Biosynthesis of Zinc Oxide Nanoparticles From Plectranthus Amboinicus and Its Photocatalytic Effect on Wastewater Treatment

Nadana Raja Vadivu Ganapathy, Vasumathi Krishnan, Aruna Janani Veeraraghavan, Varatharajan and Gokul Devaraj

Abstract*: Photocatalysis using semiconductor Zinc Oxide (ZnO) is a promising technology for water purification. The current work is aimed at improving the reduction of organic carbon of domestic wastewater by a combination of photocatalysis and Green synthesis. Synthesized zinc oxide nanoparticles from Plectranthus amboinicus was characterized by UV spectroscopy, FTIR, SEM, and XRD. Degradation of organic matter in effluent using Zinc Oxide and Plectranthus amboinicus was examined by the photocatalytic reaction. The reduction of organic carbon was analyzed by COD and pH analysis on synthesized ZnO nanoparticles. The decrease in COD from 800 mg/l to 50 mg/l and an increase in pH from 6.8 to 7.4 results in degradation of organic matter in the effluent. These advantages enable us to reuse the treated water for various purposes such as flushing, gardening, cleaning.

Keywords*: Zinc Oxide, Plectranthus amboinicus, Photocatalytic reaction, Effluent..

I. INTRODUCTION

Various metal oxides performed as a catalyst and applied in the field of environment as it reduces toxicity in water sources. ZnO has the benchmark application in field of environment and in wastewater treatment. ZnO has a wide range of applications such as photocatalysis, self-cleaning and environmental purification. Enhancement of ZnO activity is improved by the advent of nanotechnology, also has a significant impact in photocatalysis [1,2]. Green synthesis of ZnO nanoparticles from plant-derived materials provide massive importance due to eco-friendly and improve sustainability [3,4]. The synthesis of nanomaterials is done by the polyphenols present in the plant materials [5]. Sewage discharged from households, and public places are referred to as wastewater. Water pollution, water scarcity, ecosystem, fisheries, agriculture, health issues, etc., are greatly affected due to inadequate infrastructure for wastewater treatment and its maintenance. Green synthesized metal oxide nanoparticles from plant-derived compounds are used for biological treatment.

Plectranthus amboinicus is an aromatic herb native to Cuba and the Pacific Islands used for curing diseases like respiratory issues, cancer prevention, treats fever, etc., [6] Our main objective is to (i) synthesize ZnO nanoparticles using *P. amboinicus* leaf extract (ii) study the photo-catalytic degradation of sewage water.

II. II.METHODOLOGY

A. Extract preparation

The leaves of *P. amboinicus* were collected from the Department of Biotechnology, KARE. The Collected leaves were cleaned and further surface sterilized with 75% ethanol. The sterilized leaves were washed with distilled water before use. 25 g of *P. amboinicus* leaves were cut into small pieces and boiled in 30 ml of water for 15 minutes. The extracts were filtered using Whatman No.1 filter paper and refrigerated at 4ºC until future use.

B. ZnO nanoparticle synthesis

0.05 M Zinc acetate and 0.1 M NaOH were prepared. Later, 10ml of NaOH was added dropwise to 10ml of 0.1M Zinc acetate hexahydrate aqueous solution and magnetically stirred. The white color precipitated would be appeared. 10ml leaf extract was added slowly to the solution and kept in Magnetic stirred for four hours. Then, the mixed solution centrifuged at 10000 rpm for 10 minutes to collect the settled particles. The collected particles were subsequently washed with water, and subjected to centrifugation at 1000 rpm for 10 minutes. The centrifuged sample was collected and dried in a hot air oven at 80°C for 3 hours, and the dried powder was used for further analysis.

C. Characterization of ZnO nanoparticles

Synthesized nanoparticles were analyzed for the optical property by UV absorption spectra (300-800nm). The functional group's characterization of ZnO nanoparticles was analyzed using FTIR.

Revised Manuscript Received on December 05, 2019

Nadana Raja Vadivu Ganapathy*, Department of Biotechnology, School of Bio and Chemical engineering, Kalasalingam Academy of Research and Education, Krishnakoil-626126,

Vasumathi Krishnan, Department of Biotechnology, School of Bio and Chemical engineering, Kalasalingam Academy of Research and Education, Krishnakoil-626126,

Aruna Janani Veeraraghavan, Department of Chemical Engineering, School of Bio and Chemical engineering, Kalasalingam Academy of Research and Education, Krishnakoil-626126,

Varatharajan Department of Chemical Engineering, School of Bio and Chemical engineering, Kalasalingam Academy of Research and Education, Krishnakoil-626126,

Gokul Devaraj Department of Chemical Engineering, School of Bio and Chemical engineering, Kalasalingam Academy of Research and Education, Krishnakoil-626126,

The surface morphology was analyzed using SEM. The x-ray diffraction pattern was used for identifying the various form of zinc oxide nanoparticles.

D. Treatment of wastewater treatment

The wastewater collected from the Sewage Treatment Plant of Kalasalingam Academy of Research and Education. 50 ml of wastewater sample mixed with 0.005g of ZnO (0.1g/L). And the sample kept in sunlight for 5 hours. The COD value of the wastewater calculated for each one-hour time interval by using a standard titrating procedure. Finally, the ZnO separated from the wastewater by using primary filtration techniques. pH meter is used for determining the pH level in various treatments

III. RESULTS AND DISCUSSION

A. UV analysis of ZnO NP

UV Spectrum of biosynthesized ZnO NPs showed a strong UV emission at 374 nm; a weak emitting band at 420 nm (blue emission) was observed (Fig. 1). The UV emission reflects the band edge emission of the wide band gap of ZnO NPs. The room temperature should be prominent to the purity and crystallinity of the synthesized ZnO NPs. At the same time, the band gap of the material calculated using blue emission as 2.99eV. This shows that the material can go to excited state at the visible light region. So which can able to use as solar photocatalyst. The band gap at 420 nm is 2.99ev which is shorter compared to band gap at 374 nm, facilitates the movement of ZnO NP to excited state at a visible region which enables us to use biosynthesized ZnO NP as solar photocatalyst [7].

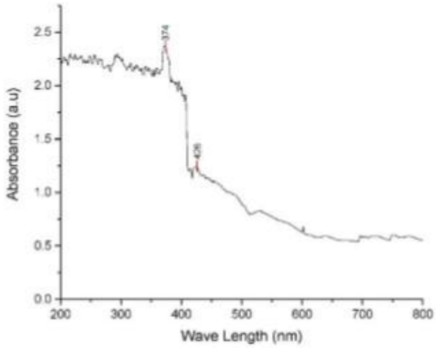

Fig 1: UV Spectrum of ZnO nanoparticles. Two peaks were obtained at 374 nm and 420 nm.

B. FTIR analysis of ZnO NP

FTIR spectra between 500 cm^{-1} and 4000 cm^{-1} were examined for *P. amboinicus* leaf extract (Fig. 2). The absorption bands at 3294 cm^{-1} due to the stretching vibrations of the primary and secondary amines. The intense absorbance at 2194.47 cm^{-1} and 2150 cm^{-1} showed the stretching of C-N. The presence of amide band was observed at 1655 cm^{-1} with the stretching of amide linkages [8,9]. The spectral ranges of FTIR for biosynthesized ZnO NPs were shown in Fig (3). The characteristic bands at 449 cm^{-1} and 619 cm^{-1} corresponds to the stretch band of Zinc Oxygen. The peaks at 1024 cm^{-1}, 1051 cm^{-1} were assigned to be symmetric C-N vibration associated with a C-O-SO3 [10].

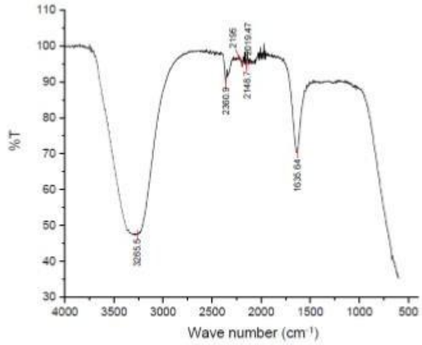

Fig 2: FTIR Spectrum of Plant Leaf Extract. The bands showed the presence of amines, C-N and amide linkages.

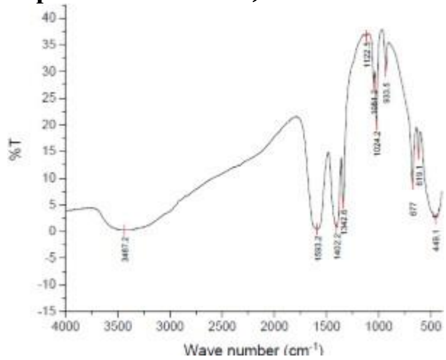

Fig 3: FTIR Spectrum of ZnO NPs.

C. SEM and XRD analysis

The SEM image of ZnO NPs shown in the Fig.4. The morphology of ZnO nanoparticles appeared to be spherical shaped and is in correlation with the previous studies [11]

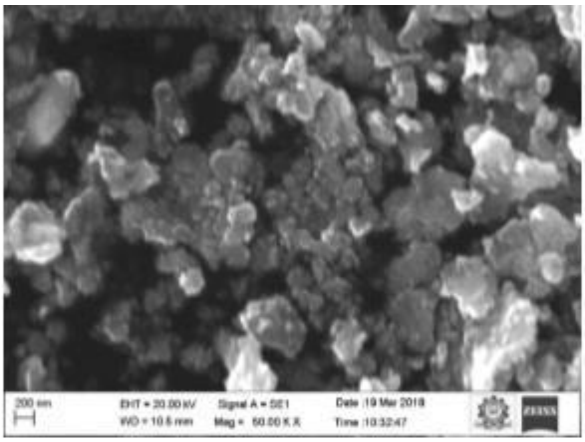

Fig 4: SEM image of ZnO NP

The result of XRD analysis showed that the green synthesized ZnO NPs were observed to be pure and crystalline in nature. The peaks of XRD analysis revealed various ranges at 31.72˚, 34.40˚, 36.22˚, 47.52˚, 56.66˚, 62.66˚, 67.98˚, 69.16˚ and it can have indexed to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2) and (2 0 1) reflection lines of hexagonal wurtzite ZnO NPs. The average grain size is calculated using

$$D = K\lambda/\beta \cos\theta \text{ Å} \quad (1)$$

Where D is an average crystallite size in Å, K is the shape factor, λ is the wavelength of X-ray (1.5406 Å) Cu -Kα radiation, θ is the Bragg angle, and β is the corrected line broadening of the NPs. The average grain size is measured to be 38.1808 nm [12].

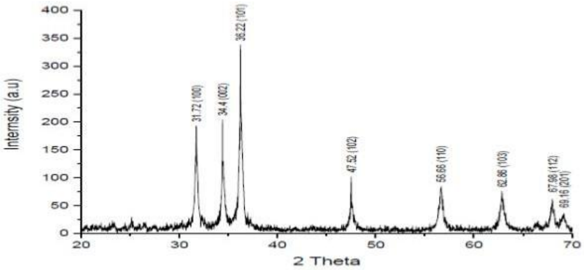

Fig 5: XRD pattern of ZnO NP

D. Treatment of Domestic Wastewater

Domestic wastewater treatment without ZnO NPs was kept under sunlight for 5 hours. The COD of the sample was found to be constant after the 5 hours of treatment. The COD of the sample was 700 mg/L. The result indicated that solar radiation has no impact on the COD reduction of wastewater within five hours.

Whereas the degradation of wastewater using ZnO NPs under dark region was performed, COD of the sample slightly decreased from 800 mg/L to 750 mg/L. The COD of the sample decreased due to adsorption of ZnO NPs. This shows that the adsorption rate constant is very low.

Treatment of Wastewater using ZnONPs and solar radiation was analyzed for photocatalytic effect. The band gap of the Green synthesized ZnO NPs is 2.99 eV. It was capable of reaching an excited state in the visible region. So sunlight used as a light source to treat the wastewater. 0.005 g of ZnO NPs added for 50 ml wastewater and kept in sunlight for five hours. COD reduction was calculated for each one-hour time interval. COD of the wastewater decreased up to 93.75%. This shows that ZnO NPs can reach an excited state and can form free radicals by utilizing photon in solar radiation [13,14]

Table 1: COD reduction with respect to time

Time (hours)	COD (mg/l)
0	800
1	500
2	300
3	150
4	100
5	50

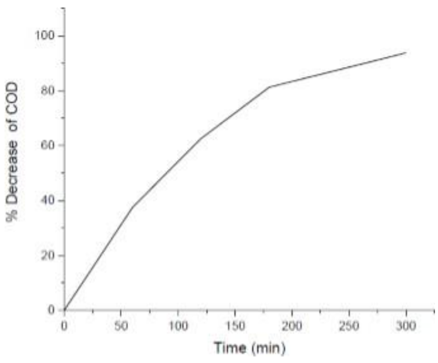

Fig 6. Photocatalytic – ZnO NP treatment shows a drastic reduction of COD.

pH level remained constant after the 5 hours when Domestic Wastewater treatment without ZnO NPs. The pH of the sample retained as 6.82. This showed that solar radiation has no impact on pH without ZnO Nps.

The pH slightly decreased from 6.80 to 6.85 upon degradation of Wastewater using ZnO NPs under the dark region. The increase of pH observed in the treatment of wastewater using ZnO NPs and solar radiation observed for 5 hours, due to the radical formation [15,16].

Table 2 : Effect of pH with respect to time in wastewater treatment using ZnO NP and solar radiation

Time (h)	pH
0	6.80
1	6.92
2	7.14
3	7.29
4	7.37
5	7.40

IV. CONCLUSION

The biosynthesized ZnO nanoparticles using *P. amboinicus* is a low-cost, simple, and effective method to treat wastewater. Biosynthesized ZnO nanoparticles do not allow bacteria to grow because of its antibacterial activity[7]. The COD of the wastewater decreased to less than 50 mg/L. At the same time the pH of the wastewater maintained less than 7.5. Our results suggest that the treated wastewater could be used for various purposes and provide an effective outcome for a sustainable environment.

ACKNOWLEDGMENT

Authors would like to thank Kalasalingam Academy of Research and Education (KARE) management for providing facilities to perform this study in the Department of Biotechnology.

REFERENCES

1. Kumar, Surabhi Siva, et al. "Synthesis, characterization and optical properties of zinc oxide nanoparticles." International Nano Letters, 3.1, 2013, pp. 30.
2. Velmurugan, R., and M. Swaminathan. "An efficient nanostructured ZnO for dye sensitized degradation of Reactive Red 120 dye under solar light." Solar Energy Materials and Solar Cells, 95.3, 2011, pp. 942-950..
3. Elumalai, K., et al. "Bio-approach: plant mediated synthesis of ZnO nanoparticles and their catalytic reduction of methylene blue and antimicrobial activity." Advanced Powder Technology, 26.6, 2015, pp .1639-1651.
4. Kharissova, Oxana V., et al. "The greener synthesis of nanoparticles." Trends in biotechnology, 31.4, 2013, 240-248..
5. Singh, Henam Premananda, et al. "Biogenic synthesis of metal nanocatalysts using Mimosa pudica leaves for efficient reduction of aromatic nitrocompounds." RSC Advances, 4.71, 2014, pp . 37816-37825.
6. Asiimwe, Savina, et al. "Chemical composition and Toxicological evaluation of the aqueous leaf extracts

of Plectranthus amboinicus (Lour.) Spreng." Int. J. Pharm. Sci. Invent, 3, 2014, pp .19-27.

7. Vijayakumar, S., et al. "Plectranthus amboinicus leaf extract mediated synthesis of zinc oxide nanoparticles and its control of methicillin resistant Staphylococcus aureus biofilm and blood sucking mosquito larvae." Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 137, 2015, pp . 886-891.
8. Basavaraja, S., et al. "Extracellular biosynthesis of silver nanoparticles using the fungus Fusarium semitectum." Materials Research Bulletin, 43.5, 2008, pp . 1164-1170.
9. Philip, Daizy. "Biosynthesis of Au, Ag and Au–Ag nanoparticles using edible mushroom extract." Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 73.2, 2009, pp . 374-381..
10. Annamalai, A., et al. "Green synthesis, characterization and antimicrobial activity of Au NPs using Euphorbia hirta L. leaf extract." Colloids and Surfaces B: Biointerfaces, 108, 2013, pp . 60-65..
11. Lingaraju, K., et al. "Biogenic synthesis of zinc oxide nanoparticles using Ruta graveolens (L.) and their antibacterial and antioxidant activities." Applied Nanoscience, 6.5, 2016, pp . 703-710.
12. Fatimah, Is, Rizqi Yulia Pradita, and Annisa Nurfalinda. "Plant extract mediated of ZnO nanoparticles by using ethanol extract of Mimosa pudica leaves and coffee powder." Procedia engineering, 148, 2016, pp . 43-48.
13. Vaiano, Vincenzo, and Giuseppina Iervolino. "Facile method to immobilize ZnO particles on glass spheres for the photocatalytic treatment of tannery wastewater." Journal of colloid and interface science, 518 ,2018, pp . 192-199.
14. Gawade, V. V., et al. "Green synthesis of ZnO nanoparticles by using Calotropis procera leaves for the photodegradation of methyl orange." Journal of Materials Science: Materials in Electronics, 28.18, 2017, pp . 14033-14039
15. Rajamanickam, D., and M. Shanthi. "Photocatalytic degradation of an organic pollutant by zinc oxide–solar process." Arabian Journal of Chemistry, 9 , 2016, pp . 1858-S1868
16. Adam, Rania E., et al. "Synthesis of ZnO nanoparticles by co-precipitation method for solar driven photodegradation of Congo red dye at different pH." Photonics and Nanostructures-Fundamentals and Applications,32,2018, pp . 11-18