TRENDS IN SCIENCES 2024; 21(11): 8219 RESEARCH ARTICLE
https://doi.org/10.48048/tis.2024.8219

A Comparative Study of Congo Red Textile Dye Photodegradation Using ZnO Al and ZnO Al+Mn Nanoparticles

Aprilion Krisandi[1,*], Heru Harsono[1] and Nurfina Yudasari[2]

[1]Department of Physics, Brawijaya University, Jawa Timur 65145, Indonesia
[2]Research Center for Photonics, National Research and Innovation Agency,
South Tangerang 15314, Indonesia

([*]Corresponding author's e-mail: aprilionkris@student.ub.ac.id)

Received: 20 March 2024, Revised: 27 April 2024, Accepted: 4 May 2024, Published: 1 October 2024

Abstract

Photodegradation of Congo Red textile dye was successfully carried out using ZnO Al and ZnO Al+Mn nanoparticles synthesized using the bottom-up coprecipitation method. Powder X-ray diffraction provides information that Al and Mn doping successfully inserted in the host crystal structure while maintaining the Hexagonal Wurtzite crystal structure. However, a shift in the diffraction peak caused by the lattice distance changes with the addition of doping. FE-SEM EDS provides information that both nanoparticles are nonuniform sphere-like due to the addition of dopping, and each dopping is detected through EDS spectra. There is a decrease in the gap energy in each sample. ZnO Al nanoparticles have a gap energy of 3.29 eV, and ZnO Al+Mn nanoparticles have a gap energy of 3.28 eV. However, the decrease in the gap energy is not directly related to the percentage and kinetic rate of Congo Red photodegradation. Adding 5 mg of ZnO Al Nanoparticles powder could degrade Congo Red up to 97.9 % within 120 min using UV A radiation or 0.03504/min. At the same time, adding ZnO Al+Mn Nanoparticles powder with the same parameters could only degrade 67.6 % or 0.00759/min.

Keywords: ZnO Al/Mn Nanoparticles, Photodegradation, Congo red

Introduction

Textiles are the dominating industry in various countries. This dominance occurs because the need for multiple types of textiles increases along with the population increase. It has a good impact on economic growth in various related industrial sectors. Nevertheless, it still leaves many problems in the environmental industry. Related and binding laws always accompany industrialization. One of them is the waste from textile production, whose processing has been regulated by state regulations. Unfortunately, not all industrial centers follow these rules due to the high cost of handling waste. This textile industry waste is disposed of in public disposal, directly impacting the environment. One of the wastes that this research focuses on is textile dye waste [1]. In Indonesia, especially in cultural tourism centers such as Bali, Yogyakarta, Pekalongan and several regions producing typical regional fabrics, some industry players still dispose of fabric dye waste, especially Congo Red, into the river. This organic dye is a type of textile dye that is used directly on textiles. Congo Red is also categorized as a residual compound and is highly toxic. The long half-life of Congo Red in soil and water causes this compound to be known and suspected as a carcinogen. Humans can suffer serious harm from its toxic properties, such as kidney damage, nervous system disorders and reproductive disorders. The presence of this pigment in aquatic ecosystems causes blockage of solar radiation, reducing the photosynthetic efficiency of aquatic plants and thus disrupting the balance of marine ecosystems [2-4].

Many parties have carried out countermeasures for textile dye pollution using various methods such as adsorption, filtration, coagulation and enzymatic. However, as reported by previous studies, these methods need to be more effective. One of the methods offered and being developed is degradation using semiconductor nanomaterials. One of the semiconductor nanomaterials developed is Zinc Oxide (ZnO); this nanomaterial has a gap energy of 3.37 eV in the Ultra Violet (UV) spectrum, a significant binding energy of about 60 MeV at room temperature, and naturally has n-type electrical conductivity [5,6]. The mechanism of ZnO nanoparticles in degrading textile dye waste is called photodegradation through a photocatalyst process. Here is the mechanism: Molecular reactions occur on the surface of the photocatalyst agent during the radiation process of Ultraviolet, Visible or Infrared light. This irradiated photon energy will excite electrons in the valence band to the conduction band so that the valence band leaves a hole. Then, the electrons in the conduction band are reduced with O_2 to produce superoxide anion radicals, while the holes in the valence band are oxidized with H_2O to form hydroxyl radicals. These 2 oxidative solid radicals are the agents that play an essential role in degrading the bonds of organic compounds in textile dyes [7,8].

One method of modifying nanoparticles to reduce the energy gap is dopping using transition, post-transition and noble metals. Post-transition doping has attracted the attention of many researchers because it can effectively change optical properties, such as decreasing the energy gap. Aluminum is one of the post-transition metals used for the main doping of ZnO semiconductors. Aluminum metal, which produces Al^{3+} ions, has a smaller atomic size than the primary Zn atom. This positively affects changes in lattice parameters that can increase Reactive Oxygen Species (superoxide anion and hydroxyl radicals). So, based on research by Sholeha *et al.* [9], Single dopping ZnO Al can reduce the energy gap from the initial 3.37 to 3.30 eV. This has the potential for ZnO doping Al to increase the percentage of photodegradation and the kinetic rate of photodegradation in its application as a photodegradation agent for textile dye waste [9]. This increases the possibility of Al-doped ZnO nanoparticles being used as a photodegradation agent for Congo Red textile dye waste. After a literature study, ZnO nanoparticles doping Al as a photodegradation agent were used for various textile dyes such as Rhodamine, Methylene Blue, Metanil Yellow and Congo Red [10-12]. This process is reported to be quite effective in degrading the chemical bonds of textile dyes. The next challenge faced is how to maximize the photodegradation process. One of the things under development is co-doping using transition metals. Co-doping ZnO-Al nanoparticles with transition metals can effectively minimize electron-hole recombination to maximize the excitation process. This is expected to lead to photocatalysts using visible light [13,14]. Some researchers have reported co-doping ZnO-Al with one of the transition metals, such as Ni. Ni co-doping ZnO-Al is said to be able to reduce charge recombination during the photocatalyst process, which increases its degradation capability [8]. The element Mn is also one of the exciting transition metals to be used as a co-doping candidate; according to Al-Gariaa, 2023 [15] ZnO in single doping with Mn can degrade cefotaxime waste effectively; this happens because Mn^{2+} ions have a larger size, thus preventing charge carriers for electron-hole recombination. When tested photocatalytically using UV radiation, this Mn-doped ZnO could degrade cefotaxime by 99 % for 2 h [15].

From the research that has been done before and to answer the challenges faced, this research wants to focus on combining the ability of ZnO nanoparticles, both single-doping Al and co-doping Al+Mn, to reduce the gap energy and increase the ability of Congo Red textile dye waste photodegradation rate. The synthesis method used in this research is the bottom-up coprecipitation nanoparticle synthesis method with parameters referring to supporting journals [16,17]. The material composition was determined using the equation $Zn_{0.95-x}Al_{0.05}Mn_x$ with x values of 0 and 0.01.

Materials and methods

Materials

In this study, the materials used include Zinc acetate dihydrate $Zn(CH_3COO)_2\cdot 2H_2O$ (Merck, 99.9 %), Aluminum chloride $AlCl_3$ (Analysis grade 99 %) and Manganese acetate $Mn(CH_3COO)_2\cdot 4H_2O$ (Merck, 99.9 %), precipitator NaOH, solvent DI (Deionized) Water and ethanol.

Coprecipitation synthesis

All materials were prepared using the $Zn_{0.95-x}Al_{0.05}Mn_x$ concentration ratio with $x = 0$ and 0.01. Each sample with a concentration of 1M was dissolved in 200 mL of deionized water and stirred using a magnetic stirrer at room temperature for 30 min. After that, the sample solution was titrated using NaOH solution with a concentration of 1 M until it reached pH 10. The precipitate was filtered using Whatman paper size 42. This process was carried out simultaneously with washing the sample using DI water and Ethanol. After that, the sample was transferred to the crucible and dried using an oven at a temperature of 90 °C for 12 h. All samples were calcined using a High-Temperature Furnace at 800 °C for 3 h.

Photodegradation of Congo Red

Congo red photodegradation activity using Al and Al+Mn doping ZnO nanoparticles was carried out using a standard dye solution with the same ten ppm 20 mL concentration. Pure congo red sample is written as CR, congo red sample + 5 mg ZnO Al nanoparticles are referred to as S1, and congo red sample + 5 mg ZnO Al+Mn nanoparticles are called S2. Each sample is irradiated under the UV A spectrum. All samples were characterized using UV-Vis spectroscopy to determine initial absorbance before being irradiated. Afterward, the initial absorbance spectra result data is labeled “Pre”. Then, each sample was irradiated in a chamber with a magnetic stirrer and 5 UV A lamps. Each sample was stirred using a magnetic stirrer and irradiated for 15 min. After 15 min, the samples were taken for UV-Vis testing. This process lasts up to 120 min, with step testing every 15 min. Every 15 min of characterization, absorbance data is labeled as “15 m” until “120 m”.

Characterisation technique

The characterization performed was divided into 3. The crystal structure was characterized using X-ray powder diffraction (XRD) with CuKα radiation (λ = 1.5406Å) 2θ angle used from 20 - 90°. Morphological shape and material composition were characterized using Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive Spectroscopy (EDS). Optical properties to determine the gap energy were carried out with Diffuse Reflectance Spectroscopy (DRS) using 200 – 1.100 nm wavelengths.

Results and discussion

X-ray diffraction data

The XRD spectra of Al and Al+Mn doped ZnO nanoparticles are given in **Figure 1**. The blue vertical line is the JCPDS 36 - 1,451 data combined with the black line (ZnO Al) and the red dashed line (ZnO Al+Mn). From **Figure 1**, it can be seen that all spectra appear in the same hkl plane as pure ZnO. Additional peaks are also not observed in the spectra of either ZnO Al or ZnO Al+Mn nanoparticles. Both modified samples retain pure ZnO and a hexagonal Wurtzite crystal structure with space group $P6_3mc$ [18]. The observed change is a shift in the peak of ZnO Al+Mn nanoparticles. One of the enlarged peaks to be observed is the peak that shows the 101 lattice plane. The peak of pure ZnO lattice 101 is at angle 2θ 36.253°. In Al and Al+Mn doped ZnO nanoparticles, the 101 lattice peak shifts towards a larger angle of

36.320 ° in Al ZnO and 36.300 ° in Al+Mn ZnO. The shift of the ZnO Al peak towards a larger angle occurs because the 0.53 Å sized Al^{3+} ions are smaller than the host Zn^{2+} ions of 0.74 Å. Al^{3+} ions inserted in the ZnO crystal structure make the distance between the lattice larger. This results in a larger X-ray diffraction angle. After the 0.82 Å Mn^{2+} ions enter the second sample, the diffraction angle moves towards a smaller angle. The larger ion size makes the distance between lattices closer, decreasing the X-ray diffraction angle. The shifting of the diffraction peak towards a higher angle indicates a change in the lattice parameters, which is decreasing. ZnO is a semiconductor that has a hexagonal wurtzite phase. Changes in this diffraction peak will affect the lattice parameter c, which shortens with adding Al and Mn doping. The decrease in the crystal lattice affects the stronger electron bonds at each angle. This has an impact on narrowing the width of the energy band gap. This is following the hypothesis described in the introduction. Narrowing the energy band gap will make it easier for electrons to excite from the π bond to the π* bond. Electrons excited and in contact with water will produce more ROS, so the possibility of increasing photocatalyst activity is more significant [9].

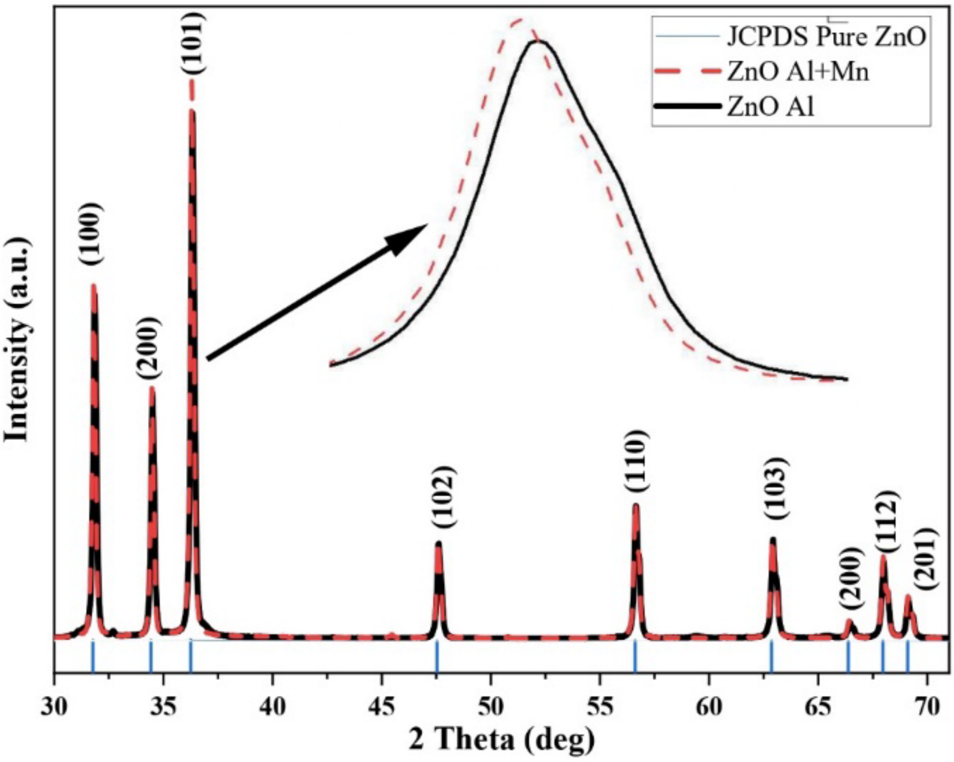


Figure 1 Powder X-ray diffraction patterns of JCPDS Pure ZnO, ZnO Al nanoparticles and ZnO Al+Mn nanoparticles.

FE-SEM EDS data

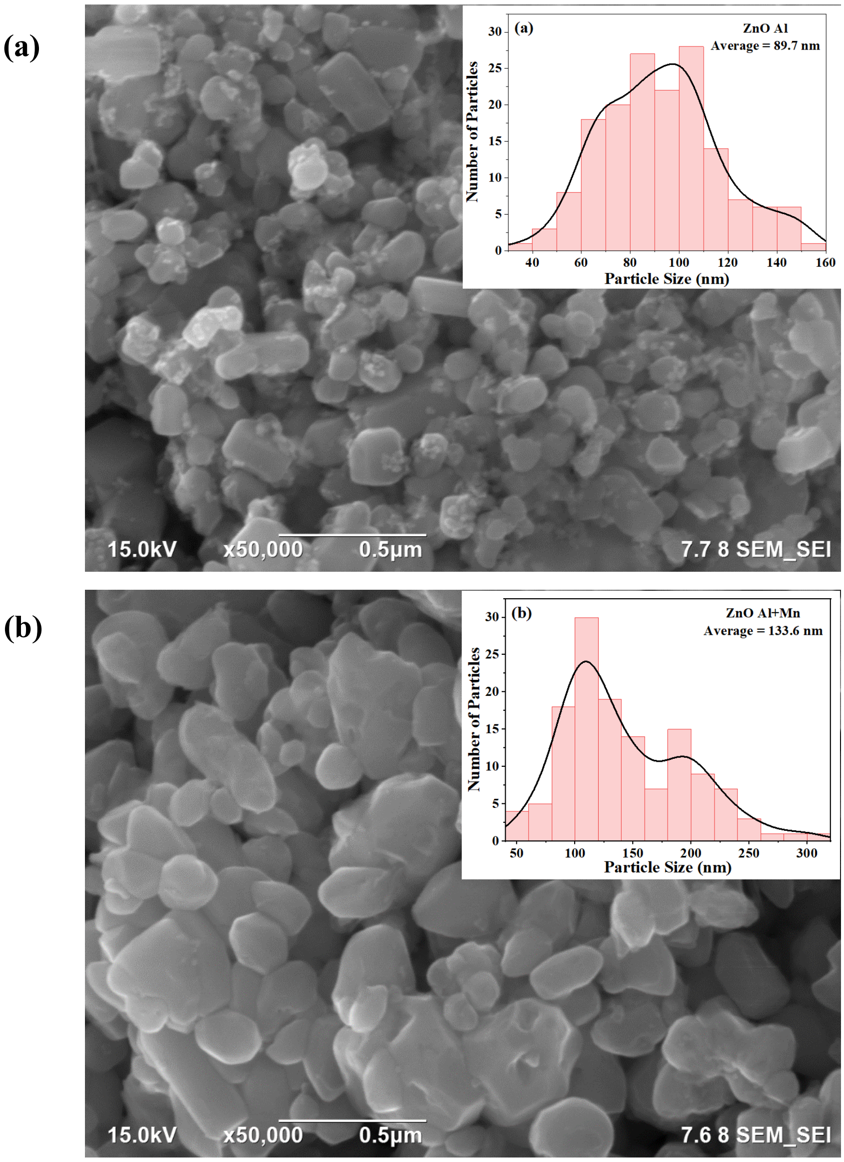
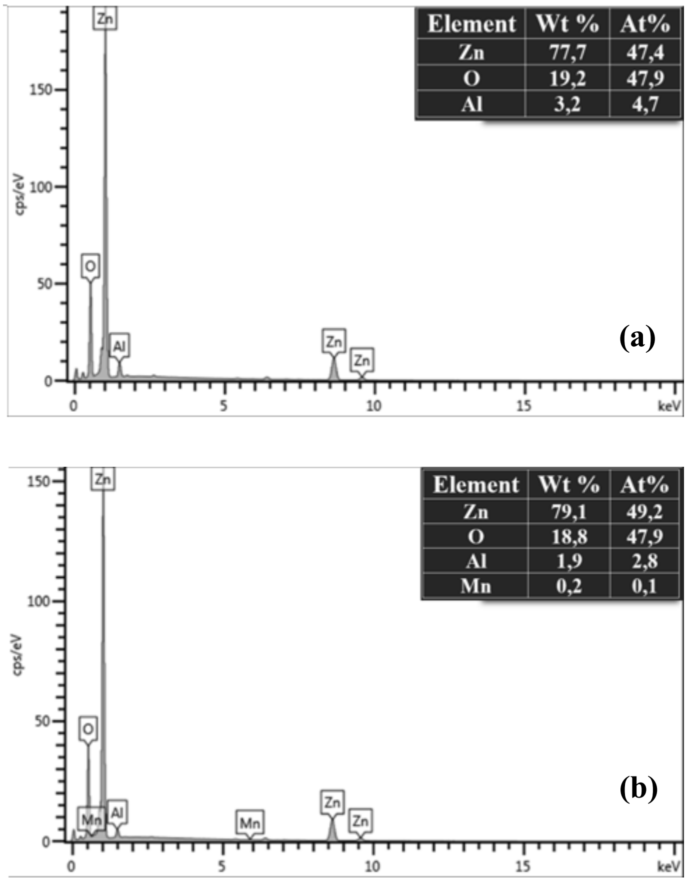


Figure 2 FE-SEM images of (a) ZnO Al nanoparticles and (b) ZnO Al+Mn nanoparticles.

FE-SEM results of Al and Al+Mn doped ZnO nanoparticles are shown in **Figure 2**. **Figure 2(a)** shows the morphology of Al-doped ZnO nanoparticles. Most particle distribution is in the range of 100 - 110 nm. However, the average ZnO Al nanoparticles have a particle size of 89.7 nm. After the addition of double doping, Mn peak particle distribution does not shift towards larger or smaller, remaining in the range of 100 - 110 nm. This happens because the added Mn elemental ions are insignificant enough to change the particle size. However, when averaged, ZnO Al+Mn nanoparticles have an average particle size of 133.6 nm. **Figure 2(a)** shows the non-uniform shape of ZnO Al nanoparticles. Most are irregularly shaped sphere-like, but they are still nanorod-shaped. This is based on research conducted by Gnanamozhi 2023 [19] that shows that adding Al doping will change the shape of nanorods into nanoparticles [19]. **Figure 2(b)** shows the morphology of the ZnO Al+Mn nanoparticle, which has a more uniform particle shape than in **Figure 2(a)**. Each doping that subtitute the ZnO host element makes it like a ZnO/Al or ZnO/Al/Mn nanocomposite arrangement. This well-dispersed aggregate is beneficial for increasing the adsorption activity of Congo Red dye molecules on the surface of the photocatalyst material. It plays a vital role in entering photon radiation as a photodegradation source. The composition of each sample was characterized using EDS, as shown in **Figures 3(a)** and **3(b)**. The mass percentage resulting from this EDS mapping indicates that the Al and Mn elements were successfully inserted into the ZnO nanoparticle structure.



Element	Wt %	At%
Zn	77,7	47,4
O	19,2	47,9
Al	3,2	4,7

Element	Wt %	At%
Zn	79,1	49,2
O	18,8	47,9
Al	1,9	2,8
Mn	0,2	0,1

Figure 3 Energy dispersive images for (a) ZnO Al nanoparticles and (b) ZnO Al+Mn nanoparticles.

Band gap study

Optical properties were observed using Ocean Optic DRS reflectance spectroscopy with a 200 - 800 nm wavelength range. Reflectance testing of materials was done to calculate the gap energy values of ZnO Al and ZnO Al+Mn nanoparticles. The extrapolation point of the linear part that meets the abscissa point will be given as the gap energy value of a material. Calculation of the gap energy value is done using Eq. (1) below [20].

$$(F(R)\,h\nu)^{\gamma}=A\left(h\nu-E_{g}\right) \tag{1}$$

where F(R) is the Kubelka-Munk function, which is the ratio of absorption coefficient and scattering coefficient, while γ is the value of ½ for indirect band gap and 2 for direct band gap, the gap energy can be obtained by plotting a graph of $(F(R)h\nu)^2$ as a function of hν.

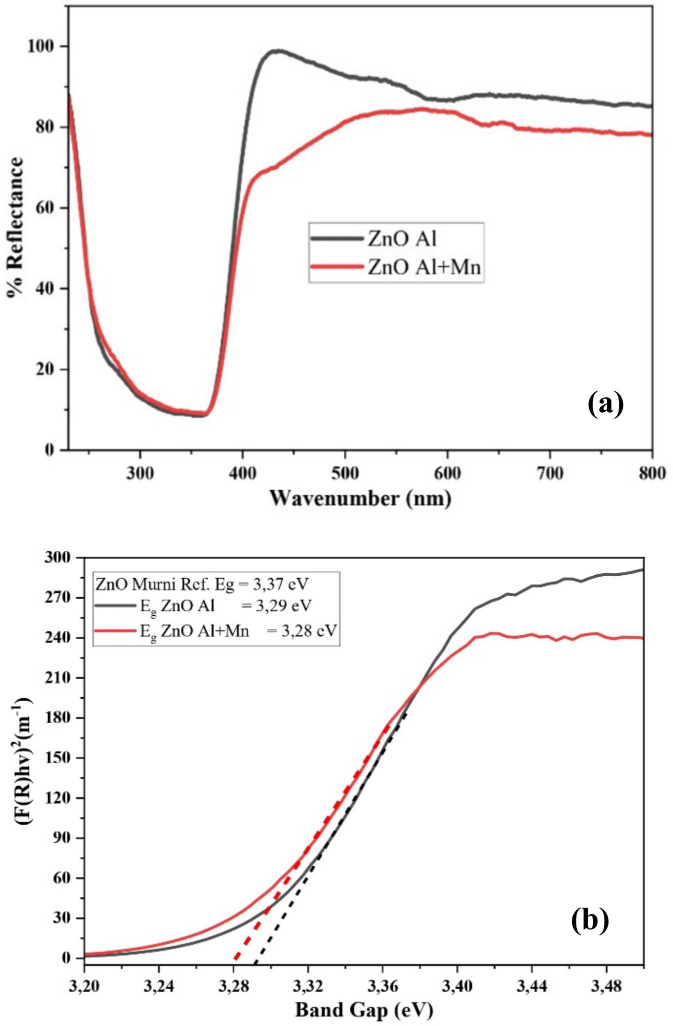


Figure 4 (a) Diffuse Reflectance Spectra (DRS) of ZnO Al and ZnO Al+Mn nanoparticles (b) plot of $(F(R)h\nu)^2$ with hv of ZnO Al and ZnO Al+Mn nanoparticles.

Figure 4(a) shows the reflectance spectra of ZnO Al and ZnO Al+Mn nanoparticle samples. The addition of Mn doping can be seen to decrease the reflectance peak around the wavelength of 400 nm. **Figure 4(b)** shows the gap energy values of the 2 nanoparticles that have been characterized. Changes in the calculated gap energy values and comparison with the reference gap energy are displayed directly in **Figure 4(b)**. All the gap energy values of the materials dropped using Al and Mn are lower than those of pure ZnO. The decrease in the percentage of reflectance is a sign that the greater the UV radiation absorbed by ZnO Al+Mn Nanoparticles than ZnO Al Nanoparticles. This occurs because of the narrowing of the energy band gap in ZnO Al + Mn nanoparticles; this results in more photon energy absorbed by electrons to move from the Ground State to the Excited State. The decrease in the percentage of reflectance is confirmed by the decrease in the energy gap, which is physically directly related to the excited behavior of electrons. This decrease in gap energy value occurs due to incorporating Al and Mn ions in the Zn lattice, creating a new recombination pattern. Gaurav Saxena described the reduction in gap energy value and the addition of Al and Mn doping as a form of p-d spin exchange interaction between localized d electrons resulting from substituting Al^{3+} and Mn^{2+} ions. ZnO Al+Mn nanoparticles produce a significant decrease in the gap energy. This is due to the strong p-d assimilation between O and Mn [21].

Photodegradation study

Figure 5(a) shows the physical changes of the congo red solution without degradation agent (CR), ZnO Al Agent (S1) and ZnO Al+Mn Agent (S2). **Figure 5(b)** shows the absorption spectrum of pure Congo Red from before irradiation to irradiation for 120 min. Without any degradation agent, the Congo Red absorption spectrum did not decrease. This means that the photodegradation process does not occur without degradation agents.

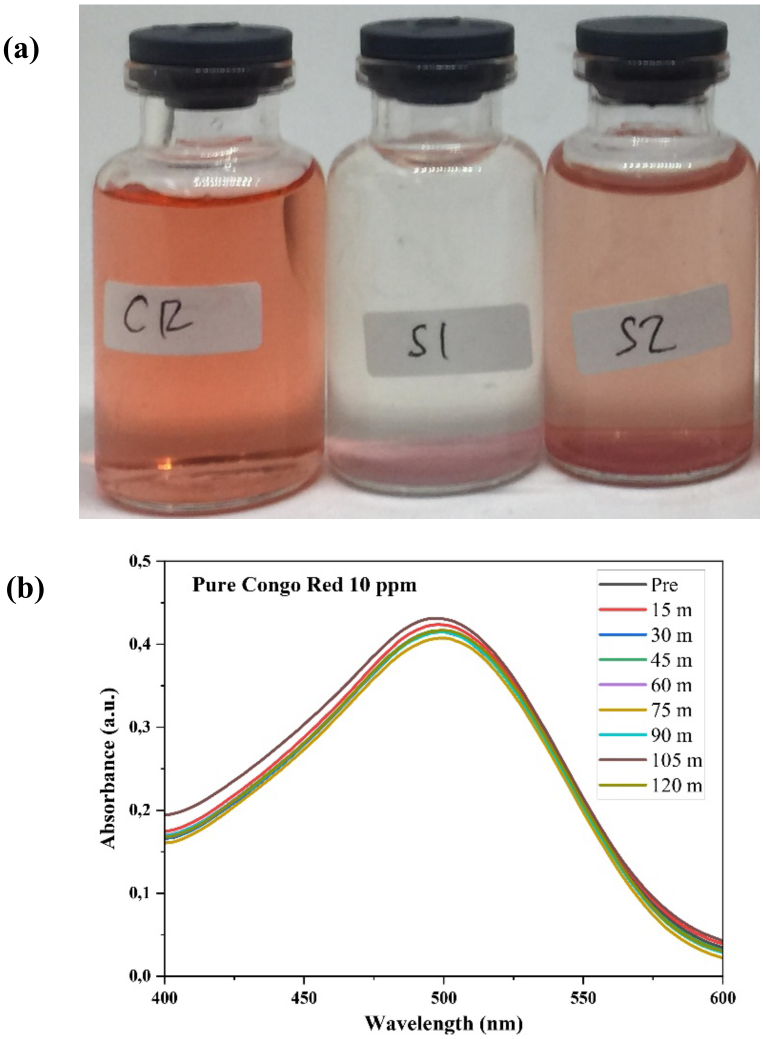


Figure 5 (a) Congo Red solution after photodegradation (b) Pure Congo Red absorbance spectra.

Visually, in **Figure 5(a)**, it can be seen that ZnO Al nanoparticles can reduce the color intensity significantly compared to ZnO Al+Mn nanoparticles. This is confirmed by **Figures 6(a)** and **6(b)**, which show a decrease in absorbance value in Congo Red dye solution. The absorption peak of Congo red dye waste is at around 498 nm wavelength. The photodegradation process was carried out every 15 min using UV A light and repeated up to 120 min of observation. When viewed, the intensity of Congo Red absorption decreases with increasing irradiation time, both in the ZnO Al nanoparticle agent and ZnO Al+Mn nanoparticles. This means that both nanoparticles successfully degrade Congo Red textile dye waste with the help of UV A radiation. In the photodegradation agent ZnO Al nanoparticles, the decrease in absorption intensity is quite significant. This is likely due to the amount of adsorption on the surface of ZnO Al nanoparticles. On ZnO Al+Mn nanoparticles, the decrease in intensity is not significant. This may occur due to the presence of Mn^{2+} ions inserted in the main ZnO crystal along with Al^{3+} ions so that the adsorption is manageable, as in ZnO Al, where there are only Al^{3+} ions.

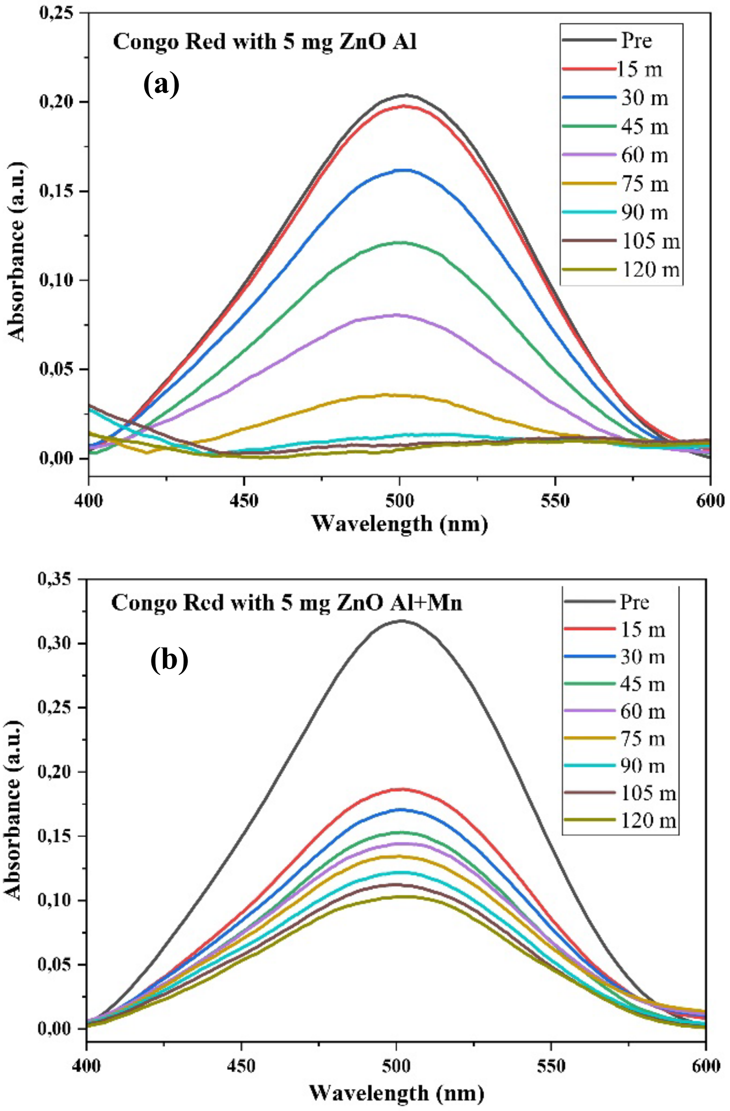


Figure 6 Absorbance spectra of Congo Red peaking at 498 nm due to the effect of (a) ZnO Al NPs and (b) ZnO Al+Mn NPs.

After the solution is irradiated using UV A light, electrons (e^-) in ZnO Al and Al+Mn nanoparticles will be excited from the ground state or valence band to the conduction band; this event leaves holes in the valence band, which then reacts with water molecules to produce products in the form of hydroxyl radicals. Then, the electrons in the conduction band have superoxide radicals, effectively reducing charge recombination. This hydroxyl radical mineralizes the Congo Red dye due to its strong oxidizing properties. Substituting Al^{3+} and Mn^{2+} ions can increase electron mobility, accelerating photocatalyst activity. The electrons from these Al^{3+} and Mn^{2+} ions produce superoxide radicals. One of the other species is Reactive Oxygen Species (ROS); when the dye interacts with ROS, this dye molecule will be absorbed by its surface, and the molecule will be degraded easily into a non-toxic solution.

The percentage of Congo Red photodegradation by ZnO Al and Al+Mn nanoparticles was calculated using absorbance data from UV-Vis characterization using Eqs. (2) - (3). C_o is the initial absorbance before UV A radiation, and C_t is the absorbance at the last radiation time. The photodegradation rate can be calculated using Eq (3). K_{app} is the photodegradation rate with units (min^{-1}) obtained from the slope value of ln C_o/C_t as a function of radiation time (t) [3,22,23].

$$\%\ degradation = \frac{C_O - C_t}{C_O} x100\% \tag{2}$$

$$\ln \frac{C_O}{C_t} = k_{app} t \tag{3}$$

Table 1 Percentage of photodegradation activity.

No	Degradation agent	% Degradation	Kapp (min^{-1})
1	ZnO Al NPs	97.9	0.03504
2	ZnO Al+Mn NPs	67.6	0.00759

After calculating the percentage of degradation using Eq. (2) and the kinetic rate of photodegradation using Eq. (3), the values presented in **Table 1** were obtained. ZnO Al nanoparticles can degrade 97.9 % of Congo Red textile dye waste using UV A radiation within 120 min. This is evident from **Figure 6(a)**, which illustrates that the absorption peak of Congo Red decreased drastically. This value is lower than the research conducted by Gnanamozhi *et al.* [19], which uses 5 % Al doping in ZnO material to degrade 99.5 % of Methylene Blue textile dye waste for 120 min using UV A radiation. **Figure 6(b)** shows the degradation ability of ZnO Al+Mn nanoparticles in Congo Red textile dye solution. The absorbance value of Congo Red decreased as the radiation time increased. The photodegradation ability from the first min of irradiation to 120 min was recorded at 67.6 %. This value is smaller than the ability of ZnO Al nanoparticles. The radiation rate expressed by K_{app} confirmed the percentage of degradation. ZnO Al nanoparticles were recorded to degrade at a rate of 0.03504/min, while ZnO Al+Mn was only able to degrade at a rate of 0.00759/min. This means that ZnO Al nanoparticles have better Congo Red photodegradation ability than ZnO Al+Mn nanoparticles. The decrease in the energy gap in Al+Mn codoping on ZnO nanoparticles does not linearly impact its photocatalyst activity. This differs from the initial hypothesis that adding Mn codoping can increase the photocatalyst activity. Saqib *et al.* [24] also experienced the same thing with this. This happens because Mn is used as codoping, so there is a possibility that Mn atoms do not replace Zn atoms due to the overlapping of atoms, so irradiation is not established ideally. This can be seen in the FE-SEM characterization results. It can be seen that particle agglomeration occurs, which indicates the imperfection of the UV irradiation exposure process. Saqib *et al.* [24] also proved by removing Al doping so that Mn is the main doping. The results of this synthesis reduced the energy gap to 1.8 eV. MB textile dye can be degraded using visible light for 150 min with this modification.

Conclusions

Congo Red is one type of organic textile dye waste that is difficult to decompose when reacting with water. Therefore, the role of nanoparticles as a photodegradation agent is a solution to this problem. The synthesis of ZnO Al and Al+Mn nanoparticles has been successfully carried out using the coprecipitation method using DI Water and 1 M NaOH at pH 10. XRD and FESEM EDS characterization was carried out to determine changes in the structure and morphology of nanoparticles. This aims to ensure that both doping inserts are perfect on ZnO nanoparticles. The incorporation of metal ions on ZnO impacts photocatalyst activity, including a decrease in the gap energy. The impact of Al doping on ZnO nanoparticles reduces the gap energy from 3.37 to 3.29 eV, while adding Al+Mn codoping reduces the gap energy to 3.28 eV. Both nanoparticle powders were photodegradation agents on Congo Red textile dye waste liquid. Each 5 mg nanoparticle powder was added to 20 mL of 10 ppm Congo Red. For 120 min, ZnO Al nanoparticles were able to degrade 97.9 % of Congo Red, while ZnO Al+Mn nanoparticles were recorded to be able to degrade 67.6 %. From this study, it can be concluded that ZnO Al nanoparticles are more effective in degrading Congo Red textile dye waste using UV A radiation for 120 min than ZnO Al+Mn nanoparticles.

Acknowledgments

The authors are grateful to the head of the Biophysics Laboratory for providing a place to synthesize ZnO nanoparticles and to BRIN Talent Management for organizing the Barista program, which helped fund the research.

References

[1] B Lellis, CZ Fávaro-Polonio, JA Pamphile and JC Polonio. Effects of textile dyes on health and the environment and bioremediation potential of living organisms. *Biotechnol. Res. Innovat.* 2019; **3**, 275-90.

[2] RE Adam, G Pozina, M Willander and O Nur. Synthesis of ZnO nanoparticles by co-precipitation method for solar driven photodegradation of Congo red dye at different pH. *Photon. Nanostructures* 2018; **32**, 11.

[3] S Boudiaf, N Nasrallah, M Mellal, B Belhamdi, C Belabed, MA Djilali and M Trari. Kinetic studies of Congo Red Photodegradation on the hetero-system $CoAl_2O_4$/ZnO with a stirred reactor under solar light. *J. Environ. Chem. Eng.* 2021; **9**, 105572.

[4] MB Mobarak, NS Pinky, F Chowdhury, MS Hossain, M Mahmud, MS Quddus, SA Jahan and S Ahmed. Environmental remediation by hydroxyapatite: Solid state synthesis utilizing waste chicken eggshell and adsorption experiment with Congo red dye. *J. Saudi Chem. Soc.* 2023; **27**, 101690.

[5] Mahesha, M Nagaraja, A Madhu, N Suriyamurthy, SS Reddy, M Al-Dossari, NSA EL-Gawaad, SO Manjunatha, K Gurushantha and N Srinatha. Chromium-doped ZnO nanoparticles synthesized via auto-combustion: Evaluation of concentration-dependent structural, band gap-narrowing effect, luminescence properties and photocatalytic activity. *Ceram. Int.* 2023; **49**, 22890.

[6] D Savitha, HKE Latha, HS Lalithamba, S Mala and YV Jeppu. Structural, optical and electrical properties of undoped and doped (Al, Al + Mn) ZnO nanoparticles synthesised by green combustion method using terminalia catappa seed extract. *Mater. Today Proc.* 2022; **60**, 988.

[7] R Ghorbali, G Essalah, A Ghoudi, H Guermazi, S Guermazi, AE Hdiy, H Benhayoune, B Duponchel, A Oueslati and G Leroy. The effect of (In, Cu) doping and co-doping on physical properties and organic pollutant photodegradation efficiency of ZnO nanoparticles for wastewater remediation. *Ceram. Int.* 2023; **49**, 33828.

[8] MR Al-Mamun, MZI Rokon, MA Rahim, MI Hossain, MS Islam, MR Ali, MS Bacchu, H Waizumi, T Komeda and MZH Khan. Enhanced photocatalytic activity of Cu and Ni-doped ZnO nanostructures: A comparative study of methyl orange dye degradation in aqueous solution. *Heliyon* 2023; **9**, e16506.

[9] N Sholeha, AM Afianti, M Diantoro, A Aripriharta and H Pujiarti. Structure, functional groups, and optical properties of Al doped ZnO nanorods thin films. *Mater. Today Proc.* 2023. https://doi.org/10.1016/j.matpr.2023.04.159.

[10] W Purwaningrum, FP Sari, Julinar, A Ahmadi and M Said. Effect of Al Concentration over ZnO-Al2O3 Physicochemical Characteristics and Removal of Remazol Red RB. *ASEAN J. Chem. Eng.* 2022; **22**, 206.

[11] F Abdulrahman, AN Abdulqodus and MA Almessiere. Biosynthesis of Al-doped ZnO nanoparticles with different Al doping ratio for methylene orange dye degradation activity. *Ceram. Int.* 2023; **49**, 34920.

[12] HJ Lee, JH Kim, SS Park, SS Hong and GD Lee. Degradation kinetics for photocatalytic reaction of methyl orange over Al-doped ZnO nanoparticles. *J. Ind. Eng. Chem.* 2015; **25**, 199.

[13] MA Nawaz. 2016, Effect of transition metals doping on the properties of ZnO thin films. Ph. D. Dissertation. The Islamia University of Bahawalpur, Bahawalpur, Pakistan.

[14] CO Chey. *Synthesis of ZnO and transition metals doped ZnO nanostructures.* Linköping University Electronic Press, Linköping, Sweden, 2015.

[15] M Al-Gariaa, GS Elasala, EH Ismail, MMH Khalil and IM El-Sewify. Photodegradation of antibacterial cefotaxime using Mn doped ZnO nanosphere. *Inorg. Chem. Comm.* 2023; **158**, 111434.

[16] S Roguai and A Djelloul. Structural, microstructural and photocatalytic degradation of methylene blue of zinc oxide and Fe-doped ZnO nanoparticles prepared by simple coprecipitation method. *Solid State Comm.* 2021; **334-335**, 114362.

[17] R Prasetyowati, D Widiawati, E Swastika and W Ariswan. Synthesis and characterization of magnetite (Fe_3O_4) nanoparticles based on iron sands at Glagah Beach Kulon Progo with coprecipitation methods at various NH_4OH concentrations. *In*: Proceedings of the Science and Science Education International Seminar, Yogyakarta, Indonesia. 2019.

[18] K Pavani and A Kumar. ZnO nanostructures: Simple routes of synthesis. *Int. J. Eng. Res. Tech.* 2015; **4**, 505-8.

[19] P Gnanamozhi, A Monamary, SD Jereil, JE Pauline, JAO Ratnam, A Ganeshkumar, V Pandiyan, AA Alothman, RA Alshgari and M Govindasamy. Effective photocatalytic degradation of methylene blue (MB) and reactive red 120 (RR120) using Al substituted ZnO nanoparticles. *Surface Interfac.* 2023; **41**, 103203.

[20] S Landi, IR Segundo, E Freitas, M Vasilevskiy, J Carneiro and CJ Tavares. Use and misuse of the Kubelka-Munk function to obtain the band gap energy from diffuse reflectance measurements. *Solid State Comm.* 2022; **341**, 114573.

[21] G Saxena, IA Salmani, MS Khan and MS Khan. Structural co-related optical properties of Al and Cu co-doped ZnO nanoparticles. *Nano Struct. Nano Objects* 2023; **35**, 100986.

[22] BCB Salgado, RA Cardeal and A Valentini. *Photocatalysis and Photodegradation of Pollutants*. *In*: R Nascimento, OP Ferreira, AJD Paula and VOS Neto (Eds.). Nanomaterials applications for environmental matrices: Water, soil, and air. Elsevier, Amsterdam, Netherlands, 2019, p. 449-88.

[23] N Yudasari, A Hardiansyah, Y Herbani, MMS Uliyanti and D Djuhana. Single-step laser ablation synthesis of ZnO-Ag nanocomposites for broad-spectrum dye photodegradation and antibacterial photoinactivation. *J. Photochem. Photobiol. A Chem.* 2023; **441**, 114717.

[24] M Saqib, SU Rahman, S Ali, SA Khan, B Ismail and AM Khan. Comparative studies of “3d” transition metals (Co, Mn, Ni) doped ZnO nanoparticles for visible light degradation of methylene blue. *Mater. Today Comm.* 2023; **37**, 107335.