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Experimental Investigation on Green Synthesis of FeNPs using *Azadirachta indica* Leaves

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Abstract

In nanotechnology, developing an environmentally friendly method for synthesizing iron nanoparticles (FeNPs) is an important aspect. According to recent studies, the use of secondary metabolites from plant leaf extract has recently emerged as a novel technology for synthesizing various nanoparticles. The leaf extract of *Azadirachta indica* was used to synthesize iron nanoparticles in this research. The effects of reactant concentrations, reaction temperature, and pH of the solution on the synthesis process of iron nanoparticles were studied. A UV-Visible Spectrophotometer that analyzed absorbance spectra was used to monitor the formation of iron nanoparticles in dispersion. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) characterized the morphology of iron nanoparticles, and results reveal the particles are spherical with an average size of 48 nm. The optimum conditions for synthesis are as follows: 15 % leaf extract, [$FeCl_3$] = 1.0 mM, pH 6.0, and temperature 60 °C. The FTIR technique confirms that plant biomolecules induce the reduction of Fe^{3+} ions to FeNPs and act as a capping and stabilizing agent. Therefore, they have good stability for various applications.

Keywords: Green synthesis; *Azadirachta indica*; Iron nanoparticles; Experimental investigation.

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1. Introduction

Iron nanoparticles (FeNPs) are among the most promising metallic nanoparticles for various applications due to their reactivity and high surface area to volume ratio [1]. Several physical and chemical methods are used to synthesize iron nanoparticles, such as co-precipitation [2], sol-gel [3], hydrothermal [4], micro-emulsion [5], and sonochemical method [6]. The physical technique includes high energy, pressure, and temperature intake, while the chemical technique requires dangerous and harmful chemicals that lead to environmental contamination [7]. Research is focused tirelessly on achieving a green nanoparticle synthesis process that is easy, efficient, and accurate. Several species serve as safe, environmentally friendly, and green precursors to develop stable and well-defined functionalized nanoparticles. [8]. Biosynthesis of nanoparticles using microorganisms and

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plant extracts has been recommended as a feasible eco-friendly substitute to chemical and physical methods [9]. Plant extracts are possibly preferred biological resources over microorganisms for the biosynthesis of nanoparticles due to their easy availability in nature, biohazards, and rigorous cell culture maintenance process [10]. In terms of eco-friendly alternatives, this method is beneficial for toxic chemicals that can be processed in comparatively less time, feasible, and can provide immense applications [11]. During synthesis, there are three steps to fabricate particles like reducing metal ions to zero-valent particles, growth, and stabilization, respectively [12]. It depicts the nanoscale creation, shape, characterization, and application of particles. Green nanotechnology has a great recognition to use in numerous fields such as catalyst [13], environmental remediation [14,15], Agriculture [16], and food industries [17]. However, iron nanoparticles and their composites have other recent applications in different fields, including biomedical, tissue engineering, thermal stabilization, and wastewater treatment [18-21].

Utilizing a more convenient and environmentally friendly method to synthesize iron nanoparticles is a significant advancement in nanomaterial production. Existing literature reports a successful synthesis of iron nanoparticles through green routs that include leaf extracts of *Eucalyptus tereticornis, Melaleuca nesophila, and Rosemarinus officinal* [22], *Plantago major* [23], *Mangifera indica, Murraya Koenigii, Azadiracta indica, Magnolia champaca* [24], and other plant extract used as reducing and capping agent. The source of the plant extract influences characteristics of nanoparticles contains a unique combination and concentration of biomolecules as reducing agents [25]. Iron nanoparticles of various sizes and morphologies have been synthesized using Lantana Camara leaf extract as a reducing and capping agent. The average particle size was 10-20 nm, with nanorods, crystalline, and very stable morphologies [26]. Iron nanoparticles of various sizes and morphologies (spherical, platelets, and nanorods) were also formed instantaneously using aqueous tea extracts [27]. The size and crystallinity (hexagonal metallic iron, amorphous iron, and R-Fe_2O_3) of the synthesized iron nanoparticles depended on the concentration of the tea extract in the reaction mixture. The iron nanoparticles were effectively capped by the tea polyphenols, extending their stability. Although the synthesis of metallic nanoparticles using plant materials has been reported, a rapid, cost-effective biosynthetic protocol for bulk synthesis of stable metallic nanoparticles has not been developed. This approach is essential to understand the full potential of these nanoparticles in environmental remediation and other industrial applications.

This study reports the biosynthesis of iron, a nanoparticle, via a single-step reduction of iron ions using aqueous leaf extract from the Indian medicinal plant *Azadirachta indica* (Neem). The reduction of the metal ions using aqueous *Azadirachta indica* extracts is rapid and results in moderately stable colloids. Terpenoids, nimbaflavone, sugar, and other biomolecules are present in neem leaves extract and are responsible for metal ion reduction with capping agents [28]. These biological compounds are water-soluble, non-toxic, and biodegradable, affording a green synthesis process. *Azadirachta indica* leaf extracts with high levels of freely extractable phenolic compounds are potentially more cost-effective and advantageous for the bulk synthesis of metallic nanoparticles. The synthesis process results were influenced by several parameters such as reactant concentrations, temperature, and pH, and synthesized plant-mediated FeNPs were characterized using various instrumental techniques.

2. Material and Method

2.1. *Chemical and materials*

Ferric chloride (E. Merck) and neem (*Azadirachta indica*) leaf extract were used to synthesize iron nanoparticles. Based on cost-effectiveness and ease of availability, the plant *Azadirachta indica* was chosen from Kota, Rajasthan, India. New, healthy leaves were collected, thoroughly rinsed, and allowed to dry at room temperature. 10 g of these finely incised leaves were stirred for 20 min on a magnetic stirrer at 80 °C. The extract was filtered twice through Whatman filter paper and stored in Erlenmeyer flasks at 4°C for further testing. Sterile conditions were maintained during the experiment to ensure the feasibility and precision of the findings.

2.2. *Instrumentation*

UV-Vis spectra were obtained as a function of the reaction time on a double beam spectrophotometer (UV 3000+ LAB INDIA) with a resolution of 1 nm. The functional groups of biomolecules in the leaves extract of Azadirachta indica were identified by the spectrum recorded using an FTIR model (ALPHA-T Bruker, Germany) transmittance mode operating at a resolution of 4 cm^{-1}. Morphological study of the Iron nanoparticles was carried out with scanning electron microscopy (SEM) (Model-Nova Nano FE-SEM 450 (FEI)) and Transmission electron microscope (TEM) (Model-FEI Techni G2S2 Twin) instrument. The presence of metal in the sample was investigated using the energy dispersive spectroscopy (EDS) technique. A pH meter (Model-MSW-552) was used to determine the pH of the reaction mixture.

2.3. *Iron nanoparticle synthesis*

1 mM ferric chloride ($FeCl_3$) aqueous solution in a 250 mL Erlenmeyer flask was prepared, and the mixture was kept on magnetic stirring at 60 °C. Then 15 % leaf broth was added dropwise to reduce Fe^{+3} ions. Periodic sampling and scanning with a UV-Visible spectrophotometer to record time and color change. The color change from light yellowish to colloidal brownish-black confirmed the complete reduction of Fe^{+3} ions. The colloidal solution was sealed and stored correctly for further use. Different spectrophotometric techniques further confirmed the formation of iron nanoparticles. The effects of different concentrations of $FeCl_3$ solution, percentage of leaf extract, temperature, and pH on the synthesis rate were also investigated.

3. Results and Discussion

3.1. *Effect of leaf extract's percentage*

The dispersion changed color from yellow to brownish-black due to the biosynthesis of FeNPs, indicating that the reduction of Fe^{+3} into Fe^0 particles can impart such color. Similar color differences have been seen in previous studies. [1,29]. According to current research, the optical properties of metal nanoparticles are influenced by their size and shape; hence, their geometry and size can control the optical reactivity of nanoparticles. [30,31]. Optical spectroscopy can be used as a primary tool for confirmation that metal nanoparticles are an aqueous solution during the synthesis process. The absorption peak was obtained at 258 nm, attributed to the SPR of Fe^0 particles or FeNPs formation [32].

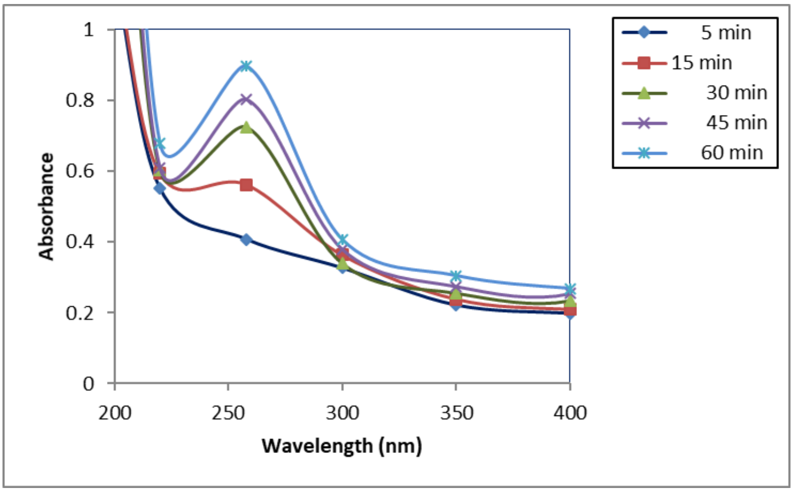

Fig. 1. UV spectra were recorded as a function of reaction at different wavelengths versus absorbance during the synthesis of iron nanoparticles at different time intervals.

The effect of different percentages of leaf extract on synthesis rate was investigated. When the leaf extract concentration was increased, a significant difference emerged between the intensity of UV–vis at 258 nm in varied extract percentage (5 to 15 %) and 1 mM $FeCl_3$ at 60 °C as shown in Fig. 2. A weak absorption peak at 258 nm was observed when a low percentage (5 %) of leaf broth was used, indicating that relatively low concentrations of iron nanoparticles were formed due to insufficient reduction. The degree of dispersion of iron nanoparticles is considered to be determined by the UV-Vis absorption peak [33]. The intensity of the absorption peak at 258 nm increases as the percentage of leaf extract (5-15 %) increases. However, the maximum absorption peak was found at 15 % neem leaf extract, indicating that this is the optimal percentage of leaf extract for iron nanoparticles synthesis.

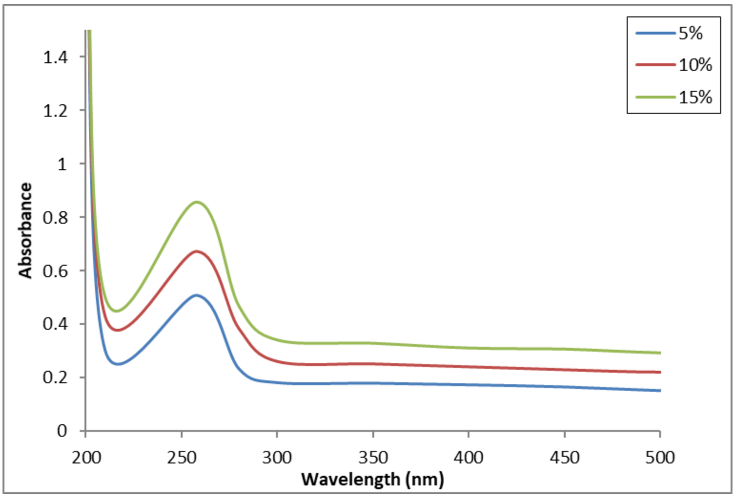

Fig. 2. UV spectra recorded as a function of reaction at different wavelengths versus absorbance during synthesis of iron nanoparticles at different Neem leaf extract 5 %, 10 %, and 15 %).

Biosynthesized iron nanoparticles are documented that polyphenols from plants leave to be encased in a thin layer of organic material that acts as a cap [34]. It is also reported that the leaf polyphenols not only capped the ensuing nanoparticles [35] but also reduced the iron salts since the reduction potential of polyphenols was in the 0.3–0.8 V range, while the reduction potential of Fe was only 0.44 V [34], leading to Fe^{+3} to be reduced to FeNPs. TEM images (Fig. 3) show that the synthesized Iron nanoparticles are spherical with an average size of 48 nm, encased in a thin layer of some capping material, and remain stable in solution for four weeks. Energy-dispersive X-ray spectroscopy (EDS) was used to calculate the elemental analysis of iron (Fig. 4). The number of X-ray counts is shown on the vertical axis, while the energy is shown on the horizontal axis. Strong signals in the iron region 7 Kev are revealed by EDS spectra, confirming the formation of nano iron in its elemental state [36]. Other than these signals for C, O are observed, which may originate from the biomolecules capped to the surface of the FeNPs, Mn, and Cl due to plant constituents and precursor salt, respectively.

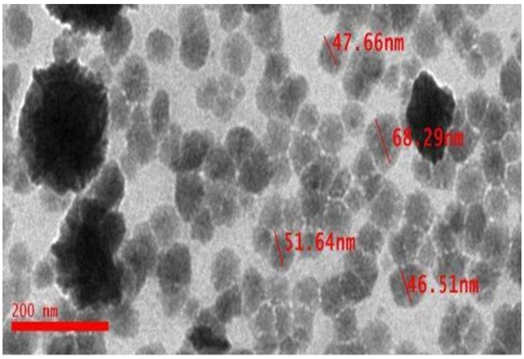

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Fig. 3. TEM image of synthesized iron nanoparticles.

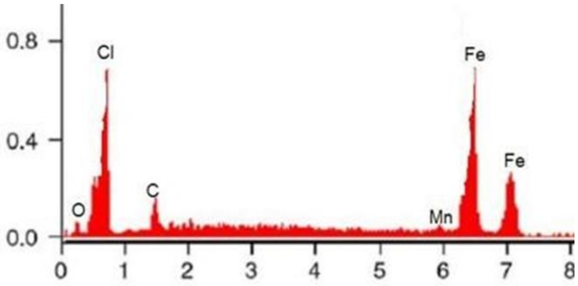

Fig. 4. Spot profile EDS spectra of synthesized iron nanoparticles.

3.2. *Effect of precursor salt concentration*

According to a previous study, there are two steps in forming metal nanoparticles in a solution. The first stage produces metal nuclei, and the second is to grow them expand [37]. As a result, it is important to control the preparation phase because iron nuclei must produce faster and develop slower, which requires better control of the initial Fe^{+3} concentration. The influence of initial precursor salt concentration on the synthesis of iron nanoparticles was examined in this study using iron chloride concentrations ranging from 0.5 to 2 mM.

The UV-Vis spectra were observed as a function of reaction at various $Fecl_3$ concentrations versus absorbance during the synthesis of iron nanoparticles at various time intervals, as shown in Fig. 5. It can be shown that as the concentration of Fe^{+3} increases, the reaction rate increases. The number of iron nuclei increases as the reaction rate increases, resulting in smaller particle sizes produced. At various $FeCl_3$ initial concentrations, SEM images of the synthesized iron nanoparticles were recorded, as shown in Fig. 6. The SEM results reveal that excess nuclei are produced when the reactant concentration is too high (2 mM). As a result, nuclei cluster together, and particle size increases. This may be due to collision between small particles, which leads to particle growth [38]. Therefore, synthesis of iron nanoparticles, the optimal initial concentration of $FeCl_3$ is 1 mM at 15 % leaf extract, 60 °C temperature, and pH 6.0.

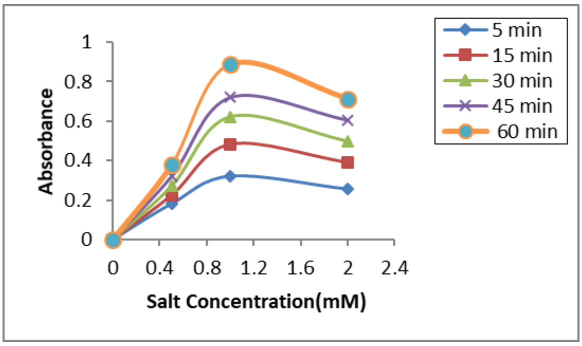

Fig. 5. Time course of iron nanoparticles synthesis with different initial concentration of $FeCl_3$ (0.5 to 2 mM), leaf extract =15 %, temperature= 60 °C, pH = 6.0.

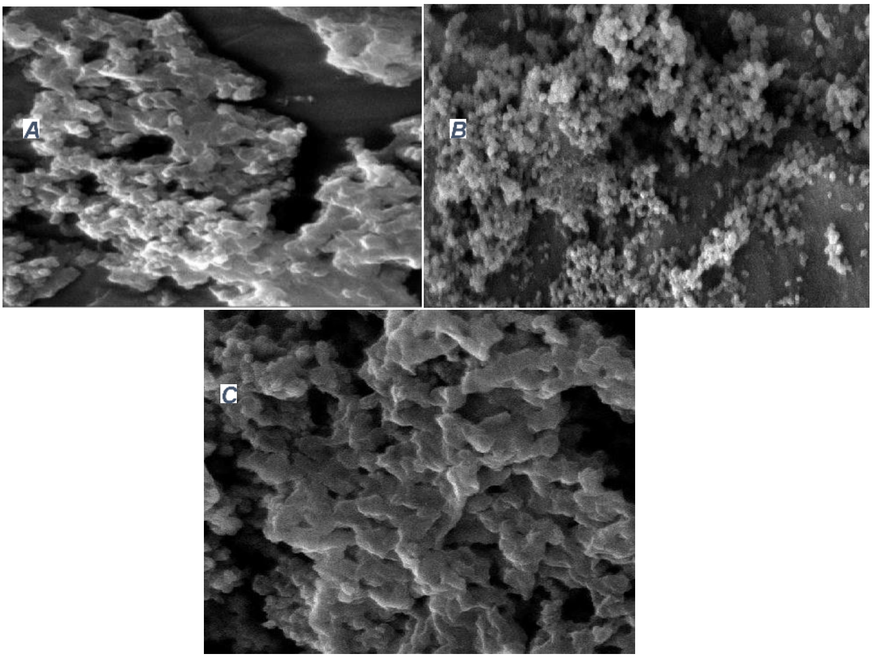

Fig. 6. SEM images of the synthesized iron nanoparticles at three concentration of the precursor salt ($FeCl_3$) (A) 0.5 mM, (B) 1.0 mM, (C) 2.0 mM.

3.3. *Effect of reaction temperature*

The present study also investigated the effect of temperature on the synthesis of nanoparticles at three different temperatures viz 50°, 60°, 70 °C, respectively. Fig. 7 shows that at higher temperature (70 °C), the nanoparticles were agglomerated, while at 60 °C are well dispersed with an average size at about 48 nm. The reduction of Fe^{+3} was increased by raising the reaction temperature. Therefore, at a high temperature, the synthesis rate is too high to regulate particle size. Harshiny *et al*. [39] are also reported that the reduction rate of iron nanoparticles increased with raising the temperature of the reaction. When a reducing agent was added to the precursor solution at 70 °C, the rate of growth, agglomeration, and nucleation of iron nanoparticles all accelerated almost simultaneously, resulting in agglomeration of the formed iron nanoparticles. It is also confirmed by SEM results Fig. 8. Therefore, moderate temperature (60 °C) should be selected to synthesize iron nanoparticles with appropriate control on size.

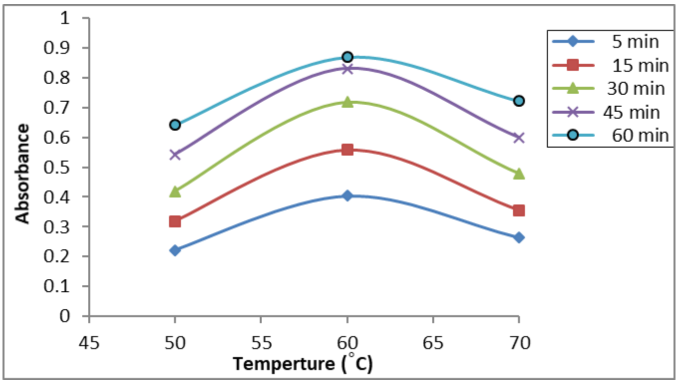

Fig. 7. Time course of iron nanoparticles synthesis with different reaction temperature (50-70 °C), $FeCl_3$ (1 mM), leaf extract= 15 % pH=6.0.

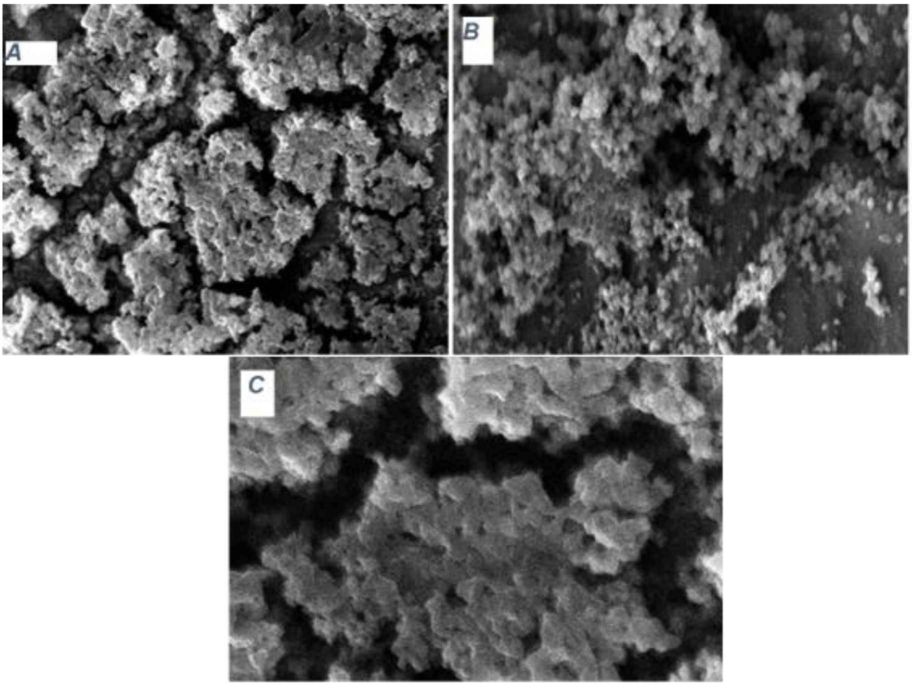

Fig. 8. SEM images of synthesized iron nanoparticles at three different temperatures (°C) (A) 50 (B) 60 (C) 70.

3.4. *Effect of pH*

The solution pH was one of the key factors for the synthesis of nanoparticles, and the rate of synthesis and morphology of NPs are affected by pH variations [40]. The effect of solution pH was studied on the synthesis of NPs by absorbance spectra, as shown in Fig. 9. At acidic pH (3), fewer particles at spectrum peak at 258 nm due to unreacted organic molecules present in the reaction solution. At almost neutral pH (6), high absorbance obtained was due to activation of phytochemicals present in the leaf extract. However, at higher pH (9), the absorbance peak was shifted, which may be an agglomeration of nanoparticles. As a result, the pH of 6.0 is favorable for FeNPs biosynthesis at 1 mM $FeCl_3$ concentration, 15 % leaf extract, and 60 °C temperature. The pH of the medium decreases during the synthesis process because the species of leaf extract release H^+ ions when they oxidize in the presence of Fe^{3+} ions [39].

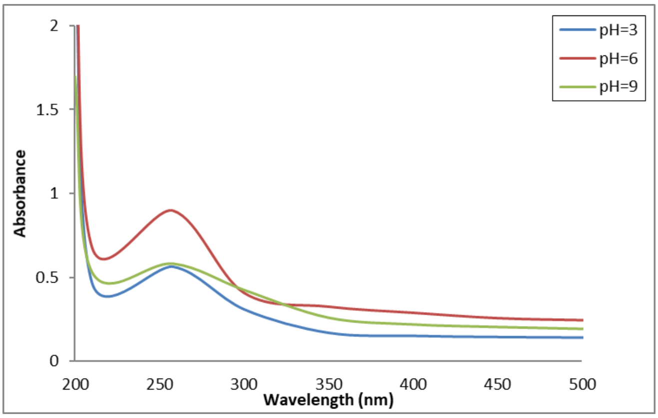

Fig. 9. UV spectra recorded as a function of reaction at different wavelengths versus absorbance during synthesis of iron nanoparticles at different solution pH (3, 6, and 9).

FTIR measurements were carried out to identify the potential functional groups of the bio-molecules in the leaf extract of Azadirachta indica (neem), which are responsible for reducing iron ions into iron nanoparticles. The synthesized FeNPs are stable for one month at 4 °C by the bio capping of Neem leaf extract, which was confirmed by the FTIR Spectra of synthesized Fe-NPs given in Fig. 10. The absorption bands observed at 3393 cm^{-1} and 1627 cm^{-1} are attributed to the O-H and C=C stretching vibrations, respectively. The band that appears at 1076 cm^{-1} is related to C-O-C and absorption peaks [41]. In general, a band observed at 1384 cm^{-1} is assigned to the germinal methyl groups. From the analysis, it is clear that flavonoids could be adsorbed on the surface of metal nanoparticles by a possible interaction through electron or carbonyl groups. The presence of reducing sugar in the leaf extract may be responsible for the formation of bio-capped FeNPs. The physisorbed leaf extract may cause steric/electrostatic barriers around the surface of FeNPs, and hence they show good stability.

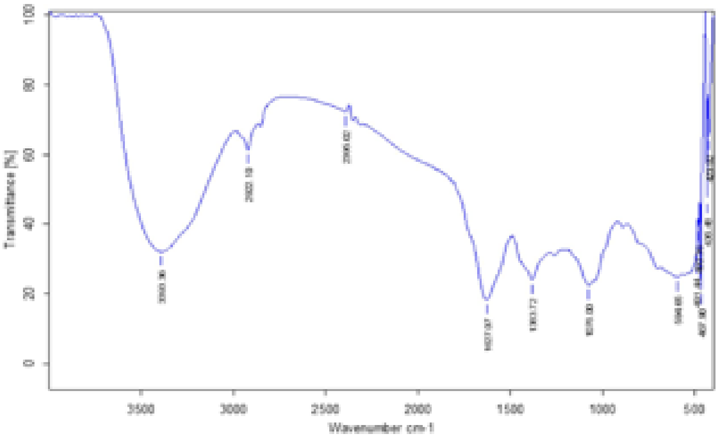

Fig. 10. FT-IR Spectra of synthesized Fe nanoparticles.

4. Conclusion

The study suggests that the synthesis route is low cost, environmentally friendly, and can be prepared in simple laboratory equipment in ambient conditions. This biological reduction of iron ions would be a boon for developing a clean, non-toxic, environmentally acceptable green approach to produce iron nanoparticles. The characterization results reveal biosynthesized FeNPs are spherical with an average size of 48 nm. Moreover, it was clearly shown that the initial concentration of reactant, reaction temperature, and pH remarkably affect particle size and agglomeration of the synthesized iron nanoparticles. The synthesized nanoparticles have good stability, thus have a potential for use in biomedical applications, and will play an important role in the field of catalysis.

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