Shaukat et al *LGU. J. Life Sci.* 2021

LGU Journal of
LIFE SCIENCES

LGU Society of Life Sciences

Research Article
Vol 5 Issue 1 Jan-March 2021

LGU J. Life. Sci
ISSN 2519-9404
eISSN 2521-0130

Synthesis, Characterization, Photocatalytic and Antimicrobial Activities of Copper Doped Silver and Nickel Oxide Nanoparticles

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ABSTRACT: *The copper-doped silver and nickel oxide nanoparticles were prepared by the co-precipitation method in which the silver oxide (Ag_2O) and nickel oxide (NiO) nanoparticles are doped with copper in 4:1 in the presence of sodium dodecyl sulfate (SDS), a surfactant. Then various analytical studies were carried out by using X-ray diffraction (XRD) and Diffuse reflectance spectroscopy (DRS). The XRD analysis revealed the crystalline structure and the size of nanoparticles was determined by using Scherrer's formula. The XRD data showed the effect of doping on crystallinity and size. It was found that the size of nanoparticles was reduced without any change in crystallinity after doping. DRS results showed that when silver oxide and nickel oxide nanoparticles were doped with copper oxide nanoparticles, the energy band gap was shifted to a lesser value, i.e., from 1.50 to 1.17 eV for Ag_2O and from 2.29 to 2.08 eV for NiO, respectively. The photocatalytic degradation of methylene blue (MB) and eriochrome black-T (EBT) by nanoparticles was monitored by UV-Vis spectroscopy. The antimicrobial activity of the synthesized nanoparticles was checked by using well diffusion assay and it was found that doped nanoparticles were more active than the undoped ones.*

Keywords: *Nanoparticles, Doping, XRD, DRS, Antimicrobial activities, Photocatalytic degradation, co-precipitation method*

INTRODUCTION

Different terminologies have been used for "nanoparticle" by various regulatory bodies both nationally and internationally. Nanoparticles (Nps) are those which have at least one dimension in 1-100 nm range (Miernicki et al., 2019). Nps are not new in nature or science. Several characterization techniques were developed to understand the phenomena and properties of matter on reducing their size from bulk to nanoscale. Many of the biological processes occurring at the nanoscale have revolutionary effects and the researchers are able to use the particles at the nanoscale and to enhance their work in different fields such as imaging, printing, catalysis, material science, computing and in medicine (Dhand et al., 2016). Nanotechnology is concerned with the dimensions of Nps. Nanotechnologist also uses the physical, chemical, biological and optical features that occur naturally at the nanoscale. There is a dramatic change in properties of matter at nanoscale in comparison with the bulk. At the nanoscale, the quantum effect deals with the behaviour and characteristics features of matter (Zhang et al., 2010). Different metals and metal oxide based Nps have been used as catalysts, absorption, sensors, antimicrobial and reducing agents due to their unique properties (Nair et al., 2011). They have high surface to volume ratio so that they have very fast reaction kinetics and increased sorption ability. There are some drawbacks of NPs regarding their applications in real life e. g. high pressure drop in flow through system; they don't have specificity for reaction in complex system. They also have weak mechanical strength (He et al., 2016).

The size of particles, surface characteristics, properties, degree of toxicity, biodegradability and biocompatibility depends on the method of preparation of Nps (Abdussalam-Mohammed, 2020).

Doping has revolutionized in the industry of semiconductors (Yang et al., 2020). There is always a challenge for the introduction of dopants into the pure Nps. For the enhancement of properties of doped Nps various kinds of interactions are feasible. These properties come from spin exchange interactions between substrate and dopant, stable isolated electronic state and from structural defects (Bharat et al., 2019).

In the present work, we synthesized the copper-doped silver oxide and nickel oxide Nps by using a simple method known as the co-precipitation method. The photocatalytic activity of the nanoparticles was elaborated by degradation of methylene blue (MB) and eriochrome black-T (EBT). The biological potential was investigated by screening Nps against various species bacteria and fungus.

MATERIALS AND METHOD

Materials

All the precursors like $AgNO_3$, $Cu(NO_3)_2$, $CuCl_2$, $NiCl_2.6H_2O$ and NaOH employed in the current study were

obtained from Sigma-Aldrich. Sodium dodecyl sulfate (SDS) and Organic dyes (MB and EBT) were purchased from Across Organics. Distilled water was obtained from the, research lab of UMT, Lahore. All these chemicals were obtained in the form of highest purity. The crystal structure of pure and doped Nps was studied by Bruker, D8/Germany X-ray diffractometer using Cu-Kα(1.5406 Å) emissions with K = 0.9. UV-Visible/NIR spectrometer (Perkin Elmer, Lambda 950/UK) was used to obtain absorbance, reflectance and transmittance up to 3300 nm.

Synthesis of metal oxide nanoparticles

A co-precipitation method is used to synthesize metal oxide nanoparticles which is very simple and easy. Firstly, 0.1 M solution of surfactant was prepared by dissolving 2.8 g of SDS in 100 mL of distilled water. The solution was continuously stirred for 20 minutes at a temperature of 60-70 ^{o}C. Then 2 g of metal salts ($AgNO_3$, $Cu(NO_3)_2$, $CuCl_2$, $NiCl_2.6H_2O$) was added separately to the above solution and the resultant mixture was sonicated for 30 minutes. Finally a 5 M solution of sodium hydroxide (NaOH) was added drop wise until a pH of 10-11 was attained. The mixture was stirred at room temperature for 3-5 hours until the precipitates of Ag_2O, CuO and NiO in nanoscale range were appeared, respectively. These nanoparticles were filtered and washed with distilled water for several times. The collected nanoparticles were dried at 85-100 °C for 3 hours. At the end the obtained nanoparticles were annealed at 500-600 ^{o}C for 30 minutes to remove the organic residue if any.

Synthesis of Doped Nanoparticles

For the preparation of doped Nps, $AgNO_3$ and $Cu(NO_3)_2$ and $CuCl_2$ & $NiCl_2.6H_2O$ were taken separately in 4:1 ratio in 100 mL of SDS solution. The obtained mixture was ultrasonicated at room temperature for dispersion for 1 hour. The fine Nps were formed in basic media, for this purpose 5M NaOH solution was added drop wise to adjust pH up to 11-12. The resulting suspension was stirred at room temperature for 30 minutes. The precipitates of doped nanoparticles were filtered and washed with distilled water repeatedly to remove excess base. After that, the resulting nanoparticles were air dried and then calcined at high temperature to remove organic residue at 500-600 ^{o}C for 30 minutes.

RESULTS AND DISCUSSION

Powder X-Ray Diffraction Studies

Fig. 1(a-d) showed the XRD spectra of pure CuO, Ag_2O and NiO Nps before and after doping. The results of XRD confirmed the crystallinity, size and purity of metal Nps and also give some information about the effect of doping on the shape and size of the Nps. It is clear from the XRD pattern that as the dopants such as copper are introduced in the silver

and nickel, the diffraction peaks get broadened and the particle size is further reduced. From peaks it is also revealed that when Cu ion is substituted into the metal oxide lattice. The overall structure of the NiO/Ag_2O Nps will remain the same as the Cu ions replaces Ni/Ag substitutionally in the lattice, instead of getting into the void spaces (Lanje et al., 2010).

Debye-Scherrer's formula was used to calculate the average crystallite size of pure CuO, NiO, Ag_2O and copper doped NiO/Ag_2O nanoparticles and presented in the Table 1. From data it was found that the doped metal oxide NPs seemed better in terms of precise crystallite size, than the undoped ones.

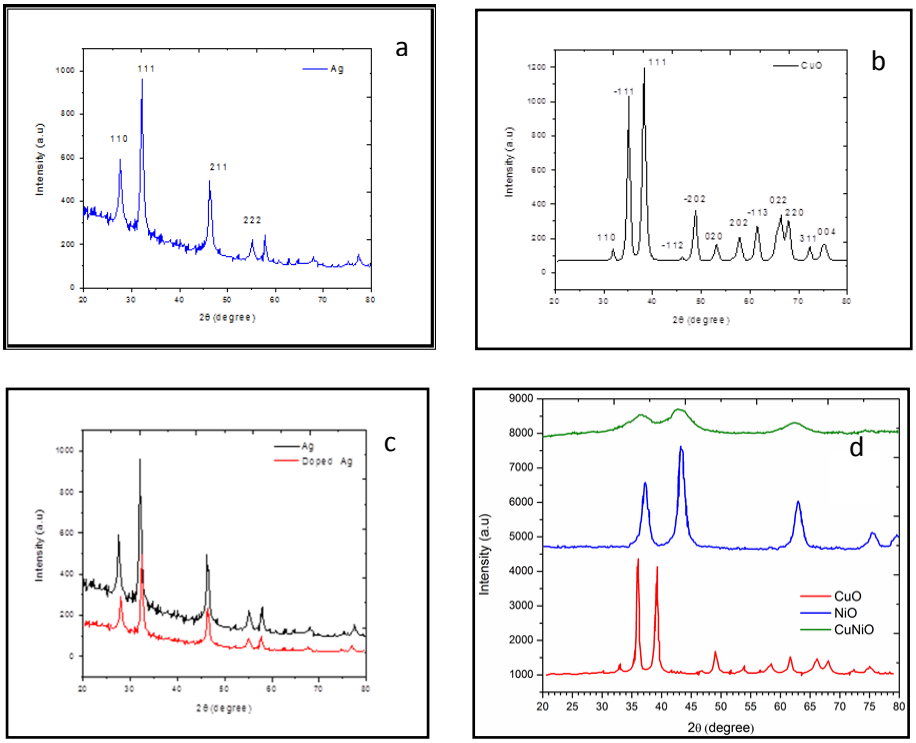


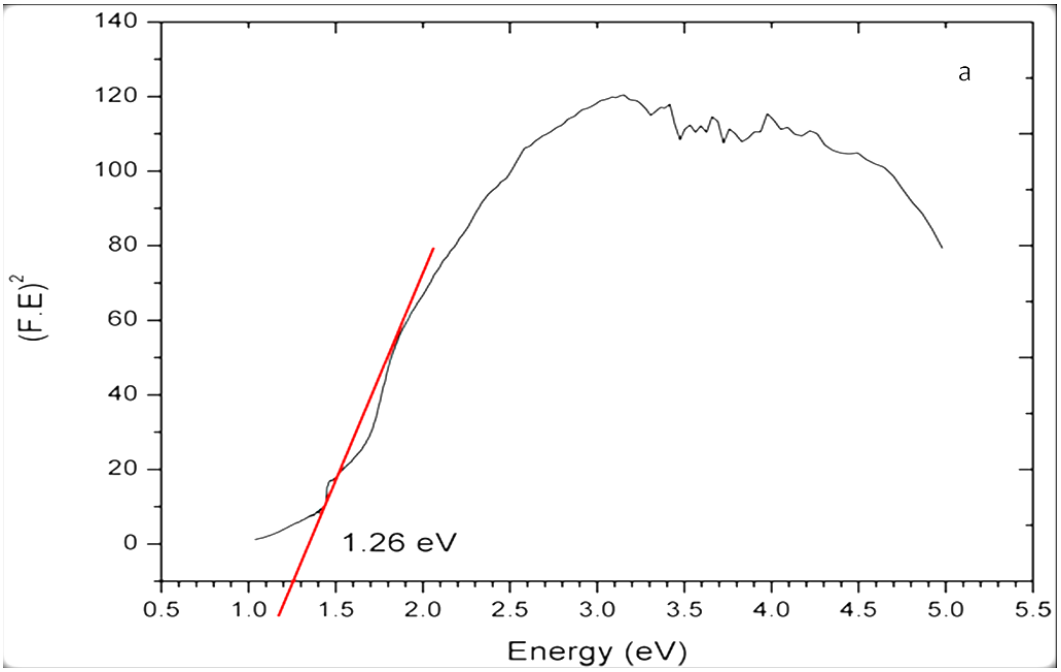
Fig. 1: Powder XRD spectra of a) Ag_2O nanoparticles (Top left) b) CuO nanoparticles (Top right) c) Cu doped Ag_2O nanoparticles (Bottom left) d) Combined spectra of CuO, NiO and Cu doped NiO nanoparticles (Bottom right)

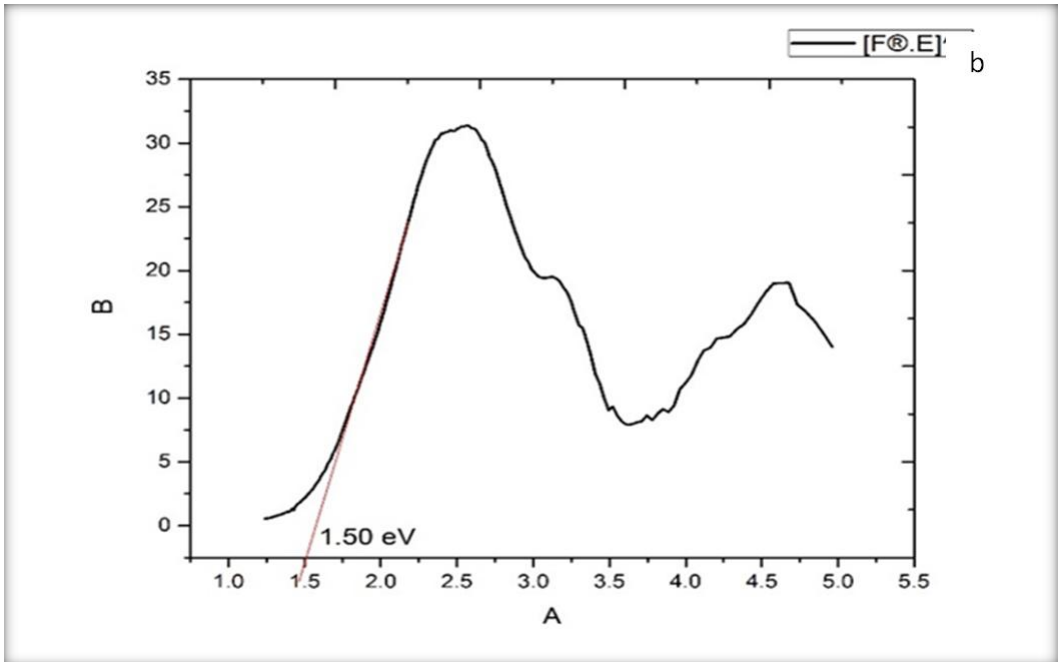
Table 1: Average particle size of the nanoparticles

Serial No	Nanoparticles	Particle size (nm)
1	CuO	11.3
2	NiO	9.1
3	Ag_2O	10.5
4	Cu doped NiO	2.4
5	Cu doped Ag_2O	5.6

Diffuse reflectance studies

DRS spectra (Fig. 2 (a-d)) showed that whenever Ag_2O/NiO nanoparticles were doped with CuO the band gap of pure metal nanoparticles was reduced. DRS spectra showed that the pure Ag_2O Nps have the band gap of 1.50 eV as demonstrated by tangent. On doping with CuO nanoparticles the band gap was decreased to 1.17 eV. Same is the case for NiO nanoparticles in which value of band gap was decreased from 2.29 to 2.08 eV on doping with CuO nanoparticles (Bashir et al., 2019).

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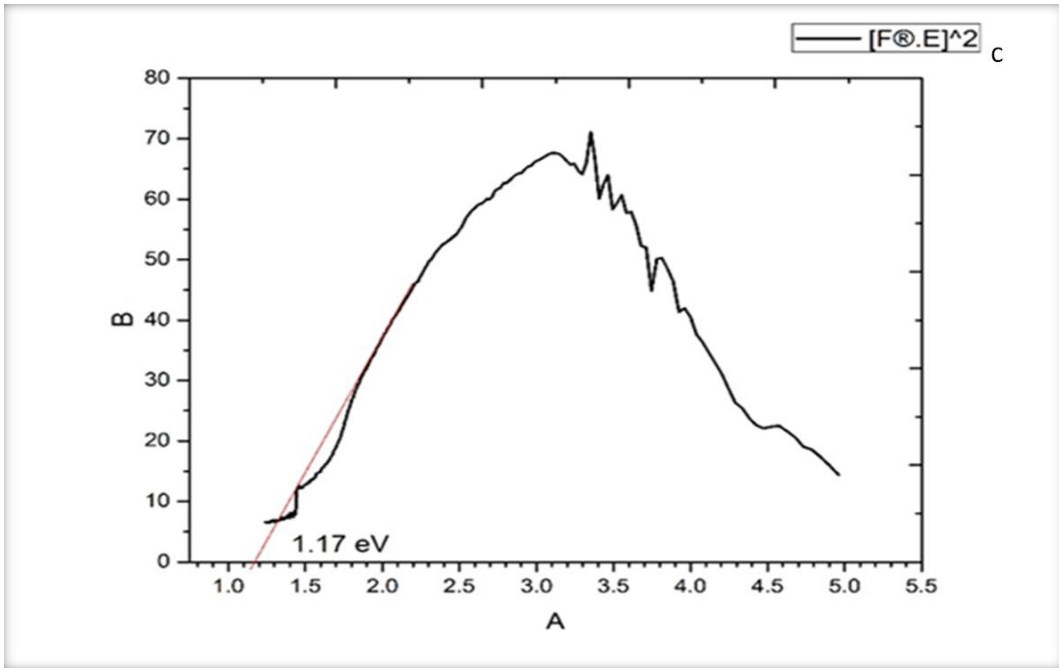
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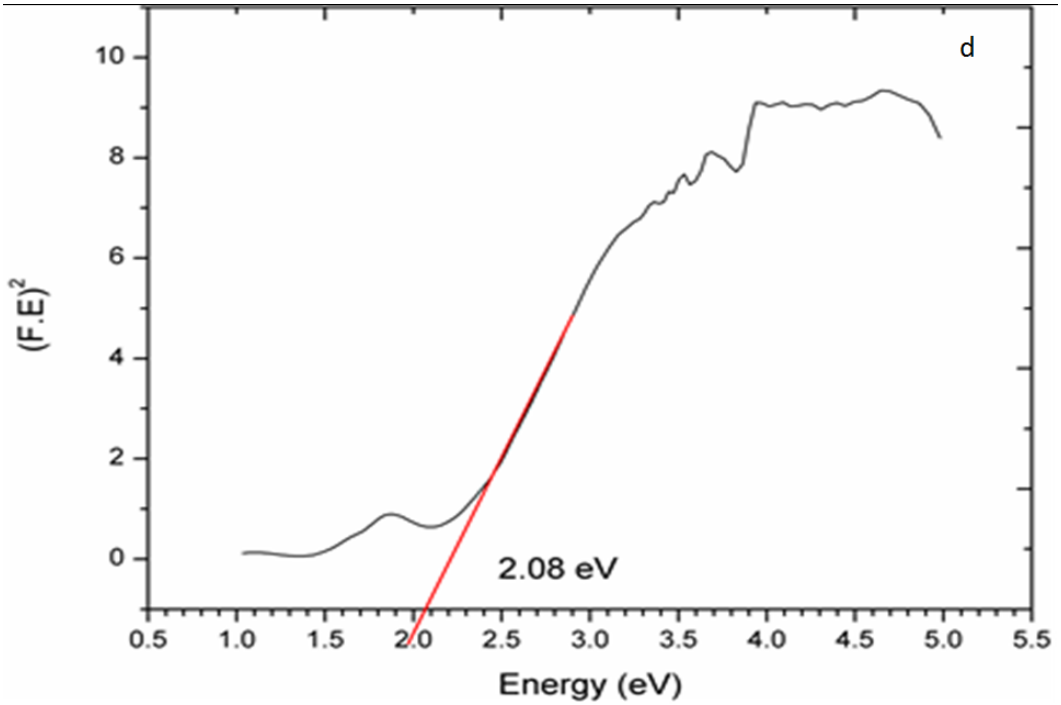

Fig. 2: DRS spectra of a) CuO nanoparticles b) Ag_2O nanoparticles c) Cu doped Ag_2O nanoparticles d) Cu doped NiO nanoparticles

Antimicrobial activity of nanoparticles

Well diffusion method is chosen to determine the antimicrobial activity of silver oxide (Ag_2O), copper oxide (CuO), nickel oxide (NiO), and copper doped Ag_2O/NiO Nps against Gram-positive bacteria including *Streptococcus mutans* and *Acinetobacter baumanii* and Gram-negative bacteria including *Pseudomonas aeruginosa*, *Escherichia coli*, and *Klebsiella pneumonia* and against a fungal specie *Candida albicans.*
For this purpose, microbes were revitalized on their respective media (Fig. 3).

(a) *Pseudomonas aeruginosa* was invigorate on nutrient media

(b) *Escherichia coli* on MacConkey's agar

(c) *Candida albicans* on chocolate agar

(d) *Streptococcus mutans* on TYCSB (tryptone yeast cysteine sucrose bacitracin) agar

(e) *Acinetobacter baumanii* on MacConkey's agar

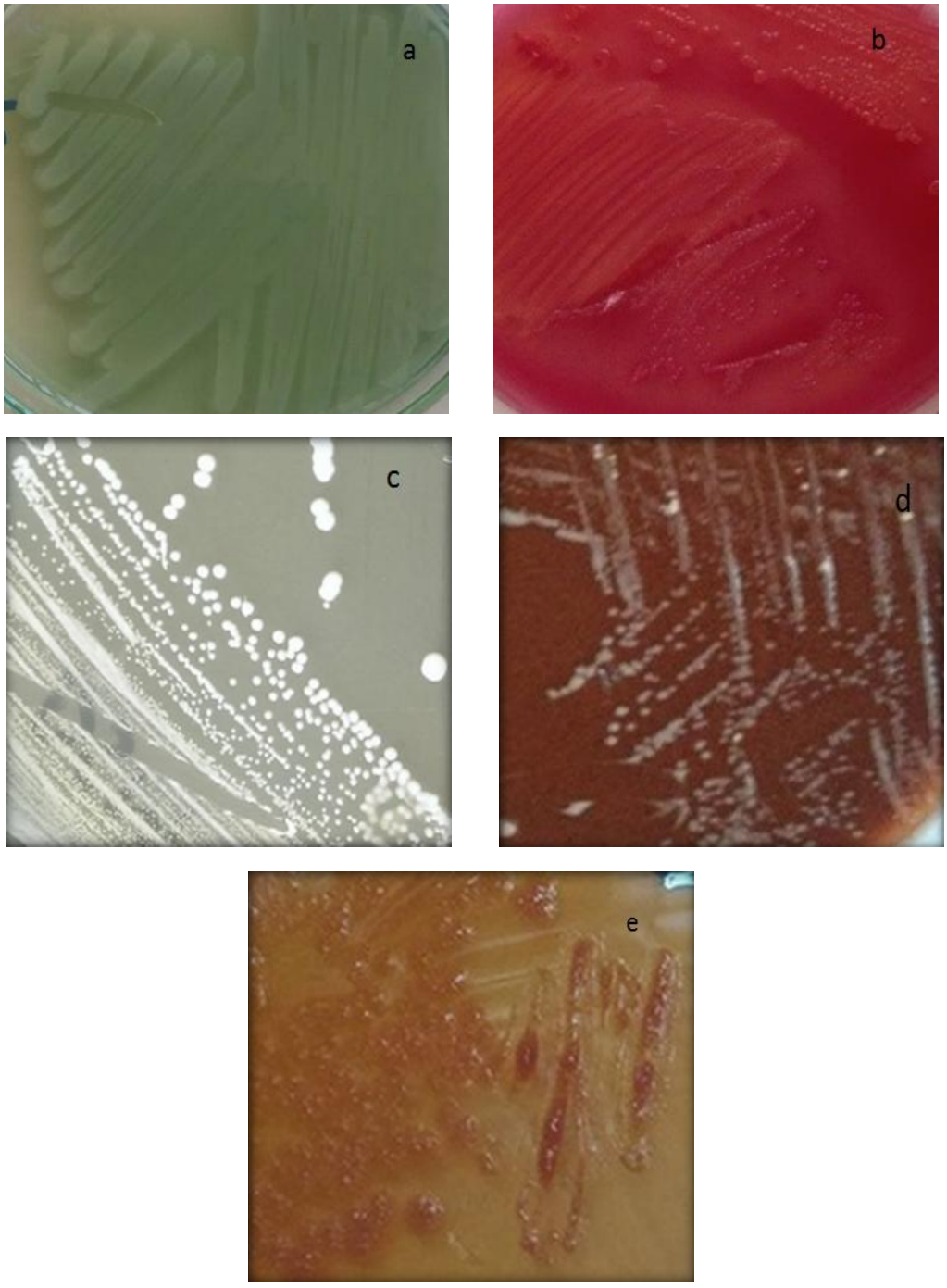

Fig. 3: Growth of microbes on different agar media: (a) nutrient agar media (b) MacConkey's agar (c) Chocolate agar (d) TYCSB agar (e) MacConkey's agar

Well diffusion assay

To evaluate the antimicrobial activity, a well diffusion assay was chosen due to its simplicity. Two concentrations of nanoparticles 200 µg/mL and 500 µg/mL were prepared for all samples. Nps were transferred into shafts and incubated at 37 ^{o}C for 24 hours to check the activity of microbes against nanoparticles (Kumar et al., 2017). The Fig. 4 (a-f) exhibited the zone of inhibition of prepared NPs against *Escherichia coli*, *Pseudomonas aeruginosa*, *Acinetobacter baumanii* and *Candida albicans.* Overall data of the antimicrobial potential shown by nanoparticles is summarized in Table 2 and in the form of histogram in Fig. 5.

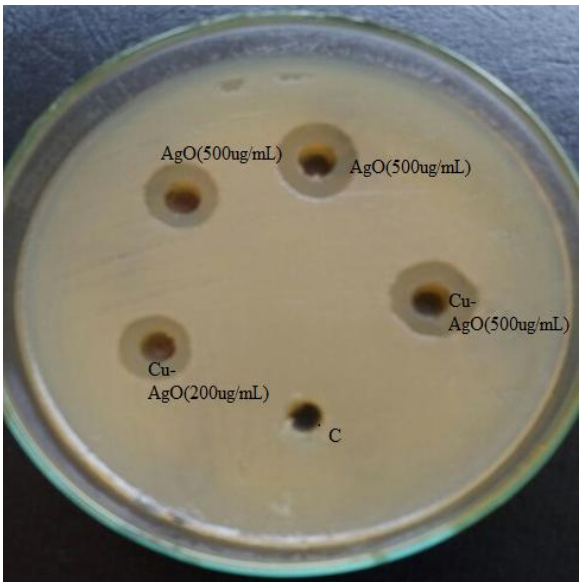

Fig. 4(a): Zone of inhibition of silver oxide, copper doped silver oxide NPs against *Escherichia coli*

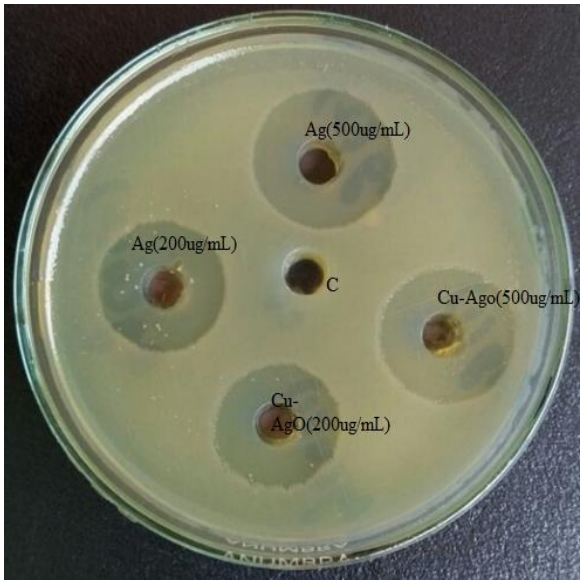

Fig. 4 (b): Zones of inhibition of silver oxide and copper doped silver oxide NPs against *Pseudomonas aeruginosa*

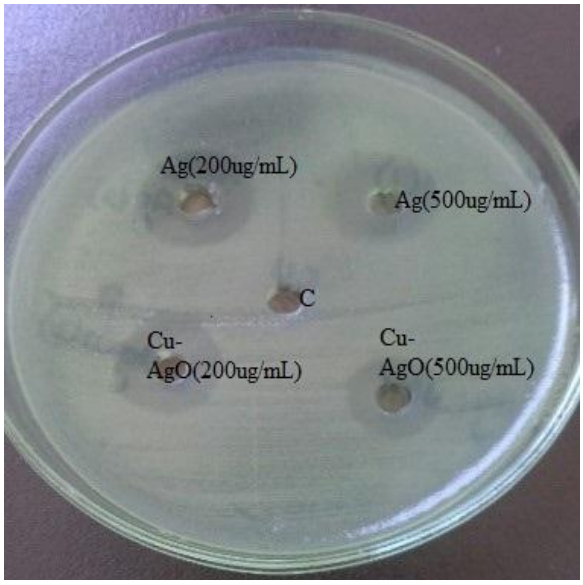

Fig. 4 (c): Zone of inhibition of silver oxide and copper doped silver oxide nanoparticles against *Pseudomonas aeruginosa*

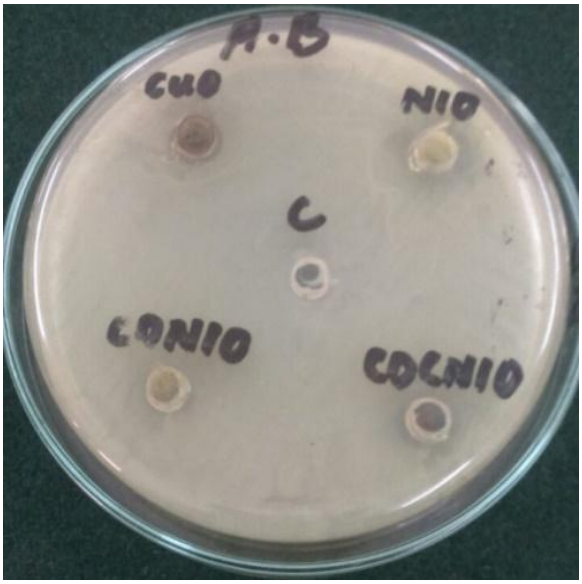

Fig. 4(d): Zone of inhibition of nickel oxide, copper oxide and copper doped nickel oxide NPs against *Pseudomonas aeruginosa*

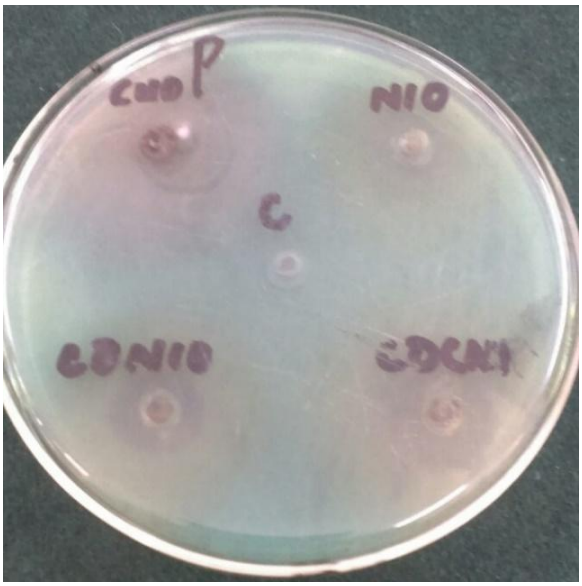

Fig. 4(e): Zone of inhibition of nickel oxide, copper oxide and copper doped nickel oxide NPs against *Acinetobacter baumanii*

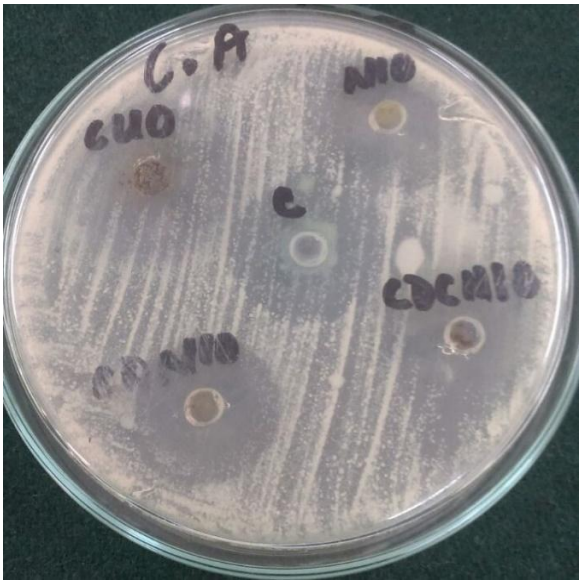

Fig. 4(f): Zone of inhibition of nickel oxide, copper oxide and copper doped nickel oxide NPs against Candida albicans

Table 2: Zone of inhibition (mm) of various microorganisms against copper oxide (CuO), silver oxide (Ag_2O), nickel oxide (NiO) and copper doped NiO/Ag_2O Nps with concentrations of 200 µg/mL and 500 µg/mL. (NZ= no zone of inhibition).

Indicator microbes	Type of microbe	Standard	Zone of inhibition (mm)	Antimicrobial activity of nanoparticles									
				CuO		Ag_2O		NiO		Cu-NiO		Cu-Ag_2O	
				Concentration (µg/mL)									
				200	500	200	500	200	500	200	500	200	500
				Zones of inhibitions (mm)									
K. pneumoniae	Gram – ve	Ampicillin	12	15	18	16	18	8	10	10	12	13	15
E. coli			19	10	15	15	17	10	12	14	16	15	18
P. aeruginosa			12	12	13	19	20	16	18	14	16	18	20
Acinetobacter	Gram + ve		14	5	8	14	16	12	14	8	10	11	15
S. mutans			12	6	8	15	16	9	11	7	9	14	16
C. albicans	Fungus	Fluconazole	10	10	15	17	20	19	22	21	23	23	25

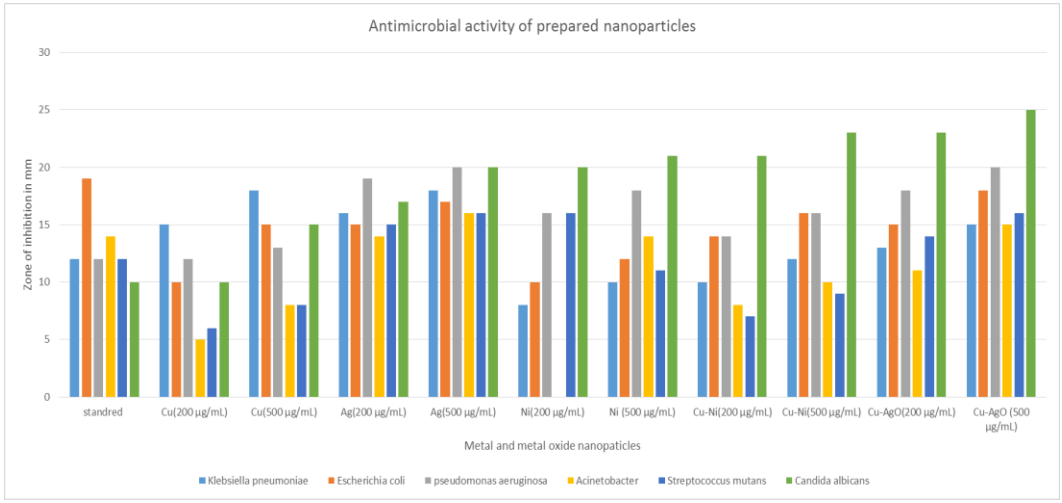

Fig. 5: Graphical illustration of antimicrobial activity of CuO, NiO, Ag_2O, Cu-NiO and Cu-Ag_2O Nps with different concentrations against *Klebsiella pneumonia, Escherichia coli, Pseudomonas aeruginosa, Acinetobacter, Streptococcus mutans,* and *Candida albicans*

The results indicated that copper oxide, silver oxide and nickel oxide Nps have antimicrobial activity against gram-negative bacteria such as *Pseudomonas aeruginosa*, *Escherichia coli*, and *Klebsiella pneumonia* and gram-positive bacteria such as *Streptococcus mutans* and *Acinetobacter baumanii* and fungus such as *Candida albicans.* They have larger regions of inhibition on higher concentration e.g., 500 µg/ml and these can be efficiently utilized as the antifungal agent (Chauhan et al., 2020).

There are various systems used to adjust the properties of metals for example doping and alloying. The doping of metals is an alluring method to change the qualities of metals. The doping of different metal Nps has been accounted for and has wide applications in different fields. The fundamental extent of the current investigation is to assess and analyze the antimicrobial action of copper oxide and silver oxide Nps with Cu doped Ag_2O/NiO Nps. The Cu doped Ag_2O Nps and Cu doped NiO Nps indicated vast antimicrobial action against microbes and parasites (Rana and Singh, 2016). Copper doped silver oxide nanoparticles showed more inhibition against *Candida albicans*. Hence it can be concluded that the doped nanoparticles are more significant against fungus as compared to bacteria (Vijayaprasath et al., 2016).

The current study demonstrates that metal Nps such as CuO, Ag_2O, NiO, Cu doped Ag_2O, and Cu doped NiO can have potential to control the antibiotic resistance issue. The precise mechanism behind the antimicrobial activity of metal is unidentified (Prabhu and Poulose, 2012).

The purposed mechanism for the antimicrobial activity of metal oxide nanoparticle is that the metal nanoparticles generate metallic ions and these ions change the permeability and destroy membrane proteins. By this, the cell membrane is damaged and cell contents are leaked out. So, by the dissolution of metal ion and free radicals, the transport of electrons through the microbial cell is stopped and cell death occurs. Due to the significant antimicrobial behavior of the CuO, NiO, and Ag_2O Nps, these are used in the formation of bone cement, sterilization and coating for devices.

Photocatalytic activity

The photocatalytic ability of Cu doped NiO Nps was compared with pure NiO Nps for the degradation of methylene blue (MB) and eriochrome black-T (EBT).

Photocatalytic Degradation of Methylene Blue

Fig. 6 and 7 showed the behavior of UV-Visible absorption spectrum of an aqueous solution of 22.4 micromolar MB against photo catalytic behavior of prepared nanoparticles. The spectra were recoded after different time intervals to check the effect on the degradation behavior of MB. The adsorption peak of MB at 665 nm is characteristic and is measured as a function of light. It can be seen that the adsorption peak diminishes sharply after 30 minutes and completely disappears after 90 minutes by using Cu doped NiO Nps. However, adsorption of the peak using pure NiO shows less reduction intensity than Cu doped NiO catalyst (Chauhan et al., 2020) (Hernández-Gordillo and González 2015; Noua et al., 2019)

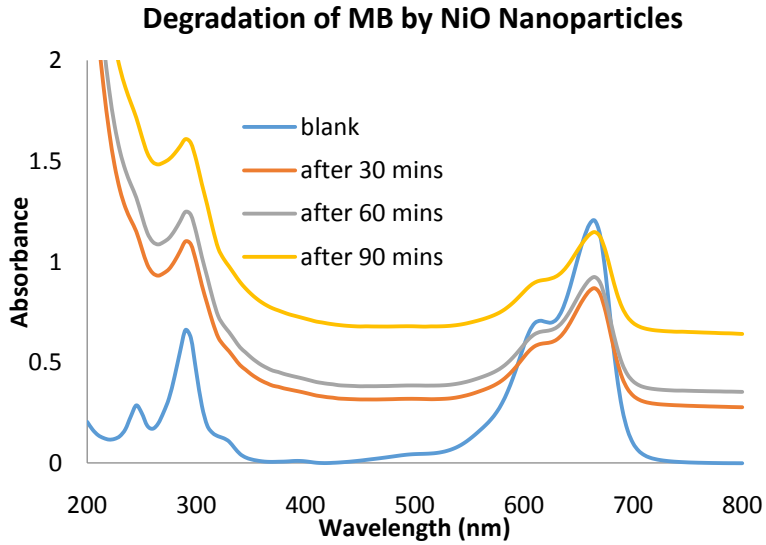

Fig. 6: Degradation of MB by NiO Nps

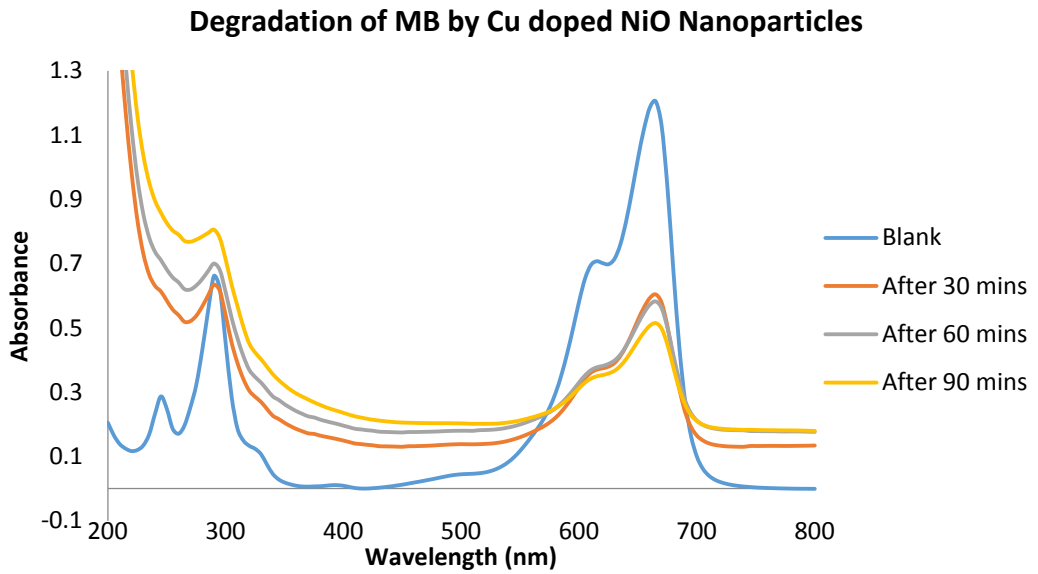

Fig. 7: Degradation of MB by Cu doped NiO Nps

Photocatalytic degradation of eriochrome black-T

Fig. 8 and 9 showed the photo catalytic degradation of EBT using pure NiO and Cu doped NiO photocatalysts respectively. It can be observed from the chart that after different intervals of time the peak height decreases very sharply using Cu doped NiO as photocatalyst compared to pure NiO. The spectra was taken after the intervals of three minutes (Jongnavakit et al., 2012).

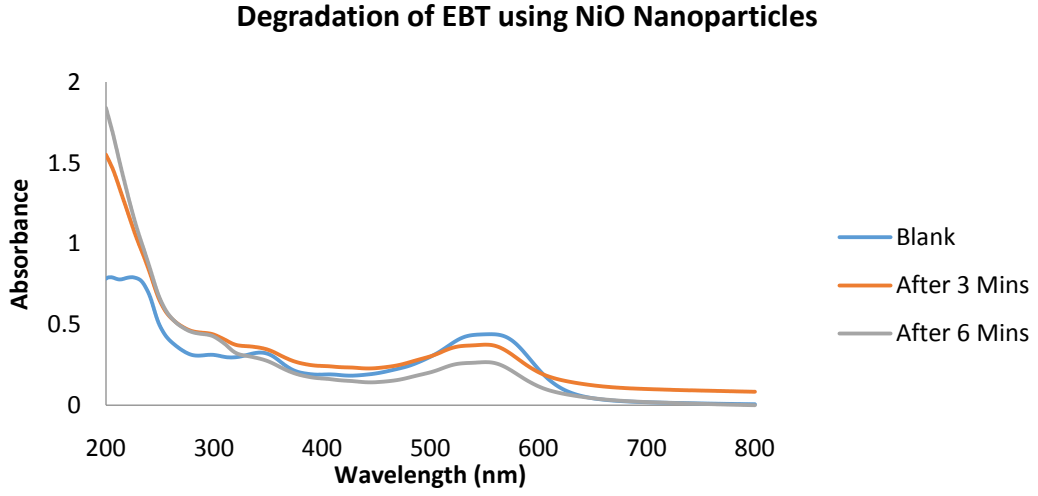

Fig. 8: Degradation of EBT by NiO Nps

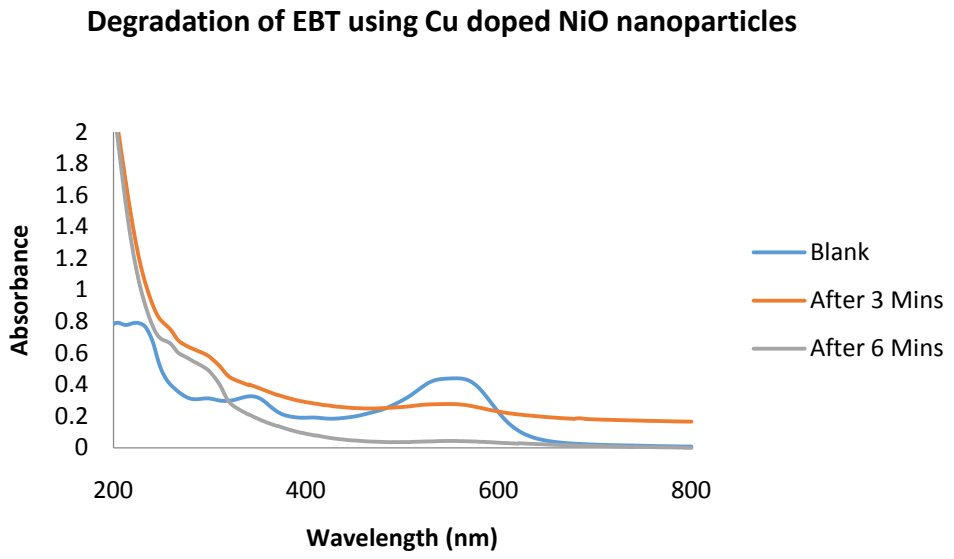

Fig. 9: Degradation of EBT by Cu doped NiO Nps

CONCLUSION

The pure and doped metal oxide nanoparticles were prepared by co-precipitation method. The XRD and DRS spectra confirm the doping of Cu with Ag_2O and NiO Nps. The antimicrobial and photocatalytic activities of prepared nanoparticles were also investigated. The studies showed that in comparison to pure NiO Nps, Cu doped NiO Nps exhibited increased photocatalytic activity towards the degradation of methylene blue (MB) and eriochrome black-T (EBT) dyes under visible light. If we see the zone of inhibition of metal oxide and doped Nps it is clear that the doped nanoparticles are more effective than pure Nps.

ACKNOWLEDGEMENT

This work was supported by the Higher Education Commission under Indigenous 5000 Program [PIN NO. 106-1087-ps6-016].

CONFLICT OF INTEREST STATEMENT

It is declared that there is no potential conflict of interest in the current study.

REFERENCES

1. Abdussalam-Mohammed, W (2020). Comparison of Chemical and Biological Properties of Metal Nanoparticles (Au, Ag), with Metal Oxide Nanoparticles (ZnO-NPs) and their Applications. Ad. J. Chem. Sec. A 3(2): 192-210.

2. Bashir A, Lew JH, Shukla S, Gupta D, Baikie T, Chakraborty S, Patidar R, Bruno A, Mhaisalkar S, Akhter Z (2019).

Cu-doped nickel oxide interface layer with nanoscale thickness for efficient and highly stable printable carbon-based perovskite solar cell. Sol. Energy. 182: 225-236.

3. Bharat TC, Mondal S, Gupta HS, Singh PK, Das AK (2019). Synthesis of doped zinc oxide nanoparticles: a review. Mat. Today: Proceed. 11: 767-775.

4. Chauhan A, Verma R, Kumari S, Sharma A, Shandilya P, Li X, Batoo KM, Imran A, Kulshrestha S, Kumar R (2020). Photocatalytic dye degradation and antimicrobial activities of Pure and Ag-doped ZnO using Cannabis sativa leaf extract. Scient. Rep. 10(1): 1-16.

5. Dhand V, Soumya L, Bharadwaj S, Chakra S, Bhatt D, Sreedhar B (2016). Green synthesis of silver nanoparticles using Coffea arabica seed extract and its antibacterial activity. Mat. Sci. Eng. 58: 36-43.

6. He L, Weniger F, Neumann H, Beller M (2016). Synthesis, characterization, and application of metal nanoparticles supported on nitrogen-doped carbon: catalysis beyond electrochemistry. Angew. Chem. Int. Ed. 55(41): 12582-12594.

7. Hernandez-Gordillo A, Gonzalez VR (2015). Silver nanoparticles loaded on Cu-doped TiO2 for the effective reduction of nitro-aromatic contaminants. Chem. Eng. J. 261: 53-59.

8. Jongnavakit P, Amornpitoksuk P, Suwanboon S, Ndiege N (2012). Preparation and photocatalytic activity of Cu-doped ZnO thin films prepared by the sol–gel method. Appl. Surf. Sci. 258(20): 8192-8198.

9. Kumar V, Prakash J, Singh JP, Chae KH, Swart C, Ntwaeaborwa OM, Swart HC, Dutta V (2017). Role of silver doping on the defects related photoluminescence and antibacterial behaviour of zinc oxide nanoparticles. Colloid. Surf. B. Biointerf. 159: 191-199.

10. Lanje AS, Sharma SJ, Pode RB, Ningthoujam RS (2010). Synthesis and optical characterization of copper oxide nanoparticles. Adv. Appl. Sci. Res. 1(2): 36-40.

11. Miernicki M, Hofmann T, Eisenberger I, von der Kammer F, Praetorius A (2019). Legal and practical challenges in classifying nanomaterials according to regulatory definitions Nat. nanotec. 14(3): 208-216.

12. Nair MG, Nirmala M, Rekha K, Anukaliani A (2011). Structural, optical, photo catalytic and antibacterial activity of ZnO and Co doped ZnO nanoparticles. Mater. Lett. 65(12): 1797-1800.

13. Noua A, Farh H, Guemini R, Zaoui O, Ounis TD, Houadsi H, Aounallah H (2019). Photocatalytic degradation of methylene blue by NiO thin films under solar light irradiation. J. Nano Res. Trans Tech Publ. 56: 152-157.

14. Prabhu S, Poulose EK (2012). Silver nanoparticles: mechanism of antimicrobial action, synthesis, medical applications, and toxicity effects. Int. Nano Lett. 2(1): 32.

15. Rana SB, Singh RP (2016). Investigation of structural, optical, magnetic properties and antibacterial activity of Ni-doped zinc oxide nanoparticles. J. Mat. Sci: Mat. Elect. 27(9): 9346-9355.

16. Vijayaprasath G, Murugan R, Palanisamy S, Prabhu NM, Mahalingam T, Hayakawa Y, Ravi G (2016). Role of nickel doping on structural, optical, magnetic properties and antibacterial activity of ZnO nanoparticles. Mater. Res. Bull. 76: 48-61.

17. Yang S, Yao J, Quan Y, Hu M, Su R, Gao M, Han D, Yang J (2020). Monitoring the charge-transfer process in a Nd-doped semiconductor based on photoluminescence and SERS technology. Light Sci. Appl. 9(1): 1-7.

18. Zhang QL, Yang ZM, Ding BJ, Lan XZ, Guo YJ (2010). Preparation of copper nanoparticles by chemical reduction method using potassium borohydride. Tran. Nonferrous Met. Soc. 20: s240-s244.