

Photocatalytic Degradation of Different Organic Dyes Under Chemically Synthesized CuO and ZnO Nanoparticles: A Comparative Study

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Abstract

Recent advancements in nanoparticle research present promising solutions for addressing the environmental impact of dyes in aquatic ecosystems. This study focuses on the synthesis and application of zinc (Zn) and copper (Cu) nanoparticles, synthesized through the co-precipitation method, to facilitate the photo catalytic degradation of various dyes. Methylene blue, crystal violet, Rhoda mine B, and brilliant blue were subjected to degradation experiments in acidic, basic, and neutral media to allow for a comprehensive comparative analysis. The synthesized nanoparticles were thoroughly characterized using XRD, SEM-EDS, and FT-IR techniques, revealing excellent crystallinity and optical properties. The nanoparticles exhibited a robust response to UV radiation, indicative of their potential in photo catalytic processes. Comparative analysis revealed that zinc nanoparticles outperformed copper counterparts, attributed to their superior photo induced electron transfer reactions and an alignment of band gap with visible light energy. Surface reactivity, a crucial factor in photo catalysis, favored zinc nanoparticles due to their more reactive surface compared to copper. Mechanistic studies, conducted in the absence of light, confirmed the exclusively photo catalytic nature of the degradation process. The rate of dye degradation demonstrated a direct correlation with the concentration of nanoparticles, highlighting that an increase in nanoparticle concentration enhances the degradation rate. Remarkably high degradation efficiencies, averaging 95% for zinc nanoparticles and 85% for copper nanoparticles, underscore the efficacy of zinc as a superior photo catalyst for remediating dye-contaminated aquatic environments. The study contributes valuable insights to the expanding field of nanoparticle-based environmental remediation, offering sustainable solutions for addressing the detrimental impact of industrial dyes on water ecosystems. Overall, the findings contribute to the knowledge base for developing environmentally friendly approaches to tackle water pollution issues. The nanoparticles utilized in this degradation process exhibit significant advantages, characterized by their non-toxic nature, eco-friendly attributes, and cost-effectiveness. Notably, these nanoparticles maintain their photo catalytic properties across multiple uses, enhancing their efficiency and enabling their repeated application in treating diverse dye solutions. The central impetus behind this research lies in mitigating the adverse impacts of industrial and individual waste discharged into water bodies.

Keywords: *Eutrophication; XRD-EDS; FT-IR; SEM-EDS; Photocatalytic degradation.*

1. Introduction

The detrimental effects of certain dyes on aquatic ecosystems stem from various factors, underscoring the urgency of addressing their proper disposal [1]-[21]. These dyes, commonly used in textiles [22]-[25], printing [26]-[29], cosmetics [30], [31], and other applications [32]-[37], can harbor diverse chemical compositions [38]-[40], with some exhibiting harmful properties that pose risks to both the environment and human health when not handled responsibly [41]-[50]. The improper disposal of these dyes can result in severe consequences for aquatic life and overall ecosystem health. One of the primary concerns associated with these dyes is their potential toxicity to aquatic organisms [51]-[65]. Upon introduction into water bodies, the chemical compounds present in many dyes can exert adverse effects on fish, invertebrates, and other aquatic species. These toxic dyes can disrupt normal physiological processes within these organisms, leading to a myriad of detrimental outcomes [66]. Among these consequences are compromised growth, diminished reproductive capabilities, and, in severe cases, mortality [67]-[69]. The disruption of these vital processes can have cascading effects throughout the aquatic ecosystem, affecting the entire food chain and ecosystem dynamics. In addition, the persistence of toxic dyes in aquatic environments exacerbates their impact on aquatic organisms. Dyes can persist in water bodies for extended periods, continually exposing organisms to their harmful effects and impeding ecosystem recovery. This persistence prolongs the duration of exposure and increases the likelihood of adverse effects on aquatic life, further amplifying the threats posed by these substances. The presence of toxic dyes in water bodies also poses challenges for water quality management. The accumulation of these compounds can lead to alterations in water chemistry and physical properties, potentially impairing water quality and ecosystem function. Additionally, the release of dyes into water bodies can result in changes in water color and clarity, further disrupting aquatic habitats and ecosystem processes. Overall, the improper disposal of certain dyes represents a significant threat to aquatic ecosystems, encompassing a range of detrimental effects on aquatic organisms and ecosystem health.

The repercussions of releasing dyes into water bodies extend beyond immediate toxicity, encompassing far-reaching consequences that disrupt the delicate equilibrium of aquatic ecosystems. The alteration of water quality due to dye contamination has cascading effects on essential environmental factors crucial for the well-being of aquatic plants and animals. Changes in water color and transparency, induced by dye release, impact sunlight penetration and oxygen availability—both critical for sustaining the health of aquatic life. Disruption in these factors can have a profound impact on the delicate balance of the aquatic food chain, posing a pervasive threat to the overall health and sustainability of the ecosystem. An alarming consequence associated with certain dyes is the induction of eutrophication. Dyes may contain nutrients that contribute to this process, leading to the excessive growth of algae and aquatic plants [70].

This unchecked growth can result in oxygen depletion in water, creating "dead zones" where life cannot thrive. Eutrophication poses a direct risk to the sustainability of aquatic ecosystems [71], further underscoring the environmental hazards associated with improper dye disposal. The bioaccumulation of dye compounds in the tissues of aquatic organisms introduces an additional layer of threat up the food chain [72]. As smaller organisms containing these compounds are consumed by larger ones, the concentration of harmful substances escalates. This bioaccumulation poses risks to predators at the top of the food chain, including humans if they consume contaminated fish, amplifying the potential for adverse health effects. Moreover, certain dyes have the capacity to disrupt the reproductive processes of aquatic species. This interference can result in diminished population sizes, leading to long-term consequences for the sustainability of aquatic ecosystems. The disruption of reproductive cycles could potentially alter the composition and dynamics of aquatic communities, with far-reaching implications for the entire ecosystem.

The aggregation of dyes and their byproducts in water bodies not only poses a threat to aquatic organisms but also significantly contributes to habitat destruction, particularly in sensitive ecosystems like coral reefs. This accumulation induces stress in resident organisms and causes harm to their habitats, adding another layer of complexity to the multifaceted threat posed by certain dyes to the delicate balance and long-term health of aquatic ecosystems. To sum up, the deleterious effects of certain dyes extend beyond direct toxicity to encompass alterations in water quality, disruptions in the aquatic food chain, eutrophication, bioaccumulation, disruptions in reproductive processes, and habitat destruction. These combined impacts underscore the urgent need for effective remediation strategies to mitigate the environmental consequences of dye contamination.

Traditional methods associated with dye removal, including physical and chemical approaches [73], [74], have shown limitations in effectively addressing the toxicity of dyes. This limitation has led to the development of advanced and efficient approaches, notably nanotechnology. Nanotechnology, involving the application of nano-sized active materials, has emerged as a promising and innovative solution due to its non-toxic nature, cost-effectiveness, and high performance in degrading dyes [74].

Nanoparticles, particularly those made of materials like CuO and ZnO are a major attraction in environmental remediation due to their unique properties [75], [76]. With high surface area, reactivity, and the potential for targeted delivery, nanoparticles can be engineered to adsorb, degrade, or immobilize contaminants, making them suitable for various remediation strategies such as adsorption, catalysis, and nano-filtration. Ongoing research in this field aims to advance the understanding of nanoparticles' interactions with contaminants and the environment. Scientists explore new types of nanoparticles, improve their efficiency, and focus on developing eco-friendly synthesis methods to minimize the environmental footprint of nanoparticle production. This continuous advancement in nanotechnology for environmental remediation holds promise for the development of sustainable and effective strategies to address the challenges posed by dye contamination in aquatic ecosystems.

In our study, the focus lies on CuO and ZnO nanoparticles (NPs) as the subjects of investigation. We synthesized these nanoparticles to analyze their photocatalytic degradation efficiency against a selection of dyes, including methylene blue, crystal violet, brilliant blue, and rhodamine-B. The synthesis of nanoparticles for the assessment of photocatalytic degradation involved employing the chemical precipitation method. To ensure a comprehensive understanding of the synthesized particles, various techniques were utilized to characterize their purity and properties. The Fourier Transform Infrared (FTIR) analysis played a pivotal role in the identification of nanoparticles, examining the transmittance or absorbance of infrared rays within the range of 4000 cm^{-1} to 400 cm^{-1} . This technique provided valuable insights into the molecular composition and functional groups present in the synthesized CuO and ZnO nanoparticles. Furthermore, X-ray Diffraction (XRD) was employed to determine essential parameters such as particle size and crystallinity of the synthesized nanoparticles. This technique allowed for a detailed examination of the crystal structure, aiding in understanding the physical characteristics of the nanoparticles. The surface morphological information of the nanoparticles was retained through the implementation of Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS). This technique enabled the observation of the nanoparticles at a microscale level, providing information about their surface structure and elemental composition.

2. Materials and Methods

2.1 Chemicals and Reagents

The experiment utilized specific reagents and chemicals to investigate the photocatalytic degradation of dyes. Rhodamine B (RB), Crystal Violet (CV), Brilliant Blue (BB), and Methylene Blue (MB) were obtained in high-grade purity (99%) from Himedia laboratories Pvt. Ltd. Mumbai, India. Sodium hydroxide pellets (NaOH), Ammonia solution (NH_4OH), Copper chloride (CuCl_2), Copper sulfate (CuSO_4), Hydrochloric acid (HCl), and Zinc chloride (ZnCl_2) were procured from various reputable suppliers with high purity grades.

All solutions were prepared using double distilled water during the experimental work. A 2.0 M NaOH stock solution was created by dissolving sodium hydroxide pellets in distilled water. The stock solutions of the dyes (RB, CV, BB, and MB) were prepared by dissolving specified amounts of each dye in 100ml of double distilled water.

The degradation of dyes was monitored using a model no. 301 UV-visible digital spectrophotometer from Eneqix Equipments Company, Thrissur, India. The spectrophotometer had 2 cell holders, and a 3.5 ml quartz cuvette with a path length of 1mm was employed to measure the absorbance of the dye solutions. The absorbance values were obtained at regular intervals of 30 minutes under the influence of UV rays to observe the complete degradation of the dyes. Control experiments were conducted by keeping a set of solutions in the dark, confirming that the observed changes were due to photocatalytic degradation rather than adsorption.

The experiments were conducted in different mediums, including acidic, basic, and neutral conditions. The comparative behavior of Cu and Zn nanoparticles in degrading the dyes in various mediums was analyzed and represented graphically. This detailed methodology provides insights into the experimental setup and procedures employed to assess the photocatalytic degradation efficiency of CuO and ZnO nanoparticles for the selected dyes.

2.2 Synthesis of Cu-nanoparticles

The synthesis of copper (Cu) nanoparticles involved the following steps:

- **Reactant Preparation:** 100ml of 0.1M copper sulfate (CuSO_4) solution was prepared by dissolving 2.4gm of CuSO_4 in 100ml of double distilled water.
- **Precipitation Reaction:** 30ml of 1M sodium hydroxide (NaOH) solution was added to the copper sulfate solution. This addition was carried out while maintaining a pH range of 10-14. The mixture was subjected to constant stirring at 750rpm.
- **Controlled Conditions:** The synthesis reaction occurred at a controlled temperature of 75°C .
- **Stirring Process:** The reaction mixture was stirred continuously for approximately 3 to 4 hours.
- **Precipitate Formation:** As a result of the reaction, a black precipitate of copper nanoparticles was formed.
- **Washing Process:** The obtained black precipitate was washed thoroughly with distilled water and ethanol.
- **pH Adjustment:** The washing process included adjusting the pH back to 7 (neutral).

The overall synthesis process involved the controlled addition of sodium hydroxide to copper sulfate, leading to the formation of copper nanoparticles as indicated by the black precipitate. The subsequent washing steps were crucial to remove impurities and adjust the pH to a neutral level. This detailed procedure ensures the production of purified copper nanoparticles suitable for further analysis or applications.

2.3 Synthesis of Zn- nanoparticles

The synthesis of Zinc Oxide (ZnO) nanoparticles involved the following steps:

- **Solution Preparation:** 6.6gm of Zinc chloride (ZnCl_2) was added to 200ml of distilled water to obtain a 0.2M solution.
- **Alkaline Addition:** About 20ml of sodium hydroxide (NaOH) solution with a concentration of 2M was added thoroughly to the ZnCl_2 solution.
- **Ammonia Addition:** Ammonia solution (25% w/w) was added dropwise (approximately 15-20ml) to the $\text{Zn}(\text{OH})_2$ solution until a white precipitate of zinc hydroxide formed.
- **Precipitate Collection:** The formed precipitate of zinc hydroxide was filtered from the solution.
- **Washing Process:** The collected precipitate was washed several times with distilled water to remove impurities.
- **Drying:** The washed precipitate was dried at a temperature of 80°C for about 16 hours.

- **Calcination:** The dried $\text{Zn}(\text{OH})_2$ nanoparticles were subjected to calcination at a high temperature of 600°C for about 6 hours.
- **Product Formation:** The calcination process resulted in the transformation of $\text{Zn}(\text{OH})_2$ nanoparticles into Zinc Oxide (ZnO) nanoparticles.

The sequential process involves the controlled addition of NaOH and ammonia to induce the formation of zinc hydroxide, which is then subjected to filtration, washing, and drying. The final step of calcination at a high temperature converts the zinc hydroxide into Zinc Oxide nanoparticles. This detailed procedure ensures the synthesis of purified ZnO nanoparticles suitable for various applications or further analysis.

3. Results and discussion

3.1 Characterization of nanoparticles

FTIR

Frontier Transmission Infrared Spectroscopy (FTIR) is a valuable analytical technique utilized in characterizing synthesized nanoparticles, offering insights into their size, shape, and nature. In FT-IR, each chemical functional group within the nanoparticles absorbs infrared light at specific wavelengths, generating a distinctive "fingerprint" that aids in identification. This is achieved by detecting the transmittance or absorbance of infrared rays over a variable range of wavelengths.

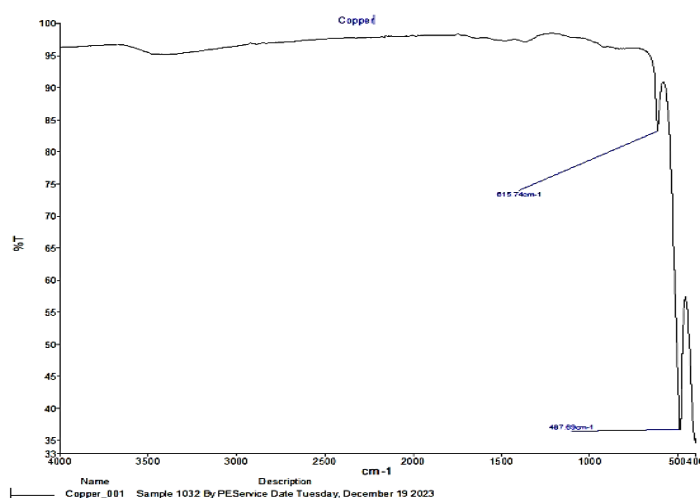


Figure 1 FTIR of CuO nanoparticles.

In the case of ZnO and CuO nanoparticles, FT-IR analysis was conducted within the range of 4000 cm^{-1} to 400 cm^{-1} . The obtained spectra provided key information about the molecular vibrations and functional groups present in the synthesized nanoparticles. For CuO nanoparticles, a well-defined peak in the FT-IR spectrum was observed at 609.10 cm^{-1} . This specific peak serves as confirmation of the formation of CuO nanoparticles. Additionally, a peak at 2981.30 cm^{-1} was noted, which can be attributed to the absorption of the O-H group present in the nanoparticles (**Figure 1**).

Similarly, for ZnO nanoparticles, the FT-IR spectrum exhibited a distinct peak at 478.34 cm⁻¹, providing confirmation of the formation of ZnO nanoparticles (**Figure 2**). These characteristic peaks in the FT-IR spectra serve as unique identifiers for the synthesized nanoparticles, allowing researchers to confirm the successful formation of CuO and ZnO nanoparticles and providing valuable information about their chemical composition and structure.

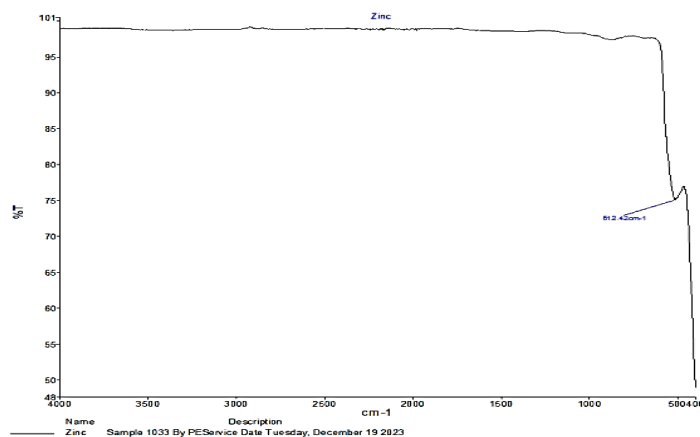


Figure 2 FTIR of ZnO nanoparticles.

XRD

X-ray Diffraction (XRD) stands as a fundamental tool in crystallography, playing a crucial role in the study of crystal structures. It provides comprehensive information about various aspects such as unit cell dimensions, lattice parameters, and interatomic distances. In the realm of nanomaterials and nanoparticles, XRD is employed to gain insights into their size, shape, and crystal structure. The figure 3 and figure 4 below illustrates the XRD patterns obtained for both Zinc (Zn) and Copper (Cu) nanoparticles, confirming their nanocrystalline form and ensuring phase purity. The graph accompanying the figure highlights the diffraction peaks observed on the XRD patterns of both nanoparticles, providing information about the intensity of these peaks. The diffraction peaks serve as distinctive markers, allowing researchers to deduce essential details about the crystalline nature of the synthesized nanoparticles. The presence and positioning of these peaks contribute to a deeper understanding of the structural characteristics, confirming the nanocrystalline nature of the particles. In summary, XRD analysis in this study plays a pivotal role in characterizing the synthesized Zn and Cu nanoparticles, providing crucial insights into their crystallographic properties, which include size, shape, and phase purity.

SEM-EDS

The Scanning Electron Microscopy (SEM) technique was employed to examine the morphology of the synthesized nanoparticles (Figure 5 and Figure 6). Based on the obtained data, the Cu nanoparticles (NPs) exhibited a spherical shape, indicating a three-dimensional structure with characteristics resembling a sphere. On the other hand, the Zn nanoparticles displayed a rod-like structure, suggesting an elongated,

cylindrical morphology. Notably, both types of nanoparticles exhibited particle sizes less than the 100nm scale, signifying their nanoscale dimensions. Additionally, the data indicated that the nanoparticles, both Cu and Zn, possessed low polydispersity. Polydispersity refers to the distribution of particle sizes within a sample. A low polydispersity index suggests that the nanoparticles have a relatively uniform size distribution, enhancing their suitability for various applications.

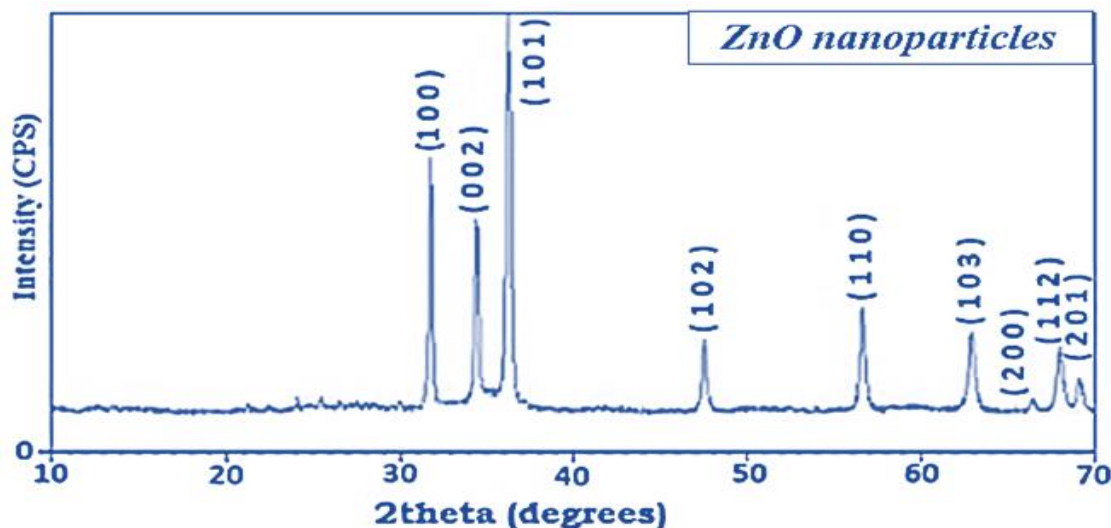


Figure 3 XRD of ZnO nanoparticles.

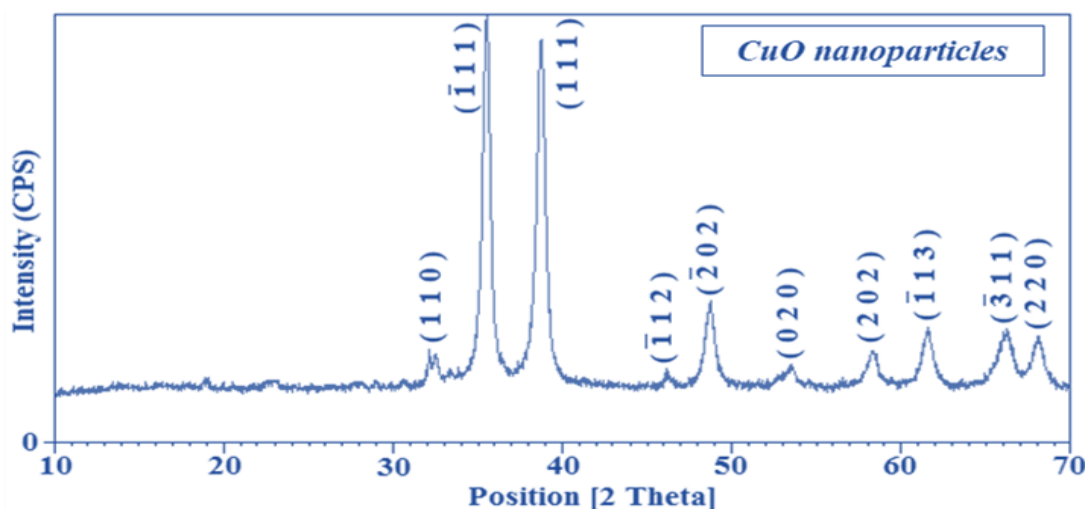


Figure 4 Figure 3 XRD of CuO nanoparticles.

In summary, the SEM analysis provided valuable information about the morphological characteristics of the synthesized nanoparticles. The spherical shape of Cu nanoparticles and the rod-like structure of Zn nanoparticles, both within the nanoscale range and exhibiting low polydispersity, contribute to their potential applications in diverse fields.

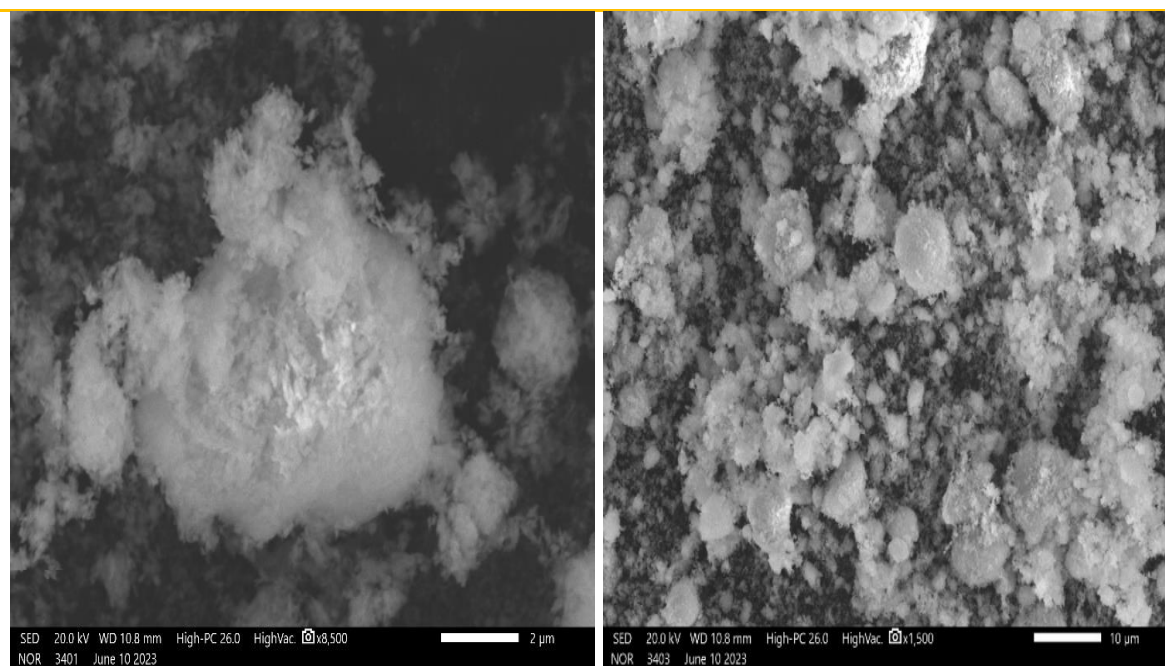


Figure 5 Scanning Electron Microscopy CuO.

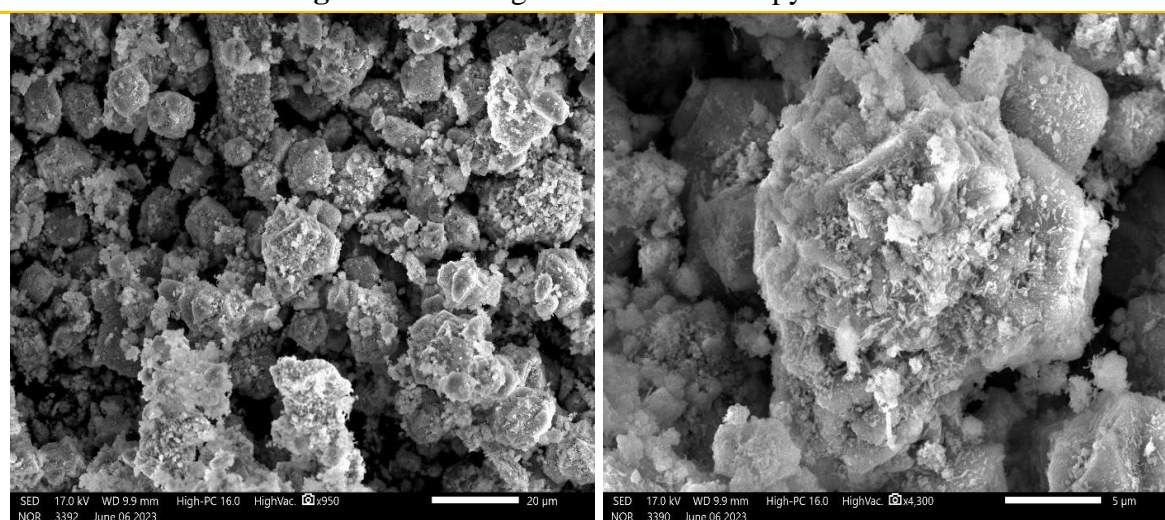


Figure 6 Scanning Electron Microscopy ZnO.

HR-TEM

High-Resolution Transmission Electron Microscopy (HRTEM) stands as an indispensable tool in the characterization of nanomaterials, providing valuable insights into their structural and morphological properties. In our research, HRTEM has been employed to analyze the ultrastructure of CuO and ZnO nanoparticles (NPs), offering a comprehensive understanding of their unique features at the nanoscale. The application of HRTEM allows for the visualization of individual nanoparticles, enabling precise measurements of size, shape, and crystallinity. This level of resolution is particularly crucial in our investigation, as it aids in elucidating the intricate details of CuO and ZnO nanoparticles.

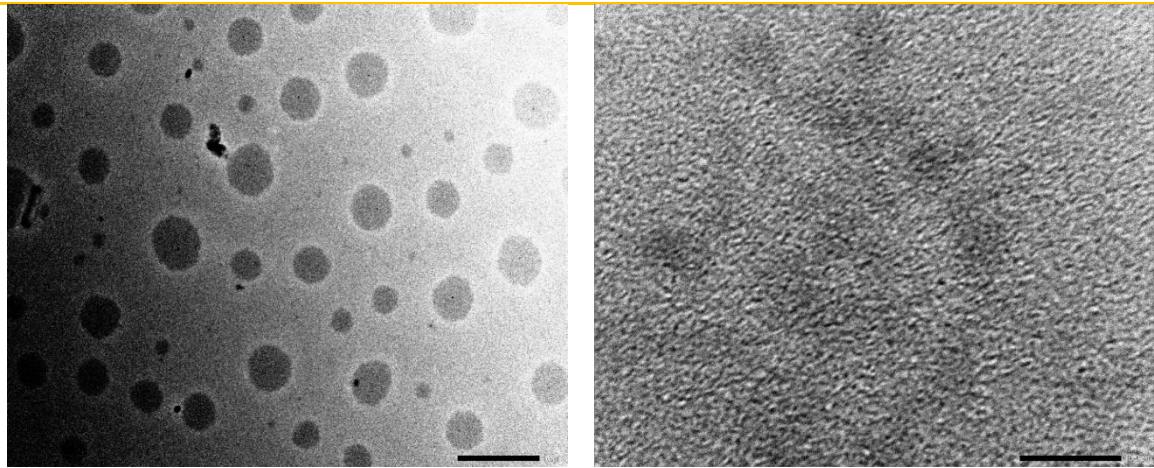


Figure 7 TEM of CuO.

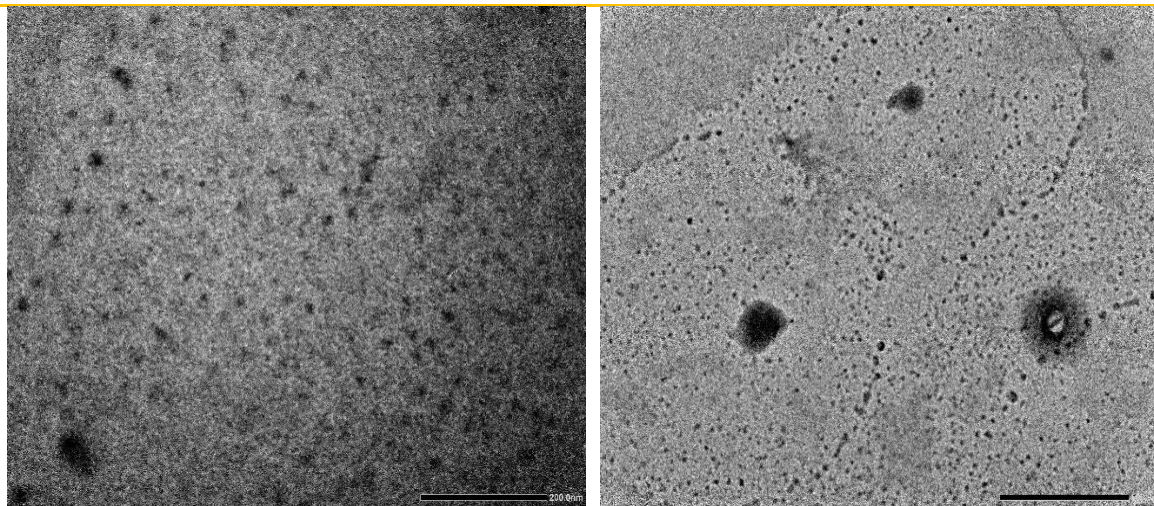


Figure 8 ZnO TEM.

The micrographs obtained through HRTEM reveal a highly ordered arrangement of specific structural features, shedding light on the inherent characteristics of the material. This detailed analysis enhances our comprehension of the nanoscale properties, paving the way for a more comprehensive understanding of CuO and ZnO nanoparticles and their potential applications.

3.2 Application

Photocatalytic degradation of dyes

The figure 9 the experimental setup employed for the photocatalytic degradation of dyes under sunlight. In this process, various dye solutions were exposed to natural sunlight to assess the photocatalytic activity of synthesized nanoparticles, specifically CuO and ZnO. The exposure to sunlight serves as the external stimulus necessary for initiating and driving the photocatalytic degradation reactions.

The experimental arrangement showcases a systematic approach to evaluate the efficacy of the nanoparticles in harnessing solar energy for the degradation of dyes, providing valuable insights into their photocatalytic performance under environmentally relevant conditions.



Figure 9 Experimental setup employed for the photocatalytic degradation

Below is a table presenting the percentage of degradation achieved for various dyes within a 3-hour experimental duration:

Table 1 Percentage inhibition of different dyes.

Dye degraded	CuO Nanoparticles	ZnO Nanoparticle
Methylene blue	98.4%	98%
Rohadamine	82%	89%
Brilliant blue	88%	90%
Crystal violet	84%	96%

This table succinctly summarizes the outcomes of the study, showcasing the effectiveness of the synthesized nanoparticles in degrading different dyes within the specified time frame.

Calculation of the rate of reaction

The efficiency of photocatalysts is significantly influenced by their band gap energy, representing the energy difference between the valence and conduction bands. In the domain of photocatalysis, aligning the band gap energy with the energy of photons in the light spectrum is crucial for optimal performance. Zinc oxide (ZnO), a widely used zinc compound in photocatalysis, demonstrates a band gap energy ranging from 3.0 to 3.4 eV, making it well-suited for ultraviolet (UV) light energy. In contrast, copper, with a considerably higher band gap energy of around 7 eV, exhibits reduced responsiveness to visible or UV light. This limitation diminishes its capacity to absorb photons and initiate photocatalytic reactions compared to zinc. Zinc oxide, particularly in the form of ZnO, exhibits robust photocatalytic activity, especially under UV light exposure.

The absorption of UV light by ZnO generates electron-hole pairs that actively participate in redox reactions with adsorbed species, such as water molecules or pollutants, resulting in their degradation or conversion. This makes zinc oxide effective for applications like water and air purification under UV irradiation. On the contrary, copper, due to its higher band gap energy and lower reactivity with light, displays lower photocatalytic activity compared to zinc-based materials. Stability and corrosion resistance are crucial considerations, with zinc oxide being known for its stability and resistance to corrosion under environmental conditions. This stability is essential for maintaining catalytic properties over time. In contrast, copper's susceptibility to oxidation and corrosion raises concerns about potential degradation or loss of catalytic activity in photocatalytic applications. Additionally, the recyclability of the catalyst is a significant parameter. Zinc-based photocatalysts, such as ZnO, often demonstrate enhanced recoverability and recyclability due to their stability, retaining catalytic activity across multiple usage cycles. This recyclability is crucial for practical applications where the ability to reuse the catalyst is a key consideration.

The degradation of rhodamine B by copper oxide (CuO) and zinc oxide (ZnO) nanoparticles at varying quantities of 0.1gm and 0.01gm for each nanoparticle has been meticulously illustrated through graphs in both acidic and basic mediums. The presented data, depicted graphically, clearly demonstrates that the rate of degradation was notably faster when utilizing ZnO nanoparticles in comparison to CuO nanoparticles. This trend was consistently observed in both acidic and basic mediums. The distinct properties of zinc and copper, both being transition metals, play a crucial role in influencing their effectiveness as photocatalysts. Notably, zinc is often regarded as a superior photocatalyst compared to copper. The graphical representation of the experimental results visually highlights the enhanced efficiency of ZnO nanoparticles in facilitating the degradation of rhodamine B under the specified experimental conditions. This observation further emphasizes the significance of selecting appropriate photocatalysts based on their unique properties, as the choice of metal oxide nanoparticles significantly impacts the overall photocatalytic performance in the degradation of dyes.

As the quantity of nanoparticles increases, the degradation process exhibits accelerated and enhanced efficiency. Figures 10 depict the graphical representation of the degradation plot for methylene blue dye using 0.01gm of zinc and copper nanoparticles, respectively, in both acidic and basic mediums. Similarly, Figures 11 illustrate the degradation plots for methylene blue dye with an increased quantity of nanoparticles (0.1gm), specifically zinc and copper, in both acidic and basic mediums. These graphs visually capture the correlation between the amount of nanoparticles and the efficiency of the photocatalytic degradation process. The observed trends provide valuable insights into the dosage-dependent impact of zinc and copper nanoparticles on the degradation of methylene blue dye under varying pH conditions.

The degradation process for each dye followed a similar approach as that observed for rhodamine B. However, due to the more pronounced and clearer results in the acidic medium, subsequent graphs focus exclusively on the degradation of dyes in the presence of 0.01gm nanoparticles under acidic conditions.

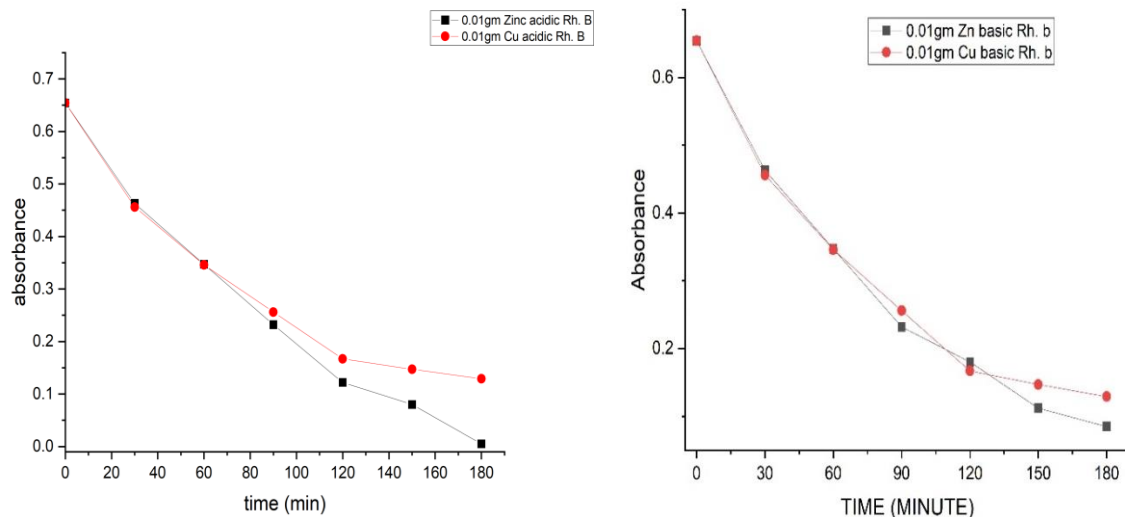


Figure 10 Graphical representation of the degradation plot for methylene blue dye using 0.01gm of zinc and copper nanoparticles.

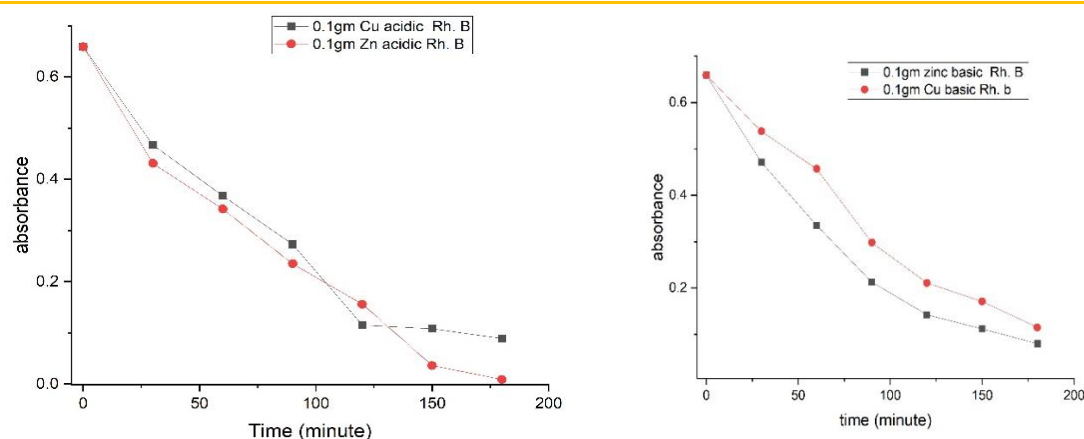


Figure 11 Degradation plots for methylene blue dye with an increased quantity of nanoparticles

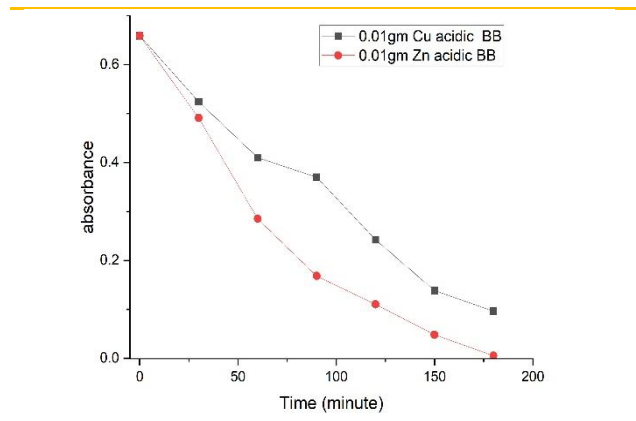


Figure 12 Degradation plot of brilliant blue dye.

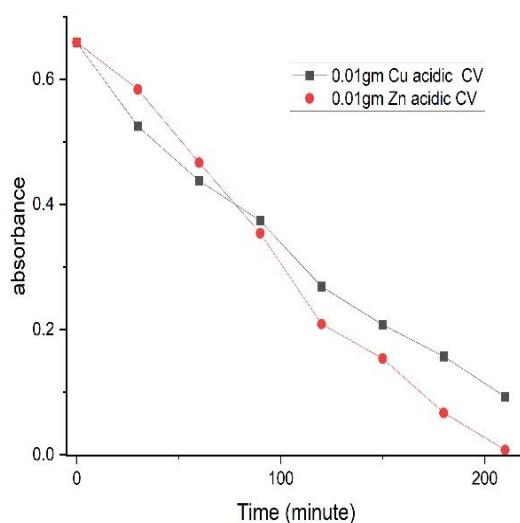


Figure 13 Degradation plot of crystal violet dye.

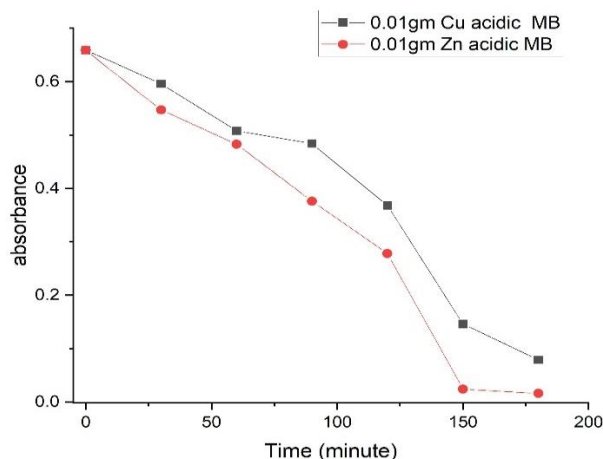


Figure 14 Degradation plot of methylene blue dye.

Figure 12 illustrates the degradation plot of brilliant blue dye when subjected to 0.01gm of copper and zinc nanoparticles separately in an acidic medium. Similarly, Figure 13 presents the degradation plot of crystal violet dye under the influence of 0.01gm copper and zinc nanoparticles in an acidic medium. Lastly, Figure 14 showcases the degradation plot of methylene blue dye using 0.01gm of copper and zinc nanoparticles in an acidic medium. These graphs not only highlight the degradation efficiency of each dye in response to the presence of nanoparticles but also emphasize the superior degrading strength of zinc nanoparticles. The enhanced responsiveness of zinc nanoparticles to UV radiation is consistently evident across all plotted figures.

Conclusion

In conclusion, the present study underscores the pivotal role of zinc (Zn) and copper (Cu) nanoparticles in the photocatalytic degradation of various dyes, offering a promising avenue for addressing the environmental impact of industrial dyes in aquatic ecosystems. The thorough synthesis of nanoparticles through the co-precipitation method, coupled with comprehensive characterization using XRD, SEM-EDS, and FT-IR techniques, has provided valuable insights into their structural and optical properties. The excellent crystallinity and robust response to UV radiation make these nanoparticles effective candidates for photocatalytic processes. The comparative analysis of zinc and copper nanoparticles reveals the superior performance of zinc in degrading dyes, attributed to its enhanced photoinduced electron transfer reactions and alignment of bandgap with visible light energy. The surface reactivity of zinc nanoparticles further contributes to their superior photocatalytic efficiency compared to copper. Mechanistic studies confirm the exclusive photocatalytic nature of the degradation process, highlighting the significance of light in driving the reaction. Furthermore, the concentration-dependent enhancement of the degradation rate emphasizes the potential scalability and efficiency of this approach. Notably, zinc nanoparticles exhibit remarkably high degradation efficiencies, averaging 95%, showcasing their effectiveness as a superior photocatalyst for remediating dye-contaminated aquatic environments. The findings contribute to the growing field of nanoparticle-based environmental remediation, offering sustainable and eco-friendly solutions to combat water pollution caused by industrial dye discharge. The non-toxic nature, cost-effectiveness, and the retained photocatalytic properties of these nanoparticles across multiple uses further enhance their applicability in treating diverse dye solutions. The central motivation behind this research, focused on mitigating the adverse impacts of industrial and individual waste on water bodies, aligns with the global pursuit of environmentally friendly approaches to address water pollution challenges. The demonstrated advantages of these nanoparticles position them as promising tools in the ongoing efforts to protect and restore the health of aquatic ecosystems.

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References

- [1] Shanker, U., Rani, M., & Jassal, V. (2017). Degradation of hazardous organic dyes in water by nanomaterials. *Environmental chemistry letters*, 15, 623-642.
- [2] Islam, A., Teo, S. H., Taufiq-Yap, Y. H., Ng, C. H., Vo, D. V. N., Ibrahim, M. L., & Awual, M. R. (2021). Step towards the sustainable toxic dyes removal and recycling from aqueous solution-A comprehensive review. *Resources, Conservation and Recycling*, 175, 105849.

- [3] Gupta, V. K., Jain, R., Mittal, A., Saleh, T. A., Nayak, A., Agarwal, S., & Sikarwar, S. (2012). Photo-catalytic degradation of toxic dye amaranth on TiO₂/UV in aqueous suspensions. *Materials science and engineering: C*, 32(1), 12-17.
- [4] Ahamad, T., Naushad, M., Eldesoky, G. E., Al-Saeedi, S. I., Nafady, A., Al-Kadhi, N. S., & Khan, A. (2019). Effective and fast adsorptive removal of toxic cationic dye (MB) from aqueous medium using amino-functionalized magnetic multiwall carbon nanotubes. *Journal of Molecular Liquids*, 282, 154-161.
- [5] Islam, A., Teo, S. H., Taufiq-Yap, Y. H., Ng, C. H., Vo, D. V. N., Ibrahim, M. L., & Awual, M. R. (2021). Step towards the sustainable toxic dyes removal and recycling from aqueous solution-A comprehensive review. *Resources, Conservation and Recycling*, 175, 105849.
- [6] Sukul, P. K., & Malik, S. (2013). Removal of toxic dyes from aqueous medium using adenine based bicomponent hydrogel. *RSC advances*, 3(6), 1902-1915.
- [7] Malik, A., Khan, A., & Humayun, M. (2019). Preparation and chemical modification of rice husk char for the removal of a toxic dye (Orange G) from aqueous medium. *Zeitschrift für Physikalische Chemie*, 233(3), 375-392.
- [8] Naseem, K., Farooqi, Z. H., Begum, R., Ghufuran, M., Rehman, M. Z. U., Najeeb, J., & Al-Sehemi, A. G. (2018). Poly (N-isopropylmethacrylamide-acrylic acid) microgels as adsorbent for removal of toxic dyes from aqueous medium. *Journal of Molecular Liquids*, 268, 229-238.
- [9] Yagub, M. T., Sen, T. K., Afroze, S., & Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption: a review. *Advances in colloid and interface science*, 209, 172-184.
- [10] Li, X., Han, D., Zhang, M., Li, B., Wang, Z., Gong, Z., & Yang, X. (2019). Removal of toxic dyes from aqueous solution using new activated carbon materials developed from oil sludge waste. *Colloids and surfaces A: physicochemical and engineering aspects*, 578, 123505.
- [11] Oladipo, M. A., Bello, I. A., Adeoye, D. O., Abdulsalam, K. A., & Giwa, A. A. (2013). Sorptive removal of dyes from aqueous solution: a review. *Adv. Environ. Biol*, 7(11), 3311-3327.
- [12] Oladipo, M. A., Bello, I. A., Adeoye, D. O., Abdulsalam, K. A., & Giwa, A. A. (2013). Sorptive removal of dyes from aqueous solution: a review. *Adv. Environ. Biol*, 7(11), 3311-3327.
- [13] Dawood, S., & Sen, T. (2014). Review on dye removal from its aqueous solution into alternative cost effective and non-conventional adsorbents. *Journal of Chemical and Process Engineering*, 1(104), 1-11.
- [14] Osagie, C., Othmani, A., Ghosh, S., Malloum, A., Esfahani, Z. K., & Ahmadi, S. (2021). Dyes adsorption from aqueous media through the nanotechnology: A review. *Journal of Materials Research and Technology*, 14, 2195-2218.
- [15] Teo, S. H., Ng, C. H., Islam, A., Abdulkareem-Alsultan, G., Joseph, C. G., Janaun, J., & Awual, M. R. (2022). Sustainable toxic dyes removal with advanced materials for clean water production: A comprehensive review. *Journal of Cleaner Production*, 332, 130039.

- [16] Kahraman, S., Yalcin, P., & Kahraman, H. (2012). The evaluation of low-cost biosorbents for removal of an azo dye from aqueous solution. *Water and Environment Journal*, 26(3), 399-404.
- [17] Kahraman, S., Yalcin, P., & Kahraman, H. (2012). The evaluation of low-cost biosorbents for removal of an azo dye from aqueous solution. *Water and Environment Journal*, 26(3), 399-404.
- [18] Naushad, M., Alqadami, A. A., AlOthman, Z. A., Alsohaimi, I. H., Algamdi, M. S., & Aldawsari, A. M. (2019). Adsorption kinetics, isotherm and reusability studies for the removal of cationic dye from aqueous medium using arginine modified activated carbon. *Journal of Molecular Liquids*, 293, 111442.
- [19] Ferreira, A. M., Coutinho, J. A., Fernandes, A. M., & Freire, M. G. (2014). Complete removal of textile dyes from aqueous media using ionic-liquid-based aqueous two-phase systems. *Separation and Purification Technology*, 128, 58-66.
- [20] Dilarri, G., de Almeida, É. J. R., Pecora, H. B., & Corso, C. R. (2016). Removal of dye toxicity from an aqueous solution using an industrial strain of *Saccharomyces cerevisiae* (Meyen). *Water, Air, & Soil Pollution*, 227, 1-11.
- [21] de Oliveira, E. H. C., Fraga, D. M. D. S. M., da Silva, M. P., Fraga, T. J. M., Carvalho, M. N., de Luna Freire, E. M. P., & da Motta Sobrinho, M. A. (2019). Removal of toxic dyes from aqueous solution by adsorption onto highly recyclable xGnP® graphite nanoplatelets. *Journal of Environmental Chemical Engineering*, 7(2), 103001.
- [22] Benkhaya, S., M'rabet, S., & El Harfi, A. (2020). A review on classifications, recent synthesis and applications of textile dyes. *Inorganic Chemistry Communications*, 115, 107891.
- [23] Sharma, J., Sharma, S., & Soni, V. (2021). Classification and impact of synthetic textile dyes on Aquatic Flora: A review. *Regional Studies in Marine Science*, 45, 101802.
- [24] Slama, H. B., Chenari Bouket, A., Pourhassan, Z., Alenezi, F. N., Silini, A., Cherif-Silini, H., & Belbahri, L. (2021). Diversity of synthetic dyes from textile industries, discharge impacts and treatment methods. *Applied Sciences*, 11(14), 6255.
- [25] Verma, M., Thakur, A., Sharma, R., & Bharti, R. (2022). Recent advancement in the one-pot synthesis of the Tri-substituted Methanes (TRSMs) and their biological applications. *Current Organic Synthesis*, 19(1), 86-114.
- [26] Gastaldi, M., Cardano, F., Zanetti, M., Viscardi, G., Barolo, C., Bordiga, S., & Roppolo, I. (2020). Functional dyes in polymeric 3D printing: applications and perspectives. *ACS Materials Letters*, 3(1), 1-17.
- [27] Rekaby, M., Salem, A. A., & Nassar, S. H. (2009). Eco-friendly printing of natural fabrics using natural dyes from alkanet and rhubarb. *The Journal of The Textile Institute*, 100(6), 486-495.
- [28] El-Sayed, G. A., Othman, H., & Hassabo, A. G. (2021). An overview on the eco-friendly printing of jute fabrics using natural dyes. *Journal of Textiles, Coloration and Polymer Science*, 18(2), 239-245.
- [29] Savvidis, G., Karanikas, E., Nikolaidis, N., Eleftheriadis, I., & Tsatsaroni, E. (2014). Ink-jet printing of cotton with natural dyes. *Coloration Technology*, 130(3), 200-204.

- [30] Gürses, A., Açıkyıldız, M., Güneş, K., Gürses, M. S., Gürses, A., Açıkyıldız, M., & Gürses, M. S. (2016). *Dyes and pigments: their structure and properties. Dyes and pigments*, 13-29.
- [31] Brudzyńska, P., Sionkowska, A., & Grisel, M. (2021). *Plant-derived colorants for food, cosmetic and textile industries: A review. Materials*, 14(13), 3484.
- [32] He, J., Jo, Y. J., Sun, X., Qiao, W., Ok, J., Kim, T. I., & Li, Z. A. (2021). *Squaraine dyes for photovoltaic and biomedical applications. Advanced Functional Materials*, 31(12), 2008201.
- [33] Khan, M. N., Parmar, D. K., & Das, D. (2021). *Recent applications of azo dyes: A paradigm shift from medicinal chemistry to biomedical sciences. Mini Reviews in Medicinal Chemistry*, 21(9), 1071-1084.
- [34] Yao, L., Xue, X., Yu, P., Ni, Y., & Chen, F. (2018). *Evans blue dye: a revisit of its applications in biomedicine. Contrast media & molecular imaging*, 2018.
- [35] Sun, Y., Sun, P., Li, Z., Qu, L., & Guo, W. (2022). *Natural flavylum-inspired far-red to NIR-II dyes and their applications as fluorescent probes for biomedical sensing. Chemical Society Reviews*.
- [36] Sun, Y., Sun, P., Li, Z., Qu, L., & Guo, W. (2022). *Natural flavylum-inspired far-red to NIR-II dyes and their applications as fluorescent probes for biomedical sensing. Chemical Society Reviews*.
- [37] Dang, Z., Liu, X., Du, Y., Wang, Y., Zhou, D., Zhang, Y., & Zhu, S. (2023). *Ultra-Bright Heptamethine Dye Clusters Based on a Self-Adaptive Co-Assembly Strategy for NIR-IIb Biomedical Imaging. Advanced Materials*, 35(46), 2306773.
- [38] Abu-Melha, S. (2019). *Synthesis of novel biologically active thiazole dyes and their applications. Pigment & Resin Technology*, 48(5), 375-382.
- [39] Mujtahid, F., Gareso, P. L., Arminah, B., & Tahir, D. (2022). *Review effect of various types of dyes and structures in supporting performance of dye-sensitized solar cell TiO₂-based nanocomposites. International Journal of Energy Research*, 46(2), 726-742.
- [40] Kumar, A., Dixit, U., Singh, K., Gupta, S. P., & Beg, M. S. J. (2021). *Structure and properties of dyes and pigments. Dyes and Pigments-Novel Applications and Waste Treatment*, 131.
- [41] Padhi, B. S. (2012). *Pollution due to synthetic dyes toxicity & carcinogenicity studies and remediation. International journal of environmental sciences*, 3(3), 940-955.
- [42] de Campos Ventura-Camargo, B., & Marin-Morales, M. A. (2013). *Azo dyes: characterization and toxicity-a review. Textiles and Light Industrial Science and Technology*, 2(2), 85-103.
- [43] Mani, S., Chowdhary, P., & Bharagava, R. N. (2019). *Textile wastewater dyes: toxicity profile and treatment approaches. Emerging and eco-friendly approaches for waste management*, 219-244.
- [44] Puvaneswari, N., Muthukrishnan, J., & Gunasekaran, P. (2006). *Toxicity assessment and microbial degradation of azo dyes*.
- [45] Brown, M. A., & De Vito, S. C. (1993). *Predicting azo dye toxicity. Critical reviews in environmental science and technology*, 23(3), 249-324.

- [46] Gičević, A., Hindija, L., & Karačić, A. (2020). Toxicity of azo dyes in pharmaceutical industry. In *CMBEBIH 2019: Proceedings of the International Conference on Medical and Biological Engineering, 16–18 May 2019, Banja Luka, Bosnia and Herzegovina* (pp. 581-587). Springer International Publishing.
- [47] Affat, S. S. (2021). Classifications, advantages, disadvantages, toxicity effects of natural and synthetic dyes: A review. *University of Thi-Qar Journal of Science*, 8(1), 130-135.
- [48] Ismail, M., Akhtar, K., Khan, M. I., Kamal, T., Khan, M. A., M Asiri, A., & Khan, S. B. (2019). Pollution, toxicity and carcinogenicity of organic dyes and their catalytic bio-remediation. *Current pharmaceutical design*, 25(34), 3645-3663.
- [49] Nohynek, G. J., Fautz, R., Benech-Kieffer, F., & Toutain, H. (2004). Toxicity and human health risk of hair dyes. *Food and Chemical Toxicology*, 42(4), 517-543.
- [50] Ramsay, J. A., & Nguyen, T. (2002). Decoloration of textile dyes by *Trametes versicolor* and its effect on dye toxicity. *Biotechnology Letters*, 24, 1757-1761.
- [51] Sharma, J., Sharma, S., & Soni, V. (2021). Classification and impact of synthetic textile dyes on Aquatic Flora: A review. *Regional Studies in Marine Science*, 45, 101802.
- [52] Tkaczyk, A., Mitrowska, K., & Posyniak, A. (2020). Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: A review. *Science of the total environment*, 717, 137222.
- [53] Garcia, V. S. G., de Freitas Tallarico, L., Rosa, J. M., Suzuki, C. F., Roubicek, D. A., Nakano, E., & Borrely, S. I. (2021). Multiple adverse effects of textile effluents and reactive Red 239 dye to aquatic organisms. *Environmental Science and Pollution Research*, 28, 63202-63214.
- [54] de Jesus Azevedo, C. C., de Oliveira, R., Soares-Rocha, P., Sousa-Moura, D., Li, A. T., Grisolia, C. K., & Montagner, C. C. (2021). Auramine dyes induce toxic effects to aquatic organisms from different trophic levels: an application of predicted non-effect concentration (PNEC). *Environmental science and pollution research*, 28, 1866-1877.
- [55] de Luna, L. A., da Silva, T. H., Nogueira, R. F. P., Kummrow, F., & Umbuzeiro, G. A. (2014). Aquatic toxicity of dyes before and after photo-Fenton treatment. *Journal of Hazardous Materials*, 276, 332-338.
- [56] Puvaneswari, N., Muthukrishnan, J., & Gunasekaran, P. (2006). Toxicity assessment and microbial degradation of azo dyes.
- [57] Darsana, R., Chandrasehar, G., Deepa, V., Gowthami, Y., Chitrikha, T., Ayyappan, S., & Goparaju, A. (2015). Acute toxicity assessment of Reactive Red 120 to certain aquatic organisms. *Bulletin of environmental contamination and toxicology*, 95, 582-587.
- [58] Berradi, M., Hsissou, R., Khudhair, M., Assouag, M., Cherkaoui, O., El Bachiri, A., & El Harfi, A. (2019). Textile finishing dyes and their impact on aquatic environs. *Heliyon*, 5(11).
- [59] Rowiński, P. M., & Chrzanowski, M. M. (2011). Influence of selected fluorescent dyes on small aquatic organisms. *Acta Geophysica*, 59, 91-109.

- [60] Croce, R., Cinà, F., Lombardo, A., Crispeyn, G., Cappelli, C. I., Vian, M., & Baderna, D. (2017). Aquatic toxicity of several textile dye formulations: acute and chronic assays with *Daphnia magna* and *Raphidocelis subcapitata*. *Ecotoxicology and Environmental Safety*, 144, 79-87.
- [61] Lellis, B., Fávaro-Polonio, C. Z., Pamphile, J. A., & Polonio, J. C. (2019). Effects of textile dyes on health and the environment and bioremediation potential of living organisms. *Biotechnology Research and Innovation*, 3(2), 275-290.
- [62] Bae, J. S., Freeman, H. S., & Kim, S. D. (2006). Influences of new azo dyes to the aquatic ecosystem. *Fibers and polymers*, 7, 30-35.
- [63] Hernández-Zamora, M., & Martínez-Jerónimo, F. (2019). Congo red dye diversely affects organisms of different trophic levels: a comparative study with microalgae, cladocerans, and zebrafish embryos. *Environmental Science and Pollution Research*, 26, 11743-11755.
- [64] Tkaczyk, A., Mitrowska, K., & Posyniak, A. (2020). Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: A review. *Science of the total environment*, 717, 137222.
- [65] Lellis, B., Fávaro-Polonio, C. Z., Pamphile, J. A., & Polonio, J. C. (2019). Effects of textile dyes on health and the environment and bioremediation potential of living organisms. *Biotechnology Research and Innovation*, 3(2), 275-290.
- [66] Puvaneswari, N., Muthukrishnan, J., & Gunasekaran, P. (2006). Toxicity assessment and microbial degradation of azo dyes.
- [67] Soni, P., Sharma, S., Sharma, S., Kumar, S., & Sharma, K. P. (2006). A comparative study on the toxic effects of textile dye wastewaters (untreated and treated) on mortality and RBC of a freshwater fish *Gambusia affinis* (Baird and Gerard). *Journal of environmental biology*, 27(4), 623-628.
- [68] Ribeiro, A. R., & Umbuzeiro, G. D. A. (2014). Effects of a textile azo dye on mortality, regeneration, and reproductive performance of the planarian, *Girardia tigrina*. *Environmental Sciences Europe*, 26, 1-8.
- [69] de Oliveira, G. A. R., de Lapuente, J., Teixidó, E., Porredón, C., Borràs, M., & de Oliveira, D. P. (2016). Textile dyes induce toxicity on zebrafish early life stages. *Environmental toxicology and chemistry*, 35(2), 429-434.
- [70] Berradi, M., Hsissou, R., Khudhair, M., Assouag, M., Cherkaoui, O., El Bachiri, A., & El Harfi, A. (2019). Textile finishing dyes and their impact on aquatic environs. *Heliyon*, 5(11).
- [71] Khan, M. N., & Mohammad, F. (2014). Eutrophication: challenges and solutions. *Eutrophication: Causes, Consequences and Control: Volume 2*, 1-15.
- [72] Yusuf, M. (2019). Synthetic dyes: a threat to the environment and water ecosystem. *Textiles and clothing*, 11-26.
- [73] Piaskowski, K., Świdarska-Dąbrowska, R., & Zarzycki, P. K. (2018). Dye removal from water and wastewater using various physical, chemical, and biological processes. *Journal of AOAC International*, 101(5), 1371-1384.
- [74] Anastopoulos, I., Hosseini-Bandegharai, A., Fu, J., Mitropoulos, A. C., & Kyzas, G. Z. (2018). Use of nanoparticles for dye adsorption. *Journal of Dispersion Science and Technology*, 39(6), 836-847.

- [75] *Primo, J. D. O., Bittencourt, C., Acosta, S., Sierra-Castillo, A., Colomer, J. F., Jaeger, S., & Anaissi, F. J. (2020). Synthesis of zinc oxide nanoparticles by ecofriendly routes: adsorbent for copper removal from wastewater. Frontiers in Chemistry, 8, 571790.*
- [76] *Akintelu, S. A., Oyebamiji, A. K., Olugbeko, S. C., & Latona, D. F. (2021). Green chemistry approach towards the synthesis of copper nanoparticles and its potential applications as therapeutic agents and environmental control. Current Research in Green and Sustainable Chemistry, 4, 100176.*