antimicrobial activity, Appl Sci, 11(7) (2021), 3134. http://doi.org/10.3390/app11073134.
22. K. O Iwuozor, L. A. Ogunfowora and I. P. Oyekunle, Review on sugarcane-mediated nanoparticles synthesis: a green approach, Sugar Tech, (2021), 1-12. http://doi.org/10. 1007/s12355-021-01038-7.
23. D. Dutta, Mukherjee R, Patra M, et al. Green synthesized cerium oxide nanoparticle: a prospective drug against oxidative harm, Colloids Surf B Bio interfaces, 147 (2016), 45-53. http://doi.org/10.1016/j. colsurfb.2016.07.045.
24. Dizaj, Solmaz Maleki, Farzaneh Lotfipour, Mohammad Barzegar-Jalali, Mohammad Hossein Zarrintan, and Khosro Adibkia. "Antimicrobial activity of the metals and metal oxide nanoparticles." *Materials Science and Engineering: C* 44 (2014): 278-284.
25. Q. Maqbool, M. Nazar, S. Naz, T. Hussain, N. Jabeen, R. Kausar, S. Anwaar, F. Abbas and T. Jan, Antimicrobial potential of green synthesized CeO2 nanoparticles from Olea europaea leaf extract, Int J Nanomedicine, 11 (2016), 5015-5025. http://doi.org/10.2147/IJN. S113508.
26. A. Miri, M. Darruodi and M. Sarani, Biosynthesis of cerium oxide nanoparticles and its cytotoxicity survey against colon cancer cell line, Appl Organometal Chem, (2019), 1-7. http://doi.org/10.1002/aoc.5308.
27. Stanić, Vojislav, and Sladjana B. Tanasković. "Antibacterial activity of metal oxide nanoparticles." In *Nanotoxicity*, pp. 241-274. Elsevier, 2020.