Green Synthesis of Magnetite (Fe_3O_4) Nanoparticles Using *Azadirachta indica* Leaf Extract and Their Characterization

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Abstract Magnetite (Fe_3O_4) nanoparticles (NPs) were prepared through green synthesis route using *Azadirachta indica* leaf extract that acted as an efficient stabilizer and capping agent of the NPs. Two types of magnetite NPs were synthesized using 5 and 10 mL *Azadirachta indica* leaf extract of the same concentration. The X-ray diffraction (XRD) analysis showed that the particles were crystalline with cubic inverse spinel structure and the crystallite size was found to be about 5.73 nm and 6.34 nm, respectively. The surface morphology of the NPs was investigated by field emission scanning electron microscopy (FESEM) which showed that NPs were spherical in shape. The Fourier transform infrared spectroscopy (FT-IR) analysis showed that the capping agents of the NPs contained the functional groups alcohol, alkane, amine, alkyne, etc. The thermal stability of Fe_3O_4 NPs was investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC showed endothermic and exothermic peaks. The percentage of weight loss was about 55% and 40%, respectively, as found from TGA. The NPs were superparamagnetic in nature with zero coercivity and zero reminance magnetization which was observed using a vibrating sample magnetometer (VSM). On the treatment of aqueous solutions of ferrous and ferric salts in alkaline medium with *Azadirachta indica* leaf extract, the rapid formation of stable iron oxide nanoparticles (Fe_3O_4-NPs) is observed to occur. The average crystallite size was determined by Scherer formula which showed that the crystallite size of the NPs gets increased with the increasing amount of *Azadirachta indica* extract used. Which support and show a good agreement with XRD and VSM analysis.

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M. Mukherjee et al. (eds.), *Advances in Medical Physics and Healthcare Engineering*, Lecture Notes in Bioengineering, https://doi.org/10.1007/978-981-33-6915-3_9

Keywords Green synthesis · NPs · Magnetic properties · Thermal analysis · Crystal structure analysis

1 Introduction

Nanoparticles have excellent recognition and acceptance due to their desirable characteristic features some of which include catalytic, optical, magnetic and electrical properties (Payman and Allan 2009; Fazlzadeh et al. 2016; Lu et al. 2010; Klokkenburg et al. 2007). These particles possess remarkably new properties when compared to their bulk counterpart. This means that nanoparticles do not necessarily behave in the same manner as larger particles in chemical reactions, but tend to be much more reactive (Sulistyaningsih et al. 2013; Davor 1993; Nicolae et al. 2014). The particles possess an enormous amount of energy in their high surface-to-volume ratio, which changes their reactivity (Parker et al. 1993; Bashar et al. 2013; Khan 1998; Ruhane et al. 2017a). Nanoparticles have a general tendency to adsorb species very readily, which has obvious kinetic advantages. Due to environmental concerns, the green route methods have become increasingly popular to synthesize nanoparticles as they are well known to be environmentally friendly and help to reduce harmful effects on environment (Ruhane et al. 2017b; Mehedi and Khan 2018; Khan et al. 2019a). Nanoparticle is a particle in the nanometer scale which usually in the range of 1–100 nm (Khan et al. 2019b; Mehedi and Khan 2019; Hassan and Khan 2020). There are a lot of applications of NPs nowadays. Our main motto to use our produced NPs for electricity generation from different leaf extracts (Khan et al. 2019c; Hazrat Ali et al. 2019).

1.1 Methods and Materials

The chemicals and reagents used in this work are of analytical grade and are used without further purification. De-ionized (DI) water with resistivity 18 MΩ-cm is used as solvent in order to prepare the solutions required in this work. The chemicals and reagents used in this work are listed here: Ferric chloride anhydrous ($FeCl_3$) (Merck, India), Ferrous chloride tetra hydrates ($FeCl_2 \cdot 4H_2O$) (Merck, India), Sodium hydroxide (NaOH) (Merck, India), Citrus limon peel extract, Acetone (CH_3COCH_3) (Merck, India), Ethanol (CH_3OH) (Merck, India), Dichloromethane (CH_2Cl_2) (Merck, India), HeLA Cell line (a human cervical carcinoma cell line), Vero Cell line (a kidney epithelial cell extracted from an African green monkey), DMEM (Dulbecco's Modified Eagle's medium), 1% penicillin streptomycin, 0.2% gentamycin, 10% fetal bovine serum, DI water, etc. Furthermore, the equipments and instruments were used for the synthesis, characterization and antibacterial application of the Fe_3O_4 NPs: Ceramic mortar, Digital balance (AB 265/S/SACT METTLER, Toleto, Switzerland), Magnetic stirrer with thermostat hotplate (GALLTMKAMP,

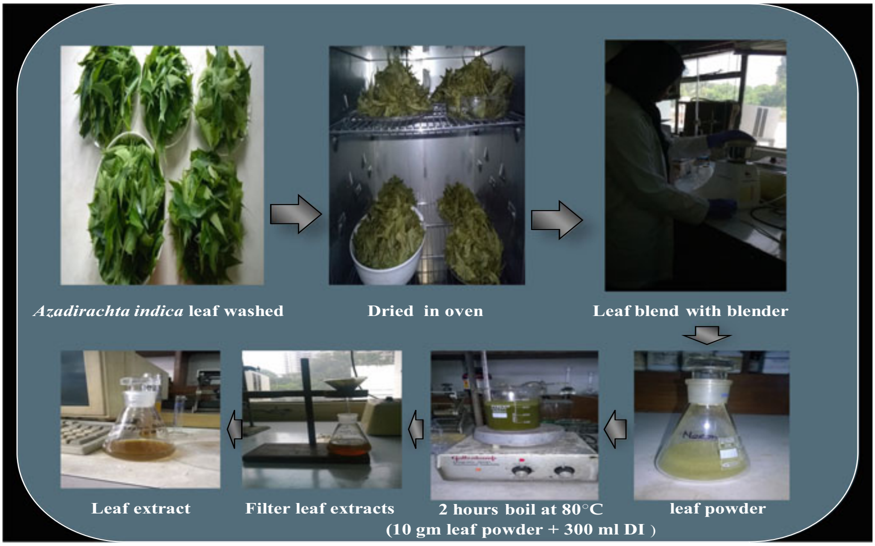


Fig. 1 Methods of *Azadirachta indica* leaf extract preparation

England), Incubator (115 V) RI 115, Electric oven (Binder), Bath sonicator (Decon FS minor), X-ray diffractometer (Philips, Expert Pro, Holland), Fourier transform infrared spectrophotometer (Jasco-FT-IR-6300), Field emission scanning electron microscopy (JSM-7600F, Tokyo, Japan), TGA machine (TA instrument, SDT Q-600) and Vibrating sample magnetometer (EV-9 Micro Sense, Germany).

Figure 1 shows the preparation of *Azadirachta indica* leaf extract preparation. Firstly, it has been taken washed *Azadirachta indica* leaf then it was dried, then the leaf was blended by a blender and then it was made leaf powder. After that this powder was mixed with DI water and heated at 80 °C for two hours, then it was filtered and we got leaf extract.

Figure 2 shows the preparation of iron oxide nanoparticles (Fe_3O_4-NPs) from *Azadirachta indica* leaf extract. It is shown that it needs seven different steps to get iron oxide nanoparticles (Fe_3O_4-NPs) from *Azadirachta indica* leaf extract.

1.2 Synthesis of Fe_3O_4 NPs

Fe_3O_4 NPs were synthesized via a facile green synthesis route where $FeCl_3$ and $FeCl_2 \cdot 4H_2O$ were used as precursor and *Azadirachta indica* leaf extract was used as a source of reducing and capping agents. To synthesize Fe_3O_4, the *Azadirachta indica* leaf extract was added to an aqueous mixture of Fe^{3+} and Fe^{2+} chloride at a 2:1 M ratio (Khan et al. 2018a, b). The chemical reaction of Fe_3O_4 precipitation is given below:

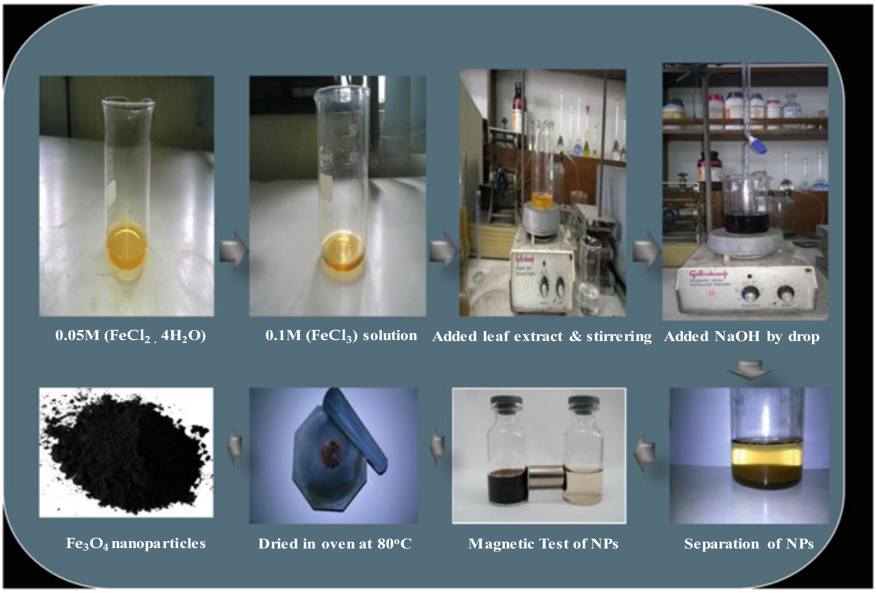


Fig. 2 Methods of NPs preparation from *Azadirachta indica*

$$\text{Azadirachta indica} + H_2O + Fe^{2+}(aq) + Fe^{3+}(aq) + OH^- \rightarrow [\text{Azadirachta indica}/Fe_3O_4]$$

2 Results and Discussion

2.1 Structural Analysis of XRD

The diffraction peaks of synthesized Fe_3O_4 NPs are assigned to the crystal planes of (220), (311), (400), (440), respectively. The analyzed diffraction peaks were matched well with the standard magnetite XRD patterns with JCPDS file no: 89.0691 which declared the crystallographic system of spherical structure (Fig. 3).

Debye–Scherrer's Formula
Equation for calculating structural parameters.

Debye–Scherrer's Formula

$$D = \frac{k\lambda}{\beta_{hkl}\cos\theta} \tag{1}$$

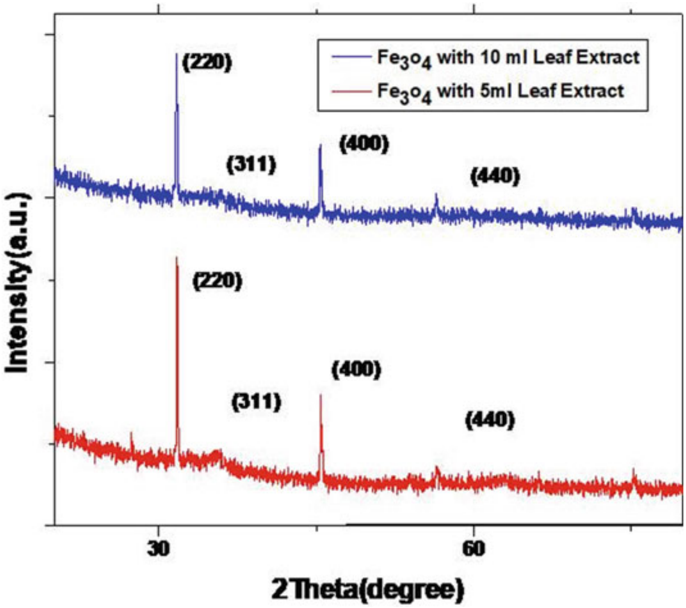


Fig. 3 Structural analysis of XRD

Table 1 Structural analysis for XRD

Leaf extract in Ml	Crystallite size *D* in (Nm) line/Nm	Micros-train (*E*) $\times 10^{-3}$
5	5.73	2.90
10	6.34	1.46

where β is the full width at half maxima (FWHM), λ is the wavelength ($\lambda = 0.15406$ Å), D the average crystallite size and θ is Bragg's angle.

Table 1 shows the crystallite size and structural parameter for different capping and stabilizing agents presentation (Fig. 4).

The crystallite size is increasing, respectively, according to the leaf extract increasing and the estimated crystallite size are 5.73 and 6.34 nm (Fig. 5).

2.2 *Fourier Transform Infrared Spectroscopy (FT-IR) Analysis*

The Fourier transform infrared spectroscopy (FT-IR) analysis showed that the capping agents of the NPs contained the functional groups alcohol, alkane, amine, alkyne, etc. (Table 2).

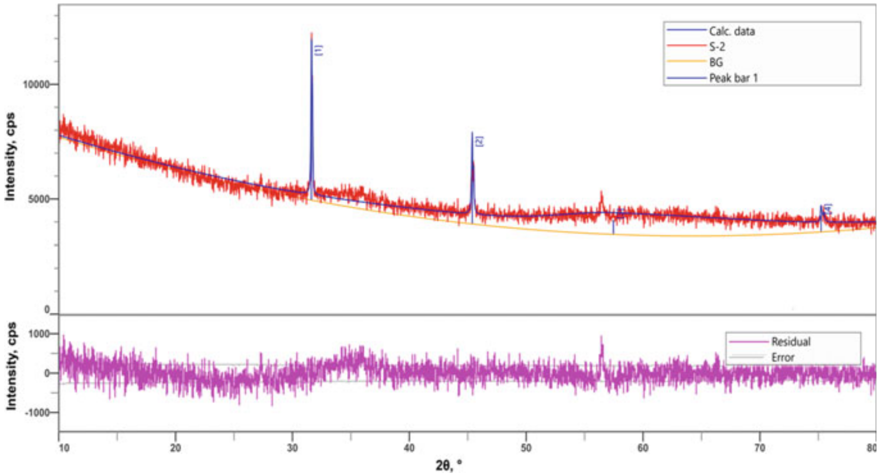
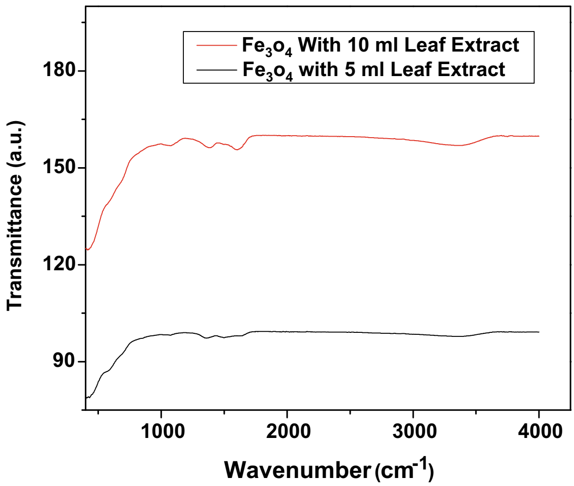


Fig. 4 Variation of intensity with 2θ

Fig. 5 Variation of transmittance (a.u.) with 2θ



2.3 Surface Morphology of the NPs

The surface morphology of the NPs was investigated by field emission scanning electron microscopy (FESEM) which showed that NPs were spherical in shape (Fig. 6).

Table 2 Table for Fourier transform infrared spectroscopy (FT-IR) analysis

Functional group	Peak position (sample-1)	Peak position (sample-2)	Attribution
– OH	3450.29	3456.65	Stretching vibration of –OH functional group
N–H	3324.09	3327.92	N–H stretching and bending vibration of amine group NH_2
Azadirachta indica	3415.29	3416.05	The involvement of functional groups of *Azadirachta indica* in the reduction process
– C≡C–	2424.78	2429.65	Alkyne group presents in phytoconstituents of extracts
Fe–0	1623.85	1622.13	Stretching vibration of Fe–O bond
– CH_3	1370.72	1375.01	Bending alkanes
C–O	1076.06	1133.44	Stretching carbonyl
– O–H	939.21	942.88	Bending hydroxyl

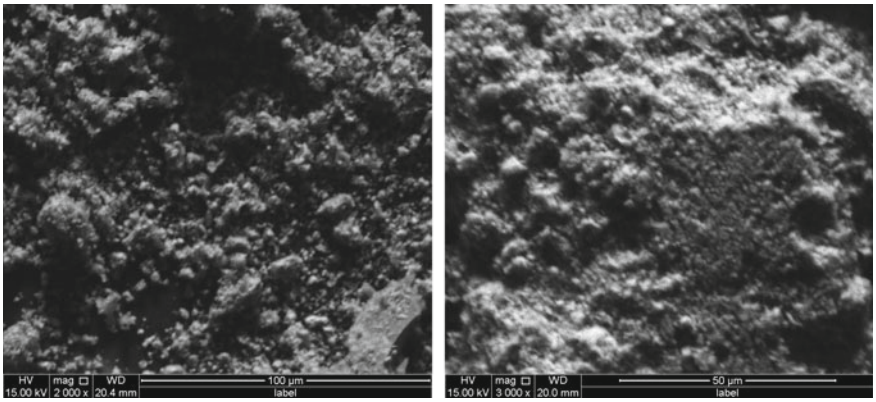
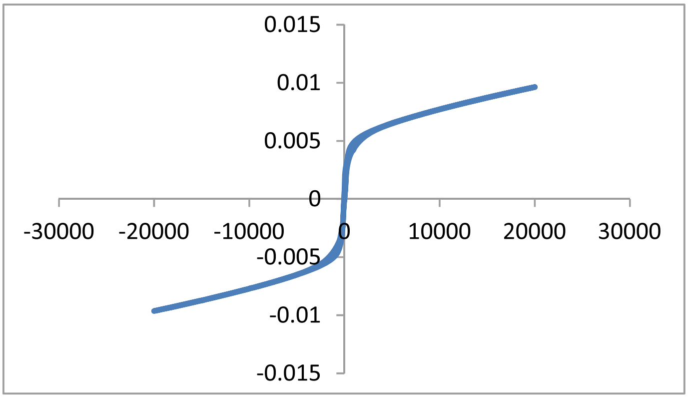


Fig. 6 Surface morphology of the NPs

2.4 VSM Analysis of NPs

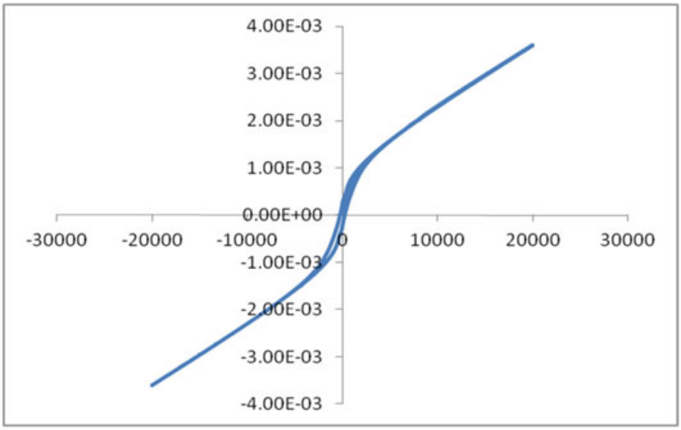
The NPs were superparamagnetic in nature with zero coercivity and zero reminance magnetization which was observed (Figs. 7 and 8).

Finally, we can say that the saturation magnetization (Ms) of the Fe_3O_4 indicates the presence of non-magnetic surface layers resulting from the strong chemical



Magnetization Vs Applied field (Oe) graph

Fig. 7 Magnetization curve of Fe_3O_4 NPs of sample-1 as a function of applied field



Magnetization Vs Applied field (Oe) graph

Fig. 8 Magnetization curve of Fe_3O_4 NPs of sample-2 as a function of applied field

attachment of the stabilizing agent of *Azadirachta indica* leaf extract to the Fe_3O_4s surface which also observed by FT-IR spectroscopy.

2.5 DSC Analysis of NPs

In DSC curve, exothermic and endothermic peak are observed, and the sharp exothermic peak occurred in between 800 to 840 °C due to the physical state change

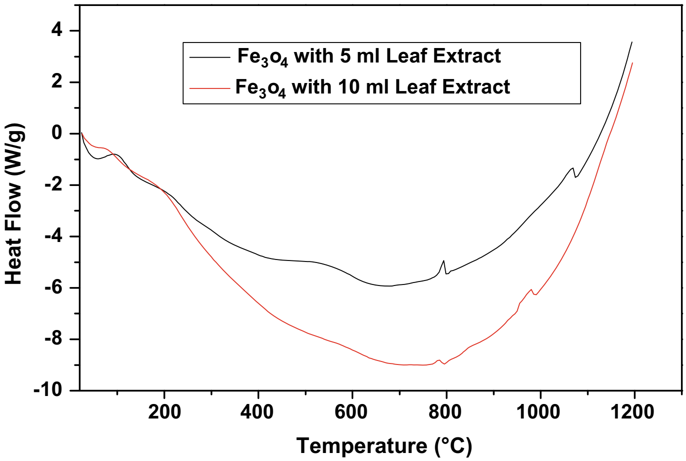


Fig. 9 DSC plot as a function of temperature of Fe_3O_4 NPs

of water. The result of DSC demonstrated that the magnetite is unstable at high temperature and it gets transferred to hematite at high temperature (Fig. 9).

3 Conclusions

Magnetite NPs were successfully synthesized through green synthesis method using *Azadirachta indica* leaf extract. Leaf extract acts as capping and stabilizing agent that prevents the conglomerated of magnetite NPs formed during synthesis. Crystallinity, surface morphology, magnetic property and thermal properties are analyzed here. From the XRD, FT-IR, FESEM, TGA, DSC and VSM analysis, it can be concluded that we have successfully synthesized crystalline Fe_3O_4 NPs.

Acknowledgements The authors are grateful to the GARE (Grant of Advanced Research in Education) project, Ministry of Education, GoB for financing during the research work (Project/User ID: PS2019949).

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