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Green Synthesis of Silver-based Nanocomposites Using Indigenous Plant Waste and their Lab Scale Application for Targeted Environmental Remediation

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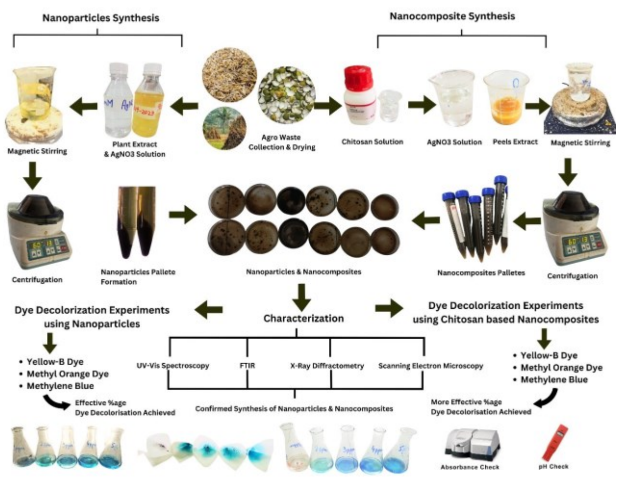
Graphical abstract



ABSTRACT

Green nanotechnology is a multidisciplinary field that has emerged as a rapidly developing research area, serving as an important technique that emphasizes on making procedures that are clean, nonhazardous, and especially environment friendly, in contrast with chemical and physical methods currently employed for nano-synthesis. The present work concentrated on the green synthesis of Silver Nanoparticles (AgNPs) and Chitosan based Silver Nanocomposites (CS-AgNCs) using aqueous extracts of some indigenous plants; optimizing the different experimental factors required for the formation and stability of AgNPs and CS-AgNCs. The optimum conditions were found to be 0.05 M and 0.1 M concentration of silver nitrate solution, a 1:10 ratio extract of the peels, and an incubation period of 24-48 h at 4 °C. The synthesized AgNPs were characterized using UV-VIS Spectroscopy, XRD, FTIR, and SEM and CS-AgNCs were characterized by UV-VIS Spectroscopy and FTIR. FTIR analysis showed the presence of polyphenolic functional groups which confirmed the biogenic synthesis of nanoparticles. Furthermore, these nanoparticles and their composites showed promising properties for the decolorization of azo dyes. Nanoparticles and nanocomposites of *Citrus paradisi* peels showed 100 % decolorization of Methylene Blue, while the nanocomposites of *Oryza sativa* husk showed more decolorization about 80 % than its nanoparticles having 47 % of the same dye. Hence, they can be a very good choice for application in targeted environmental remediation e.g., industrial wastewater treatment.

Keywords: Biowaste valorization, Citrus fruit peels, rice husk, silver nanoparticles, chitosan-based silver nanocomposites, dyes decolorization, wastewater treatment

1. Introduction

Global waste is projected to rise from 2.01 billion to 3.4 billion tons in three decades, emphasizing the need for change. Pakistan alone contributes 87 out of 998 million tons of the global annual agrowaste production including crops, food processing, and hazardous materials like pesticides (Zamare *et al.* 2016). In the last decade, circular economy has become popular as a solution for sustainable development as increasing MSW generation presents both challenges and opportunities for advancing this. Researchers are investigating nanotechnology's potential as green chemistry is one of the most attractive and applicable solutions for tackling this challenge (Ncube *et al.* 2023). Creating unique nanomaterials in nanotechnology poses challenges in achieving precise control over size, shape, composition, and surface properties while addressing issues in stability, reproducibility, scalability, and safety during synthesis

(Tariq *et al.* 2023). The importance of nanomaterials (NMs) becomes clear as research reveals that their particle size significantly influences properties such as chemical, electrical, mechanical, and optical attributes.

Nanoparticles can be synthesized using physical, chemical, and biological methods. However, chemical and physical methods have environmental drawbacks and complexity, while biological pathways offer rapid, cost-effective, and eco-friendly alternatives (Ingale *et al.* 2013). Various plant parts have been studied for nanoparticle synthesis, offering scalability and simplified processes compared to cell cultures. The biomolecules in plants and extracts act as both reducing and capping agents, as they serve as key stabilizers and enhancers for nanoparticle synthesis (Hasan *et al.* 2018). Biologically synthesized nanoparticles find applications in pollution control, catalysis, antimicrobial agents, and photochemical reactions.

Despite the benefits of green-synthesized nanoparticles, they tend to clump together, reducing their effectiveness. When the bare nanoparticles are used alone, they pose a significant threat & toxicity to biotic systems including humans. For this reason, making nanocomposites from nanoparticles is an ideal solution to increase their stability, prevention of agglomeration, and biosafety. Nanocomposites improve properties like strength, conductivity, and stability due to better dispersion and reduced agglomeration. These nanocomposites can be classified based on structure and matrix type, such as polymer-based or non-polymer-based (Motshekga *et al.* 2015). Chitosan nanocomposites exhibit unique physical features like thickness, swelling behavior, and strong transparent films due to the presence of reactive amine-hydroxyl groups (Ahmad *et al.* 2020). Their growing popularity stems from remarkable biocompatibility and antimicrobial traits, finding application in water treatment, tissue engineering, drug delivery, wound dressing, packaging, electronics, etc. (Ramachandran *et al.* 2019).

The objective of this study is therefore, the synthesis of Chitosan-based Silver Nanocomposites using Citrus and Rice Husk waste to play a role in sustainable waste management and lab-scale application of these nanomaterials for dye decolorization.

2. Materials and methods

2.1. Collection of waste & extracts preparation

The locally collected peels of Grape Fruit *(Citrus paradisi),* Mosambi *(Citrus limetta),* and Rice husk (*Oryza sativa)* were ground into fine powder. All extracts were prepared in distilled water in 1:100, one with boiling for 3-4 minutes and the other with stirring at room temperature for 30 minutes.

2.2. Estimation of phenols & antioxidant potential

For plant extracts, qualitative and quantitative phenolic content estimation was conducted through Lead Acetate, Ferric Chloride Tests, and Folin-Ciocalteu's assay. Additionally, antioxidant properties were evaluated using the 2,2-Diphenyl-1-picrylhydrazyl (DPPH) free radical scavenging method as described by (Tamilselvi *et al.* 2012; Shirazi *et al.* 2014). The percentage of inhibition of DPPH by the extracts was calculated using the following formula:

$$\% \text{ Inhibition} = \frac{A - B}{A} \times 100 \tag{6}$$

2.3. Synthesis of silver nanoparticles and chitosan silver nanocomposites

Silver nanoparticles were synthesized with a plant extract ratio of 1:100 and 1 mM $AgNO_3$ solution. Optimization included varying extract ratios, $AgNO_3$ concentrations (1 mM, 0.05 M, 0.1 M, 0.5 M), and adjusting volumes and compositions of extracts. Time and temperature impacts on nanoparticles yield were studied. Purification was achieved through centrifugation at 6000 rpm. Chitosan Silver Nanocomposites were synthesized by dissolving 2 g of Chitosan in acetic acid, mixing it with 100 ml of $AgNO_3$, and then adding plant extract. Nanocomposites were purified by centrifugation at 4500 rpm and subsequently dried.

2.4. Characterization of AgNPs & CS-AgNCs

The synthesized AgNPs were characterized using UV-Vis Spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy, and X-ray Diffractometry. The synthesized CS-AgNCs were characterized using UV-Vis Spectroscopy and FTIR.

2.5. Application for Dye Decolorization

The dye decolorization efficacy of synthesized Silver Nanoparticles (AgNPs) and Chitosan Silver Nanocomposites (CS-AgNCs) were tested against the Methyl Orange, Yellow (B), and Methylene Blue Dyes.

3. Results and discussion

3.1. Estimation of Phenols

The qualitative detection of phenols yielded positive results in all prepared aqueous extracts of *Citrus limetta, Citrus paradisi* peels, and *Oryza sativa* Husk. For quantitative estimation, Folin-Ciocalteu's assay indicated that among boiled peel extracts in a 1:100 ratio, *Citrus paradisi* extract exhibited a higher Phenolic Content (21 %) compared to *Citrus limetta* (16 %). While *Oryza sativa* husk in a 1:10 ratio, displayed a high phenol content with an antioxidant potential of 83% due to its concentrated extract ratio.

3.2. Synthesis of AgNPs and CS-AgNCs

Among all the experiments performed, they showed that 0.05 M and 0.1 M of $AgNO_3$ with a 1:10 ratio of plant extracts of citrus peels and rice husk, respectively, were found optimal for maximum yield of AgNPs and CS-AgNCs. Aqueous plant extracts prepared with boiling were found more successful for AgNPs & CS-AgNCs synthesis. Upon the synthesis of AgNPs color changes of the solutions were observed from yellow to dark brown and in the case of CS-AgNCs from pale white to dark brown after the complete reduction of Ag^+ ions.

3.3. Characterization of AgNPs and CS-AgNCs

3.3.1. UV-Vis Spectroscopy

The synthesis of AgNPs and CS-AgNCs using extracts of *Citrus limetta*, *Citrus paradisi* peels, and *Oryza sativa* husk were confirmed by UV-VIS as Figure 1. shows the absorption peak of their AgNPs at 420, 430, and 440 nm, respectively (Mahmoud, 2021). It also showed the absorption peak of biosynthesized CS-AgNCs at 340 nm which is different from AgNPs, indicating their difference of formation.

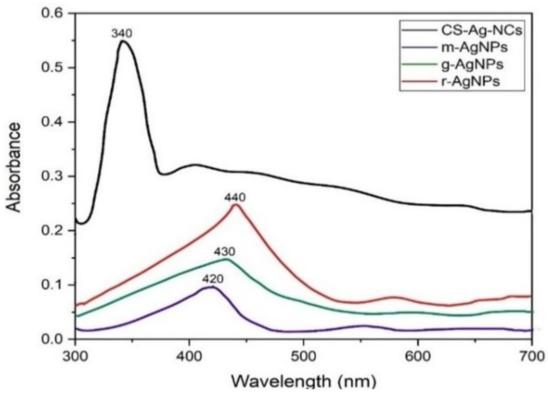


Figure 1. UV-Visible spectrum showing the AgNPs of *Citrus limetta* (m-AgNPs), *Citrus paradisi* (g-AgNPs) peels, and *Oryza sativa* husk (r-AgNPs) and CS-AgNCs.

3.3.2. Fourier Transform Infrared Spectroscopy

FTIR analysis confirmed the functional groups present in *Citrus limetta*, *Citrus paradisi* peels, and *Oryza sativa* husk extracts, acting as capping or reducing agents for AgNPs synthesis. In Figure 2., in the FTIR spectra of *Oryza sativa* husk (R.H), *Citrus limetta* (M.P), and *Citrus paradisi* (G.F.P) peels, shifts in peaks of O-H, C≡C, C–H, C=O, C=C, C-C, and C–O stretching occurred in both AgNPs and CS-AgNCs that confirming the presence of key functional groups in their extracts as well as in their AgNPs and AgNCs. Unique peaks at 1379 and 1146 in NCs. The absence of the C=O, OH, and C≡C stretch in NCs of *Oryza sativa* husk, *Citrus limetta*, and *Citrus paradisi* peels, respectively present in extracts, suggests its utilization that contributes to the AgNCs formation. Unique peaks in the FTIR graphs of NCs at 1377 and 1148 of *Oryza sativa* husk, 1379 and 1146 of *Citrus limetta peels*, and 1376 and 1148 of *Citrus Paradisi peels*, while absent in their AgNPs, indicate silver incorporation into chitosan.

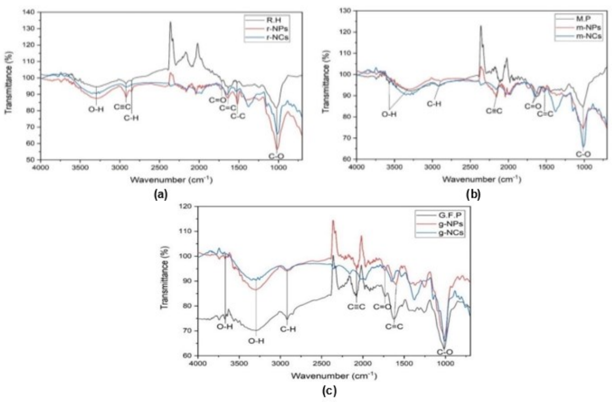


Figure 2. FTIR Spectrum of **(a)** *Oryza sativa* husk, r-AgNPs, r-CSAgNCs **(b)** *Citrus limetta* peels, m-AgNPs, m-CSAgNCs **(c)** *Citrus paradisi* peels, g-AgNPs, g-CSAgNCs

3.3.3. X-Ray Diffractometry

X-ray diffraction confirmed the crystalline nature of biosynthesized AgNPs. In Figure 3., *Citrus limetta* (m-AgNPs), *Citrus paradisi* (g-AgNPs) peels, and *Oryza sativa* husk (r-AgNPs) displayed five, six and four peaks, respectively that corresponded to crystal lattice planes of Ag. All peaks are consistent with the face-centered cubic crystalline structure of metallic silver, which is closely connected with the JCPDS (Card No. 04–0783) for silver (Ali *et al.* 2023; Jiamboonsri *et al.* 2021).

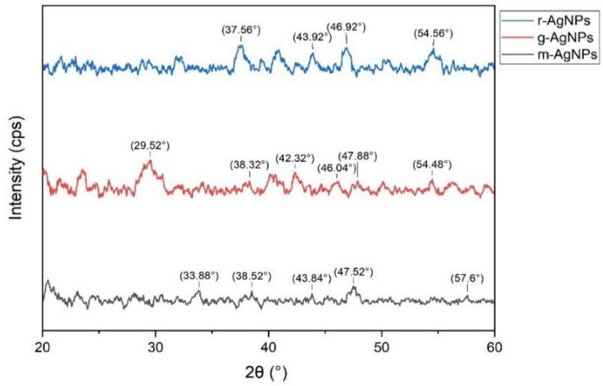


Figure 3. XRD spectrum of the AgNPs of *Citrus limetta* (m-AgNPs), *Citrus paradisi* (g-AgNPs) peels, and *Oryza sativa* husk (r-AgNPs).

3.3.4. Scanning electron microscopy

Images of *Citrus paradisi* peel (g-AgNPs) and *Oryza sativa* husk (r-AgNPs) revealed polymorphic shapes, including irregularly granulated, ellipsoidal, and highly aggregated structures (Figure 4). The average particle sizes from SEM analysis were 213.75 nm for g-AgNPs and 66.46 nm for r-AgNPs, confirming their nano-scale dimensions.

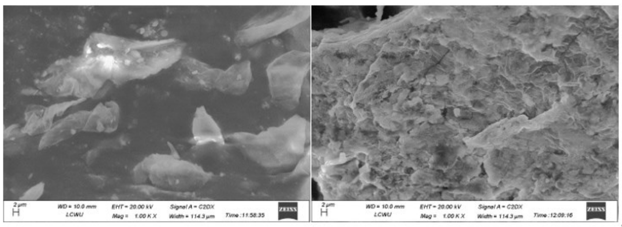
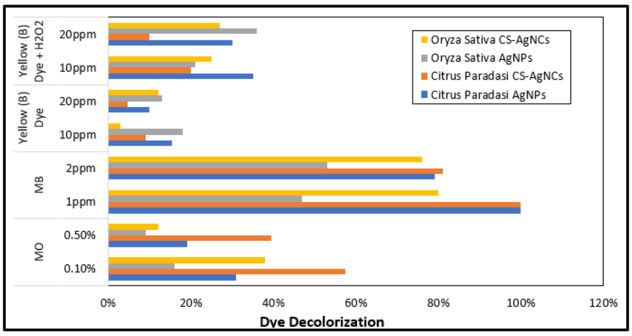


Figure 4. SEM images of AgNPs of *Citrus paradisi* peels (left) and of *Oryza sativa* husk (right)

3.4. Percentage dye decolorization

Decolorization experiments demonstrated the superior efficacy of CS-AgNCs over AgNPs in decolorizing Methyl Orange and Methylene Blue dyes. However, AgNPs assisted with H_2O_2 proved more effective for Yellow (B) dye decolorization. The results indicated that *Citrus paradisi* CSAgNCs achieve the highest decolorization for MO and MB, with significant results at 57.5% and 100%, respectively. For Yellow (B) Dye, decolorization is generally lower, with *Citrus paradisi* AgNPs and *Oryza sativa* CS-AgNCs performing better than their counterparts. Overall, *Citrus paradisi* CS-AgNCs are the most effective across different dyes. The detailed results are illustrated in the accompanying graph:



Graph 1. %age Dye Decolorization using AgNPs & CS-AgNCs

4. Conclusion

Organic waste has massive undiscovered potential for the synthesis of nanomaterials, that could not only solve the problem of organic waste management at landfill sites but also reduce the costs of managing waste. Silver Nanoparticles and Chitosan-based Silver Nanocomposites were successfully synthesized and characterized using UV-vis, FTIR, XRD, and SEM techniques. Leveraging Organic Plant Waste for nanomaterial synthesis, the study also explored their potential, focusing on dye degradation. Results highlighted CS-AgNCs' superior performance in dye decolorization compared to AgNPs, as AgNPs and CS-AgNCs of *Citrus paradisi* peels showed 100 % decolorization of Methylene Blue, while the CS-AgNCs of *Oryza sativa* showed more decolorization about 80 % than its AgNPs of 47 % for the same dye. Further optimization can be incorporated, including catalyst to enhance AgNPs & CS-AgNCs yield and improve their percentage dye decolorization.

Acknowledgment

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