Biological solid waste mediated synthesis of silver nanoparticles for removal of anthropogenic pollutant: Optimization modelling by RSM, ANN & DFT studies

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INTRODUCTION

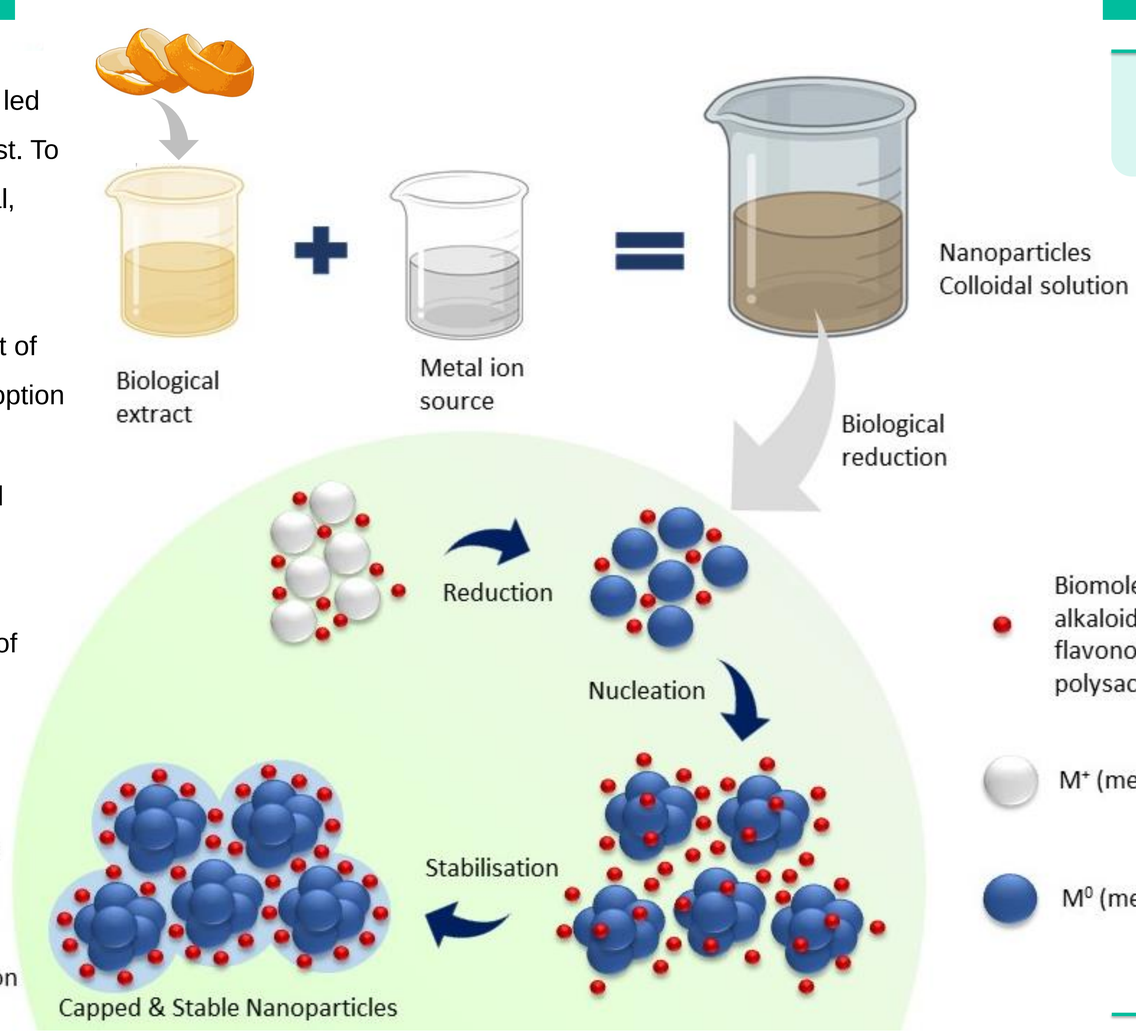
Silver nanoparticles (AgNPs) have piqued considerable interest on account of their unique properties, which has led to their application in several areas of commercial interest. To fulfill the increasing demand for AgNPs, different physical, chemical methods have been reported for its synthesis. However, the majority of these technologies are costly, energy-intensive, use toxic chemicals, and/or produce lot of by-products. Green chemistry has emerged as a viable option to synthesize AgNPs cost-effectively and sustainably.

Citrus tangerina is one of the most important commercial fruits with 37.43 million tonnes of global production annually. It contains 8 - 10% peel, which is a valuable biodegradable by-product and a rich source of a variety of functional compounds, yet generally dumped as waste. Hence, aqueous extracts from widely available biowaste *C. tangerina* peels were employed in this work as a novel reducing, capping, and stabilizing agent for the effective and eco-friendly synthesis of highly stable silver nanoparticles.

Reaction Parameters

Temperature
Reaction time
Reactant concentration

Overview of the mechanism



METHODS

AgNPs Synthesis
C. tangerina peels extract was prepared and utilised for AgNPs fabrication with silver nitrate solution.

Optimization by RSM
Central composite design (CCD) of response surface methodology was used for optimization of parameters.

Optimization by ANN
Mathematical modelling of process parameters was done by artificial neural network (ANN).

AgNPs Characterization
Characterization of synthesized AgNPs was done by various techniques.

Pollutant degradation
4-nitrophenol (4-NP) reduction to 4-aminophenol (4-AP) by AgNPs was evaluated.

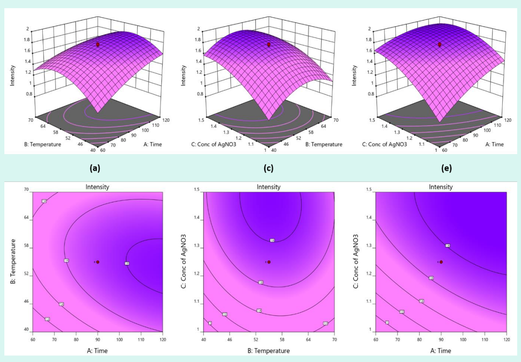
DFT studies
Quantum chemical studies were carried out for the compounds present in extract.

RESULTS & DISCUSSION

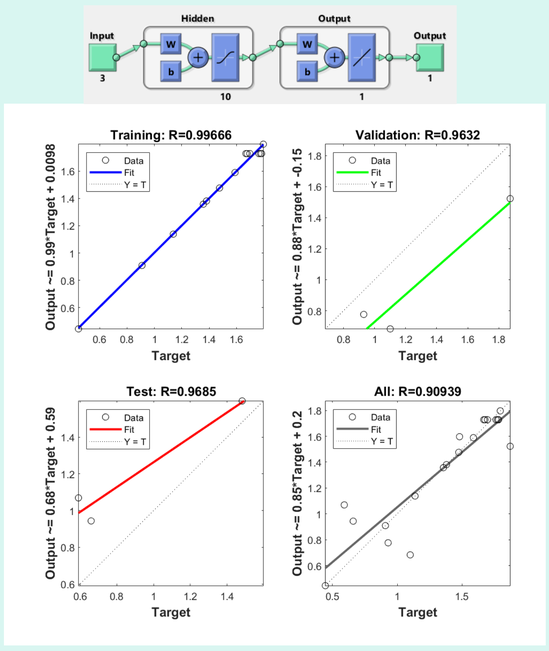
Optimization by RSM & ANN

The experimental parameters, time, temperature and $AgNO_3$ conc., were used to establish the set of optimal qualities for *C. tangerina* peel extract mediated production of AgNPs by RSM and ANN.

Factors	Independent variables	Coded levels -α	-1	+1	+α
X1	Time (min)	39.54	60	120	140.45
X2	Temp (°C)	29.77	40	70	80.22
X3	$AgNO_3$ Conc (mM)	0.83	1.00	1.50	1.67

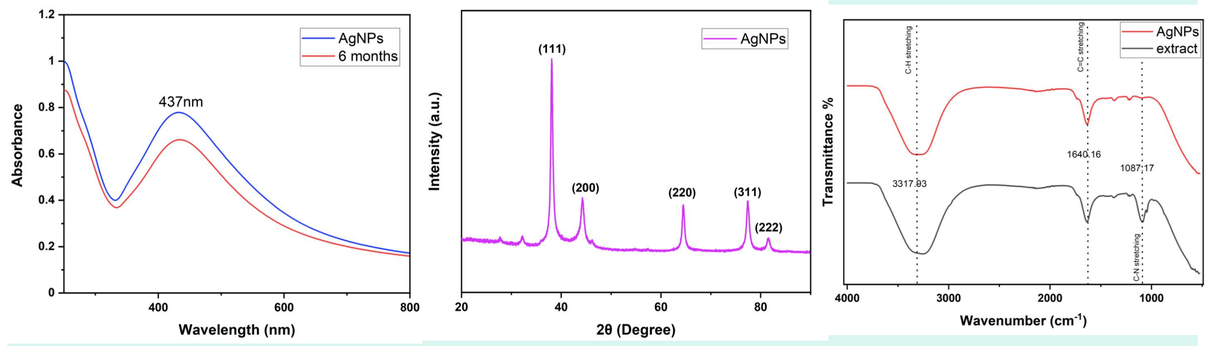


3D and 2D response surface plots between the process parameters time, temperature and conc. of $AgNO_3$.



ANN structure and evaluated modelling parameters

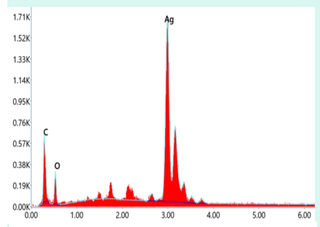
Characterization



UV- Visible spectra of synthesized AgNPs with high stability

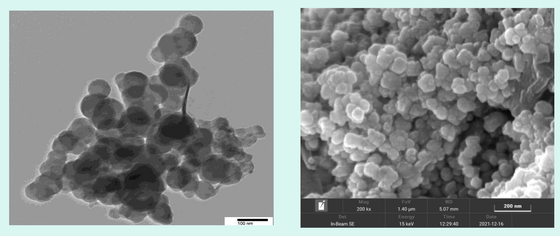
Powder XRD diffraction pattern representing polycrystalline FCC silver

FTIR spectrum showing the reduction done by compounds present in extract



Element	Weight %	MDL	Atomic %	Error %
C K	9.6	0.31	37.4	11.1
O K	9.4	0.49	27.4	14.7
Ag L	81.1	0.95	35.2	4.0

EDX Mapping confirms the presence of silver.

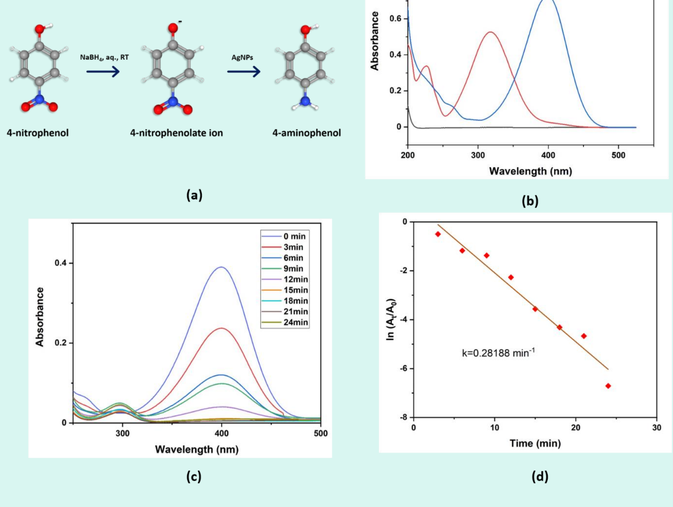


TEM and SEM micrographs confirm the spherical morphology of the synthesized AgNPs with a size of 40-60nm in diameter.

The characterization confirms the green synthesis of AgNPs which are spherical in shape and 40-60nm in size.

Pollutant degradation

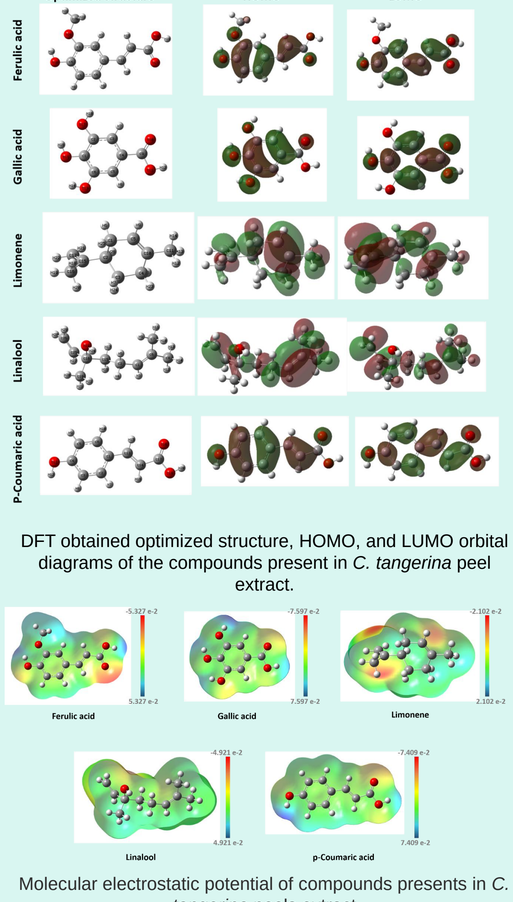
4-NP is a major hazardous pollutant in water resources due to its high toxicity. The ability of biowaste-mediated AgNPs to catalyse the reduction of 4-NP to 4-AP in presence of $NaBH_4$ was evaluated. 4-NP could be degraded successfully and AgNPs can be recycled.



(a) Scheme of 4-NP degradation by AgNPs; **(b)** Absorbance spectra of 4-NP in the absence and presence of $NaBH_4$; **(c)** Time-dependent UV–vis spectra of Ag NPs catalyzing the reduction of 4-NP to 4-AP; **(d)** ln (A_t/A_0) versus reaction time with linear relationship.

DFT studies

Quantum chemical and frontier molecular investigations were carried out to investigate the overall reduction behaviour of important chemicals found in the extract of *Citrus tangerina* peels, such as ferulic acid, gallic acid, limonene, linalool, and p-coumaric acid using the using the Gaussian 09W software with B3LYP functional method and 6-31G(d) electron basis set.



DFT obtained optimized structure, HOMO, and LUMO orbital diagrams of the compounds present in *C. tangerina* peel extract.

Molecular electrostatic potential of compounds presents in *C. tangerina* peels extract

CONCLUSION

- The study discovered that the green synthesis of AgNPs utilizing biowaste extract from C. tangerina peels is a cost-effective, fast, one-pot, and environmentally friendly.
- $AgNO_3$ conc. of 1.5 mM, a reaction period of 120 min, and a temperature of 60 °C were determined to be the optimized reaction conditions. The derived CCD quadratic model was statistically significant, with p-value < 0.0001 and F value of 16.40.
- The resulted spherical AgNPs have an average hydrodynamic diameter of 60 nm and colloidal stability even after 6 months.
- AgNPs showed excellent, recyclable, and rapid catalytic ability at a low catalyst dose for the degradation of 4-NP with a rate constant k equal to 0.281 min^{-1} .
- The DFT investigations demonstrated that the ferulic acid found in the C. *tangerina* peels extract likely played an important part in the decrease of Ag^+ and is a better stabilizing agent than other extract components such as gallic acid, p-coumaric acid, limonene, and linalool.

References: Karthik, R., et al., 2016. J. Colloid Interface Sci. 468, 163–175. https://doi.org/10.1016/J.JCIS.2016.01.046; Lee, S.J., et. al., 2021. Environ. Pollut. 269, 116174. https://doi.org/10.1016/J.ENVPOL.2020.116174; Li, H., Miao, et. al., 2020. Chem. Eng. J. 381, 122680. https://doi.org/10.1016/J.CEJ.2019.122680 .