Green synthesis of zinc oxide from aqueous fruit extract of *Dovyalis abyssinica* (Koshem) and application for water purification

Mekuriaw Assefa Kebede[1,*], Tessera Alemneh Wubieneh[2], Yonas Beyene Yohannes[1], Kinjal J. Shah[3]
[1]Bahir Dar University, Science College, Department of Chemistry, 79, Ethiopia

[1]Bahir Dar University, Science College, Department of Chemistry, 79, Ethiopia
[2]Bahir Dar University, Science College, Department of Material Science and Engineering, PO Box 79, Ethiopia
[3]College of Urban Construction, Nanjing Tech University, Nanjing, 211800, China

Received: 15 February 2022 **Accepted**: 21 November 2022 **Published**: January 2023

ABSTRACT

This article reports the green synthesis of ZnO nanoparticles using an endemic plant called *Dovyalis abyssinica*, locally known as *Koshem*, for the degradation of malachite green dye in photocatalytic process. An aqueous extract from the ripe fruits of the plant was incorporated into the sol-gel synthesis process to obtain ZnO NPs with the size of 17 nm. XRD data and UV-Vis absorption at 390 nm confirmed that the synthesis was successful. In addition, the FTIR result showed a characteristic absorption peak at 543 cm^{-1} for the presence of Zn-O stretching and additional peaks also appeared from the plant source, suggesting that the natural functionalities are present together on ZnO particles as a capping agent. The ZnO NPs produced were used as a photocatalyst to degrade the organic dye malachite green. The results showed that ZnO nanomaterials synthesized in green removed 98.5% of the dye from the aqueous solution by photo-degradation under visible light. This study contributes to efforts that try to develop efficient techniques for removing organic pollutants from wastewater treatment.

Key words: Zinc oxide; Nanoparticles; Photo-degradation; Malachite green; Waste-water
DOI: https://dx.doi.org/10.4314/ejst.v16i1.1

INTRODUCTION

Since water is one of nature's most precious resources, its conservation is so important in order to sustain the life of living things. However, the dynamic behavior of the human lifestyle and population affects its availability and purity (Gedda *et al.*, 2021). Various companies discharge their wastewater, which contains contaminants such as organic dyes and heavy metals, into water bodies (Domınguez *et al.*, 1998; Williams *et al.*, 1998; Kadirvelu *et al.*, 2001; Vasseghian *et al.*, 2021). People also use chemicals like oils, detergents, soap in cooking, washing and cleaning at home that also affect the purity of the water (Gedda *et al.*, 2021). As the availability of drinking

* Corresponding author: Meku.assefa65@gmail.com

water in urban areas is at risk, finding simple, inexpensive, and applicable scientific techniques for removing water pollutants should be a timely focus of research.
Malachite green (MG) is an organic dye. It is a green crystal powder with a metallic sheen, which is readily soluble in water and ethanol with a blue-green solution and is used as a dye in the textile, leather, and paper industries (Meena *et al.*, 2016). However, such organic dyes have carcinogenic properties and are major sources of water pollution because of their easy solubility.

Therefore, it is necessary to find an effective way to decompose and/or remove them from industrial wastewater in order to mitigate their dangerous effects (Saikia *et al.*, 2015). Various techniques such as photocatalytic degradation by oxidation (Iqbal *et al.*, 2021), physical adsorption (Sartape *et al.*, 2017; Alalwan *et al.*, 2021; Dutta *et al.*, 2021), ion exchange (Laszlo, 1996; Sinha *et al.*, 2021), electrochemical (Aoudj *et al.*, 2021; Rodríguez-Narváez *et al.*, 2021), and coagulation - flocculation (Mahecha *et al.*, 2021) techniques are used to remove organic pollutants. To remove it from the water, the oxidation processes is considered to be an inexpensive and very efficient method (Xu *et al.*, 2013; Ekennia *et al.*, 2021).

Metallic nanoparticles such as TiO_2 and ZnO are well-known catalysts for removing organic- based pollutants such as MG dyes, which are present in wastewater through oxidative photo-degradation process in the presence of light sources. The photocatalytic removal of MG dye from water using nanoparticle catalysts has been reported in various references, which mainly affects the degradation efficiency (Chen *et al.*, 2007; Saikia *et al.*, 2015; El-Hout *et al.*, 2020). However ZnO is more suitable in the presence of sunlight because of its low cost (Sakthivel *et al.*, 2003). ZnO nanoparticles (ZnO-NPs) can be produced by hydrothermal, sol-gel, combustion, precipitation, electro-deposition, spray pyrolysis and green synthesis techniques (Hasnidawani *et al.*, 2016; Kumaresan *et al.*, 2017; Chankhanittha and Nanan, 2018; Zare *et al.*, 2019; Ganesan *et al.*, 2020). Each method has its own contributions to tuning the shape and size of ZnO-NPs, which in turn affects their catalytic performance. The green synthesis of nanoparticles is an up-to-date technique for the synthesis of metallic nanoparticles. With this method, organic natural substances from plants, bacteria or enzymes act as reducing agents and stabilizers instead of synthetic reducing agents. It is also preferred because it is available, cheap, simple and environmentally friendly natural compound that may be involved in the synthesis process. Green synthesis of ZnO-NPs extracts of plants include: *Azadirachta indica (Neem)* (Bhuyan *et al.*, 2015; Singh *et al.*, 2019; Bhatti *et al.*, 2021), *Amomum longiligulare* (Liu *et al.*, 2020) , *Gynostemma pentaphyllum* (Park *et al.*, 2021), *Tectona grandis* (Senthilkumar *et al.*, 2017), *Thymus vulgaris* (Zare *et al.*, 2019), *Calotropis procera* (Rajashekara *et al.*, 2020), *Polygonum chinese* (Sultana *et al.*, 2017), *Mimosa pudica* (Fatimah *et al.*, 2016; Balogun *et al.*, 2020), *Moringa oleifera* (Matinise *et al.*, 2017; Ngom *et al.*, 2021), *Aloe barbadensis miller* (Sangeetha *et al.*, 2011). ZnO-NPs were successfully synthesized from *Aloe vera* extract and were used for the removal of MG dye in waste-water under sunlight (Ekennia *et al.*, 2021; Jose *et al.*, 2021).

D. abyssinica (*DA*) is an endemic tree found in Ethiopia that provides yellowish citrus fruits that are edible. Aqueous extract of this plant has been used for silver and gold nanoparticles which show good antibacterial properties (Abera Beyene and Mekonnen, 2021). However, the application of such a plant to the synthesis of ZnO nanomaterials is limited. Therefore, in this study, an aqueous extract from the fruits of *koshem* was used for the synthesis of ZnO-NPs and the nanomaterial produced was used as a photocatalyst for the degradation of MG dye dissolved in water.

MATERIALS AND METHODS

Preparation of Crude Extract of the fruit

The freshly ripened fruits were collected from Bahir Dar city, Ethiopia. The fruits were cleaned with distilled water, peeled and crushed with an electric mixer to obtain the raw crude juice. Then 50 g of juice was diluted with 200 ml of distilled water in 1 liter Erlenmeyer flask and heated to 60 °C in water bath for 1 h. The hot solution was filtered to remove the residue through a microfiltration setup and crude extract filtrate of *D. abyssinica* was obtained, which was stored in the refrigerator at 4 °C for the next process.

Preparation of ZnO-NPs

A sol-gel process was used to synthesize ZnO-NPs (Hasnidawani *et al.*, 2016; Ganesan *et al.*, 2020). In detail, 50 mL aqueous solution (0.1 M) of Zn $(NO_3)_2$. $6H_2O$ (purchased from Bulux Laboratories, India) was mixed with 5 ml of plant extract in a round bottom flask. Then 1M NaOH solution was prepared from which 12 ml was added to the above mixture to make the pH around 12. The flask was then immersed in water bath at a temperature of 60 °C for 1 h. Then the precipitate was separated by decantation and placed in a 65 °C oven overnight using a ceramic crucible. Finally, the dried powder was calcined in the furnace at 400 °C for 2 h to obtain the final ZnO-NPs powder.

Photocatalytic degradation reaction

The catalytic performance experiment was done based on the method described by Saikia *et al.* (2015) and Ullah *et al.* (2008) with minor modifications. Typically, 5% wt./wt of the reaction mixture (MG to ZnO-NPs) was prepared by mixing 25 mg of ZnO-NP catalyst in 50 ml of 25 ppm malachite green hydrochloride (MG) dye in a transparent glass container. The dye was purchased from HIMEDIA Laboratories, India. The mixture was stirred in the dark for 30 minutes before irradiation. Then the

reaction mixture was placed in a cartoon box and irradiated with visible light from a 200 W tungsten bulb for 80 minutes. The distance between the light source and the sample holder was approximately 30 cm. The effects of dye concentration, the amount of catalyst, the reaction rate and the recyclability were then examined under similar reaction conditions.

The percentage of degradation (%) was calculated by using the following relation.
% Degradation = $(C_0 – Ct)/C_0 * 100\ \% = (A_0 – A)/A_0 * 100\%$
Where C_0 is the initial dye concentration and Ct is the dye concentration after photo-degradation; A_0 and A are UV-Vis absorbance of the dye before and after the photocatalytic reaction, respectively. The photocatalytic degradation efficiency was determined by the extinction peak of the MG dye, which was observed at 617 nm and appeared in the visible range. Here the effect of the dye concentration and the amount of the ZnO-NPs catalyst on percentage degradation was also evaluated by using the same experimental procedure.

Characterization

UV-Vis spectrometer, Fourier transmission spectrometer (FTIR) and X-ray powder diffraction (XRD) instrument were used for the characterization of the synthesized catalyst.

RESULTS AND DISCUSSION

ZnO-NPs catalyst characterization

The synthesized ZnO-NPs were collected as fade yellow powders. This may be due to the color of the yellowish extract that appeared with the powder. The fruit extract (DA) and a synthesized ZnO-NPs were subjected to FTIR analysis to assess the functional groups of the plant that were present before and after synthesis of the nanoparticles. The FTIR spectral data is shown in Figure 1 below. The spectrum of the extract shows an intense absorption peak at 3424 cm^{-1}, which is due to the presence of hydroxyl groups (OH), which can be derived from polyphenols and flavonoids. The peak at 1733 cm^{-1} is assigned to the C = O stretching in polyphenols, flavonoids, and reducing sugars. Other peaks at 1635 cm^{-1} has been attributed to the NH bending of amines (Ekennia *et al.*, 2021). Other peaks at 1389 cm^{-1}, and 1090 cm^{-1} were found for the alkyl C-H and C-O stretching, which can result from different functionalities in the extract of the fruit. In the case of ZnO-NPs, however, the OH peak was observed at 3462 cm^{-1}. The peaks at 1639 cm^{-1} and 1388 cm^{-1} reappeared indicating the presence of natural metabolites with ZnO as a capping agent. The disappearance of other peaks may be due to the chemical change during the synthesis. In general, a peak observed at 543 cm^{-1} indicates the presence of metal–oxygen (Zn - O) bonding vibrations of ZnO-NPs (Ekennia *et al.*, 2021) why the intensity of O-H absorption increased in the spectrum of ZnO-NP.

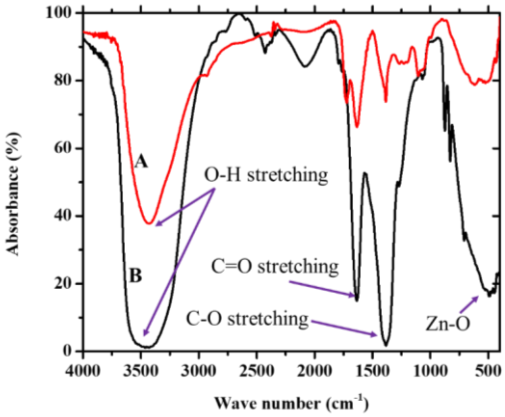

Figure 1. FTIR spectrum of A) *D. abyssinica* fruit extract; B) synthesized ZnO-NPs

Figure 2 shows the UV-VIS results. The broad absorption band at 390 nm is attributed to ZnO-NPs. The second peak at 300 nm is also due to that of the plasmonic absorption band of nano-sized ZnO particles (Ekennia *et al.*, 2021).

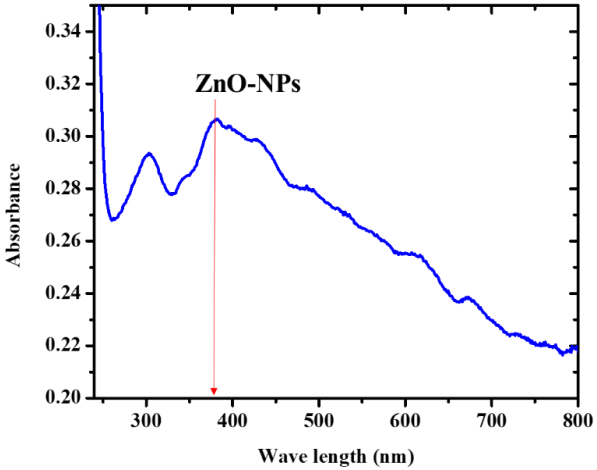

Figure 2. UV-Vis absorbance data of synthesized ZnO-NPs

To estimate the crystalline particle size, X-ray diffraction (XRD) measurements were performed as shown in Figure 3 by using Cu Kα radiation. The collected intensity over 2θ range of 10-80° shows the diffraction peaks at angles of 31.68°, 33.8°, 36.4°, 47.6°, 56.5°, and 62.9° and correspond to the reflection from (100), (002), (101), 102),

(110), and (103) crystal planes of the hexagonal ZnO structure agreed with the reported JCPDS data of Card No. 36-1451.

By using the diffraction peak intensity of (101) the synthesized ZnO nanoparticles from Debye-Sherrer equation was calculated to be 17 nm.

$$D = \frac{0.9\lambda}{FWHM\ cos\acute{o}}$$

Where D is crystalline size, λ is the x-ray wavelength (0.1514 nm), FWHM is the full width at half-maximum intensity in radians, and θ is the diffraction Bragg angle.

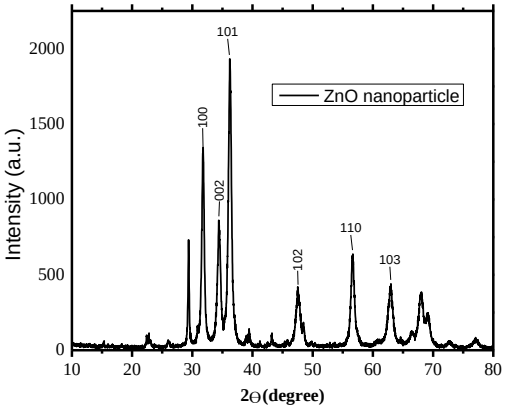

Figure 3. XRD data of synthesized ZnO nanoparticles.

Effect of dye concentration on dye removal efficiency

Different dye concentrations were used to determine the best performance of ZnO-NPs. From the first step, however, 45 mg ZnO-NP were suspended in 50 ml of aqueous solutions of MG dye at 25 ppm concentrations. The result shown in Figure 4 indicates that after a reaction of 80 min, the blue solution of dye had completely disappeared. Thus, it was confirmed that prepared ZnO-NPs were effective to remove MG dye from water under visible light.

As indicated in Figure 4B, the best performance was achieved when 98.5% dye was degraded during 25 ppm concentration whereas the least (73.3 %) dye was degraded at a concentration 5 ppm. The least degradation obtained in the case of diluted concentration may be due to less probability of the contact between the dye molecules and ZnO particles at the given reaction time. The achieved performance (98.5%) is attributed to the fact that plant-mediated nanoparticles are mostly known for their large specific surface area, controlled surface activity, high interface, and catalytic, optical and volume effects (Ekennia *et al.*, 2021)

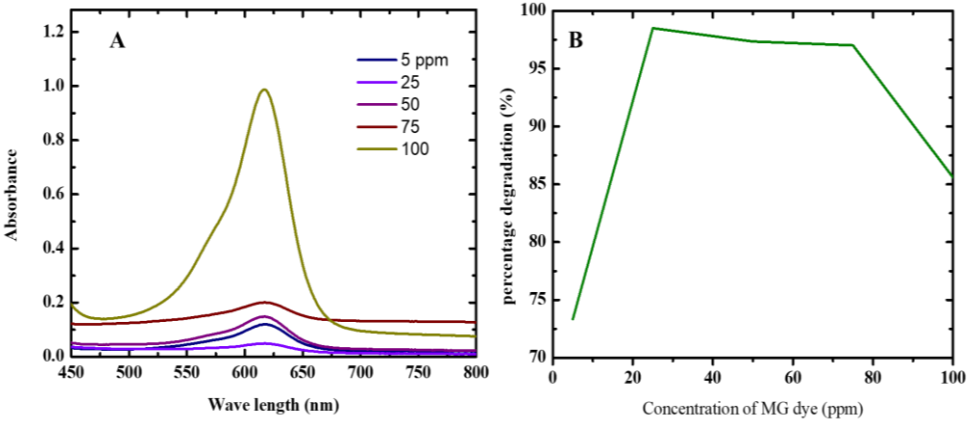

Figure 4. UV-Vis absorbance measurement data A) taken to study the effect of MG dye concentration; B) Calculated percentage degradation performance for each concentration.

Effect of ZnO-NPs amount on dye removal efficiency

The investigation of the influence of the ZnO-NP load was carried out using various amounts of ZnO-NPs from 0.03 - 1.5 wt% the dye concentration being fixed at 25 ppm. The optimum amount of ZnO-NPs for the highest photo-degradation efficiency was 0.09 wt%., thereby removing 98.5% of the dye as shown in Figure 5(B). In principle, the amount of catalyst is proportional to the number of active radicals such as OH and O_2, which quickly break down the adsorbed MG dye. However, beyond 0.09% of the catalyst, the degradation efficiency was slightly reduced. This may be due to the agglomeration of the catalyst at higher concentrations, which in turn reduces the accessibility of active sites that would adsorb dye molecules. In addition, at higher concentration of solid catalyst particles, the particles suspended and make the reaction solution more turbid. Since turbidity influences the effective formation of photosensitized particles due to quenching by ground state molecules, the catalytic efficiency will be minimal (Neppolian *et al.*, 2002).

Kinetic study

The rate of photocatalytic degradation of the MG dye was determined by measuring the absorption during the course of the reaction at various time intervals as presented in Figure 6(A). The absorbance has decreased in the first stage of the reaction that shows the degradation was faster in the early stage of the reaction and got slower later. Hence, the absorbance data was then used to calculate dye concentration at a time of reading (Ct). The initial concentration was also calculated by taking the absorbance of the reaction mixture after dark stirring step. Then the graph of C_0-Ct/C_0 against time

(min) was plotted as shown in Figure 6(B). As a result, the MG dye degradation rate by using the given ZnO-NP was 0.1 ppm/min.

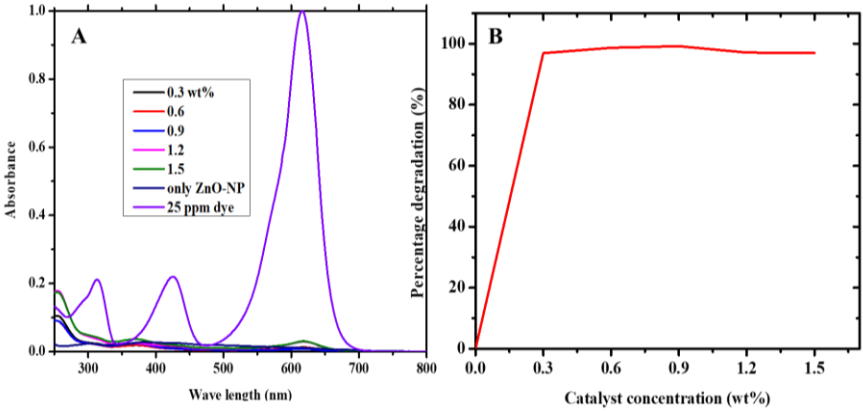

Figure 5. UV-Vis absorbance measurement data A) taken to study the effect of concentration of ZnO-NPs catalyst; B) Calculated percentage degradation performance for each concentration of the catalyst.

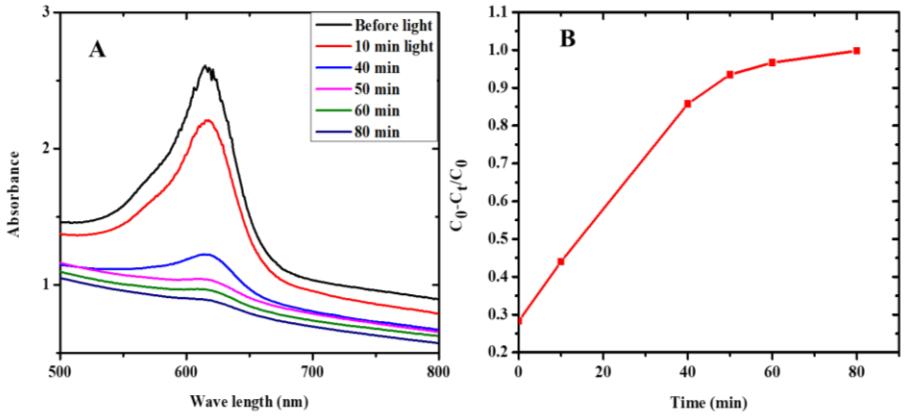

Figure 6. A) UV-vis absorbance data at different time (t) during photocatalysis reaction and B) Rate of MG dye photocatalytic degradation by ZnO-NPs catalyst

Reusability of the catalyst

The resulting optimized concentration of dye and catalyst, which shows better degradation performance, was used for the reusability study. The normalized UV-Vis measurement data was used to calculate the percentage of degradation in each cycle of catalyst application as indicated in Figure 7(A). The performance of the catalyst

remained similar up to the 2nd cycle but there was significant variation (decrease) as the cycle increased to the 5th round of catalyst used (Figure 7 B).

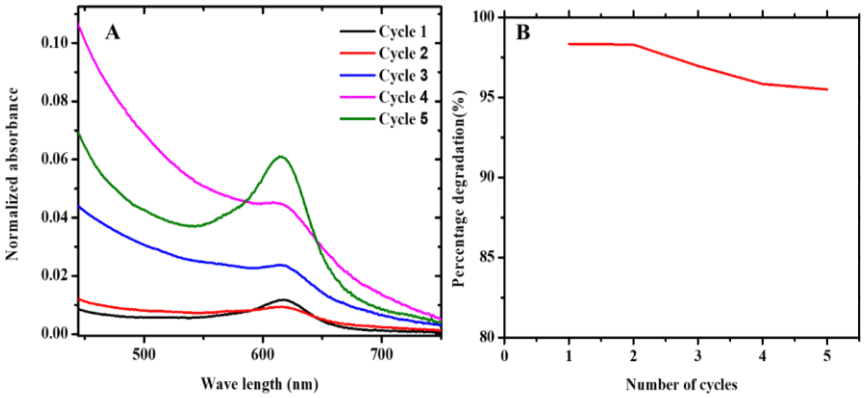

Figure 7. UV-Vis absorbance measurement data A) taken to study cycle of recovery of ZnO-NPs catalyst; B) Calculated percentage degradation performance for each cycle.

CONCLUSION

The aqueous extract of the *D. abyssinica* fruit was incorporated during the sol-gel process of nano-sized ZnO particles preparation. The XRD and UV-Vis result showed the successful synthesis of ZnO-NPs with the size of about 17 nm. In addition, FTIR data had also indicated the presence of natural organic functionalities derived from the fruit extract. Then the manufactured nanomaterial was used as a photocatalyst for the breakdown of MG dye, which is used as an organic pollutant in the leather, textile and other similar industries for safe disposal in water bodies. Therefore, the photocatalytic oxidative degradation of malachite green dye by ZnO-NP was very effective in removing the dye from aqueous solution. In this study, the influence of the initial amount of catalyst, the dye concentration, the degradation rate and the recovery cycle were investigated. Hence, 25 ppm dye has shown better performance with 98.5% degradation, while 0.09% was the optimum amount of catalyst which shows maximum performance under these circumstances. By using optimized catalyst amount, the rate of degradation reaction was 0.1 ppm/min. Finally, the recovery study shows us that it is possible to use the given catalyst loading up to 5 times with a considerable power range. Nonetheless, the first two were very effective, removing about 98% of the dye. Here the role of plant compounds on ZnO-NPs can be helpful to improve the dye adsorption on the particle, which in turn increases the catalytic efficiency. Therefore, the observed result is promising for the removal of other

dangerous organic dye contaminants from wastewater discharged from factories under natural sunlight.

Conflict of interest

Authors do not have any conflict of interest.

REFERENCES

Abera Beyene & Mekonnen, A. (2021). Synthesis, characterization and functional evaluation of gold nanoparticles prepared using *Dovyalis abyssinica* leaf extracts as reducing and surface capping agent. *Ethiopian Journal of Science and Technology* **14**: 171–190.

Alalwan, H.A., Mohammed, M.M., Sultan, A.J., Abbas, M.N., Ibrahim, T.A., Aljaafari, H.A and Alminshid, A.A. (2021). Adsorption of methyl green stain from aqueous solutions using non-conventional adsorbent media: Isothermal kinetic and thermodynamic studies. *Bioresource Technology Reports* **14**: 100680.

Aoudj, S., Bahloul, K and Khelifa, A. (2021). Degradation of dyes by electrochemical advanced oxidation processes. *Advanced Removal Techniques for Dye-containing Wastewaters.* Springer.

Balogun, S.W., James, O.O., Sanusi, Y.K and Olayinka, O.H. (2020). Green synthesis and characterization of zinc oxide nanoparticles using bashful (*Mimosa pudica*), leaf extract: a precursor for organic electronics applications. *Sn Applied Sciences* **2**: 1–8.

Bhatti, M.A., Tahira, A., Dad Chandio, A., Almani, K.F., Bhatti, A.L., Waryani, B., Nafady, A and Ibupoto, Z.H. (2021). Enzymes and phytochemicals from neem extract robustly tuned the photocatalytic activity of ZnO for the degradation of malachite green (MG) in aqueous media. *Research on Chemical Intermediates* **47**: 1581–1599.

Bhuyan, T., Mishra, K., Khanuja, M., Prasad, R and Varma, A. (2015). Biosynthesis of zinc oxide nanoparticles from *Azadirachta indica* for antibacterial and photocatalytic applications. *Materials Science in Semiconductor Processing* **32**: 55–61.

Chankhanittha, T and Nanan, S. (2018). Hydrothermal synthesis, characterization and enhanced photocatalytic performance of ZnO toward degradation of organic azo dye. *Materials Letters* **226**: 79–82.

Chen, C.C., Lu, C.S., Chung, Y.C and Jan, J.L. (2007). UV light induced photodegradation of malachite green on TiO2 nanoparticles. *Journal of Hazardous Materials* **141**: 520–528.

Domınguez, C., Garcıa, J., Pedraz, M., Torres, A and Galan, M. (1998). Photocatalytic oxidation of organic pollutants in water. *Catalysis Today* **40**: 85–101.

Dutta, S., Gupta, B., Srivastava, S.K and Gupta, A.K. (2021). Recent advances on the removal of dyes from wastewater using various adsorbents: a critical review. *Materials Advances* **2:** 4497–4531.

Ekennia, A.C., Uduagwu, D.N., Nwaji, N.N., Oje, O.O., Emma-Uba, C.O., Mgbii, S.I., Olowo, O.J and Nwanji, O.L. (2021). Green synthesis of biogenic zinc oxide nanoflower as dual agent for photodegradation of an organic dye and tyrosinase inhibitor. *Journal of Inorganic and Organometallic Polymers and Materials* **31**: 886–897.

El-Hout, S.I., El-Sheikh, S.M., Gaber, A., Shawky, A and Ahmed, A.I. (2020). Highly efficient sunlight-driven photocatalytic degradation of malachite green dye over reduced graphene oxide-supported CuS nanoparticles. *Journal of Alloys and Compounds* **849**: 156573.

Fatimah, I., Pradita, R.Y and Nurfalinda, A. (2016). Plant extract mediated of ZnO nanoparticles by using ethanol extract of *Mimosa pudica* leaves and coffee powder. *Procedia Engineering* **148:** 43–48.

Ganesan, V., Hariram, M., Vivekanandhan, S and Muthuramkumar, S. (2020). Periconium sp. (endophytic fungi) extract mediated sol-gel synthesis of ZnO nanoparticles for antimicrobial and antioxidant applications. *Materials Science in Semiconductor Processing* **105**: 104739.

Gedda, G., Kolli Balakrishna, R.U.D and Shah, K.J. (2021). Introduction to conventional wastewater treatment technologies: Limitations and recent advances. *Advances in Wastewater Treatment I* **91**: 1–36.

Hasnidawani, J., Azlina, H., Norita, H., Bonnia, N., Ratim, S and Ali, E. (2016). Synthesis of ZnO nanostructures using sol-gel method. *Procedia Chemistry* **19**: 211–216.

Iqbal, M., Bhatti, H.N., Younis, S., Rehmat, S., Alwadai, N., Almuqrin, A.H and Iqbal, M. (2021). Graphene oxide nanocomposite with CuSe and photocatalytic removal of methyl green dye under visible light irradiation. *Diamond and Related Materials* **113**: 108254.

Jose, L.M., Raj, R.A., Sajan, D and Aravind, A. (2021). Adsorption and photocatalytic activity of biosynthesised ZnO nanoparticles using *Aloe vera* leaf extract. *Nano Express* **2**: 010039.

Kadirvelu, K., Thamaraiselvi, K and Namasivayam, C. (2001). Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. *Bioresource Technology* **76**: 63–65.

Kumaresan, N., Ramamurthi, K., Ramesh Babu, R., Sethuraman, K and Moorthy Babu, S. (2017). Hydrothermally grown ZnO nanoparticles for effective photocatalytic activity. *Applied Surface Science* **418**: 138–146.

Laszlo, J.A. (1996). Preparing an ion exchange resin from sugarcane bagasse to remove reactive dye from wastewater. *Textile Chemist & Colorist* **28**: **28**:13-17.

Liu, Y.C., Li, J., Ahn, J., Pu, J., Rupa, E.J., Huo, Y and Yang, D.C. (2020). Biosynthesis of zinc oxide nanoparticles by one-pot green synthesis using fruit extract of *Amomum longiligulare* and its activity as a photocatalyst. *Optik* **218**: 165245.

Mahecha, F.C., Parra, D.C., Sandoval, J.A., Mayorga, M.A and Ortiz, S.A. (2021). Removal of cationic dyes utilizing natural coffee pulp coagulant. *Chemical Engineering Transactions* **87**: 487-492.

Matinise, N., Fuku, X., Kaviyarasu, K., Mayedwa, N and Maaza, M. (2017). ZnO nanoparticles via *Moringa oleifera* green synthesis: Physical properties & mechanism of formation. *Applied Surface Science* **406**: 339–347.

Meena, S., Dipti, V and Das, B. (2016). Photocatalytic degradation of Malachite Green dye by modified ZnO nanomaterial. *Bulletin of Materials Science* **39**: 1735–1743.

Neppolian, B., Choi, H., Sakthivel, S., Arabindoo, B and Murugesan, V. (2002). Solar/UV-induced photocatalytic degradation of three commercial textile dyes. *Journal of Hazardous Materials* **89**: 303–317.

Ngom, I., Ngom, B., Sackey, J and Khamlich, S. (2021). Biosynthesis of zinc oxide nanoparticles using extracts of *Moringa oleifera*: Structural & optical properties. *Materials Today: Proceedings* **36:** 526–533.

Park, J.K., Rupa, E.J., Arif, M.H., Li, J.F., Anandapadmanaban, G., Kang, J.P., Kim, M., Ahn, J.C., Akter, R and Yang, D.C. (2021). Synthesis of zinc oxide nanoparticles from *Gynostemma pentaphyllum* extracts and assessment of photocatalytic properties through malachite green dye decolorization under UV illumination-A green approach. *Optik* **239**: 166249.

Rajashekara, S., Shrivastava, A., Sumhitha, S and Kumari, S. (2020). Biomedical applications of biogenic zinc oxide nanoparticles manufactured from leaf extracts of *Calotropis gigantea* (L.) Dryand. *BioNanoScience* **10**: 654–671.

Rodríguez-Narváez, O.M., Picos, A.R., Bravo-Yum, N., Pacheco-Alvarez, M., Martínez-Huitle, C.A and Peralta-Hernández, J.M. (2021). Electrochemical oxidation technology to treat textile wastewaters. *Current Opinion in Electrochemistry* 100806.

Saikia, L., Bhuyan, D., Saikia, M., Malakar, B., Dutta, D.K and Sengupta, P. (2015). Photocatalytic performance of ZnO nanomaterials for self sensitized degradation of malachite green dye under solar light. *Applied Catalysis A: General* **490**: 42–49.

Sakthivel, S., Neppolian, B., Shankar, M.V., Arabindoo, B., Palanichamy, M and Murugesan, V. (2003). Solar photocatalytic degradation of azo dye: Comparison of photocatalytic efficiency of ZnO and TiO2. *Solar Energy Materials and Solar Cells* **77**: 65–82.

Sangeetha, G., Rajeshwari, S and Venckatesh, R. (2011). Green synthesis of zinc oxide nanoparticles by *Aloe barbadensis* miller leaf extract: Structure and optical properties. *Materials Research Bulletin* **46**: 2560–2566.

Sartape, A.S., Mandhare, A.M., Jadhav, V.V., Raut, P.D., Anuse, M.A and Kolekar, S.S. (2017). Removal of malachite green dye from aqueous solution with adsorption technique using *Limonia acidissima* (wood apple) shell as low cost adsorbent. *Arabian Journal of Chemistry* **10**: S3229–S3238.

Senthilkumar, N., Nandhakumar, E., Priya, P., Soni, D., Vimalan, M and Potheher, I.V. (2017). Synthesis, anti-bacterial, antiarthritic, anti-oxidant and in-vitro cytotoxicity activities of ZnO nanoparticles using leaf extract of *Tectona grandis* (L.). *New Journal of Chemistry* **41**: 10347–10356.

Singh, A., Neelam and Kaushik, M. (2019). Physicochemical investigations of zinc oxide nanoparticles synthesized from *Azadirachta indica* (Neem) leaf extract and their interaction with Calf-Thymus DNA. *Results in Physics* **13**: 102168.

Sinha, A.K., Sasmal, A.K., Pal, A., Pal, D and Pal, T. (2021). Ammonium phosphomolybdate [(NH4) 3PMo12O40] an inorganic ion exchanger for environmental application for purification of dye contaminant wastewater. *Journal of Photochemistry and Photobiology A: Chemistry* **418**: 113427.

Sultana, F., Barman, J and Kalita, M. (2017). Biogenic synthesis of ZnO Nanoparticles using *Polygonum chinense* leaf extract and their antibacterial activity. *International Journal of Nautical Archaeology* **11:** 155–165.

Vasseghian, Y., Hosseinzadeh, S., Khataee, A and Dragoi, E.-N. (2021). The concentration of persistent organic pollutants in water resources: A global systematic review, meta-analysis and probabilistic risk assessment. *Science of The Total Environment* 149000.

Williams, C., Aderhold, D and Edyvean, R. (1998). Comparison between biosorbents for the removal of metal ions from aqueous solutions. *Water Research* **32**: 216–224.

Xu, F., Yuan, Y., Wu, D., Zhao, M., Gao, Z and Jiang, K. (2013). Synthesis of ZnO/Ag/graphene composite and its enhanced photocatalytic efficiency. *Materials Research Bulletin* **48**: 2066–2070.

Zare, M., Namratha, K., Thakur, M.S and Byrappa, K. (2019). Biocompatibility assessment and photocatalytic activity of bio-hydrothermal synthesis of ZnO nanoparticles by *Thymus vulgaris* leaf extract. *Materials Research Bulletin* **109**: 49–59.