

1. A Review on Bio-Mediated Nanoparticles and their Applications

Pratibha Attri, Sangeeta Garg, Jatinder Kumar Ratan

Department of Chemical Engineering,
Dr. B.R. Ambedkar National Institute of Technology,
Jalandhar, India.

Ardhendu Sekhar Giri

Department of Chemical Engineering,
Indian Institute of Science Education and Research,
Bhopal, India.

Abstract:

Studies showed that chemically produced nanoparticles are more expensive to produce and have limited applications due to the use of hazardous chemical reagents and toxic solvents. Exposure to these nanoparticles may have harmful impacts on living creatures and the environment. Therefore, a green and non-toxic approach to the synthesis of eco-friendly and environmentally acceptable metal oxide nanoparticles is required. Biological approaches for the preparation of metal oxide nanoparticles are an environmentally safe and green alternative because they do not require harmful chemicals or toxic solvents. Biological methods employ microorganisms (bacteria, fungi, and algae) and plant extracts for the synthesis of metal oxide nanoparticles. Green synthesis is a simple, single-step bio reduction method that requires relatively low energy to initiate the reaction. Therefore, biosynthesis is a cost-effective method for the production of metal oxide nanoparticles.

Keywords:

Green Synthesis, Nanoparticles, Biological methods, Non-toxic.

1.1 Introduction:

Nanoparticles (NPs) have gained significant attention in photocatalysis due to their unique properties such as chemical, optical, electrical and mechanical properties because of the quantum confinement effect (Pande et al., 2008; Trinh et al., 2020). Instead of bulk material as a catalyst, nano particles such as TiO₂, ZnO, Fe₂O₃, WO₃, SnO₂, ZrO₂, CdS, SrTiO₃ and Cu₂O can be used to improve the efficiency of photocatalytic reactions (Abbas et al., 2018; Falah & Mackenzie, 2020; Rani & Shanker, 2019, 2021). The surface to volume ratio property of nanoparticles especially as a catalyst increases efficiency hundred percent as compared to bulk materials (Dewangan et al., 2012). Studies showed that chemically produced NPs were costlier in production and have limited application due to the use of hazardous chemical reagents and toxic solvents. Furthermore, environmental exposure to these NPs may have harmful impacts on living creatures and the environment.

Therefore, a green and non-toxic approach for the manufacture of ecologically acceptable metal oxide nanoparticles is required. Biological approaches for the manufacture of metal oxide NPs are an environmentally safe and green alternative because they do not require dangerous chemicals or toxic solvents.

Biological methods employ microorganisms (bacteria, fungi and algae) and plant extracts for the synthesis of metal oxide NPs (Singh et al., 2018). The NPs synthesised using these methods are known as bio-mediated NPs. Green synthesis is a simple and single step bio-reduction method that requires relatively low energy to initiate the reaction (Kalpana & Devi Rajeswari, 2018). Therefore, biosynthesis is a cost-effective method for the production of metal oxide NPs.

1.2 Different types of Bio-mediated nanoparticles:

The distinct properties of nanoparticles depend upon the different method used for synthesis (Figure 1.1). Bio-mediated synthesised NPs have numerous applications in different fields such as photocatalysts, electrode active materials, solar cells and antibacterial activity. Due to presence of natural surfactants and stabilizing agents which are rich biological activity.

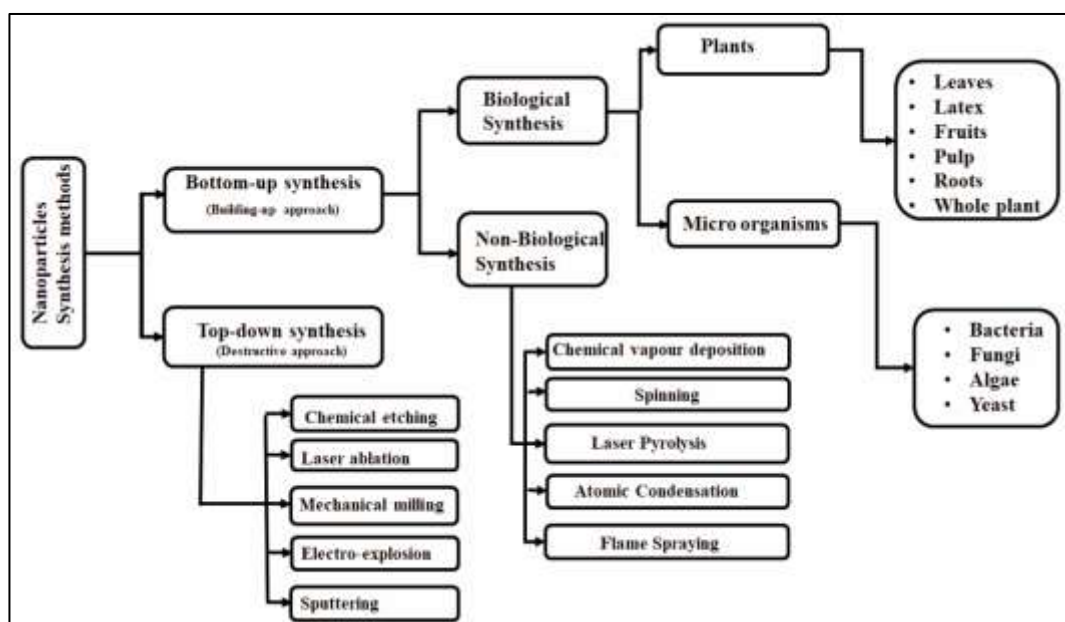


Figure 1.1: Different methods used for the synthesis of nanoparticles

1.3 Silver nanoparticles (Ag NPs):

Ag NPs have been prepared by various methods including spark discharging, electrochemical reduction, solution irradiation and cryo chemical synthesis. The size of synthesized nanoparticles was smaller than 100 nm and consisted of about 20-15,000 silver atoms (Chen & Schluesener, 2008). Ag NPs have been widely used as antimicrobial agents in commercial medical and consumer products (Rai et al., 2009; Ravindra et al., 2010). Ag

NPs preparation using plants (inactivated plant tissue, plant extracts and living plant) is an important branch of biosynthesis processes. It was reported that different plant leaves have the potential to reduce metal ions to zero valent metal nanoparticles (Makarov et al., 2014). Bio-mediated Ag NPs showed their applications in industries such as photocatalysts, in hospitals it was used for treating burns, and medical bandages because of its nano size and antimicrobial properties (Kirubaharan et al., 2012; Muthu & Priya, 2017; Pang et al., 2021; Vigneshwaran et al., 2007).

(Bankar et al., 2010) synthesised Ag NPs using banana peel extract. It was reported that Ag NPs have antimicrobial activity against fungal as well as bacterial cultures. *Tabernaemontana divaricate* leaf extract was used for the reduction of silver ions to Ag NPs by (Arun et al., 2014). The synthesised Ag NPs exhibited size of 22 nm with excellent stability for six months and cytotoxic activity against human breast cancer cell line (MCF-7). In a similar study (Ramesh et al., 2015) fabricated Ag NPs in an aqueous medium using *Emblca officinalis* fruit extract as a stabilizer and reducing agent. It was examined that the synthesized Ag NPs were spherical in shape (78 nm) and showed inhibition against both gram-positive and gram-negative bacterial strains.

Furthermore, bio-synthesis of Ag NPs using aqueous extract of Neem (*Azadirachta indica*) leaves was done by (Verma & Mehata, 2016). Synthesized Ag NPs were crystalline in nature, and poly dispersed because of which they exhibited high energy surface plasmon resonance band at around 400 nm and a strong photoluminescence band at 450 nm. Bio-mediated Ag NPs showed enhanced antibacterial activity against the bacterial colony and were used in the field of medicine, food and cosmetic industries.

The synthesis of Ag NPs using *Azadirachta indica* (neem) was done by (Nagar & Devra, 2019). Prepared Ag NPs were applied as the catalyst for the degradation of methyl orange (MO) in an aqueous solution and real wastewater. The degradation of MO followed pseudo-first order kinetics and maximum degradation of MO reached 88% in 40 min in aqueous solution and 80 min in real wastewater. (Küp et al., 2020) prepared Ag NPs from aqueous extract leaf of *Aesculus hippocastanum* (horse chestnut). It was observed that horse chestnut leaves have reduction potential as well as being a capping agent to produce well-defined nanoscale silver particles. Bio-mediated Ag NPs using *Aesculus hippocastanum* exhibited strong antibacterial activity against tested bacterial species but have no effect against fungal strains. Bio fabricated Ag NPs (25 nm) were prepared using *Nepeta leucophylla* extract by (Singh & Dhaliwal, 2020). Synthesised Ag NPs exhibited Surface Plasmon Resonance band at 430 nm in the ultraviolet-visible spectrum and showed 82.8 % photocatalytic degradation of methylene blue dye from the aqueous solution in the presence of light and 61.2 % in dark in 180 min.

Ag NPs were prepared through in-situ reduction by aminated alkaline lignin by (Pang et al., 2021). Results showed that Ag NPs has a good catalytic performance for the reduction of 4-nitrophenol after recycling eight times. Ag NPs/aminated alkaline lignin composite exhibited cyclic catalytic activity due to the strong binding force between the amine groups of lignin and Ag NPs. Photocatalytic activity and spectral properties of Ag NPs fabricated using *Ferula assafoetida* were evaluated by (Subramaniam et al., 2022). Using halogen lamp, studies explored that the photocatalytic activity of Ag NPs against the methylene blue dye was 96 % in 90 min.

(Hashemi et al., 2022) synthesized bio based Ag NPs using *Sambucus ebulus* extract as a stabilizing, capping and reducing agents for the evaluation of efficient antibacterial, anticancer, and photocatalyst activities. TEM and FE-SEM analysis showed that Ag NPs were spherical in shape with a size range of 35–50 nm. The biosynthesized Ag NPs showed anti-cancer activity against breast (MCF-7) and gastric (AGS) cancer cell lines. The biogenic Ag NPs showed high catalytic activity with 95 % degradation of methyl orange dye under sun-light irradiation in 11 min.

1.4 Cu₂O NPs:

Cu₂O NPs have attracted the attention of researchers due to their tuneable direct bandgap, p-type conductivity, non-toxicity, abundance and low-cost productivity (Minami et al., 2016; Nandy et al., 2013). The p-type behaviour of cuprous oxide nanoparticles is due to the special configuration of the valence band, formed by 3d¹⁰ levels of the Cu⁺ cation. The existence of these different levels contributes to a less localized population of holes, which improves the mobility of these charges (Matsuzaki et al., 2008). Cu₂O NPs have shown unique properties in different fields such as solar energy, gas sensing, photocatalysis and magnetic storage devices because of their capacity to absorb visible light (Huang et al., 2009; Kumar et al., 2018; Li et al., 2021).

A comparison of previous studies with present study is shown in Table 1.1 (Jassal et al., 2016) synthesised α -Fe₂O₃ nanoparticles using *Sapindus mukorossi* and showed the 81 % degradation efficiency for 4-Aminopyridine in 1440 min. (Kerour et al., 2018a) showed the 70 % degradation of methylene blue in 10 min using Cu₂O nanoparticles prepared using Aloe Vera extract. Results demonstrated that the performance and catalytic activity of Cu₂O NPs towards the degradation of various toxic dyes using different source of light was very effective. In the present study 80 % degradation of 4-Aminopyridine has been achieved using Cu₂O NPs with 82 % COD and 65 % of TOC removal.

Table 1.1: Comparison of Bio- mediated synthesised Cu₂O NPs with other chemically synthesized

Reference	Methods			Degradation Efficiency and Mineralization		Time (min)
	Nanoparticles And Reaction conditions	Plant Extract	Pollutant	Removal Efficiency	COD Removal	
(Behera & Giri, 2016)	Cu ₂ O 500 W Xenon lamp	<i>Calotropis Giganetea</i>	Methylene blue (20 ppm)	90 %	-	120
(Borah et al., 2016)	Cu ₂ O	<i>Syzygium jambos (L.) Alston plant</i>	Ary boronic acid (0.041 mmol / 5ml)	95%	-	300

Reference	Methods			Degradation Efficiency and Mineralization		Time (min)
	Nanoparticles And Reaction conditions	Plant Extract	Pollutant	Removal Efficiency	COD Removal	
(Jassal et al., 2016)	α -Fe ₂ O ₃ nanoparticles	<i>Sapindus mukorossi</i>	4-Aminopyridine (25 mg/L)	81%	-	1440
(Mousavi-Kamazani et al., 2017)	Cu/Cu ₂ O 250W Mercury lamp	<i>Pomegranate marc peels (PMP)</i>	Methylene blue (25 mg/L)	99%	-	150

1.5 Conclusion:

Studies showed that bio-mediated NPs are cheaper to produce and have wide applications in various fields due to the use natural surfactants. Biologically synthesized NPs are non-toxic, eco-friendly and environmentally acceptable. Green synthesis of nanoparticles was found to be simple, single-step and low energy initiator. Bio-mediated prepared NPs were found to comparatively more effective as compare to chemically synthesise. Therefore, biosynthesis is a cost-effective method for the production of NPs.

1.6 References:

1. Abbas, M., Adil, M., Ehtisham-ul-Haque, S., Munir, B., Yameen, M., Ghaffar, A., Shar, G. A., Asif Tahir, M., & Iqbal, M. (2018). *Vibrio fischeri* bioluminescence inhibition assay for ecotoxicity assessment: A review. *Science of the Total Environment*, 626, 1295–1309. <https://doi.org/10.1016/j.scitotenv.2018.01.066>
2. Arun, R., Aarti, C., & Kumari, P. (2014). Synthesis and characterization of silver nanoparticles using *tabernaemontana divaricata* and its cytotoxic activity against MCF-7 cell line. *International Journal of Pharmacy and Pharmaceutical Sciences*, 6(8), 86–90.
3. Bankar, A., Joshi, B., Kumar, A. R., & Zinjarde, S. (2010). Banana peel extract mediated novel route for the synthesis of silver nanoparticles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 368(1–3), 58–63. <https://doi.org/10.1016/j.colsurfa.2010.07.024>
4. Behera, M., & Giri, G. (2016). Inquiring the photocatalytic activity of cuprous oxide nanoparticles synthesized by a green route on methylene blue dye. *International Journal of Industrial Chemistry*, 7(2), 157–166. <https://doi.org/10.1007/s40090-016-0075-y>
5. Borah, R., Saikia, E., Bora, S. J., & Chetia, B. (2016). On-water synthesis of phenols using biogenic Cu₂O nanoparticles without using H₂O₂. *RSC Advances*, 6(102), 100443–100447. <https://doi.org/10.1039/c6ra22972g>
6. Chen, X., & Schluesener, H. J. (2008). Nanosilver: A nanoparticle in medical application. *Toxicology Letters*, 176(1), 1–12. <https://doi.org/10.1016/j.toxlet.2007.10.004>

7. Dewangan, R., Sharma, A. K., Kumar, N., Maiti, S. K., Singh, H., Gangwar, A. K., Shrivastava, S., Sonal, & Kumar, A. (2012). In-vitro biocompatibility determination of bladder acellular matrix graft. *Trends in Biomaterials and Artificial Organs*, 25(4), 161–171.
8. Falah, M., & Mackenzie, K. J. D. (2020). Photocatalytic nanocomposite materials based on inorganic polymers (Geopolymers): A review. *Catalysts*, 10(10), 1–20. <https://doi.org/10.3390/catal10101158>
9. Hashemi, Z., Mizwari, Z. M., & Mohammadi-aghdam, S. (2022). Sustainable green synthesis of silver nanoparticles using *Sambucus ebulus* phenolic extract (AgNPs@SEE) : Optimization and assessment of photocatalytic degradation of methyl orange and their in vitro antibacterial and anticancer activity. *Arabian Journal of Chemistry*, 15(1), 103525. <https://doi.org/10.1016/j.arabjc.2021.103525>
10. Huang, L., Peng, F., Yu, H., & Wang, H. (2009). Preparation of cuprous oxides with different sizes and their behaviors of adsorption, visible-light driven photocatalysis and photocorrosion. *Solid State Sciences*, 11(1), 129–138. <https://doi.org/10.1016/j.solidstatesciences.2008.04.013>
11. Jassal, V., Shanker, U., & Gahlot, S. (2016). Green synthesis of some iron oxide nanoparticles and their interaction with 2-Amino, 3-Amino and 4-Aminopyridines. *Materials Today: Proceedings*, 3(6), 1874–1882. <https://doi.org/10.1016/j.matpr.2016.04.087>
12. Kalpana, V. N., & Devi Rajeswari, V. (2018). A Review on Green Synthesis, Biomedical Applications, and Toxicity Studies of ZnO NPs. *Bioinorganic Chemistry and Applications*, 2018. <https://doi.org/10.1155/2018/3569758>
13. Kerour, A., Boudjadar, S., Bourzami, R., & Allouche, B. (2018). Eco-friendly synthesis of cuprous oxide (Cu₂O) nanoparticles and improvement of their solar photocatalytic activities. *Journal of Solid State Chemistry*, 263(April), 79–83. <https://doi.org/10.1016/j.jssc.2018.04.010>
14. Kirubaharan, C. J., Kalpana, D., Lee, Y. S., Kim, A. R., Yoo, D. J., Nahm, K. S., & Kumar, G. G. (2012). Biomediated silver nanoparticles for the highly selective copper(II) ion sensor applications. *Industrial and Engineering Chemistry Research*, 51(21), 7441–7446. <https://doi.org/10.1021/ie3003232>
15. Kumar, M., Das, R. R., Samal, M., & Yun, K. (2018). Highly stable functionalized cuprous oxide nanoparticles for photocatalytic degradation of methylene blue. *Materials Chemistry and Physics*, 218(November 2017), 272–278. <https://doi.org/10.1016/j.matchemphys.2018.07.048>
16. K p, F.  .,  o kun ay, S., & Duman, F. (2020). Biosynthesis of silver nanoparticles using leaf extract of *Aesculus hippocastanum* (horse chestnut): Evaluation of their antibacterial, antioxidant and drug release system activities. *Materials Science and Engineering C*, 107(November 2017). <https://doi.org/10.1016/j.msec.2019.110207>
17. Li, X., Raza, S., & Liu, C. (2021). Journal of Environmental Chemical Engineering Directly electrospinning synthesized Z-scheme heterojunction TiO₂@Ag@Cu₂O nanofibers with enhanced photocatalytic degradation activity under solar light irradiation. *Journal of Environmental Chemical Engineering*, 9(5), 106133. <https://doi.org/10.1016/j.jece.2021.106133>
18. Makarov, V. V., Makarova, S. S., Love, A. J., Sinitsyna, O. V., Dudnik, A. O., Yaminsky, I. V., Taliansky, M. E., & Kalinina, N. O. (2014). Biosynthesis of stable iron oxide nanoparticles in aqueous extracts of *hordeum vulgare* and *rumex acetosa* plants. *Langmuir*, 30(20), 5982–5988. <https://doi.org/10.1021/la501192a>

19. Matsuzaki, K., Nomura, K., Yanagi, H., Kamiya, T., Hirano, M., & Hosono, H. (2008). Epitaxial growth of high mobility Cu₂O thin films and application to p -channel thin film transistor. *Applied Physics Letters*, 93(20), 3–6. <https://doi.org/10.1063/1.3026539>
20. Minami, T., Nishi, Y., & Miyata, T. (2016). Cu₂O-based solar cells using oxide semiconductors. *Journal of Semiconductors*, 37(1). <https://doi.org/10.1088/1674-4926/37/1/014002>
21. Mousavi-Kamazani, M., Zarghami, Z., Rahmatolahzadeh, R., & Ramezani, M. (2017). Solvent-free synthesis of Cu-Cu₂O nanocomposites via green thermal decomposition route using novel precursor and investigation of its photocatalytic activity. *Advanced Powder Technology*, 28(9), 2078–2086. <https://doi.org/10.1016/j.appt.2017.05.014>
22. Muthu, K., & Priya, S. (2017). Green synthesis, characterization and catalytic activity of silver nanoparticles using *Cassia auriculata* flower extract separated fraction. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 179, 66–72. <https://doi.org/10.1016/j.saa.2017.02.024>
23. Nagar, N., & Devra, V. (2019). A kinetic study on the degradation and biodegradability of silver nanoparticles catalyzed Methyl Orange and textile effluents. *Heliyon*, 5(3), e01356. <https://doi.org/10.1016/j.heliyon.2019.e01356>
24. Nandy, S., Banerjee, A., Fortunato, E., & Martins, R. (2013). A review on Cu₂O and CuI-based p-type semiconducting transparent oxide materials: promising candidates for new generation oxide based electronics. *Reviews in Advanced Sciences and Engineering*, 2(4), 273–304. <https://doi.org/10.1166/rase.2013.1045>
25. Pande, S., Jana, S., Basu, S., Sinha, A. K., Datta, A., & Pal, T. (2008). Nanoparticle-catalyzed clock reaction. *Journal of Physical Chemistry C*, 112(10), 3619–3626. <https://doi.org/10.1021/jp7106999>
26. Pang, Y., Chen, Z., Zhao, R., Yi, C., Qiu, X., Qian, Y., & Lou, H. (2021). Facile synthesis of easily separated and reusable silver nanoparticles/aminated alkaline lignin composite and its catalytic ability. *Journal of Colloid and Interface Science*, 587, 334–346. <https://doi.org/10.1016/j.jcis.2020.11.113>
27. Rai, M., Yadav, A., & Gade, A. (2009). Silver nanoparticles as a new generation of antimicrobials. *Biotechnology Advances*, 27(1), 76–83. <https://doi.org/10.1016/j.biotechadv.2008.09.002>
28. Ramesh, P. S., Kokila, T., & Geetha, D. (2015). Plant mediated green synthesis and antibacterial activity of silver nanoparticles using *Embllica officinalis* fruit extract. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 142, 339–343. <https://doi.org/10.1016/j.saa.2015.01.062>
29. Rani, M., & Shanker, U. (2019). Degradation of tricyclic polyaromatic hydrocarbons in water, soil and river sediment with a novel TiO₂ based heterogeneous nanocomposite. *Journal of Environmental Management*, 248(August), 109340. <https://doi.org/10.1016/j.jenvman.2019.109340>
30. Rani, M., & Shanker, U. (2021). Journal of Colloid and Interface Science Synergistic effects of zinc oxide coupled copper hexacyanoferrate nanocomposite: Robust visible-light driven dye degradation. *Journal of Colloid And Interface Science*, 584, 67–79. <https://doi.org/10.1016/j.jcis.2020.09.079>
31. Ravindra, S., Murali Mohan, Y., Narayana Reddy, N., & Mohana Raju, K. (2010). Fabrication of antibacterial cotton fibres loaded with silver nanoparticles via “Green Approach.” *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 367(1–3), 31–40. <https://doi.org/10.1016/j.colsurfa.2010.06.013>

32. Singh, J., & Dhaliwal, A. S. (2020). Plasmon-induced photocatalytic degradation of methylene blue dye using biosynthesized silver nanoparticles as photocatalyst. In *Environmental Technology (United Kingdom)* (Vol. 41, Issue 12). Taylor & Francis. <https://doi.org/10.1080/09593330.2018.1540663>
33. Singh, J., Dutta, T., Kim, K. H., Rawat, M., Samddar, P., & Kumar, P. (2018). “Green” synthesis of metals and their oxide nanoparticles: Applications for environmental remediation. *Journal of Nanobiotechnology*, 16(1), 1–24. <https://doi.org/10.1186/s12951-018-0408-4>
34. Subramaniam, S., Kumarasamy, S., Narayanan, M., & Whangchai, K. (2022). Spectral and structure characterization of *Ferula assafoetida* fabricated silver nanoparticles and evaluation of its cytotoxic, and photocatalytic competence. *Environmental Research*, 204(PA), 111987. <https://doi.org/10.1016/j.envres.2021.111987>
35. Trinh, V. T., Nguyen, T. M. P., Van, H. T., Hoang, L. P., Nguyen, T. V., Ha, L. T., Vu, X. H., Pham, T. T., Nguyen, T. N., Quang, N. V., & Nguyen, X. C. (2020). Phosphate Adsorption by Silver Nanoparticles-Loaded Activated Carbon derived from Tea Residue. *Scientific Reports*, 10(1), 1–13. <https://doi.org/10.1038/s41598-020-60542-0>
36. Verma, A., & Mehata, M. S. (2016). Controllable synthesis of silver nanoparticles using Neem leaves and their antimicrobial activity. *Journal of Radiation Research and Applied Sciences*, 9(1), 109–115. <https://doi.org/10.1016/j.jrras.2015.11.001>
37. Vigneshwaran, N., Ashtaputre, N. M., Varadarajan, P. V., Nachane, R. P., Paralikal, K. M., & Balasubramanya, R. H. (2007). Biological synthesis of silver nanoparticles using the fungus *Aspergillus flavus*. *Materials Letters*, 61(6), 1413–1418. <https://doi.org/10.1016/j.matlet.2006.07.042>