Journal of Nanoscience and Technology 2(4) (2016) 189–191

ISSN: 2455-0191

Contents List available at JACS Directory

Journal of Nanoscience and Technology

journal homepage: www.jacsdirectory.com/jnst

Green Synthesis of Magnetite Nanoparticles through Leaf Extract of *Azadirachta indica*

K.C. Maheswari[1], P. Sreenivasula Reddy[2,*]

[1]Department of Biotechnology, Sri Venkateswara University, Tirupati – 517 502, AP, India.
[2]Department of Zoology, Sri Venkateswara University, Tirupati – 517 502, AP, India.

ARTICLE DETAILS

Article history:
Received 09 December 2016
Accepted 17 December 2016
Available online 30 December 2016

Keywords:
Azadirachta indica
Magnetite Nanoparticles
Green Synthesis

ABSTRACT

Biological synthesis of nanoparticles favors the eco-friendly development of nanotechnology. A novel approach to synthesize magnetite nanoparticles through green route has been developed. In the present study *Azadirachta indica* leaf extract was used as reducing and capping agent in the biosynthesis of iron oxide nanoparticles. The successful synthesis of magnetite nanoparticles was confirmed by UV-Visible spectroscopy and characterized by transmission electron microscopy, X-Ray diffraction, energy dispersive X-ray analysis, atomic force microscopy and Fourier transform infra-red spectroscopy. Stable magnetite nanoparticles of average 3-8 nm size with spherical shape were obtained. These phytogenic nanoparticles possess characteristic magnetic property and DPPH free radical scavenging activity.

1. Introduction

In the current scenario, nanoscience and nanotechnology are evolving as new trends in the world of science and technology. The increase in concern to pursue the nanoparticles with nanoscale dimensions is considerably growing since the past decade. This is because of their unique physical, chemical, optical, electrical, mechanical, catalytic and magnetic properties when compared to their large counterparts [1]. In general these properties depend upon the size and shape of the particles [2]. Nanoparticles have wide range of applications and implications in various fields like medicine, pharmaceuticals, biotechnology, agriculture etc. Magnetite (Fe_3O_4) is a common, naturally occurring iron oxide mineral with useful magnetic properties [3]. Magnetic iron oxides are often used in magnetic storage [4], including their application in magnetic layer of hard discs, floppy discs and cassette tapes. Magnetite nanoparticles also act as sorbent in the removal of Arsenic (II), Arsenic (III), Arsenic (V) and Chromium (IV) from water [5-7]. They have anticorrosion property and are used in paints and coatings [8]. These magnetic nanoparticles have appreciable quest in genetic and tissue engineering [9], medical diagnosis and therapy including MRI imaging, cancer hyperthermia [10] and drug delivery [11,12]. Recently, it was demonstrated that magnetite nanoparticles can boost crop production and quality [13].

Numerous methods were developed for the synthesis of magnetite nanoparticles, which include sol gel process [14], co-precipitation [15], sono-chemical method [16], hydrothermal techniques [17], non-aqueous synthesis [18], ultra sound irradiation [19], thermal reduction of metal organic compounds such as $Fe(acac)_3$ [20], $Fe(CO)_5$ [21], micro emulsion method [22] etc. All these physical and chemical methods require high pressures and temperatures, even involving harmful chemicals. In contrast, biogenic synthesis involves the synthesis of nanoparticles using live models such as plants and microbes or their extracts. Microbial synthesis is time consuming and somewhat risky method, since it involves the maintenance of microbial cultures under sophisticated, aseptic laboratory conditions. Of all, green synthesis using plants and plant extracts is currently under exploitation. It is ecofriendly, safe, non-toxic [23] and cost effective approach having high rate of reaction. Recently leaf extracts of *Pistachio* [24], *Carob* [25] and *Tridax procumbens* [26] were used for the production of iron oxide nanoparticles.

The present study focuses on the synthesis of magnetite nanoparticles (MNPs) by one-pot reaction using leaf extracts of *Azadirachta indica* (neem) and characterization of nanoparticles using UV-Visible spectroscopy, transmission electron microscopy, X-Ray diffraction, energy dispersive X-ray analysis, atomic force microscopy and Fourier transform infra-red spectroscopy.

2. Experimental Methods

2.1 Synthesis of Magnetite Nanoparticles through Green Route

2.1.1 Preparation of Azadirachta indica Leaf Extract

Young, healthy and fresh neem leaves were collected from *Azadirachta indica* at Sri Venkateswara University campus, Tirupati. The collected leaves were thoroughly washed several times with double distilled water. These were then shade dried for a week. The dried leaves were made into powder to prepare the leaf extract. 5 g of neem leaf powder was added in 100 mL of distilled water and heated at 80 °C for 5 minutes. It is allowed to cool down to room temperature and filtered through Whatman No. 1 filter paper. The filtrate was centrifuged at 1200 rpm for 5 minutes. The supernatant was used as leaf extract for the synthesis of nanoparticles.

2.1.2 Preparation of Magnetite Nanoparticles

Ferrous chloride tetra hydrate ($FeCl_2.4H_2O$) and ferric chloride hexa hydrate ($FeCl_3.6H_2O$) were taken in 1:2 molar ratio and dissolved in sterile deionized water. This solution was heated at 80 °C under mild stirring using a magnetic stirrer for 5 minutes. After 10 minutes, leaf extract was added slowly into the solution. After 5 minutes, 1 N NaOH was added into the solution drop by drop for uniform precipitation of magnetite nanoparticles. The solution was left undisturbed and allowed to cool down to room temperature. The black colored nanoparticles get deposited at the bottom. Decantation was done in order to remove the unwanted particles that were not precipitated. The deposited nanoparticles were washed with sterile distilled water. This solution was subjected to centrifugation at 10,000 rpm for 10 minutes. Pellet containing the nanoparticles was dried in hot air oven overnight at 80°C and subjected for characterization.

2.2 Characterization of Magnetite Nanoparticles

The change in color from yellowish to black in a sequence during the process of synthesis of magnetite nanoparticles is the key sign for the identification of the production of nanoparticles. Magnetite nanoparticles synthesized through green route were further subjected to characterization to know their size, shape, surface texture and chemical constituents. The nanoparticles were characterized using UV-Visible

*Corresponding Author
Email Address: psreddy1955@gmail.com (P. Sreenivasula Reddy)

Cite this Article as: K.C. Maheswari, P. Sreenivasula Reddy, Green synthesis of magnetite nanoparticles through leaf extract of *Azadirachta indica*, J. Nanosci. Tech. 2(4) (2016) 189–191.

spectrophotometer (Hitachi, model UV-2900). Transmission electron microscopy (TEM) observations were performed on Hitachi H-8100 microscope at 200KV. Energy dispersive atomic spectroscopy (EDX) analysis was done using energy dispersive X-ray spectrometer of Hitachi. Atomic force microscopy (AFM) analysis was done using NOVA NT-MDT, SOLVERNEXT. Fourier transform infra-red spectroscopy (FTIR) analysis was done using FTIR spectrometer of model ALPHA interferometer, manufactured in Germany. To know the magnetic behavior, aqueous solution of magnetite nanoparticles were placed next to the magnetic bead.

2.3 DPPH Assay

Oxygen free radical scavenging activity of MNPs was estimated [27]. A solution of DPPH (0.135 mM) in methanol was prepared and 1 mL of this solution was mixed with 1 mL of varying concentrations (500 ppm, 1000 ppm and 2000 ppm) of the aqueous solutions of MNPs. The reaction mixture was vortexed thoroughly and left in the dark at room temperature for 30 min. The absorbance of the mixture was measured at 517 nm. The ability to scavenge DPPH radical was calculated using the formula:

$$\text{DPPH scavenging activity (\%)} = [(Abs_{control} - Abs_{sample}) / Abs_{control}] \times 100$$

where, $Abs_{control}$ was the absorbance of DPPH radical + methanol; Abs sample was the absorbance of DPPH radical + aqueous solution of MNPs.

3. Results and Discussion

3.1 UV-Visible Spectroscopy

The synthesis of magnetite nanoparticles was confirmed by the UV-visible spectral analysis (Fig. 1). A strong peak at 234 nm was observed in UV-visible spectrophotometer. It is the characteristic absorption peak for iron oxide nanoparticles.

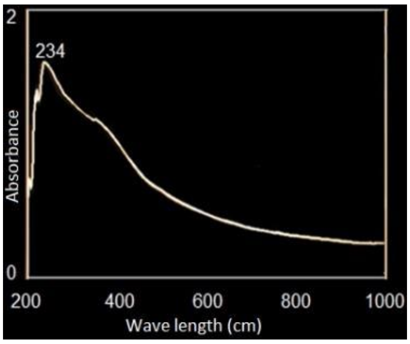

Fig. 1 UV-Visible absorption spectrum of MNPs

3.2 TEM Analysis

TEM analysis shows that all the magnetite nanoparticles synthesized were of small size and in the range of 3-8 nm. All the particles are surrounded by the capping agent of the neem leaf extract (Fig. 2).

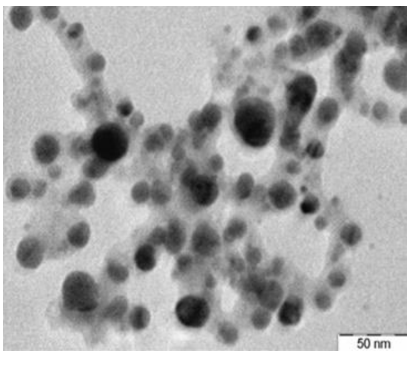

Fig. 2 TEM micrograph of MNPs

3.3 Energy Dispersive X Ray Spectroscopy

EDX analysis showed the nanoparticles contain iron and oxygen atoms with atomic% of 47.04 and 52.96, and weight% of 75.61 and 24.39 respectively (Fig. 3). This confirms that MNPs synthesized were pure without any impurities.

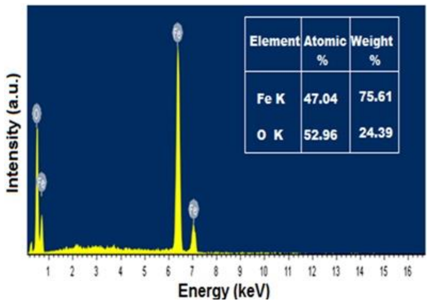

Fig. 3 EDX showing the composition of MNPs

3.4 Powder X-Ray Diffraction

XRD pattern revealed the diffraction peaks at 30.1°, 35.5°, 43.21°, 57.01° and 62.61°, respectively indexed to (220), (311), (400), (511) and (440) planes of the face-centered cubic crystal phase of magnetite nanoparticles (JCPDS 89-3854) and confirmed the crystalline nature of the synthesized magnetite nanoparticles (Fig. 4). MNPs size was calculated using the Debye-Scherrer formula,

$$D = K\lambda/\beta\cos\theta$$

where, D is the average crystalline domain size perpendicular to the reflecting planes, K is a shape factor, λ is the X-ray wavelength, β is the full width at half maximum (FWHM) and θ is the diffraction angle. The calculated average particle size of MNPs was 6 nm.

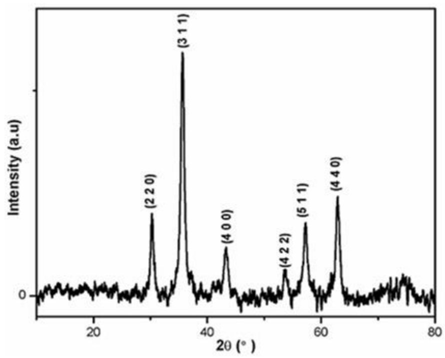

Fig. 4 XRD pattern of MNPs

3.5 FTIR Analysis

Fourier transform infra-red (FTIR) spectra of magnetite nanoparticles synthesized using neem leaf extracts was shown in Fig. 5. A broad band was obtained between 3389 cm^{-1} and 3195 cm^{-1}. This may be due to N-H stretch of amines present in the neem leaf extract. A strong peak at 1619 cm^{-1} represents the N-H bending of amide group. This indicates the presence of proteins of leaf extract in the magnetite nanoparticles synthesis. The presence of magnetite nanoparticles can be confirmed by the strong peaks at 513 cm^{-1}, 460 cm^{-1} and 440 cm^{-1} in the FTIR region. Thus, it can be confirmed that the primary amide of carbonyl group in the leaf extract acts as reducing and stabilizing agent in the formation of iron oxide nanoparticles.

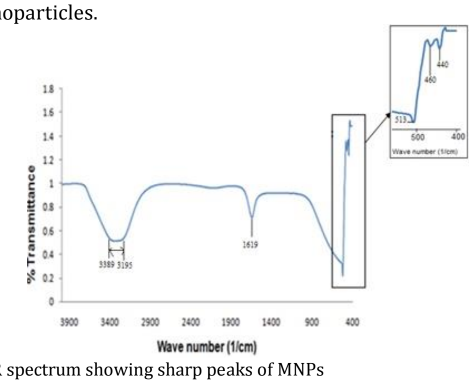

Fig. 5 FTIR spectrum showing sharp peaks of MNPs

3.6 AFM Analysis

The 3D topograph (Fig. 6) of AFM confirms the spherical shape of the magnetite nanoparticles. Difference in height represents the various sizes of the nanoparticles.

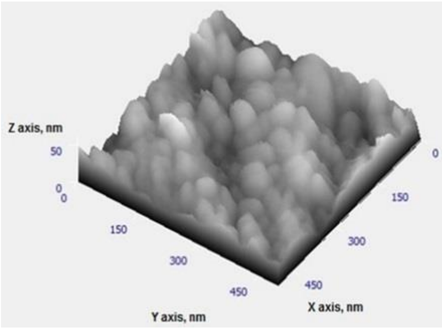

Fig. 6 AFM 3D-Topograph of MNPs

3.7 Magnetic Behavior of Magnetite Nanoparticles

Magnetite nanoparticles in the aqueous solution were attracted towards the magnetite bead placed next to it and got deposited in front of the bead (Fig. 9). When the magnetic bead is rotated, the deposited MNPs were also rotated along with the bead. This was not observed without the external magnetic field.

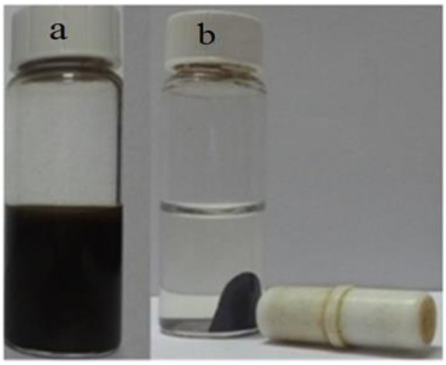

Fig. 7 Aqueous solution of MNPs a) without external magnetic field and b) under external magnetic field

3.8 DPPH Scavenging Activity (%)

MNPs of different aqueous concentrations (500 ppm, 1000 ppm and 2000 ppm) were subjected to DPPH assay. DPPH scavenging activity (%) was decreased with increase in the concentration of magnetite nanoparticles. This confirms that MNPS possesses significant free radical scavenging potential (Fig. 7).

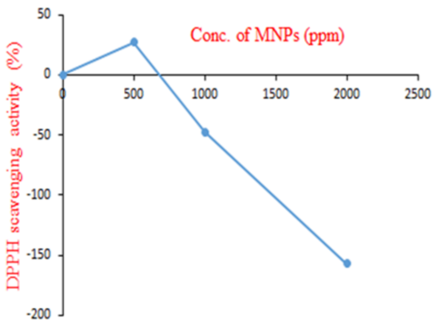

Fig. 8 DPPH scavenging activity (%) of MNPs

4. Conclusion

In the present study, magnetite nanoparticles were synthesized using leaf extract of *Azadirachta indica* and characterized. Neem leaf extract acts as reducing and stabilizing agent in the synthesis of iron oxide nanoparticles. Magnetite nanoparticles of average particle size of 3-8 nm were obtained. These phytogenic magnetite nanoparticles are stable, safe to use, easy to handle and are cost effective. They possess significant antioxidant activity. Experiments using the phytogenic MNPs on the growth of selected microorganisms are in progress in this laboratory.

Acknowledgement

KCM is thankful to University Grants Commission for providing financial support under the scheme Basic Scientific Research - Research Fellowship in Sciences for Meritorious Students to conduct the research.

References

[1] B.H. Sohn, R.E. Cohen, Processible optically transparent block copolymer films containing super paramagnetic iron oxide nanoclusters, Chem. Mater. 9 (1997) 264-269.

[2] G. Schmid, D. Fenske, Metal clusters and nanoparticles, Phil. Trans. R. Soc. A. 368 (2010) 1207-1210.

[3] R.M. Cornell, U. Schwertmann, The iron oxides structure, properties, reactions, occurrences and uses, Wiley, New York, 2003.

[4] Z. Ullah, S. Atiq, S. Naseem, Influence of Pb doping on structural, electrical and magnetic properties of Sr-hexaferrites, J. Alloy. Compd. 555 (2013) 263-267.

[5] J. Hu, I.M.C. Lo, G. Chen, Removal of Cr (VI) by magnetite nanoparticles, Water. Sci. Technol. 50 (2004) 139-146.

[6] J.T. Mayo, C. Yavuz, S. Yean, L. Cong, H. Shipley, et al, The effect of nanocrystalline magnetite size on arsenic removal, Sci. Technol. Ad. Mater. 8 (2007) 71-75.

[7] A. Khodabakshi, M. Amin, M. Mozaffari, Synthesis of magnetite nanoparticles and evaluation of its efficiency for arsenic removal from simulated industrial wastewater, Iran. J. Environ. Health. Sci. Eng. 8 (2011) 189-200.

[8] J. Alam, U. Riaz, S.M. Ashraf, S. Ahmad, Corrosion-protective performance of nano polyaniline/ferrite dispersed alkyd coatings, J. Coat. Technol. Res. 5 (2008) 123-128.

[9] K. Shimizu, A. Ito, M. Arinobe, Y. Murase, Y. Iwata, et al, Effective cell-seeding technique using magnetite nanoparticles and magnetic force onto decellularized blood vessels for vascular tissue engineering, J. Biosci. Bioeng. 103 (2007) 472-478.

[10] D. Maity, P. Chandrasekharan, C.T. Yang, K.H. Chuang, B. Shuter, et al, Facile synthesis of water-stable magnetite nanoparticles for clinical MRI and magnetic hyperthermia applications, Nanomedicine 5 (2010) 1571-1584.

[11] S.S. Shankar, A. Rai, B. Ankamwar, A. Ahmad, M. Sastry, Biological synthesis of triangular gold nanoprisms, Nat. Mater. 3 (2004) 482-488.

[12] J. Kim, J.E. Lee, J. Lee, J.H. Yu, B.C. Kim, et al, Magnetic fluorescent delivery vehicle using uniform mesoporous silica spheres embedded with monodisperse magnetic and semiconductor nanocrystals, J. Amer. Chem. Soc. 128 (2006) 688-689.

[13] C. Kole, P. Kole, K.M. Randunu, P. Choudhary, R. Podila, et al, Nanobiotechnology can boost crop production and quality: first evidence from increased plant biomass, fruit yield and phytomedicine content in bitter melon (*Momordica charantia*), BMC Biotechnol. 13(37) (2013) 1-10.

[14] O.M. Lemine, K. Omri, B. Zhang, L. El Mir, M. Sajieddine, A. Alyamani, M. Bououdina, Sol–gel synthesis of 8 nm magnetite (Fe_3O_4) nanoparticles and their magnetic properties, Superlattices. Microstruct. 52 (2012) 793-799.

[15] T. Ahn, J.H. Kim, H.M. Yang, J.W. Lee, J.D. Kim, Formation pathways of magnetite nanoparticles by coprecipitation method, J. Phys. Chem. C. 116 (2012) 6069-6076.

[16] X. Wang, J. Zhuang, Q. Peng, Y.D. Li, A general strategy for nanocrystal synthesis, Nature 437 (2005) 121-124.

[17] C.Y. Haw, F. Mohamed, C.H. Chia, S. Radiman, S. Zakaria, N.M. Huang, H.N. Lim, Hydrothermal synthesis of magnetite nanoparticles as MRI contrast agents, Ceram. Int. 36 (2010) 1417-1422.

[18] N. Pinna, S. Grancharov, P. Beato, P. Bonville, M. Antonietti, M. Niederberger, Magnetite nanocrystals: Nonaqueous synthesis, characterization, and solubility, Chem. Mater. 17 (2005) 3044-3049.

[19] R.V. Kumar, Y. Koltypin, X.N. Xu, Y. Yeshurun, A. Gedanken, I. Felner, Fabrication of magnetite nanorods by ultrasound irradiation, J. Appl. Phys. 89 (2001) 6324-6328.

[20] I.C. Masthoff, M. Kraken, D. Mauch, D. Menzel, J.A. Munevar, E.B. Saitovitch, F.J. Litterst, G. Garnweitner, Study of the growth process of magnetic nanoparticles obtained via the non-aqueous sol–gel method, J. Mater. Sci. 49 (2014) 4705-4714.

[21] S.F. Chin, S.C. Pangand, C.H. Tan, Green synthesis of magnetite nanoparticles (via thermal decomposition method) with controllable size and shape, J. Mater. Environ. Sci. 2 (2011) 299-302.

[22] Z.H. Zhou, J. Wang, X. Liu, H.S.O. Chan, Synthesis of Fe_3O_4 nanoparticles from emulsions, J. Mater. Chem. 11 (2001) 1704-1709.

[23] H.A. Salam, P. Rajiv, M. Kamaraj, P. Jagadeeswaran, S. Gunalan, R. Sivaraj, Plants: Green route for nanoparticle synthesis, Int. J. Biol. Sci. 1 (2012) 85-90.

[24] N.M. Salem, A.M. Awwad, New route for synthesis magnetite nanoparticles from ferrous ions and Pistachio leaf extract, Nanosci. Technol. 3 (2013) 48-51.

[25] A.M. Awwad, N.M. Salem, A Green and facile approach for synthesis of magnetite nanoparticles, Nanosci. Nanotechnol. 2 (2012) 208-213.

[26] M. Senthil, C. Ramesh, Biogenic synthesis of Fe_3O_4 nanoparticles using *Tridax procumbens* leaf extract and its antibacterial activity on *Pseudomonas aeruginosa*, Dig. J. Nanomater. Bios. 7 (2012) 1655-1660.

[27] C.M. Liyana-Pathirana, F. Shahidi, Antioxidant activity of commercial soft and hard wheat (*Triticum aestivum* L.) as affected by gastric pH conditions, J. Agric. Food. Chem. 53 (2005) 2433-2440.