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RESEARCH ARTICLE

Green Approach for Synthesis of Manganese Nanoparticle using Banana Peel *(Musa paradiasca)* and its Characterization

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Highlights

- Multifunctional manganese nanoparticle was synthesized using banana peel as the reducer and stabilizer.
- As synthesized samples were characterized spectroscopically via UV-vis, EDX, XRD and FT-IR.
- UV-absorption peak observed at 450 nm confirmed for the formation of manganese nanoparticles.
- Diffraction pattern revealed formation of crystalline natured nanoparticles.

Abstract

This research mainly aims at implementing green approach for synthesizing multifunctional manganese nanoparticles (MnNPs) using aqueous extract of banana peel (Musa paradiasca) and potassium permanganate ($KMnO_4$) as the precursor. As synthesized MnNPs were confirmed initially by color change and later on characterized by UV-visible (UV-vis) Spectrophotometer, Energy Dispersive Spectroscopy (EDX), X-ray Diffraction Spectroscopy (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR). Green approach was carried at various parameters like concentration of precursor solution, reaction time, temperature etc for optimization. Formation of MnNPs was confirmed by the presence of surface plasmon absorbance band (450 nm) and band at 6 and 6.5 keV of EDX spectrum. Likewise, so formed MnNPs were crystalline nature depicted from the sharp peak observed at 28.5° and 41° in X-ray diffraction pattern. Various types of biomolecules associated with the banana peel extract acting as natural reducer and stabilizer were analyzed from characteristic absorption bands present in the FT-IR spectrum..

Keywords: *Diffraction pattern, Musa paradiasca, MnNPs, Precursor, Spectroscopy.*

Introduction

In recent years, the green approach has been given a great consideration for producing a substantial amount of nanoparticles, and for environmentally nature [1-3]. Green approach seemed to be based on three essentials parameters such as a) reductants, b) stabilizer, and c) solvent [4]. Literatures revealed that various types of secondary metabolites such as terpenoids, glycosides, polyschharides, polyhydroxyphenols, alkaloids, flavonoids, phenolics, proteins are crucial reducing and stabilizing agents [5]. The green route of fabrication of nanoparticles (NPs) uses various plant parts root, leaf, stem, bark, flower, microbes *etc*. For instance, the silver nanoparticles synthesized from *Manilkara hexandra* stem bark were found in the range of 15-50 nm size [2], [6-8]. Similarly, *Momosa pudica* and *Rhyza stricta* root extract were used as natural reducing and the stabilizing agents [9 -10].

Various kinds of metal nanoparticles like gold, silver, platinum, iron, copper, manganese, zinc, iron, *etc* were exploited in diverse sectors from time immemorial [11-22]. In this scenario, MnNPs are considered promising materials for their outstanding physiochemical properties such as adsorbing, electrochemical, catalytic, magnetic, medicinal, bactericidal etc. Consequently,

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environment, catalytic, bio sensors, energy storage, magnetic resonance imaging, lithium ion batteries, biomedicine, drug delivery, *etc* are regarded as potential existing sectors for their application [23-27].

Hence, the objective of this research is to fabricate multifunctional manganese nanoparticles based on the green approach utilizing banana (*Musa paradisica)* peel extract (BPE) and to characterize them using various spectroscopic techniques. During the reaction, various types of phytoconstituents present in the banana peels were hypothesized to act as reducing and stabilizing agent [28].

Materials and Methods

Materials

Banana peels (collected from the local market of Kathmandu), potassium permanganate ($KMnO_4$ A. R. grade) and distilled water were used.

Preparation of banana peel extract

Firstly, the banana peels were washed with distilled water for three times to remove external dirt impurities and then cut into small pieces. Then, about 100 g of peels were allowed to boil at 80 °C in 500 mL beaker containing double distilled water for 10 minutes and filtered through filter paper twice to remove insoluble fractions and macromolecules. The resultant filtrate was stored at 4 °C and used as the banana peel extract (BPE) for green synthesis of MnNPs.

Green synthesis of manganese nanoparticles

Firstly, potassium permanganate of different concentrations: 1 mM, 2 mM, 3 mM, 4 mM and 5 mM were prepared so as to optimize the concentration for synthesis. Each of the precursor solutions were reacted with aqueous banana peel extract at 1:5 volume ratio (peel extract and $KMnO_4$) in a beaker using the protocol of literature [23]. The mixture was allowed to stir constantly using magnetic stirrer at 30-40 °C till the color changed to reddish black as the color change was the indicator of the formation of MnNPs. As-synthesized MnNPs were then purified by repeated washing and centrifugation. Finally, MnNPs were collected after oven dried at 40-50 °C and then subjected for various spectroscopic techniques.

Characterization techniques

As-synthesized MnNPs were characterized using double beam UV-vis spectrophotometer (Model LT-2802) in the wavelength range 200-700 nm, at 5 nm interval. Phase morphology of the banana peel mediated MnNPs was explored using X-ray diffraction (BUKER D2 PHASER, NAST) having CuKα radiation and Braggs angle (2θ) in the range of 5° to 90 °. The crystalline size of the MnNPs was calculated by using Debye-Scherrer's equation,

$$D = K\lambda/\beta\cos\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where, D (particle size), K (factor = 0.94), λ (emission wavelength = 1.54 Å)), β (Full width half maximum (FWHM), θ (Bragg's angle)

The energy dispersive X-ray spectroscopy of model EDX-8000 was used to study the elemental composition of the sample. For the identification of functional group associated with the organic biomolecules of the BPE, Fourier Transform Infrared Spectroscopy (FT-IR) Tracer 100 was used in ATR mode in the range of 400 - 4000 cm^{-1} with a resolution of 4 cm^{-1}.

Results and Discussion

Visual inspection

Firstly, the appearance of reddish black color on stirring the reacting solutions for 15 minutes inferred about the presence of nanoparticles. The color change attributes for the reduction of $KMnO_4$ from biomolecules of the extract [29-30].

UV-vis spectroscopy

The UV- vis spectrum of biosynthesized MnNPs using BPE and $KMnO_4$ (3mM) (Fig.1) clearly displayed a maximum

absorption at 450 nm which attributes to the surface plasmon resonance of electrons present at the surface of nanoparticle. The reported wavelength of maximum absorbance is slightly higher than that of literature [23], [31] which may be due to difference in g

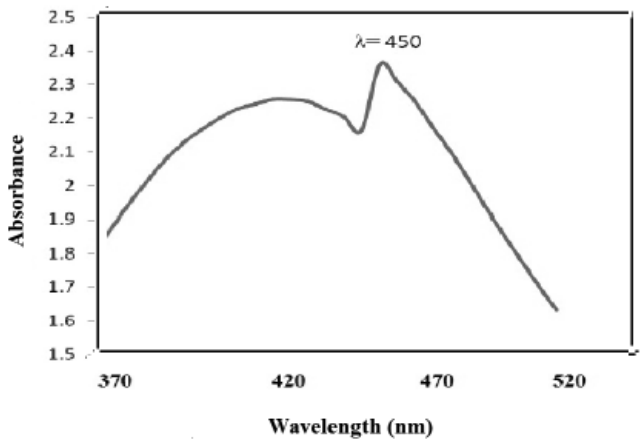

Fig 1: *UV-vis spectrum of biosynthesized MnNPs, using aqueous extract with $KMnO_4$ at volume ratio 1:5*

From the literatures, distinct UV-vis absorption band in the spectrum indicates presence of smaller sized, nanoparticles [32]. Similarly, the absorption band with single and double peaks indicates the presence of spherical and ellipsoidal nanoparticles. [29]. Formation of the single peak in the UV-vis spectrum inferred about the formation of spherical MnNPs. For the confirmation, it needs to be analyzed by using scanning electron microscope (SEM) and transmission electron microscope (TEM).

Optimization of concentration of precursor ($KMnO_4$)

Biosynthesis of MnNPs was performed varying the concentration of the $KMnO_4$; 1 mM to 5 mM with volume ratio 1: 5 (BPE: $KMnO_4$) keeping other parameters (like time, temperature) constant. Fig. 2 presents the UV-vis absorbance bands at concentration variation from 1 mM to 5 mM. All of the curves depict peaks at 450 nm, the assigned peak of the MnNPs as mentioned before. The Fig. 2 depicts that the absorbance increases with increasing the concentration of the precursor ($KMnO_4$ from 1 mM (curve a) to 3 mM (curve c) due to formation of larger amount of MnNPs. But, upon increasing the concentration beyond 3 mM the intensity of absorbance decreases slightly (curve d & e) due to formation of agglomeration of nanoparticles [33]. As the considerable amount of MnNPs are formed by 3 mM $KMnO_4$ solution with respect to others, it is assumed to be optimized concentration for synthesis of MnNPs.

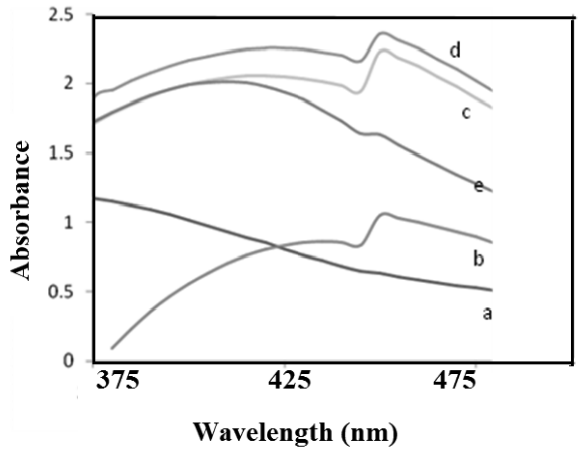

Fig 2: *UV-visible spectra of MnNPs at different concentration of $KMnO_4$ solution; (a) 1 mM, (b) 2 mM, (c) 3 mM., d) 4 mM and e) 5 mM*

Optimization of time

The aqueous banana peel extract (BPE) and precursor solution (3 mM) at volume ratio 1: 5 were stirred at 40 °C for different

time intervals like 15, 25, 35, 55 & 65 min for optimization of the time. The absorption spectra of as synthesized MnNPs with time variation (Fig. 3) shows that intensity of maximum absorbance of MnNPs gradually decreases with time; the peak intensity of MnNPs at 15 minutes (curve a) is greater with respect to other samples; 25 min (b), 35 min (c), 45 min (d), 55 min (e) & 65 min (f). The formation of considerable amount of NPs at initial 15 minutes attributes to the existence of large amount of reductants. The Fig. also indicates no significant change in size of NPs with times [30], [34-35]. The UV-vis result indicates optimized time as 15 minutes for the biosynthesis.

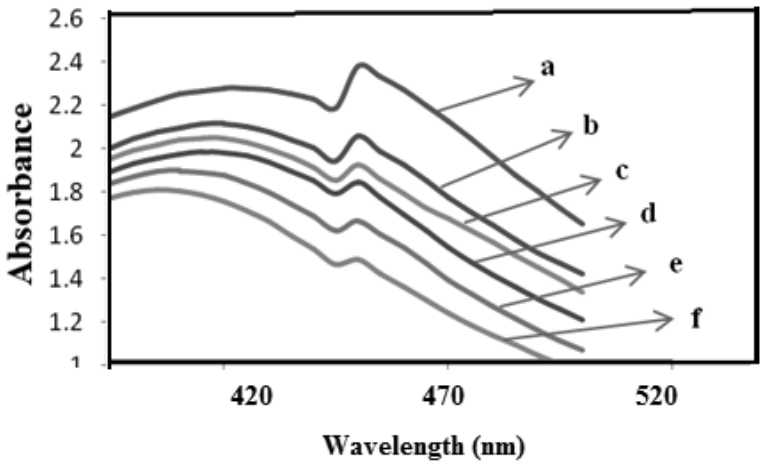

Fig 3:*UV-Visible spectra of MnNPs at different time interval at (a) 15 min, (b) 25 min, (c) 35 min, (d) 45 min, (e) 55 min and (f) 65 min.*

Optimization of temperature

Fig. 4, the UV-vis spectrum of temperature variation shows that maximum absorption bands are not so significantly changed. The absorption bands of MnNPs at 20 ºC & 40 ºC appeared at 450 nm, (curve a & c) and that of 30 ºC is at 455 nm (curve b). However, the peak of MnNPs at 30 °C (b) is slightly shifted from (a) & (c) which attributes to the formation of slightly bigger sized nanoparticles [23]. The result revealed that biosynthesis can be carried out conveniently at temperatures from 20 °C to 40 °C as the assigned peak of MnNPs are appeared at all temperatures.

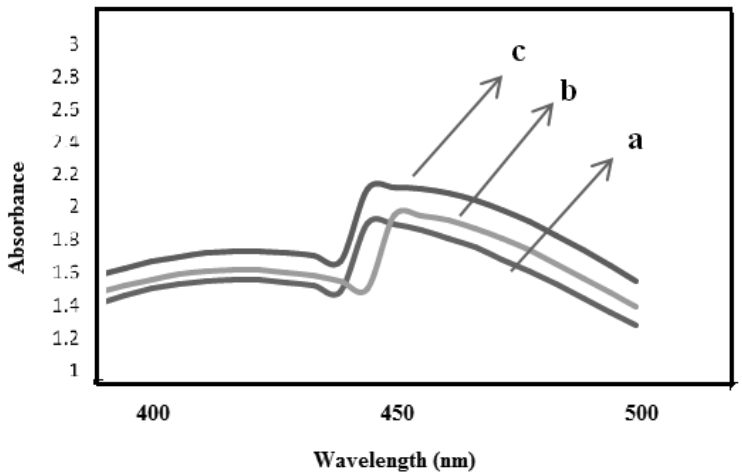

Fig 4: *UV-visible spectra of MnNPs at different temperature (a) 20 °C, (b) 30 °C and (c) 40 °C*

Energy Dispersive X-ray Spectroscopy (EDX)

As-synthesized MnNPs was analyzed by using EDX spectroscopy for elemental composition and purity. EDX pattern (Fig.

5) clearly displays the energy absorption bands at 6 and 6.5 keV indicating the presence of manganese as in the literature [36]. Additionally, the EDX spectrum indicates the presence of 76% of Mn by weight (Fig. 5) along with other elements like K, Cl, Si, Ca, P, Zn, *etc* as impurities which may arise from sampling process.

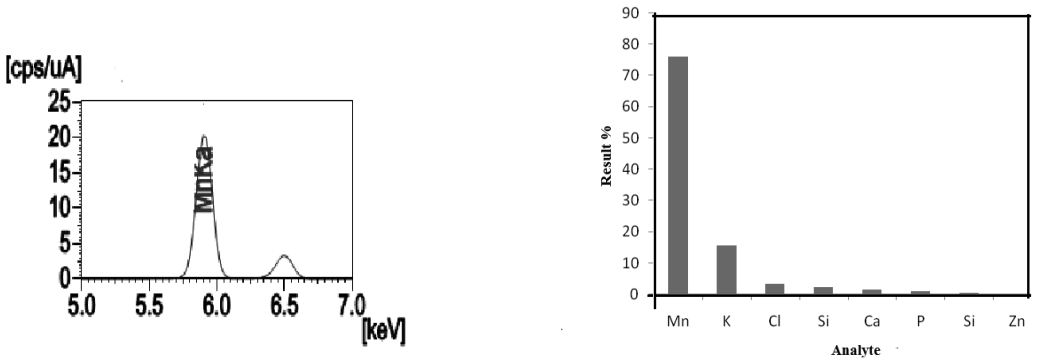

Fig 5: *a) EDX Spectrum of biosynthesized MnNPs using aqueous BPE and 3mM $KMnO_4$; b) Quantitative analysis of elements*

X-Ray Diffraction (XRD) Spectroscopy

The XRD is basically used to study the phase morphology of the NPs. Diffraction pattern of banana peel mediated synthesized MnNPs is presented in Fig. 6. Diffraction pattern comprise of two broad peaks at diffraction angles (2Θ) 28.5° & 41° which are indexed to face centered cubic manganese nanoparticles following the JCPDS No. 4-0326 as revealed in the literature [29]. Consequence of the XRD result confirmed for the formation of crystalline manganese nanoparticle. The crystallite size estimated to be 8.92 Å (~ 1 nm). Broad natured diffraction pattern owes to the formation of small sized nanoparticles and biosurfactant associated at the surface of NPs as revealed by [36].

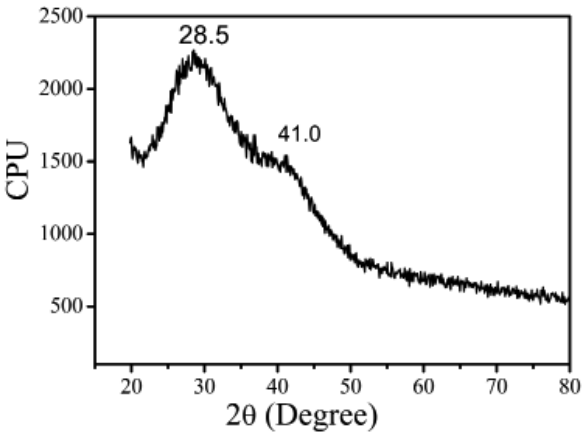

Fig 6: *Diffraction pattern of biosynthesized MnNPs using BPE and 3 mM $KMnO_4$ (Vol. ratio 1:5)*

Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectrum of MnNPs (Fig. 7) shows the broad peak around 3240 cm^{-1} attributing for -OH bending vibration of polyphenolic groups present in banana peel extract as reported by literature [23]. Likewise, absorption bands at 2885 cm^{-1} indicate C–H stretching [32], 1646 cm^{-1} refers to C=C and C=O stretching vibration [37- 38]. Bands 1395 cm^{-1} and 1014 cm^{-1} represents C=O stretch of amide and C-O-C stretching, respectively [23]. Banana peels are mainly composed of pectin, cellulose and hemicelluloses. Thus FTIR spectrum confirmed that the presence of various biopolymers along with proteinaceous compounds at the surface of MnNPs which act as reducing and stabilizing agent during biosynthesis of MnNPs [39].

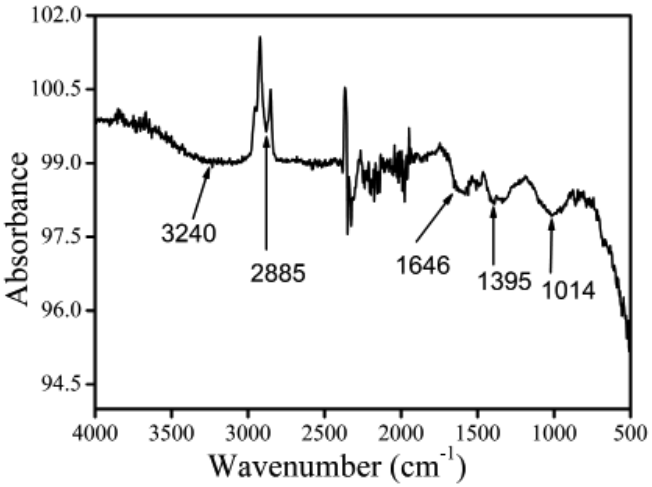

Fig 7: *Fourier Transform Infrared (FT-IR) spectrum of biosynthesized MnNPs using peel extract*

Conclusions

Manganese nanoparticles were successfully synthesized from eco-friendly and low cost green approach using aqueous banana peel extract. Formation of reddish brown colored precipitate provided the preliminary evidence of formation of MnNPs. Results of UV-vis spectroscopy confirmed the fabrication of manganese nanoparticles providing the assigned absorption band of MnNP at 450 nm. Further, presence of Mn of 65 % by weight in the as-synthesized sample was confirmed from strong energy absorption band at 6 and 6.5 keV of the EDX spectrum. Result of X-ray diffraction revealed formation of crystalline nature manganese nanoparticles possessing the crystallite size of about 8.92 Å (~1 nm). Similarly, various absorption bands appeared in FT-IR spectrum suggested for the presence of non toxic biomolecules which showed crucial role of reducing and stabilizing agent during the fabrication of manganese nanoparticles. Size controlled synthesis of MnNPs and exploration of catalytic properties of MnNPs can be the interesting research topic for future.

Acknowledgements

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