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Biosynthesis of zinc oxide nanoparticles as a potential adsorbent for degrading organochlorines

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ABSTRACT: Water pollution due to organic contaminants has been a serious issue in developing countries because of the acute toxicities and carcinogenic nature of these pollutants. Among various water treatment methods, adsorption is purported to be one of the best because it is cheap and easy to prepare and use. Initially, activated carbon was being used in water treatment to remove contaminants but it proved to be expensive and also it did not degrade these contaminants after adsorption. For this reason, zinc oxide nanoparticles are synthesized for recommended use in the degradation of pesticides. The zinc oxide nanoparticles were synthesized using *Cissus quadrangularis* plant leaf extract. The surface analysis of the synthesized nanoparticle was analyzed using a particle analyzer and X-ray diffraction (XRD) crystallography. The synthesized nanoparticles were found to have a mean diameter of 14.83 nm and the XRD pattern revealed the formation of ZnO nanoparticles showing crystallinity. The synthesized ZnO nanoparticle showed a characteristic peak at a wavelength of 368 nm for electron excitation. This simple and cost-effective phytochemical approach for the formation of ZnO nanoparticles has a promising application in biosensing, photocatalysis, electronics, and photonics.

Keywords: Water pollution, Organic contaminants, nanoparticle, Carcinogenic, adsorption

1 INTRODUCTION

Nanoparticles or ultrafine particles are particles of matter that are between 1 and 100 nanometers (nm) in diameter. The term at times is used for larger particles, up to 500 nm, or fibers and tubes that are less than 100 nm in only two directions (Trojanowski & Fthenakis 2019). The various methods used to synthesize nanoparticles include coprecipitation, hydrothermal synthesis, inert gas condensation, ion sputtering scattering, microemulsion, microwave, pulse laser ablation, sol–gel, sonochemical, spark discharge, template synthesis, and biological synthesis (Rane, Kanny, Abitha, & Thomas 2018). Among these methods it is noted that "Green synthesis" (biological synthesis) of nanoparticles makes use of environment-friendly, non-toxic, and safe reagents (Mirzaei & Darroudi 2017). Nanoparticles synthesized using biological techniques or green technology have diverse natures, with greater stability and appropriate dimensions since they are synthesized using a one-step procedure (Parveen, Banse, & Ledwani 2016).

The principal parameters of nanoparticles which make them unique in chemical reactions and reactivity are their shape, size, and the morphological structure (Ealias & Saravanakumar 2017). Nanoparticles can be present as an aerosol (mostly solid or liquid phase in air), a suspension (mostly solid in liquids), or an emulsion (two liquid phases). However, in the presence of chemical agents (surfactants), the surface and interfacial properties may be modified (Saxena, Goswami, Dhodapkar, Nihalani, & Mandal 2019). Indirectly nanoparticles can stabilize against coagulation or aggregation by conserving particle charge and by modifying the outmost layer of the particle (Hong 2019). Nanoparticles have been in use in a wide range of technologies, including adhesion, lubrication, stabilization, and controlled flocculation of colloidal dispersions (Raghu, Parkunan, & Kumar 2020).

Nanoparticles such as colloidal gold may intrude into complex folded biological molecules which are 1 nm in size to both plants and animals which are normally evidenced through immunolabeling and related surface functionalization techniques to target nanoparticles to biomolecules as markers for high-resolution transmission electron microscopy and optical imaging systems (Nativo, Prior, & Brust 2008).

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Green routes are used for the synthesis of zinc oxide nanoparticles because of the small number of chemicals that are used, which then produces the least amount of pollutants, and they are energy efficient and cost-effective. A number of natural products such as plants, fungi, algae, bacteria, and viruses can be used to synthesize the zinc oxide nanoparticles (Naveed Ul Haq et al. 2017).

In the past zinc oxide nanoparticles have been in gas sensors, biosensors, cosmetics, storage, optical devices, window materials for display, solar cells, and drug delivery, due to their unique properties (Pascariu & Homocianu 2019). Zinc oxide nanoparticles have diameters of less than 100 nanometers. Their large surface area relative to their size results in higher catalytic activity (Siripireddy & Mandal 2017).

Nanomaterials can function in the phytoremediation system through directly removing pollutants, promoting plant growth and increasing pollutant bioavailability to ease the remediation process. This means the development of nanotechnology can provide an effective way of cleaning the environment with less cost and harmful end products.

Zinc oxide (ZnO) nanoparticles have a wide bandgap semiconductor with an energy gap of 3.37 eV at room temperature which then allows the transfer of electrons in the presence of light to initiate the phytoremediation reactions. The pathway in Figure 1 shows iron nanoparticles being used in environmental cleanup.

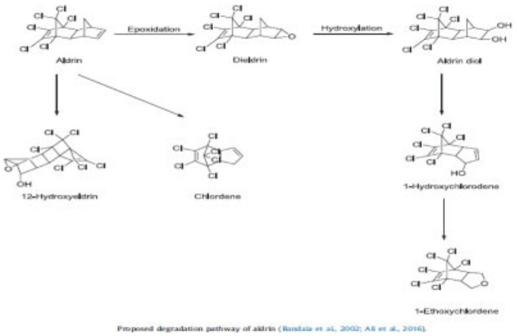

Figure 1. Proposed pathway for degradation of Aldrin.

2 LITERATURE REVIEW

Nanoparticle have proved to be very useful in the modern field of science because of their unique properties that have been used in catalysis, medicine, and electronics (Sharma et al. 2019). Nanoparticles have been used primarily in photocatalysis, which involves the use of light to initiate chemical reaction, such as degrading methyl blue to a harmless end product. Nanoparticles were used in this chemical reaction because it had a mobile valence electron between the conduction band and the valence band that is activated in the presence of light to initiate a reduction reaction to methyl blue (Boruah, Samantaray, Madras, Modak, & Bose 2020). This property of nanoparticles has made them a very important new technology for the development of adsorbents to remediate environmental pollutants to less harmful products. Specifically, nanoparticles have been used in remediating trace amounts of dyes, heavy metals, and pesticides from contaminated environments, i.e., soil and water (Mehta et al. 2019).

Nanoparticles can be prepared primarily by two methods: chemical methods and green synthesis (Sanjukta et al. 2016). Green synthesis is thought to be the best method since it uses less toxic reagents in the synthesis of nanoparticles, hence resulting in the release of less toxic by-products into the environment. In the case of green synthesis, a plant which contains either in its leaves, bark, or any other part a natural product component, which has the capability of enhancing binding of the nanoparticles, is selected for the synthesis of the nanoparticle (Saratale et al. 2018).

A nanoparticle which is friendly to the environment should be selected for phytoremediation so that it ensures that the end products of the adsorption process are not harmful to the environment or introduce pollutants to the environment (Kuppusamy, Palanisami, Megharaj, Venkateswarlu, & Naidu 2016).

Cissus quadrangularis plant was chose in the synthesis of the nanoparticles because it contains natural products that are essential in the binding of the synthesized nanoparticles (Velammal, Devi, & Amaladhas 2016). These compounds include flavonoids, glycosides, tannins, phenolics, triterpenoids, saponins, and glycosides (Dhanasekaran 2020).

ZnO nanoparticles have been employed in the photodegradation of dyes and pesticides to render these pollutants to less harmful products (Ong, Ng, & Mohammad 2018). For these reasons ZnO nanoparticles were synthesized as a potential adsorbent for the degradation of organochlorines which are persistent in the environment.

2.1 *Research design*

The research was carried out in Kenya. The research design was done at Moi university in the chemistry laboratory.

2.2 *Apparatus and reagents*

99% pure zinc nitrate, 99% pure methanol, and filter paper grade 1 were both obtained from Sigma Aldrich Chemicals Co., USA.

Cissus quandangularis plants were collected from Kisumu County 0°06′00.2″S 34°46′59.5″E.

2.3 *Synthesis of zinc oxide nanoparticles*

The cleaned, healthy plant materials were cut into small sections. They were dried under shade for 3 weeks. The dried material was ground into fine powder in an electric grinder. The powder obtained was then stored in desiccators to await extraction. Extraction was carried out using 1 g of each sample of coarsely powdered plant material with 25 mL of methanol solvent (HPLC) and kept for 48 hrs with slight shaking. All the extraction was performed at room temperature. All the extracts were filtered through Whatman No.1 paper to get filtrate as extracts which was dried to concentrate the samples (Prabhavathi, Prasad, & Jayaramu 2016). 50 mL of *Cissus quadrangualis* leaf extract was measured into a conical flask, which was then boiled at 60–80°C by a stirrer heater. 5g of zinc nitrate was added to the solution when the temperature reached 60°C. The mixture was heated until the suspension turned deep yellow in color. The paste was then collected in a ceramic crucible where it was transferred into an air furnace followed by heating at 400°C for 2 hrs. A light white colored solid of zinc oxide was collected and then powdered to form zinc oxide nanoparticles (Fazlzadeh et al. 2017).

2.4 *Characterization of zinc oxide nanoparticles*

The UV–Vis reflectance spectra (U–Vis DRS) measurements were carried out with UV140404B in the wavelength range of 200–850 nm in reflectance mode. The crystalline structure of the samples was analyzed by using PANalytical X'PERT PRO model X-Ray diffractometer, with the instrument operating at a voltage of 50 kV and a current of 30 mA.

3 RESULTS AND DISCUSSION

The following were the data from the zinc oxide nanoparticles after characterization using particle analyzer, scanning electron microscopy, and UV–Vis spectroscopy.

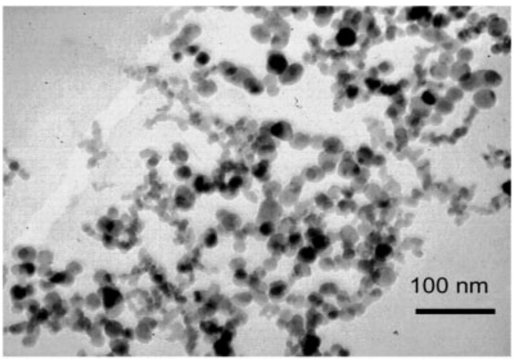

Figure 2. SEM image of agglomerated ZnO nanoparticles.

From the above data the synthesized nanoparticle using the*Cissus quandangularis* plant extract had a mean radius of 14.83 nm from Figure 3, which makes the process of synthesis viable for the synthesis of nanoparticles because the dimension of the synthesized particles were in the range of 1–100 nm, i.e., the required range for nanoparticles (Sun & Xia 2003).

Optical properties of the as-prepared ZnO nanostructure sample were revealed by UV–Vis spectroscopy at room temperature, as shown in Figure 4.

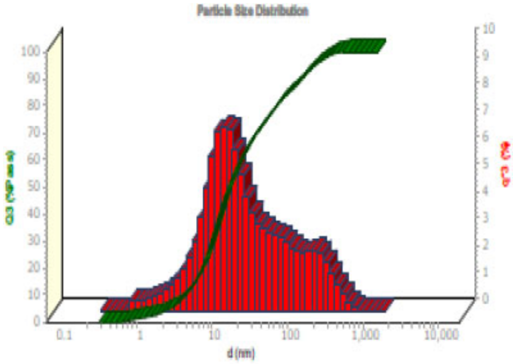

Figure 3. Particle analyzer analysis of ZnO nanoparticles.

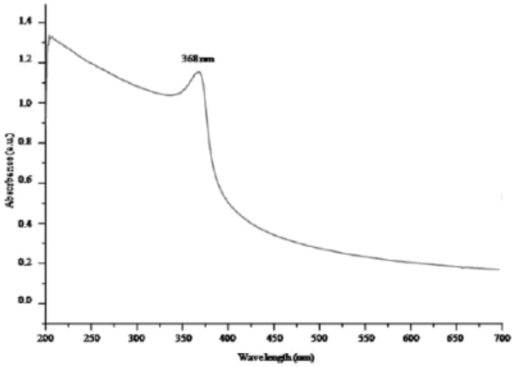

Figure 4. UV–Vis absorption spectrum of as-prepared ZnO NPs, treated *Cissus quandangularis* using optimal 0.5 mL volume in the proposed incubation cum precipitation method.

It can be seen from Figure 4 that there was intensive absorption in the ultraviolet band of about 200–400 nm. The absorption wavelength at about 368 nm of ZnO suggested the excitonic character at room temperature (Sun & Xia 2003).

The ZnO NPs embedded in *Cissus quandangularis* matrix with little agglomeration had sizes of about 5 nm throughout the carbon-coated copper grid and average particle size and shape in the range of 5–40 nm. The SEM image revealed that the particles are spherical and granular nanosized in nature, as shown in Figure 2.

4 CONCLUSION

My findings could be targeted for promising potential applications including biosensing devices and nanoelectronics because of the pollution-free and eco-friendly approach. This green synthesis approach shows that the environmentally benign and renewable latex of *Cissus quandangularis* can be used as an effective stabilizing and reducing agent for the synthesis of zinc oxide nanoparticles. Zinc oxide nanoparticles synthesized by this approach are quite stable and no visible changes are observed even after a month. Synthesis of zinc oxide nanoparticles using *Cissus quandangularis* is an alternative to chemical synthesis. We anticipate that the smaller particles are mostly stabilized by alkaloids and proteins. Further experiments on the systematic mode of mechanism of size-selective synthesis of zinc oxide nanoparticles using this very useful *Cissus quandangularis* should be done. Moreover, further research should be done on the applicability of the synthesized nanoparticles in remediation.

5 RECOMMENDATION

A study should be done to study the photoluminescence and luminescence properties of ZnO NPs synthesized from *Cissus quandangularis* plant extract.

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REFERENCES

Bandala, E. R., Gelover, S., Leal, M. T., Arancibia-Bulnes, C., Jimenez, A., & Estrada, C. A. (2002). Solar photocatalytic degradation of Aldrin. *Catalysis Today*, *76*(2–4), 189–199.

Boruah, B., Samantaray, P. K., Madras, G., Modak, J. M., & Bose, S. (2020). Sustainable photocatalytic water remediation via dual active strongly coupled AgBiO3 on PVDF/PBSA membranes. *Chemical Engineering Journal*, 124777.

Dhanasekaran, S. (2020). Phytochemical characteristics of aerial part of Cissus quadrangularis (L) and its in-vitro inhibitory activity against leukemic cells and antioxidant properties. *Saudi Journal of Biological Sciences*.

Ealias, A. M., & Saravanakumar, M. P. (2017, November). A review on the classification, characterisation, synthesis of nanoparticles and their application. In *IOP Conf. Ser. Mater. Sci. Eng* (Vol. 263, p. 032019).

Hong, N. H. (2019). Introduction to nanomaterials: basic properties, synthesis, and characterization. In *Nano-Sized Multifunctional Materials* (pp. 1–19). Elsevier.

Kuppusamy, S., Palanisami, T., Megharaj, M., Venkateswarlu, K., & Naidu, R. (2016). Ex-situ remediation technologies for environmental pollutants: a critical perspective. In *Reviews of Environmental Contamination and Toxicology Volume 236* (pp. 117–192). Springer, Cham.

Mehta, A., Mishra, A., Basu, S., Shetti, N. P., Reddy, K. R., Saleh, T. A., & Aminabhavi, T. M. (2019). Band gap tuning and surface modification of carbon dots for sustainable environmental remediation and photocatalytic hydrogen production–A review. *Journal of environmental management*, *250*, 109486.

Mirzaei, H., & Darroudi, M. (2017). Zinc oxide nanoparticles: Biological synthesis and biomedical applications. *Ceramics International*, *43*(1), 907–914.

Nativo, P., Prior, I. A., & Brust, M. (2008). Uptake and intracellular fate of surface-modified gold nanoparticles. *ACS nano*, *2*(8), 1639–1644.

Naveed Ul Haq, A., Nadhman, A., Ullah, I., Mustafa, G., Yasinzai, M., & Khan, I. (2017). Synthesis approaches of zinc oxide nanoparticles: the dilemma of ecotoxicity. *Journal of Nanomaterials*, *2017*.

Ong, C. B., Ng, L. Y., & Mohammad, A. W. (2018). A review of ZnO nanoparticles as solar photocatalysts: synthesis, mechanisms and applications. *Renewable and Sustainable Energy Reviews*, *81*, 536–551.

Parveen, K., Banse, V., & Ledwani, L. (2016, April). Green synthesis of nanoparticles: their advantages and disadvantages. In *AIP conference proceedings* (Vol. 1724, No. 1, p. 020048). AIP Publishing LLC.

Pascariu, P., & Homocianu, M. (2019). ZnO-based ceramic nanofibers: Preparation, properties and applications. *Ceramics International*, *45*(9), 11158–11173.

Raghu, H. V., Parkunan, T., & Kumar, N. (2020). Application of Nanobiosensors for Food Safety Monitoring. In *Environmental Nanotechnology Volume 4* (pp. 93–129). Springer, Cham.

Rane, A. V., Kanny, K., Abitha, V. K., & Thomas, S. (2018). Methods for synthesis of nanoparticles and fabrication of nanocomposites. In *Synthesis of inorganic nanomaterials* (pp. 121–139). Woodhead Publishing.

Riley, J. K., Matyjaszewski, K., & Tilton, R. D. (2018). Friction and adhesion control between adsorbed layers of polyelectrolyte brush-grafted nanoparticles via pH-triggered bridging interactions. *Journal of colloid and interface science*, *526*, 114–123.

Sanjukta, R. K., Samir, D., Puro, K., Ghataak, S., Shakuntal, L., & Sen, A. (2016). Green synthesis of silver Nanoparticles using plant. *Int J Nanomed Nanosurg*, *2*(2).

Saratale, R. G., Saratale, G. D., Shin, H. S., Jacob, J. M., Pugazhendhi, A., Bhaisare, M., & Kumar, G. (2018). New insights on the green synthesis of metallic nanoparticles using plant and waste biomaterials: current knowledge, their agricultural and environmental applications. *Environmental Science and Pollution Research*, *25*(11), 10164–10183.

Saxena, N., Goswami, A., Dhodapkar, P. K., Nihalani, M. C., & Mandal, A. (2019). Bio-based surfactant for enhanced oil recovery: Interfacial properties, emulsification and rock-fluid interactions. *Journal of Petroleum Science and Engineering*, *176*, 299–311.

Sharma, G., Kumar, A., Sharma, S., Naushad, M., Dwivedi, R. P., ALOthman, Z. A., & Mola, G. T. (2019). Novel development of nanoparticles to bimetallic nanoparticles and their composites: a review. *Journal of King Saud University-Science*, *31*(2), 257–269.

Siripireddy, B., & Mandal, B. K. (2017). Facile green synthesis of zinc oxide nanoparticles by Eucalyptus globulus and their photocatalytic and antioxidant activity. *Advanced Powder Technology*, *28*(3), 785–797.

Sun, Y., & Xia, Y. (2003). Gold and silver nanoparticles: a class of chromophores with colors tunable in the range from 400 to 750 nm. *Analyst*, *128*(6), 686–691.

Trojanowski, R., & Fthenakis, V. (2019). Nanoparticle emissions from residential wood combustion: A critical literature review, characterization, and recommendations. *Renewable and Sustainable Energy Reviews*, *103*, 515–528.

Velammal, S. P., Devi, T. A., & Amaladhas, T. P. (2016). Antioxidant, antimicrobial and cytotoxic activities of silver and gold nanoparticles synthesized using Plumbago zeylanica bark. *Journal of Nanostructure in Chemistry*, *6*(3), 247–260.