Characterization and Application of Nanomaterials (2023) Volume 6 Issue 2
doi:10.24294/can.v6i2.3573

ORIGINAL RESEARCH ARTICLE

Photocatalytic degradation of organic dyes using transition metal based mixed metal oxide nanocomposite under different illumination

R. Biju

Department of Physics, TKM College of Arts and Science (Affiliated to University of Kerala), Karicode, Kollam 691005, Kerala, India; bijur4u@gmail.com

ABSTRACT

Nowadays, copper and zinc nanoparticles are widely employed in a variety of applications. With nanoscale particle sizes, copper oxide/zinc oxide composite is easily synthesized using a variety of techniques, including hydrothermal, microwave, precipitation, etc. In the current work, chemical precipitation is used to create a copper oxide/zinc oxide nanocomposite. XRD analysis was used to determine the nanocomposite's structural characteristics. Through SEM analysis, the surface morphological properties are investigated. EDAX is used to study the chemical composition of produced materials, while UV/Visible spectroscopy is used to determine their optical properties. The assessment of the copper oxide/zinc oxide nanocomposite's degrading property on dyes like methyl red and methyl orange under UV and visible light are the main objectives of the current work.

Keywords: nanocomposite; metal oxide; photocatalysis; methyl orange; methyl red

ARTICLE INFO

Received: 8 November 2023
Accepted: 10 December 2023
Available online: 26 December 2023

1. Introduction

Materials that contain multiple naturally occurring materials, one of which is in the nano form, are called nanocomposite materials. The three main types of nanocomposite materials are ceramic matrix, metal matrix, and polymer matrix. Each form of nanocomposite material consists of a continuous component known as the matrix portion and a dispersed part. One of the technologies that is frequently employed for a variety of purposes is nanotechnology. People are typically drawn to items that are colorful. Many sectors consider coloring agents to be essential because of their demand. The plastics, cosmetics, paper, leather, pharmaceutical, and printing industries are among those that use dyes or coloring chemicals extensively. The textile industry has around 80% of utilization of various type of dye materials. In the present study we are selected methyl orange (MO) and methyl red (MR) as dye materials for photocatalytic degradation Various studies conducted by different scientists reported that Methyl orange is highly susceptible for development of cancer, development of tumour and genetic disorder moreover it is a very toxic azo dye[1]. The common source of discharging methyl orange to environment is occurred by industries such as fabric manufacturing, medicine. The use of MO as a pH indicator in research laboratories and industries also discharge huge amount into water resources. Some of the potential hazards property of MO include stability, great solubility, bright color, and low biodegradability[2,3]. Whereas MR is also an Azo dye with some potential health risks; largely used in microbiological application such as "Methyl red test". MR is considered as an acute toxic material. Over dose of MR may be leads to irritation in skin and eye, it also responsible for breathing problems.

Recent research shows that different synthetic dye coloring ingredients have severely contaminated the world's primary water resources. Because of its extreme solubility These kinds of contaminants are not amenable to the traditional ways of purifying water. Water use and recycling are always kept under check by nature. Nature recycles water in a variety of ways. Numerous industries have developed as a result of the industrial revolution. A necessary component of most enterprises is water. The current state of affairs surpasses the ability of natural processes to supply clean water. Numerous studies demonstrate that almost all naturally occurring sources of drinking water are found to be unclean and contaminated with a variety of contaminants, hazardous chemicals, and pathogenic organisms. Using catalytic nanocomposite materials, the very hazardous compounds can break down during photocatalysis. In photocatalysis, ultraviolet light activates a semiconductor surface, which readily produces free radicals. Through the process of photocatalysis, we may convert extremely poisonous industrial colors into innocuous material by using capable nanoscale catalytic material. These methods are among the best candidates for treating water because of their environmentally beneficial qualities. Studies on the topic of copper-based nanocomposites have revealed a wide range of applications. For example, copper oxide nanoparticles are utilized to make gas sensors[4]. Catalytic actions are employed to remove organic pollutants like dyes. According to certain research, copper oxide may find application as a semiconductor[5].

The shortage of fresh water is one of the major threats to humankind. Numerous organic contaminants have severely contaminated the majority of the water resources. These kinds of contaminants cannot be removed from water using the traditional methods of water filtration. The extremely hazardous substance can be broken down into CO_2 and water using photocatalysis using nanocomposite materials. One of the most effective and environmentally beneficial methods of treating water is photocatalysis. Wastewater treatment basically involves three key techniques. These techniques include chemical, biological, and physical ones. Biological treatment techniques often require extensive spaces and operational protocols due to their intricate architecture. One drawback of chemical treatments is sludge formation. In addition, the sludge itself produces fresh trash. There are many different kinds of chemicals needed for the process. Adsorption techniques and membrane filtration technologies are two popular physical methods. The membrane filtration techniques have a limited lifespan. It is discovered that the adsorption method is costly because activated carbon is used in it. Photocatalysis process in which two stages, as a liquid and a solid. Molecules may be photo excited by UV rays during this process. In this process, hydroxyl radicals or free holes are the oxidizing species produced is termed as heterogeneous photocatalysis[6].

The process of heterogeneous photocatalysis commences when a photocatalyst absorbs light radiation. Consequently, the semiconductor experiences the generation of photoinduced electron-hole pairs. Holes are created in the valence band when a photon is absorbed by the semiconductor and excites the valence band electrons to move into the conduction band. An electron acceptor, such as oxygen in the solution, is reduced by the photoinduced electron. In a similar manner, an electron produced by a donor species can join with a hole that has moved to the surface. Oxygen serves as an electron acceptor in semiconductor photocatalysts. It is understood that the electron generated by photoreaction can reduce oxygen molecules into oxygen radicals $O_2^{\bullet-}$. These radicals undergo several succeeding processes and harvest various types of reactive species such as $HO_2^{\bullet}$, HO_2^{-}, H_2O_2 and possibly $HO^{\bullet}$ radicals. The organic electron donor may oxidize as a result of the presence of activated oxygen species. Similarly, holes created when a photon is absorbed can oxidize the electron donor and result in the production of HO. When the two reactions mentioned above work together, organic contaminants are broken down into mineral acids, carbon dioxide, and water.

The process of heterogeneous photocatalysis involves several steps. There are two primary processes that produce the hydroxyl radicals. During the first stage, the catalyst absorbs light radiation, creating valance band holes. When the generated holes interact with water molecules, a water molecule splits into a proton and a hydroxyl-free radical. In the alternative mechanism, hydroxyl free radicals can be created when the valance band holes react with hydroxyl groups (OH-)[7].

2. Materials and methods

Well-known chemical method co-precipitation process was used for the preparation of copper oxide/zinc oxide (CuO/ZnO) nanocomposites. Precursors for the preparation include copper nitrate, zinc nitrate, ethylene diamine tetra acetic acid (EDTA) and sodium hydroxide. The Precursors were purchased from local laboratory chemical supplier all chemicals are AR grade with purity 99.4% manufactured by Loba Chemie Pvt Ltd. Mumbai, Maharashtra, India.

3. Preparation of CuO/ZnO nanocomposite

Preparation begins with making of 20 mL solutions of 0.15 M copper nitrate, 0.15 M zinc nitrate, and 0.0254 M EDTA are used in the preparation process. They were all placed in a conical flask and thoroughly mixed. A 250 mL solution of 2 M sodium hydroxide was placed in a burette and the aforesaid solution was allowed to gradually fall at a steady pace. A thick copper hydroxide/zinc hydroxide precipitate formed after five hours of continuous stirring using a magnetic stirrer at an RPM of 2000. In the reaction described above, EDTA functions as a capping agent to stop the agglomeration and as a stabilizer. The precipitate that was formed above is extracted by filtering it with ultra-filter paper. Afterwards, it undergoes many washings using triple-distilled water, ethanol, and acetone to eliminate any leftover contaminants. After the obtained powder was dried in a hot air oven set at 60 °C for 12 h, the dried powder is heated for six hours at 500 °C in a muffle furnace. Final product is CuO/ZnO (CZ5) with a black color was obtained.

4. Results and discussions

4.1. Analysis of XRD pattern

X-ray diffraction (XRD) is used to assess the crystalline clarity and structural purities. **Figure 1** displays the XRD pattern for the nanocomposites. It is abundantly obvious that the XRD patterns shows prominent peaks, which occur during the creation of nanocomposites, are indicative of the nanocomposite's crystalline character. The Scherrer equation, $d = 0.9\lambda/\beta \cos\theta$[8], was utilized to calculate the particle sizes of the synthesized nanocomposite. The FWHM (full width at half maximum) of the XRD lines is represented by β, whereas $\lambda = 1.54060$ Å. The samples that were annealed at 500 °C had average crystallite sizes of 31 nm. The XRD pattern of CZ5 nanocomposite individually matched with ICDD standard diffraction data of copper oxide and zinc oxide. The obtained XRD pattern for CuO was found to match well with ICDD pattern number 801916 with monoclinic phase and edge centered geometry. Similarly, ZnO was in well agreement with ICDD pattern number 750576 with primitive geometry and wurtzite (hexagonal) phase[9].

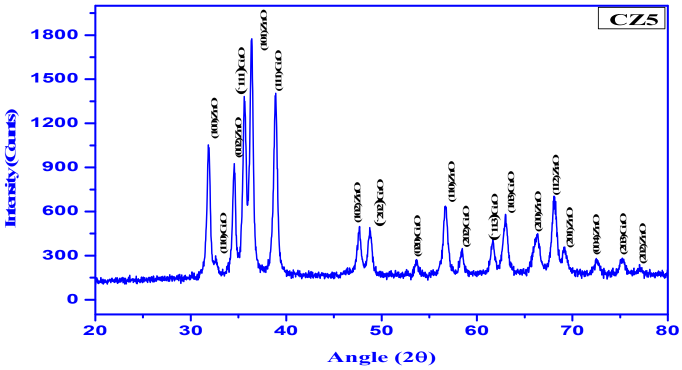


Figure 1. XRD pattern of CZ5 nanocomposite annealed 500 °C.

4.2. UV spectral studies

With the aid of a UV/Visible spectrophotometer with a 1 nm resolution, the UV spectrum of a CuO/ZnO nanocomposite sintered at 500 °C was conducted in the wavelength range of 200 to 900 nm, as illustrated in **Figure 2**. UV spectra provide amazing details regarding the material's optical bandgaps. By using Tauc formula, $\alpha\ \alpha h\upsilon = A(h\upsilon - Eg)^n$, where A is a constant, $h\upsilon$ is the photon energy ($\upsilon = c/\lambda$), Eg is the bandgap, and n = 1/2 for an allowed direct transition, the material's energy band and the absorption coefficient α are connected. The Tacu plot[10] is used to compute the direct optical bandgap, which is shown in **Figure 3**. CuO/ZnO nanocomposite annealed at 500 °C has a direct optical bandgap of 2 eV and 3.78 eV. Presence of multiple band gap is the clear-cut representation of nanocomposite formation.

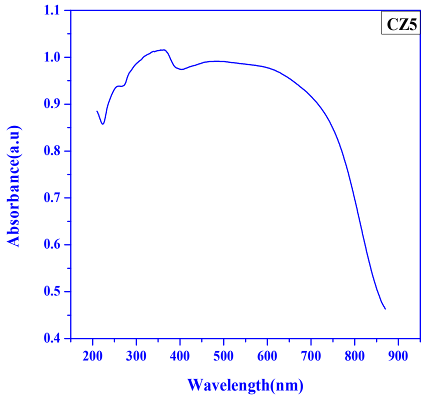


Figure 2. UV-visible spectrum of CZ5.

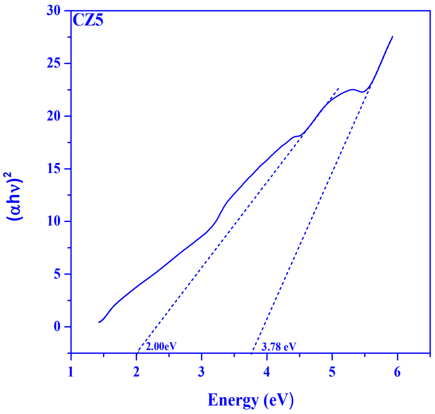


Figure 3. Tauc plot of CZ5.

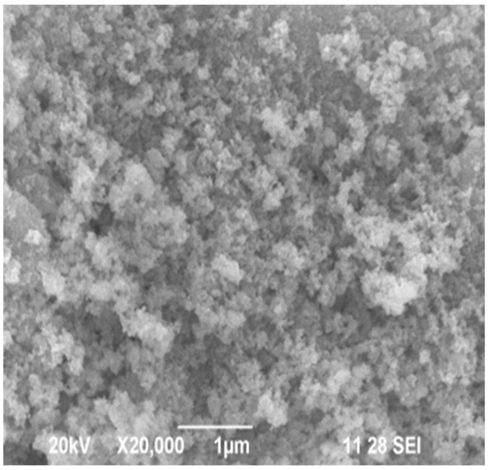


Figure 4. SEM image of CZ5.

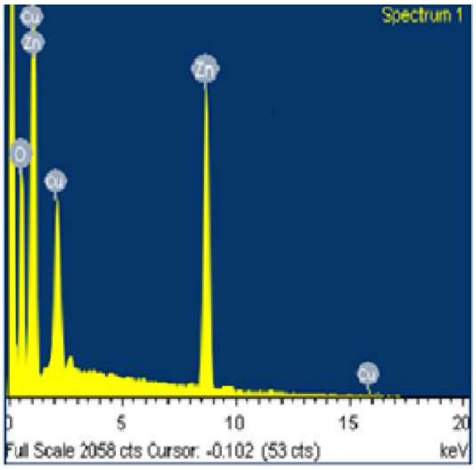


Figure 5. EDAX spectrum of CZ5.

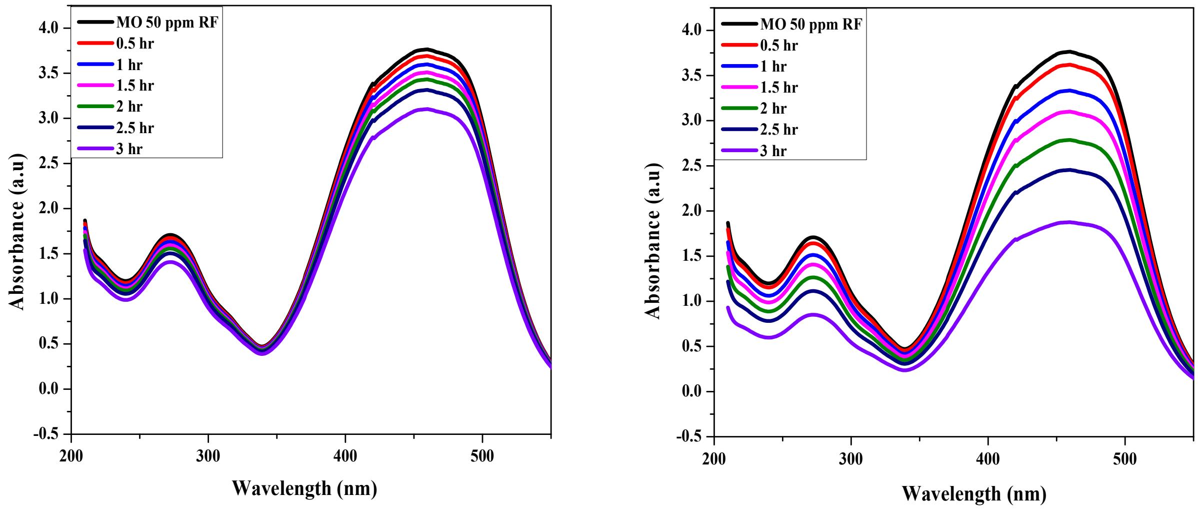
Figures 4 displays the SEM image of the CZ5 nanocomposite. The particles have a substantially agglomerated appearance and are roughly uniform in shape. **Figure 5** displays the nanocomposite's EDAX pattern. The presence of oxygen, zinc, and copper in the nanocomposite was confirmed by the EDAX results. The mass percentage of different elements in the sample obtained from EDAX analysis are oxygen 26.96%, copper 34.38% and zinc 38.66%, which confirms the formation of nanocomposite.

5. Photocatalytic studies

Photocatalytic degradation ability of CZ5 was studied using methyl orange and methyl red under UV and visible radiation. In the present study, the parameters such as dose rate of photocatalyst is fixed at 0.1 gm. The amount of catalyst load increased the number of active sites on the photocatalytic surface which increase the photocatlatitic efficiency[11]. The entire reaction was carried out in a constant temperature. Using the UV-Vis spectroscope, the initial absorbance of the blank solution was recoded. Thereafter at each half an hour 10 mL dye solution was collected from the cell and absorbance were recorded. The variations in absorbance with wavelength at a time ranging from 0.5 to 3 h in an interval of half an hour are shown in the **Figures 6** and **7**.

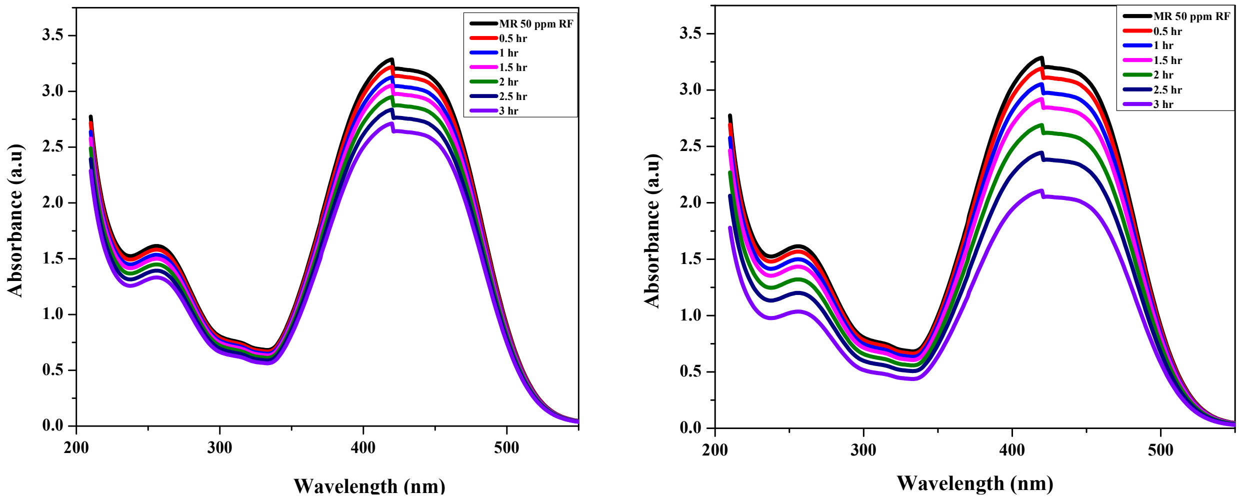
The mechanism proposed for the degradation of organic dyes methyl orange and methyl red by CZ5 is relatively due to the high band gap in the synthesized CZ5 nanocomposite the presence of two different transition metal oxide is helped to prevent the recombination of photo generated electron and holes this will leads to the production of more and more reactive species such as $OH^{\bullet}$ and $O_2^{\bullet-}$ involved in the degradation process. Additionally, the enhanced surface area of mixed metal oxide nanocomposite also enhances the photocatalytic activity of the morphology and surface sites of nanocomposite increases the adsorption process of dye molecules on the surface of the catalyst. As the adsorption of dye molecule on the surface of the photocatalyst increases the more photocatalyst sites. Are available and the degradation processes get enhanced.

Both studies revealed that the photocatalytic is higher at UV illumination as compared with visible radiation. The surface morphological parameters of the material are also playing a vital role in the case of catalytic activity the SEM image of the CZ5 shows the spherical homogeneous structure of the material. As the means that a crystal is arranged and structured will decide the performance of the atoms that represent the crystal and catalytic activity depends upon the surface structure of a crystal. the previous studies suggested that copper oxides with dominant (111) facet have higher photocatalytic activity compared with those don't have it[12].



(a) (b)

Figure 6. (a) Degradation of methyl orange under visible radiation; **(b)** Degradation of methyl orange under UV radiation.



(a) (b)

Figure 7. (a) Degradation of methyl red under visible radiation; **(b)** Degradation of methyl red under UV radiation.

From experimental results shows that the illumination radiation has dominant significance to degradation efficiency. The degradation of organic dye may arise from the high surface areas of the nanocomposite and the multiple band gap produced due to the composite formation. Another reason behind the photocatalytic degradation of organic dyes may be due to the oxidation and reduction. The relatively high band gap in the synthesized CZ5 nanocomposite material is probable to avoid the recombination of photo generated free electron and holes, which are liable for the creation of reactive free radicals such as $OH^{\bullet}$ and $O_2^{\bullet-}$. They are responsible for the degradation of organic dyes into carbon dioxide and water[13–15]. The nanocomposite of CZ5 with spherical morphology was found to have high band gap values and hence its higher activity can be accounted. Further, its high surface area and spherical morphology might have contributed to its efficiency. **Figure 8** represents the mechanism of photocatalytic degradation of dyes under UV or Visible radiation using CZ5 as photo catalyst. In the case of both dye materials maximum photocatalytic degradation efficiency was obtained for UV illumination.

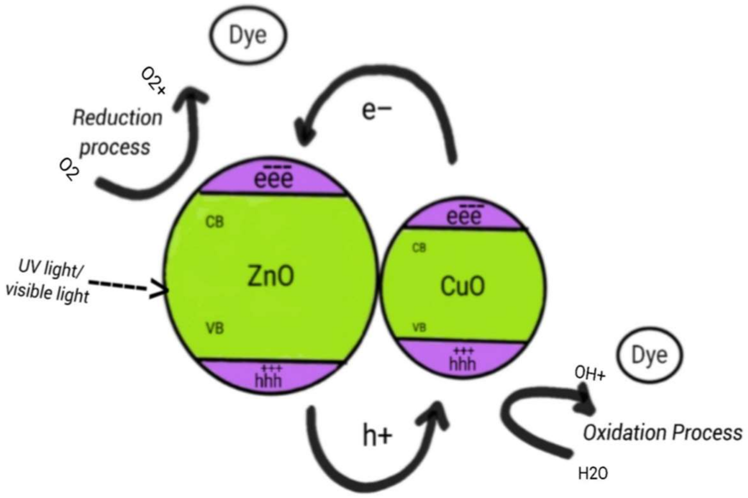


Figure 8. Proposed photocatalytic mechanism of CZ5 nanocomposite.

$$CZ5 + h\nu \rightarrow CZ5\ (e^-_{CB} + h^+_{VB})$$

$$h^+_{VB} + H_2O \rightarrow OH^\bullet + H^+$$

$$h^+_{VB} + OH^- \rightarrow OH^\bullet$$

Oxygen can react with conduction band electrons formed from semiconductors and thereby convert them into superoxide ions ($O_2^{\bullet -}$). These superoxide ions can react with hydrogen ions forming $HO_2^\bullet$.

$$e^-_{CB} + O_2 \rightarrow O_2^{\bullet -}$$

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^\bullet$$

Three distinct processes can be used to describe how H_2O_2 produces hydroxyl radicals. It directly absorbs light energy and transforms it into hydroxyl free radicals in the first process. Hydrogen peroxide absorbs super oxide ions to create hydroxyl free radicals in the following process. Finally, H_2O_2 absorbs electrons and instantly transforms into hydroxyl free radicals[16–18].

$$H_2O_2 + e^-_{CB} \rightarrow OH^\bullet + HO^-$$

According to the theoretical principle, one hydroxyl radical can only be produced with three electrons. However, one prerequisite for the production of hydroxyl free radicals is the presence of holes. It is evident from that hole reactions generate the majority of hydroxyl free radicals. One crucial element needed to keep the reaction going is the presence of the oxygen that absorbs electrons. Superoxide radicals and the prevention of electron-hole recombination both require oxygen to exist[19–21].

$$\text{Organic Dye} + CZ5/h\nu \rightarrow CO_2 + H_2O$$

6. Conclusion

Nanocomposite of copper oxide/zinc was synthesized by co-precipitation method and was annealed at 500 °C. XRD patterns of the sample can be considered as an express suggestion of its nanocrystalline nature. The particle sizes of the nanocomposite 31 nms. The direct optical bandgaps of the samples were calculated using Tauc relation and were found to be 2.00 eV and 3.78 eV. Surface morphological studies are carried out using SEM images. EDAX pattern confirms the chemical composition of nanocomposite. The photocatalytic studies reveal that copper Zin oxide nanocomposite have better degradation power in methyl red and methyl orange under UV irradiation.

Conflict of interest

The author declares no conflict of interest.

References

1. Ali I, Irina B, Evgeny G, et al. High-speed and high-capacity removal of methyl orange and malachite green in water using newly developed mesoporous carbon: Kinetic and isotherm studies. *ACS Omega* 2019; 4(21): 19293–19306. doi: 10.1021/acsomega.9b02669
2. Alghamdi AA, Al-Odayni AB, Saeed WS, et al. Adsorption of azo dye methyl orange from aqueous solutions using alkali-activated polypyrrole-based graphene oxide. *Molecules* 2019; 24(20): 3685. doi: 10.3390/molecules24203685
3. Akansha K, Chakraborty D, Sachan SG. Decolorization and degradation of methyl orange by *Bacillus stratosphericus* SCA1007. *Biocatalysis and Agricultural Biotechnology* 2019; 18: 101044. doi: 10.1016/j.bcab.2019.101044
4. Mustafa G, Tahir H, Sultan M, Akhtar N. Synthesis and characterization of cupric oxide (CuO) nanoparticles and their application for the removal of dyes. *African Journal of Biotechnology* 2013; 12(47): 6650–6660. doi: 10.5897/AJB2013.13058
5. Kida T, Oka T, Nagano M, et al. Synthesis and application of stable copper oxide nanoparticle suspensions for nanoparticulate film fabrication. *Journal of the American Ceramic Society* 2007; 90(1): 107–110. doi: 10.1111/j.1551-2916.2006.01402.x
6. Zhang W, Guo F, Wang F, et al. Synthesis of quinazolines via CuO nanoparticles catalyzed aerobic oxidative coupling of aromatic alcohols and amidines. *Organic & Biomolecular Chemistry* 2014; 12(30): 5752–5756. doi: 10.1039/c4ob00569d
7. Prince Joshua J, Krishnan S, Vidhya Raj DJ, et al. Novel synthesis of tenorite (CuO) nanoparticles by wet chemical method. *International Journal of ChemTech Research* 2014; 6(3): 2002–2004.
8. Mohan AC, Renjanadevi B. Preparation of zinc oxide nanoparticles and its characterization using scanning electron microscopy (SEM) and X-ray diffraction (XRD). *Procedia Technology* 2016; 24: 761–766. doi: 10.1016/j.protcy.2016.05.078
9. Biju R. Evaluation of the antibacterial properties of copper-based mixed metal oxide nanocomposite. *Nano and Medical Materials* 2023; 3(2): 261. doi: 10.59400/nmm.v3i2.261
10. Kumar H, Rani R. Structural and optical characterization of ZnO nanoparticles synthesized by microemulsion route. *International Letters of Chemistry, Physics and Astronomy* 2013; 19: 26–36.
11. Wang H, Xie C, Zhang W, et al. Comparison of dye degradation efficiency using ZnO powders with various size scales. *Journal of Hazardous Materials* 2007; 141(3): 645–652. doi: 10.1016/j.jhazmat.2006.07.021
12. Zhang Y, Deng B, Zhang T, et al. Shape effects of Cu_2O polyhedral microcrystals on photocatalytic activity. *The Journal of Physical Chemistry C* 2010; 114(11): 5073–5079. doi: 10.1021/jp9110037
13. Biju R, Ravikumar R, Thomas C, Indulal CR. Enhanced photocatalytic degradation of Metanil Yellow dye using polypyrrole-based copper oxide–zinc oxide nanocomposites under visible light. *Journal of Nanoparticle Research* 2022; 24(6): 117. doi: 10.1007/s11051-022-05495-3
14. Biju R, Ravikumar R, Thomas C, et al. Optimization and multifunctional applications of polypyrrole-modified copper oxide–zinc oxide nanocomposites. *Arabian Journal for Science and Engineering* 2023; 48(1): 919–937. doi: 10.1007/s13369-022-07199-1
15. Supin KK, Parvathy Namboothiri PM, Vasundhara M. Enhanced photocatalytic activity in ZnO nanoparticles developed using novel *Lepidagathis ananthapuramensis* leaf extract. *RSC Advances* 2023; 13(3): 1497–1515. doi: 10.1039/D2RA06967A
16. Güell F, Galdámez-Martínez A, Martínez-Alanis PR, et al. ZnO-based nanomaterials approach for photocatalytic and sensing applications: Recent progress and trends. *Materials Advances* 2023; 4(17): 3685–3707. doi: 10.1039/D3MA00227F
17. Bayat F, Sheibani S. Enhancement of photocatalytic activity of CuO-Cu_2O heterostructures through the controlled content of Cu_2O. *Materials Research Bulletin* 2022; 145: 111561. doi: 10.1016/j.materresbull.2021.111561
18. Alsulmi A, Mohammed NN, Soltan A, et al. Engineering S-scheme CuO/ZnO heterojunctions sonochemically for eradicating RhB dye from wastewater under solar radiation. *RSC Advances* 2023; 13(19): 13269–13281. doi: 10.1039/D3RA00924F
19. Tariq SR, Niaz Z, Chotana GA, et al. Photocatalytic degradation of imidacloprid using Ag_2O/CuO composites. *RSC Advances* 2023; 13(28): 19326–19334. doi: 10.1039/D3RA02109B
20. Dien ND, Ha PTT, Vu XH, et al. Developing efficient CuO nanoplate/ZnO nanoparticle hybrid photocatalysts for methylene blue degradation under visible light. *RSC Advances* 2023; 13(35): 24505–24518. doi: 10.1039/D3RA03791F
21. Anjum F, Shaban M, Ismail M, et al. Novel synthesis of CuO/GO nanocomposites and their photocatalytic potential in the degradation of hazardous industrial effluents. *ACS Omega* 2023; 8(20): 17667–17681. doi: 10.1021/acsomega.3c00129