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Green synthesis of nickel nanoparticles using *Sterculia foetida* leaf extract and application of antioxidant, photocatalytic and antibacterial activity

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The synthesis of nanoparticles (NP) and their applications have been increasing rapidly. The chemical synthesis of NP by using harsh chemicals may be deleterious. Thus, in the present study, the nickel nanoparticles (NiNPs) synthesized through green route and application were studied. *S. foetida* aqueous leaf extract was used for preparing NiNPs without any chemical reducing agent. Synthesized nickel nanoparticles were characterized by using UV spectroscopy, X-ray diffractrometry, FTIR and SEM coupled with EDS techniques. Size of nanoparticle was found to be 10 μm and spherical in shape. On the other hand, the synthesized NiNPs exhibit potent free radical scavenging activities, photocatalytic activity and antibacterial activities. The characterization and pharmacological results suggest that *Sterculia foetida* is a reliable source for synthesis of nickel nanoparticles.

Keywords: Nickel, nanoparicles, *Sterculia foetida,* green synthesis, nickel nanoparticles.

Introduction

Nanoparticles (NPs) have special characteristics such as smaller in size and having greater surface to volume ratio, thereby exhibiting significant properties. NPs have a wide range of applicability in various areas like magnetic storage media, sensors, target drug delivery, magnetic resonance imaging, magnetic inks, biomolecular detection, diagnostics, and micro-electronics[1]. Conventionally, nanoparticles are synthesized by harsh chemicals and physicochemical methods. Usage of chemicals are later on become accountable for various risk due to their general toxicity so that solving the objective of biological approaches is coming up to fill all these gaps. The plant-mediated synthesis process undergoes highly controlled approaches for making them suitable for metal nanoparticle synthesis. *S. foetida* is, a soft wood tree, is also commonly known as bastard poon tree, java olive tree, hazel *sterculia* and wild almond tree[2,3]. The species are distributed in India, Taiwan, Indochina, the Philippines, United States, Indonesia, Ghana, Australia, Mozambique and Togo[4]. The chemical constituents like sterols, phenolic compounds, tannins, saponins, steroids, alkaloids and flavonoids have been reported in different parts of the *S. foetida* plant like leaves, seed and bark by various authors[5–14]. Most of the phyto constituents have the reducing property and can be used as a reducing agent for synthesis of nanoparticles. Synthesis of nickel nanoparticles has attracted great focus of many scientists due their wide ranging applications in the various fields like permanent magnets, magnetic fluids, magnetic recording media, solar energy absorption, fuel cell electrodes, catalysts, biological activity[15]. The green synthesis is an eco-friendly pathway for the synthesis of nanoparticles. The present work is aimed at synthesizing the nickel nanoparticles by using *Sterculia foetida* (*S. foetida*) mediating reducing property. In this present work, *S. foetida* leaf extracts were used for synthesis of NPs. The free radical scavenging activities, photocatalytic activity and antibacterial activities of nickel nanoparticles have been studied and found that these show reliable antioxidant, photocatalytic and antibacterial activities.

Materials and methods:

Materials:

Nickel nitrate was purchased from Sigma Aldrich, India. Ciprofloxacin manufactured by Cipla Ltd., Mumbai was purchased in local market. All the chemicals were used without any further purification.

Bacteria strains used:

Two Gram-positive (*Bacillus subtilis* - MTCC – 1427, *Staphylococcus aureus* - MTCC – 1430) and two Gram-negative bacteria (*Pseudomonas aeruginosa* - MTCC – 1748, *Escherichia coli* - MTCC – 294) were studied for antimicrobial activity of synthesized nickel nanopartilces.

Preparation of plant aqueous extract:

Fresh leaves of *S. foetida* plant were collected at fields of Nizampatnam Port, Guntur, Andhra Pradesh, India. The collected leaves were washed thrice thoroughly with tap water and shade dried. Leaves were cut into small pieces and about 20 g of leaves were soaked in 100 mL of distilled water for 24 h with constant stirring. Extract was filtered by using crucible filtration apparatus and then centrifuged to remove impurities. The obtained sample is vaporized and lyophilized for further purpose.

Synthesis of nickel nanoparticles by green route:

Nickel nanoparticles were synthesized[16] by a simple reduction method. First 10 mL of 1 mM nickel nitrate solution was mixed in 10 mL of urea solution. Later 20 mL of aqueous extract of *S. foetida* was added in mixture and pH was adjusted then to 10. The initial colour of the solution was green. Then the mixture was shaken vigorously for 10 min and placed in hot air oven at 80°C for 90 min. There was a distinct change in colour (light to dark green) after the reducing reaction. The prepared sample was dried at 100°C for two weeks. Dried Ni NPs were stored in sample vial for further use.

Characterization of nickel nanoparticles:

The characteristic maximum wavelength of the synthesized nanopartilces was determined by using ultraviolet visible spectrophotometer in a wide range of wavelengths from 200–800 nm. The X-ray diffraction (XRD) measurement of NiNPs powder was conducted with RIGAKU instrument operated at a voltage of 40 kV and 30 mA current with copper target and CuKα radiation at a wavelength of 1.5405 Å. Fourier transform infrared (FTIR) spectroscopy analysis was carried out by using BRUKER IR spectrophotometer. The spectra were recorded between 4000 and 400 cm^{1}. The size, morphology and dispersion characteristics of the as-synthesized powder were determined by using a Scanning Electron Microscope (SEM).

DPPH inhibition activity of nickel nanoparticles:

The synthesized NiNPs by green synthesis was conducted at different concentrations along with the precursors (NiCl and plant aqueous extract). To assess the scavenging ability on DPPH[17], the plant extract (10–150 µg/ml) was mixed with 1 ml of methanolic solution containing DPPH radicals (0.2 mM). The mixture was shaken vigorously and left to stand for 30 min in the dark before measuring the absorbance at 517 nm against a blank. Then the scavenging ability of nanoparticles was calculated using the following formula:

$$\% \text{ Inhibition} = (A_{\text{blank}} - A_{\text{sample}})/A_{\text{blank}} \times 100$$

A_{blank} - absorbance of the control reaction (containing all reagents except the test compound) and A_{sample} - the absorbance of the test compound.

Photocatalytic studies:

Numerous methods for the heterogeneous photocatalytic decolourization of dyes have been investigated and reported especially in laboratory scale. Rhodamine B (RhB) is a dye compound used in various fields. It is suspected to be carcinogenic and thus, the products containing it must contain a warning on its label[18]. In the present work, the Rhodamine B was selected as the model chemical for the evaluation of the photocatalytic efficiency of the Ni NPs.

The experiment was carried out in a 250 mL capacity beaker reactor and total of 100 mg of Ni NPs was loaded into 100 ml of simulating pollutant such as RhB (10 ppm) for achieving a concentration of 1 mg/ml^{-1} [19].The suspension was subjected to magnetic stirring for 45 min for uniform mixing and then aliquots of 3 ml were sampled and centrifuged at 6000 rpm for 20 min at frequent time intervals. Then the absorbance of supernatant was recorded at 554 nm using UV-Visible spectrophotometer. Finally the photocatalytic degradation efficiency (PDE) percentage was calculated by using the below formula:

$$\text{PDE } (\%) = \frac{(\text{Absorbance})_0 - (\text{Absorbance})_t}{(\text{Absorbance})_0} \times 100$$

$(\text{Absorbance})_0$ - absorbance before irradiation and $(\text{Absorbance})_t$ - absorbance at time t.

Antibacterial activity:

Agar well diffusion method was conducted for determining antimicrobial activity[20,21] on nutrient Agar media. The nutrient Agar media agar plates were swabbed with selected bacteria and six wells were bored using sterile cork borer. The wells were filled with 50 μL of nickel metal solution and synthesized nanoparicles in selected concentrations. Commercially available Gentamycin (10 μg) was used as the positive control and distilled water as negative control. An amount of 50 ml of each sample was added to the respective well. The plates were incubated for 24 h at 37°C and zone of inhibition recorded.

Results and discussion

Of late, the synthesis of metal nanoparticles by green synthesis approach has become a new and promising field of research. Synthesis of metal nanoparticles like silver (Ag), gold (Au), zinc oxide (ZnO), copper (Cu), iron (Fe), cadmium (Cd) and other metal oxides by various chemical and physical approaches as well as the biological approaches mediated by number of microorganisms have been actively found. Plant-mediated synthesis approaches are found to be more reliable and economic route to synthesize these metal nanoparticles and are used as potential pharmaceutical agents for various diseases such as malaria, HIV, cancer, hepatitis and other diseases. In the present work, the leaves extract of *S. foetida* plant has completed the reduction of nickel chloride particles in to nickel nanoparticles within 6 h of reaction time. Reduction of nickel was physically verified by colour change from green to dark brown and confirmed by UV-Visible spectrophotometer, showing sharp spectral band at 270 nm (Supplementary Fig. S1). *S. foetida* phytoconstituents are used not only to reduce nickel chloride but also to stabilize newly formed NP. Natural reducing chemicals (flavanoids, phenolic compounds, alkaloids, terpinoids etc.) present in the *S. foetida* responsible for reducing reaction. Previous studies were reported the presence of sterols, phenolic compounds, tannins, saponins, steroids, alkaloids and flavonoids in different parts of the *S. foetida* plant like leaves, seed, bark by various authors[5–14].

Furthermore, the green synthesized nanoparticles were characterized by different analytical techniques. X-Ray diffraction analysis was used for identifying the phase and crystallinity of NPs. The XRD pattern of NiNPs was prepared by green route and is shown in Fig. 1. The sharp diffraction peak emerges at 2θ angles of green synthesized NiNPs, corresponds to 111, 200 and 221 crystal planes. FTIR spectroscopy was used for studying changes in chemical composition of the mixture. Supplementary Fig. S2 shows the IR spectra of NiNPs synthesized by green method recorded in the range of 400–4000 cm^{-1}. The NiNPs cover an absorption band at 678.28, 706.00, 739.66, 486.80, 824.6, 1014.28, 1096.37, 1218.71, 1307.10, 1242.16, 1427.94, 1487.15, 1522.21, 1677.14 and 3321.71 cm^{-1} refers to OH stretching, cross-linked CC stretching, stretching vibration of carboxylic acids, carbonyl C=O bonding and amine groups in the plant. This proves that the bio active alkaloids and flavanoids were involved in the formation and bio reductions of nickel. The

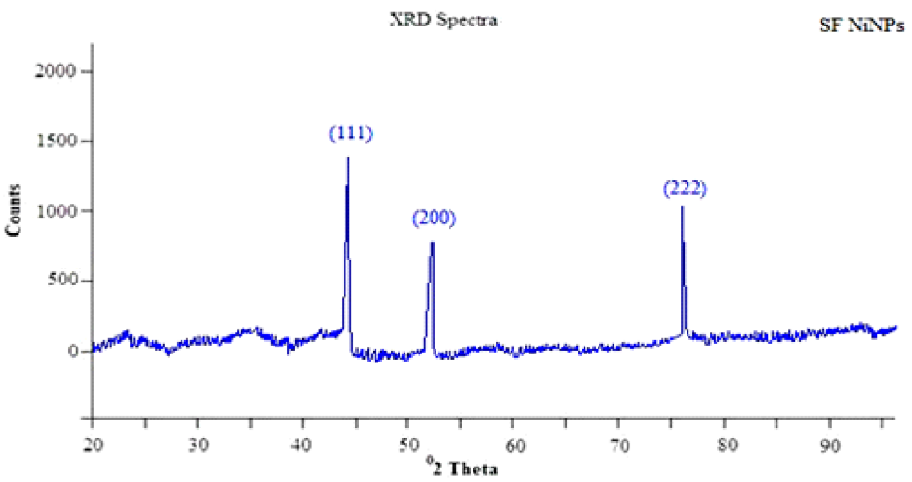
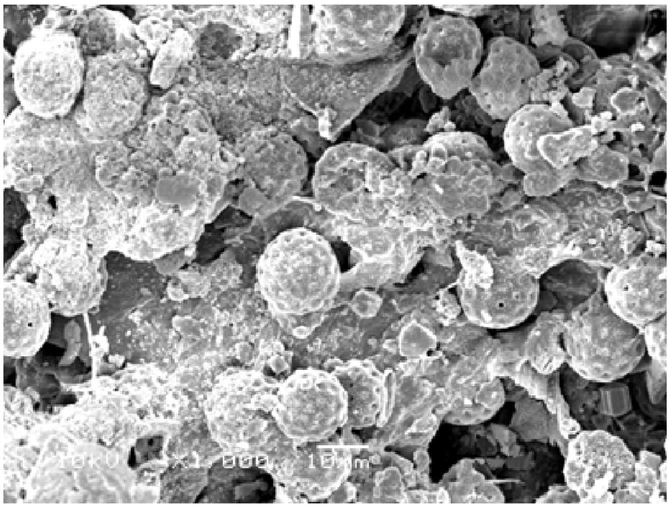


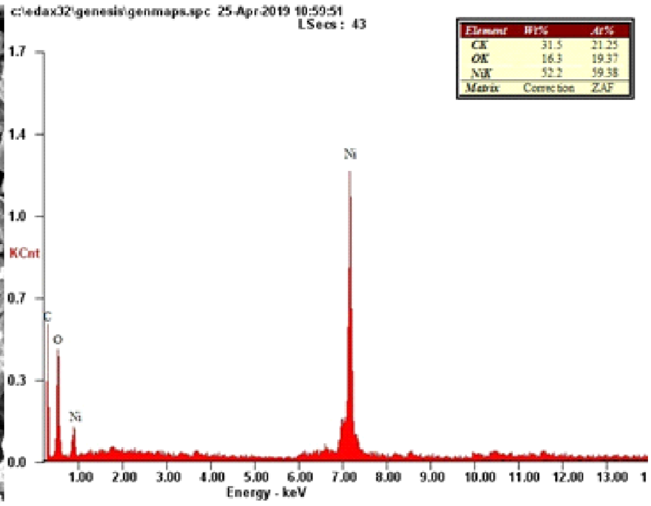
Fig. 1. X-Ray diffractometry spectrum of nickel nanoparticles by green route and showed different peaks at 2θ angles at 111, 200, 222.

SEM images confirmed that Ni nanoparticles are in a nano range where the size of nanoparticle was found to be 10 µm. The shape of the nanoparticle was found spherical shape.

The SEM images are shown in Fig. 2 and Fig. 3. The EDS results clearly indicate that the presence of nickel about 52.2% in the synthesized nanomaterial. Thus, it proves that the formation of nickel and phyto-constituents from the plant leaf extracts attached together and formed into complex mixture with spherical nickel nanopartilces.

DPPH scavenging activity is widely used for monitoring chemical reactions where involving radicals as it generates the violet color in DPPH solution in its radical form and the colour changes to pale yellow when a hydrogen atom is donated to the molecule. Thus, the higher antioxidant potential of NiNPs suggests the presence of additional moiety in the NP that participates in free radical scavenging action (Table 1 and Fig. 4). The green synthesized nickel nanoparticles were successfully removed the dye material in the solution. Only 51 (IC_{50}) minutes were taken for removing the 50% of the dye material in the solution. This was due to the largest absorption band edge energy, good particle size distribution and smaller sizes of uniform shapes. Therefore, this sample was used for evaluating the photocatalytic activity. The ratio of concentration of RhB dye remaining to the initial one over time is depicted in Fig. 5. Photocatalysis utilizes visible and





Figs. 2 and 3. Scanning electron microscope (SEM) images at X1000 and Energy-dispersive X-ray spectroscopy (EDS) spectra showing nickel, oxygen and carbon presence.

Table 1. Results of DPPH activity

Sl. No.	Concentration (µg/ml)	% DPPH Inhibition		
		Ascorbic acid	SF NiNPs	Aqueous plant extract
1.	10	9.68	5.27	2.57
2.	20	18.75	11.24	6.38
3.	40	34.61	26.82	13.51
4.	60	49.58	39.13	20.43
6.	80	61.08	52.25	29.95
7.	100	79.58	67.44	41.14
8.	125	91.36	81.13	57.85
9.	150	96.37	89.58	76.69

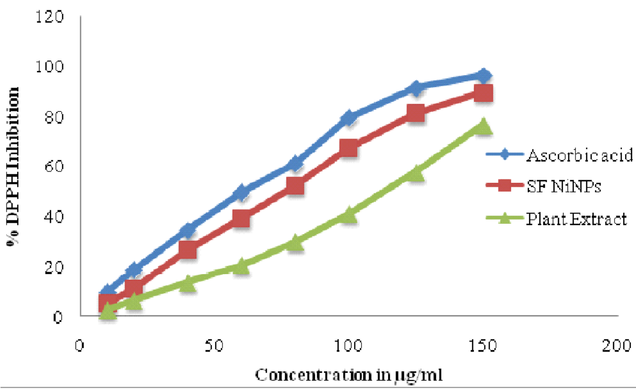


Fig. 4. Results of DPPH scavenging activity of nickel nanoparticles.

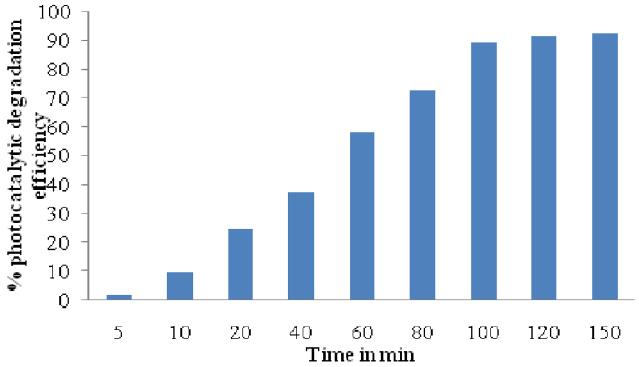


Fig. 5. Results of photocatalytic studies showing ratio of concentration of RhB dye remaining to the initial one over time is depicted.

(*Pseudomonas aeruginosa*, *Escherichia coli*). The zone of the inhibition was measured and found that the synthesized nanoparticles were sensitive to the *S. aureus* (13.4 mm zone of inhibition) than the other bacterial selected. The antimicrobial results were presented in the Figs. 6 and 7. But nearest activity was reported with remaining three bacteria. Hence it indicates that nickel nanoparticles were effective against both Gram-positive and Gram-negative bacteria. The activity was studied along with plant extract which was used for the synthesis to compare the effect of phytochemicals present in the leaf extract and naoparticles and proves that the synthesized nanoparticles are having enhanced activity than the plant aqueous extract.

Fig. 6. Illustration of zone of inhibition of synthesized nickel nanoparticles against four different bacterial strains.

ultraviolet light from a major part of the solar spectrum. Studies of the optical properties and catalytic capabilities of noble metal nanoparticles (NPs), such as gold (Au) and silver (Ag), nickel (Ni) have formed the basis for the very recent fast expansion of the field of green photocatalysis. The reason for this growth is the recognition that the localized surface plasmon resonance (LSPR) effect of nanoparticles can couple the light flux to the conduction electrons of metal NPs and the excited electrons and enhanced electric fields in close proximity to the NPs can contribute to converting the solar energy to chemical energy by photo-driven photo-catalytic reactions. Antimicrobial properties of metallic nanoparticles are influenced by the chemical composition, concentration, size, shape and photo-activation. Antimicrobial activity was synthesized and nickel nanoparticles were studied and compared with the two Gram-positive (*Bacillus subtilis*, *Staphylococcus aureus*) and two Gram-negative bacteria

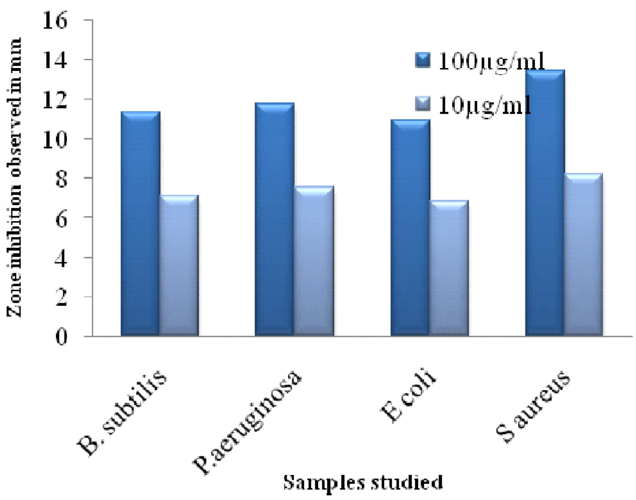


Fig. 7. Comparative results of zone of inhibition of synthesized nickel nanoparticles against four different bacterial strains.

The presented approach could be encouraging from both environmental remediation and nanoparticle production points of view. The plant-mediated synthesis process undergoes highly controlled approaches for making them suitable for metal nanoparticle synthesis. In addition, biological synthesis of metallic nanoparticles is inexpensive, one-step and eco-friendly method. The plant *S. foetida* has not only reported a rich source for phytochemical but also reported for its reducing ability of metals in to nanoparticles. Hence the present approach is novel attempt for synthesis of nickel nanoparticles with *S. foetida.* The attempt was once again proves the high reducing activity of phytochemicals present in the *S. foetida.*

Conclusion

Ni nanoparticles were successfully synthesized by reduction method which is greener and environmentally suitable, cheap. The synthesized nanoparticles were highly pure and almost homogenous in size. The antioxidant property, antibacterial activity was found to be the better by green methodology, thereby making it a good antimicrobial agent.

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