Design, Synthesis, and Characterization of First-Row Transition Metal Nano-Photocatalysts for Efficient Wastewater Treatment

Khalil Ur Rahman[1], Lala Rukh[1]

[1]*Superior university Lahore, Lahore, Pakistan*

Abstract

The existing research work is to examine the photoinduced dye degradation behavior of zinc oxide (ZnO) and copper oxide (CuO) nanoparticles (NPs). The plant extract and nitrate dihydrate salt of zinc and copper was used to synthesize ZnO and CuO NPs. The extract was of neem plant and acts as a stabilizing, capping and reducing agent. The synthesized NPs are analyzed using UV-Visible technique and the degradation efficiency of both NPs under direct sunlight was also studied. The maximum light absorbed by the NPs at specific wavelength was revealed using UV-Visible analyzer i.e., 350 and 222 nm for ZnO and CuO NPs, respectively. The degradation behavior of NPs was observed against dyes known as methylene blue (MB) and methyl orange (MO). The ZnO NPs degraded dyes to the extent of MB (93.93%) and MO (86.36%), while CuO degradation behavior was found to be MB (94.5%) and MO (93.45%). Overall, both of the NPs showed greater degradation efficiency against MB as compared to MO because MO forms stronger bonds with photocatalysts and is resistive to breakdown. The reusability study of NPs was also performed revealing that both, ZnO and CuO, NPs could be used for dye degradation up to three cycles even after every cycle NPs efficiency is reducing.

Keywords: *Azadirachta indica*; Nanoparticles (NPs); UV-Vis, Photocatalytic dye degradation

Introduction

The natural environment, which sustains life on Earth, is deteriorating at an unprecedented rate [1]. Human activities, coupled with climate change, are ravaging ecosystems, threatening biodiversity, and jeopardizing the well-being of future generations [2]. Air pollution from toxic emissions contaminates the air, causing respiratory diseases and premature deaths, while water pollution from chemical runoff and industrial waste harms aquatic life and human health [3]. Deforestation accelerates climate change, destroys habitats, and disrupts ecosystems, compromising soil fertility and threatening food production [4]. Climate change intensifies weather events, melts ice caps, and imperils global food security, economies, and human settlements [5]. Biodiversity loss undermines the delicate balance of nature, leading to species extinction, habitat destruction, and ecosystem disruption. The consequences of environmental degradation are far-reaching and devastating [6]. Health impacts include increased respiratory diseases, cancer, and mental health issues [7]. Food insecurity arises from decreased crop yields, water scarcity, and loss of arable land [8]. Economic consequences encompass damage to infrastructure, loss of productivity, and increased healthcare costs [9] while Social impacts include displacement, migration, and social unrest due to environmental degradation. Moreover, ecological collapse looms as a dire possibility, with irreversible damage to ecosystems leading to catastrophic consequences [10]. Transitioning to renewable energy, implementing sustainable practices, protecting and restoring ecosystems, enforcing environmental policies, and educating communities are crucial steps [11].

Nanoparticles play a crucial role in environmental cleaning due to their unique properties [12]. They have a high surface area-to-volume ratio, enabling enhanced reactivity and adsorption capacity [13]. Their small size allows penetration into porous materials for targeted pollution removal [14]. Nanoparticles also exhibit catalytic properties, facilitating chemical reactions for pollutant degradation [15]. Natural plant extracts offer an eco-friendly, cost-effective, and simple method for nanoparticle synthesis [16]. These extracts serve as stabilizing agents, preventing nanoparticle aggregation [17]. The benefits of plant-mediated nanoparticles are numerous. They provide environmental sustainability, low toxicity, high efficiency, cost-effectiveness,

and scalability [18]. By combining nanoparticles with natural plant extracts, we can develop innovative solutions for environmental cleaning and sustainable development. This approach ensures a healthier environment and a brighter future. Furthermore, plant-mediated nanoparticles have the potential to revolutionize wastewater treatment, soil remediation, and air purification, making them an essential tool in the fight against environmental pollution.

This study aims to develop a reproducible soft template-based method for synthesizing Neem extract-mediated nanoparticles (NPs) and correlate their dye degradation efficiency with size [17]. The goal is to address the long-standing reproducibility issue hindering NP applications in environmental remediation. By establishing a reliable size-efficiency relationship, this research will optimize NP-based technologies for efficient dye degradation and wastewater treatment.

Methodology

The reagents & chemicals used in research work are of systematic grade and sanitized. All the glassware was washed and rinsed with ethanol before its utilization. The synthesized NPs of ZnO & CuO goes through four different analytical techniques like UV-visible spectrophotometer, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Scanning electron microscopy (SEM). The NPs (1mg) and distilled water (10mg) were put in a beaker to prepare a solution (0.01%) after 10 min sonication or 2-3 min ultrasonication. Turn on UV-Visible spectrophotometer and then lamp warmed up till red light turned green. The cuvette was washed using distilled water and then cleaned with tissue paper before use. At first, for instrument calibration blank was run i.e., fill the cuvette with distilled water (a blank), placed in spectrophotometer in a way that transparent sides are in front of light and got the reading after lid is closed. Then do autozero and discard the blank in a waste bottle and now fill the $3/4^{th}$ part of cuvette with a sample of ZnO and CuO NPs. The absorbance was observed at 300-800 nm and wavelength/peak at maximum absorbance was obtained in the form of the graph.

Preparation of plant leaf extract

The leaves of *A. indica* (fresh neem) were collected from Gujrat, Pakistan and washed thoroughly using distilled water. The leaves were dried, finely chopped in hot air oven, and turned into a fine powder using mechanical grinder. The powder was stored in an airtight container. 10 g of neem dust and 100 ml of distilled water were taken in a beaker and stirred for an hour at about 60℃ to prepare neem powder solution [19]. Then the solution was cooled down at room temperature and filtered using normal filter paper to get the leafy materials as a residue. The filtrate then goes through Whatman filter paper No. 1 to collect a clear solution of light green color. The extract could be stored at 4℃ and was used as a reducing, stabilizing, and caping agent for the synthesis of ZnO and CuO nanocomposites.

Preparation of solutions for NPs synthesis

The two different solutions are prepared for NPs synthesis i.e., copper salt (copper nitrate dihydrate) and zinc salt (zinc nitrate dihydrate) solution.

Solution of zinc nitrate dihydrate

100 mM / 0.1 M solution of zinc salt was prepared by dissolving 2.3 g of zinc nitrate dihydrate in 100ml of distilled water. The solution was stirred continuously to ensure proper mixing of reagents. Molecular weight of zinc nitrate dihydrate [$Zn(NO_3)_2 \cdot 2H_2O$] = 225.4 g/mol

$$1\text{M} = \frac{1 \text{ mole}}{1 \text{ L}}$$

$$100 \text{ mM} = \frac{(100 \div 1000) \text{ mole}}{1 \text{ L}}$$

$$100 \text{ mM} = \frac{0.1 \text{ mole}}{1 \text{ L}}$$

$$100 \text{ mM} = \frac{0.1 \text{ mole} \times 225.4 \text{ g/mol}}{1 \text{ L}}$$

$$100 \text{ mM} = \frac{22.54 \text{ g}}{1 \text{ L}}$$

100 mM of zinc nitrate dihydrate per 1 liter is 22.54 g. So, per 100 ml (0.1 L), zinc nitrate dihydrate required is;

$$100 \text{ mM} = 22.54 \times 0.1 \text{ L}$$

$$100 \text{ mM} = 2.254 \text{ g/100ml}$$

$$100\ \text{mM} \approx 2.3\ \text{g per } 100\text{ml}$$

Solution of copper nitrate dihydrate

100 mM / 0.1 M solution of copper salt was prepared by dissolving 2.2 g of copper nitrate dihydrate in 100 ml of distilled water. The solution was stirred continuously to ensure proper mixing of reagents. Molecular weight of copper nitrate dihydrate [$Cu(NO_3)_2 \cdot 2H_2O$] = 223.59 g/mol

$$1\text{M} = \frac{1\ \text{mole}}{1\ \text{L}}$$

$$100\ \text{mM} = \frac{(100 \div 1000)\ \text{mole}}{1\ \text{L}}$$

$$100\ \text{mM} = \frac{0.1\ \text{mole}}{1\ \text{L}}$$

$$100\ \text{mM} = \frac{0.1\ \text{mole} \times 223.59\ \text{g/mol}}{1\ \text{L}}$$

$$100\ \text{mM} = \frac{22.359\ \text{g}}{1\ \text{L}}$$

100 mM of copper nitrate dihydrate per 1 liter is 22.359 g. So, per 100 ml (0.1 L), zinc nitrate dihydrate required is;

$$100\ \text{mM} = 22.359 \times 0.1\ \text{L}$$

$$100\ \text{mM} = 2.2359\ \text{g/100ml}$$

$$100\ \text{mM} \approx 2.2\ \text{g per } 100\text{ml}$$

Synthesis of ZnO NPs

A solution of zinc nitrate dihydrate was poured in a beaker with which 20 ml of neem extract was incorporated at room temperature, a drop at a time. The solution pH should be 12 and was adjusted using 2M NaOH solution. The solution was stirred magnetically at 60 ℃ for about 4h to attain a yellow paste which was then filtered. After filtration, the color of aqueous solution (light yellow) changes to pale white indication zinc salt reduction to ZnO NPs. The filtrate was poured in a petri dish evenly for drying in an oven at 80℃ for 12h. The dried paste was peeled off from petri dish and transformed into the ceramic crucible for calcination. The paste was calcinated for 3h at 500℃ so that light white colored powder of ZnO NPs could be obtain which was

turned into a fine white colored powder using mortar and pestle. The NPs were collected, weighed, and stored in an Eppendorf for further characterization.

Results and Discussion

A solution of copper nitrate dihydrate was placed in a beaker with which 20 ml of neem extract was incorporated drop by drop at room temperature. The solution pH should be 12 and was adjusted by the addition of 2M NaOH solution. The solution was stirred using magnetic stirrer at 60 ℃ for about 4h to attain a brown precipitate indicating CuO NPs. The solution was kept at room temperature for overnight and CuO attained was centrifuged and washed three times with distilled water. The collected precipitates are dried in a hot air oven at 80℃ for 6h and then are transformed into ceramic vessel which was placed in an air-heater furnace for 3h for calcination at 400℃ to acquire CuO NPs having black color and was turned into a fine powder using mortar and pestle. The NPs were collected, weighed, and stored in an Eppendorf for further characterization.

Photocatalytic Activity

The photocatalytic ability of synthesized nano-photocatalysts was evaluated through photodegradation of Methylene Blue (MB) and Methyl Orange (MO) after being exposed to direct sunlight [20]. The activity was performed in the hottest months of the year i.e., June and July of 2024 from 10:00 AM to 4:00 PM having average temperature and sunlight intensity of about ≥40 ℃, and 329.67 W/m^2. In 100ml dye solution, 60mg of synthesized NPs were added and the solution was sonicated in the dark for about 1h to attain adsorption-desorption equilibrium. The first reading was taken in the dark known as zero minutes reading and was analyzed using UV-Visible spectrophotometer. Then, the solutions were exposed to sunlight under ambient conditions. After being exposed, every 20 minutes 3ml of the solution/sample was collected and was analyzed after removing photocatalysts from it using centrifugation and filtration. The centrifuged suspensions were analyzed using UV-Visible spectrophotometer and degradation efficiency of MB and MO for both samples were calculated. The degradation percentage was calculated using

$$\text{Photodegradation (\%) of congo red} = \left[\frac{C_0 - C}{C_0}\right] \times 100$$

where C_0 - concentration of dyes in the absence of sunlight, and C - concentration of dyes after solar irradiation with respect to time.

The neem leaves were powdered after washing using distilled water, drying, fine chopping, and mechanical grinding. For extract preparation, neem dust and distilled water were taken in a beaker and the solution was stirred magnetically at 60°C for about 1h. The resulted solution after cooling was filtered using normal filter paper to get rid of leaves and to obtain pure and clean extract, the filtrate goes through the filter paper known as Whatman No. 1. The extract being light green in color was stored at 4°Cand the yield came out to be 50ml.

Neem leaf extract and the clear solution of zinc nitrate dihydrate were taken in a beaker to synthesize ZnO NPs. The solution pH was maintained at 12 using 2M NaOH and was stirred magnetically at 60°C for about 4h and then filtered. The pale white colored solution obtained from yellow paste after filtration was dried in an oven at 80°C for about 12h and after scrapping and grinding weighed. The white colored powder was calcined at 500°C for about 3h to decompose the extract completely and a fine powder of light white colored ZnO NPs was obtained having a yield of 111.2mg. Neem leaf extract and blue-colored solution of zinc nitrate dihydrate were taken in a beaker to synthesize CuO NPs. The solution pH was maintained at 12 using 2M NaOH and was stirred magnetically at 60°C for about 4h and then kept overnight at room temperature. The brown colored precipitates indicating CuO NPs were obtained after centrifugation and washing with distilled water and were then dried in an oven at 80°C for about 6h and after scrapping and grinding weighed. The brown colored powder was calcined at 400°C for about 3h to decompose the extract completely and a fine powder of black colored CuO NPs was obtained having a yield of 115.3mg.

UV-Visible spectrophotometer

0.01% solution of ZnO and CuO NPs were prepared and homogenized for fine dispersion of NPs in a solvent. The spectrophotometer was turned on and was allowed to heat up before the blank was run for calibration. Then both of the samples were placed in a cuvette one by one to obtain maximum absorbance at a wavelength range

of 200-800 nm. The graphs obtained revealed maximum light was absorbed at 350 nm and 222 nm by ZnO and CuO NPs, respectively, confirming their synthesis as reported in literature (Figure 12-13).

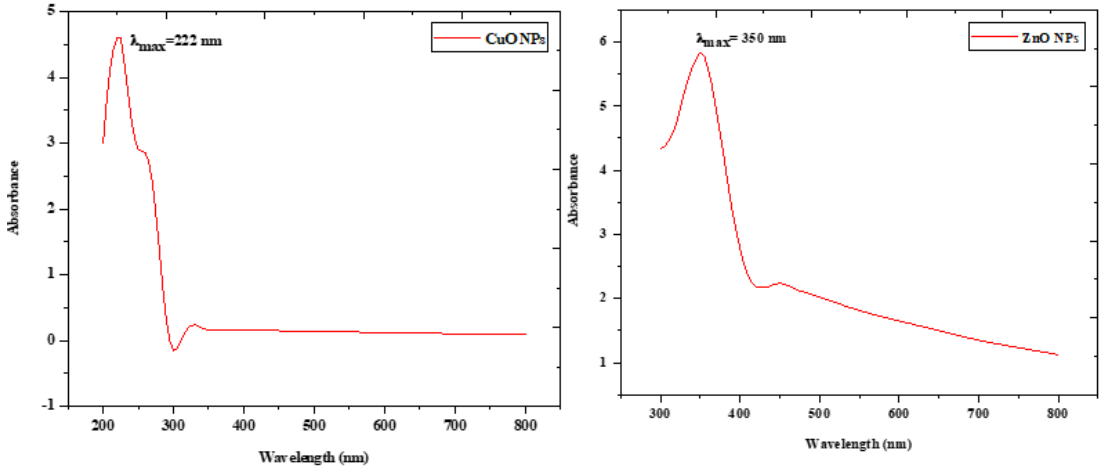

Fig. 1 UV-Visible spectra of ZnO and CuO NPs

Dye Degradations

The dyes, MB and MO, were degraded under sunlight using ZnO and CuO NPs. 10ppm dye solution was degraded using 5mg of NPs under sunlight irradiation for 120 min and the dye degradation was confirmed with the color disappearance of both dyes under continuous light exposure. The photo-induced dyes degradation efficiency was analyzed using UV-Visible spectrophotometer and are reported as ZnO NPs degraded 93.93% of MB and 86.36% of MO, while CuO NPs degraded 94.5% of MB and 93.45% of MO (Figure 14-15). The ZnO and CuO, both of the NPs showed greater photocatalytic activity towards MB as compared to MO because MB absorbance to catalyst's surface is good which in result generated more holes and OH radicals enhancing pollutant degradation to higher extent, while MO forms very strong bonds with the catalyst's surface making it less available for photocatalytic degradation due to its durability and resistance against breakdown[82].

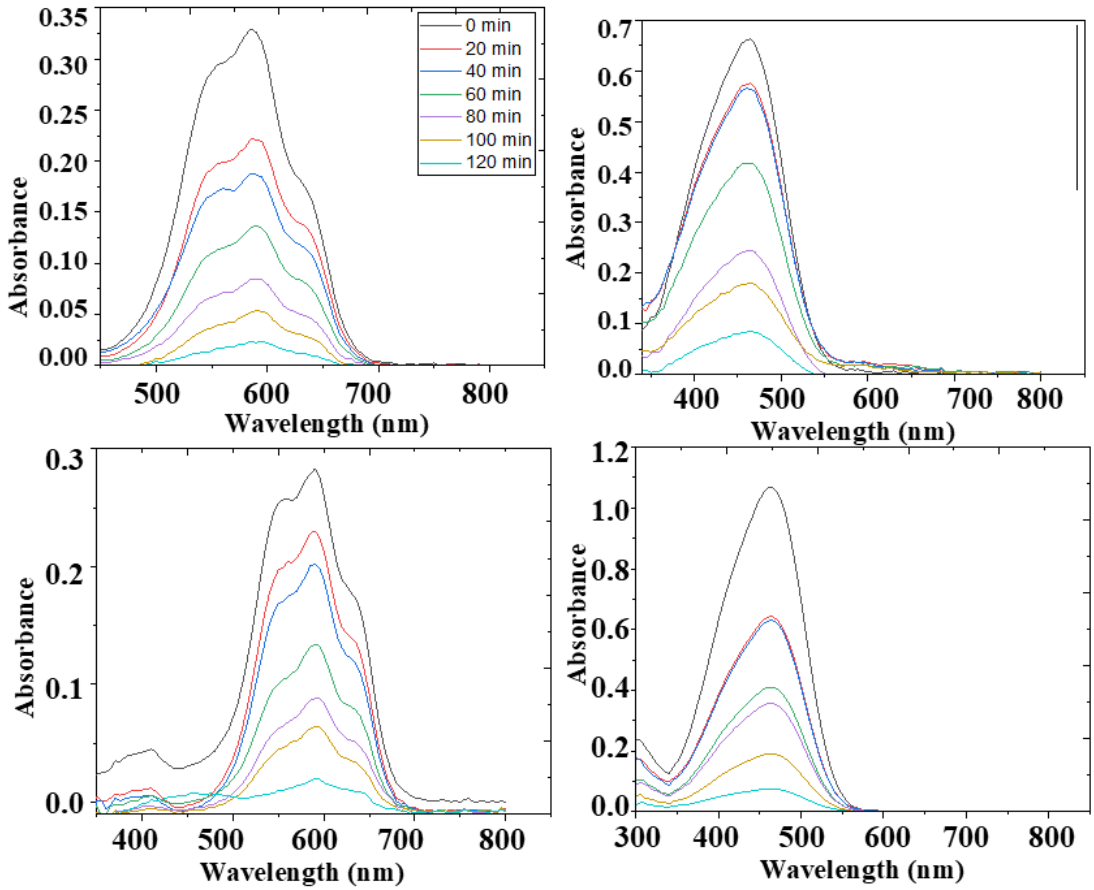

Fig. 2 Degradation of (a) MB and (b) MO using Neem mediated ZnO NPs under sunlight

The mechanism inducing degradation includes the formation of hole-electron pairs when NPs absorbs light as a result of which excited electrons move to excited state leaving positively charged hole behind. The positively charged hole reacts with the dye molecules and breakdown them by initiating oxidation reactions which in turn enhanced degradation process by forming OH radicals using water molecules. The superoxide radicals formed when molecular oxygen accepts electrons also has a great contribution in efficient dye degradation[83, 84].

Reusability Study

The synthesized ZnO and CuO NPs stability, effectiveness and photocatalytic ability in the degradation of MB and MO was evaluated through a series of reusability experiments. The results revealed that NPs could be reused for dye degradation up to three cycles even after the decline in degradation efficiency after every cycle (Figure

3 and 4). The simultaneous decline in degradation efficiency is may be due to the NPs saturation with final products indication that neem mediated ZnO and CuO NPs could show reusability[85].

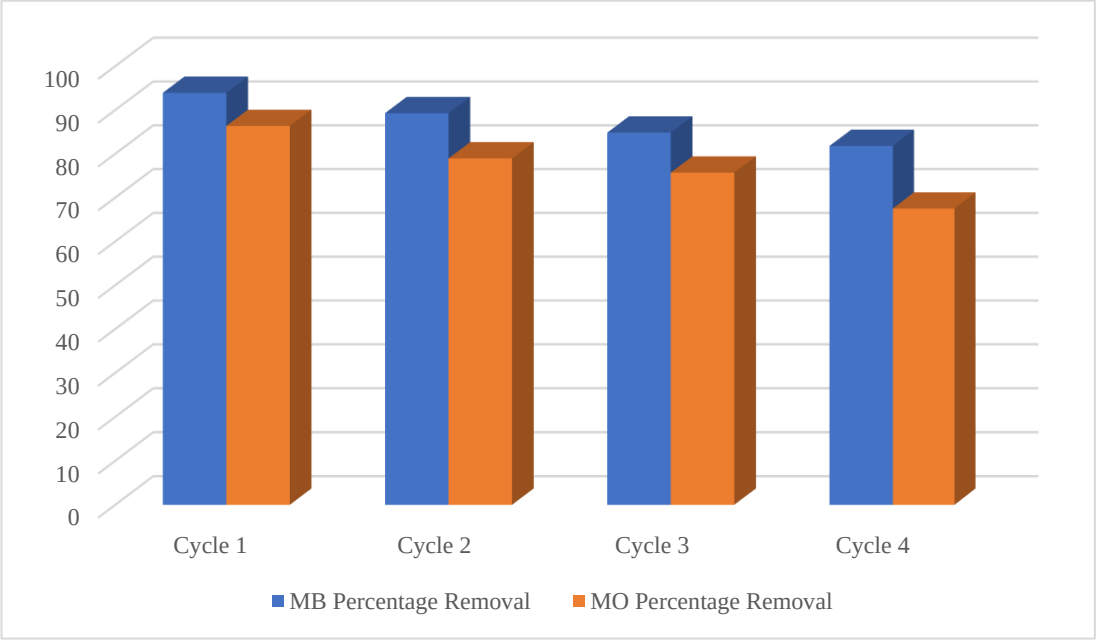

Fig. 3 Reusability status of bio-mediated ZnO NPs

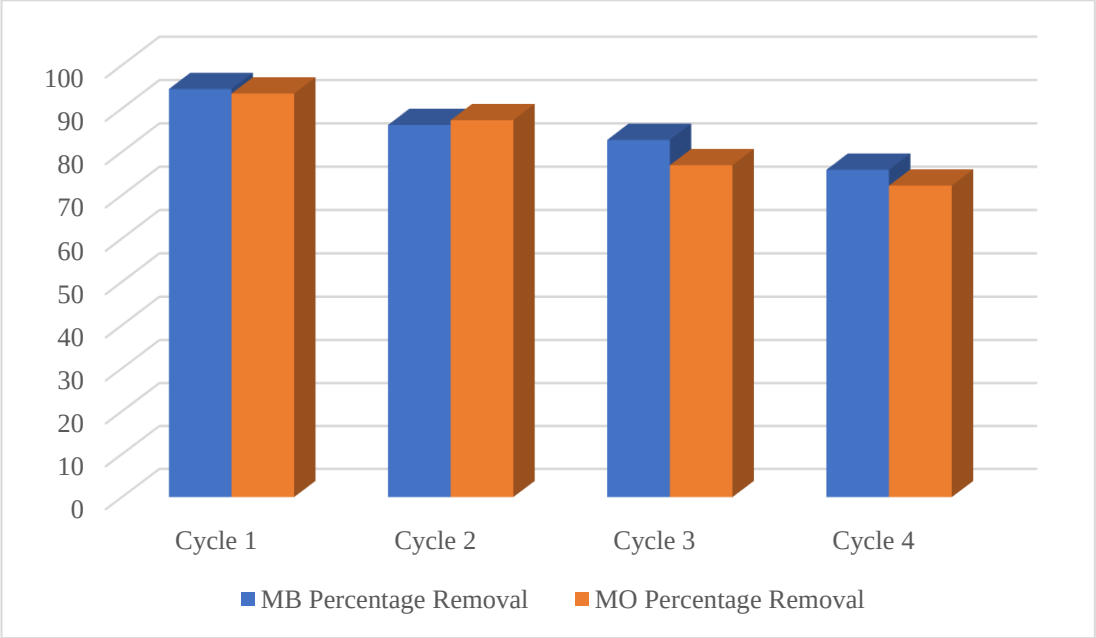

Fig. 4 Reusability status of bio-mediated CuO NPs

Conclusion

The bio-assisted approach was used to synthesize ZnO and CuO NPs because of being beneficial over chemical method such as ecofriendly, stable, non-toxic, cost-effective, large particle size and greater degradation efficiency. The NPs were synthesized using neem extract and nitrate dihydrate salts of Zn and Cu. The NPs were characterized using UV-Visible technique and the degradation behaviour of NPs under direct sunlight was also studied against two dyes i.e., MB and MO. The maximum absorbance observed using UV-Visible analyzer confirmed the synthesis of NPs as it is found to be 350 nm for ZnO NPs and 222 nm for CuO NPs. Both of the NPs degraded dyes efficiently but the photocatalytic degradation behaviour of both NPs was found to be highly efficient against MB as compared to MO because MO forms stronger bonds with catalyst that are difficult to breakdown. NPs reusability test was also performed revealing that NPs could be used for up to three cycles for dye degradation.

References

1. Abou-Elela SI, Fawzy ME, El-Shafai SA (2021) Treatment of hazardous wastewater generated from metal finishing and electro-coating industry via self-coagulation: Case study. Water Environment Research

2. Smith W (2022) Understanding the changing role of global public health in biodiversity conservation. Ambio 51:485–493. https://doi.org/10.1007/s13280-021-01576-0

3. Rodriguez Garzon S, Küpper A (2019) Pay-per-pollution: Towards an air pollution-aware toll system for smart cities. Proceedings - 2019 IEEE International Conference on Smart Internet of Things, SmartIoT 2019 361–366. https://doi.org/10.1109/SmartIoT.2019.00063

4. Manojlovic M, Cabilovski R, Bavec M (2010) Organic materials: sources of nitrogen in the organic production of lettuce. Turkish Journal of Agriculture and Forestry 34:163–172

5. Hren R, Vujanović A, Van Fan Y, et al (2023) Hydrogen production, storage and transport for renewable energy and chemicals: An environmental footprint assessment. Renewable and Sustainable Energy Reviews 173:113113. https://doi.org/10.1016/j.rser.2022.113113

6. Ali H (2010) Biodegradation of Synthetic Dyes—A Review. Water, Air, & Soil Pollution 213:251–273. https://doi.org/10.1007/s11270-010-0382-4

7. Vázquez-Vélez GE, Zoghbi HY (2021) Parkinson's Disease Genetics and Pathophysiology. Annual Review of Neuroscience 44:87–108

8. Majiya H, Adamu A, Galstyan A (2024) Photostability and photodynamic antimicrobial profile of dye extracts from four (4) plants: prospects for eco-friendly low-cost food disinfection and topical biomedical applications. Photochem Photobiol Sci 23:1179–1194. https://doi.org/10.1007/s43630-024-00585-8

9. Ren S, Hao Y, Xu L, et al (2021) Digitalization and energy: How does internet development affect China's energy consumption? Energy Economics 98:105220. https://doi.org/10.1016/j.eneco.2021.105220

10. Yao T, Huang Z, Zhao W (2020) Are smart cities more ecologically efficient? Evidence from China. Sustainable Cities and Society 102008. https://doi.org/10.1016/j.scs.2019.102008

11. Lopez G, Aghahosseini A, Child M, et al (2022) Impacts of model structure, framework, and flexibility on perspectives of 100% renewable energy transition decision-making. Renewable and Sustainable Energy Reviews 164:112452. https://doi.org/10.1016/j.rser.2022.112452

12. Hassan AU, Sumrra SH, Zafar W, et al (2022) Enriching the compositional tailoring of NLO responsive dyes with diversity oriented electron acceptors as visible light harvesters: a DFT/TD-DFT approach. Molecular Physics e2148585. https://doi.org/10.1080/00268976.2022.2148585

13. Wang D, Tian H, Zhu J, et al (2024) Enhanced photocatalytic degradation of toluene on surface C- and CN-modified TiO2 microspheres. Applied Surface Science 673:160862. https://doi.org/10.1016/j.apsusc.2024.160862

14. Muhsan MS, Nadeem S, Hassan AU, et al (2019) Synthesis of carbon nanoparticles by using seed oils. Pakistan Journal of Scientific and Industrial Research Series A: Physical Sciences 62:1–7. https://doi.org/10.52763/PJSIR.PHYS.SCI.62.1.2019.1.7

15. Hassan AU, Sumrra SH, Mustafa G, et al (2022) Efficient and tunable enhancement of NLO performance for indaceno-based donor moiety in A-π-D-π-D-π-A type first DSSC design by end-capped acceptors. Journal of Molecular Modeling 29:4. https://doi.org/10.1007/s00894-022-05402-6

16. Herms I, Jódar J, Soler A, et al (2021) Evaluation of natural background levels of high mountain karst aquifers in complex hydrogeological settings. A Gaussian mixture model approach in the Port del Comte (SE, Pyrenees) case study. Science of The Total Environment 756:143864

17. Amjad M, Mohyuddin A, Ulfat W, et al (2023) Silver hybridized polymer nanocomposite for efficient encapsulation of toxic dye from aqueous solution. Nanotechnol Environ Eng 8:891–898. https://doi.org/10.1007/s41204-023-00335-8

18. Zhao Y-G, Chen L-H, Ye M-L, et al U(VI) removal on polymer adsorbents: Recent development and future challenges. Critical Reviews in Environmental Science and Technology 0:1–23. https://doi.org/10.1080/10643389.2024.2401215

19. Batool F, Mohyuddin A, Amjad A, et al (2023) Removal of Cd(II) and Pb(II) from synthetic wastewater using *Rosa damascena* waste as a biosorbent: An insight into adsorption mechanisms, kinetics, and thermodynamic studies. Chemical Engineering Science 280:119072. https://doi.org/10.1016/j.ces.2023.119072

20. Hassan AU, Sumrra SH, Mustafa G, et al (2023) Molecular modeling of mordant black dye for future applications as visible light harvesting materials with anchors: design and excited state dynamics. J Mol Model 29:74. https://doi.org/10.1007/s00894-023-05474-y