International Journal of Chemistry and Pharmaceutical Sciences

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Green Synthesis of Iron oxide nanoparticles using *Cinnamon zeylanicum* powder extract

Priti Malhotra[1], Divya Mathur*[1], Jitendra Singh[1,2]

[1]Department of Chemistry, Daulat Ram College, University of Delhi, Delhi-110007, India
[2]Bioorganic Laboratory, Department of Chemistry, University of Delhi, Delhi- 110 007, India

A B S T R A C T

The biological synthesis of nanoparticles using plants or plant derived materials have a significant potential to boost its production without the use of harsh, toxic, and expensive chemicals commonly used in conventional physical and chemical processes. Plant extracts contain bioactive alkaloids, phenolic acids, polyphenols, proteins, sugars, and terpenoids which are believed to first reduce the metallic ions and then stabilize them. Iron oxide nanoparticles have attracted a great deal of attention among researchers because of their multivalent oxidation states, polymorphisms, unique optical, electrical, and magnetic properties and biomedical applications. However, developing a simple, eco-friendly and reliable method for low-dimensional iron oxide nanostructures is still challenging. The bark of cinnamon is one of the most popular spices used worldwide not only for cooking but also in traditional and modern medicines. The most important constituents of cinnamon is cinnamaldehyde which contributes not only to the fragrance but also to its various biological activities. In this work, Iron oxide nanoparticles have been synthesized through a green technique using *Cinnamon zeylanicum* (cinnamon bark powder) extract. The X-ray powder diffraction measurement shows that the biosynthesized particles are hematite (α-Fe_2O_3). The microstructure and particle size were investigated using scanning electron microscopy and absorption spectroscopy.

Keywords: Iron oxide nanoparticle, Biosynthesis, Cinnamon, Hematite

A R T I C L E I N F O

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Article History: Received 09 March 2016, **Accepted** 14 May 2016, **Available Online** 27 July 2016

***Corresponding Author**
Divya Mathur
Department of Chemistry,
Daulat Ram College, University of Delhi,
Delhi-110007, India
Manuscript ID: IJCPS3037

PAPER-QR CODE

Citation: Divya Mathur, *et al.* Green Synthesis of Iron oxide nanoparticles using *Cinnamon zeylanicum* powder extract. *Int. J. Chem, Pharm, Sci.*, 2016, 4(7): 366-370.

1. Introduction

Iron is the fourth most plentiful and crucial element in the Earth's crust. From being the building block of steel, nourishing plants and carrying oxygen in blood – iron has played an unparallel role in life sustenance. Nanotechnology is an emerging and rapidly growing area of research because of its potential and widespread applications [1]. Extremely small size and large surface area to volume ratio of nanoparticles is the reason for its significant biological, catalytic, mechanical, thermal and electrical conductivity properties [2]. Iron nanoparticles has carved out a niche in nanotechnology and a lot of research is being conducted on the synthesis of iron nanoparticles because of its scientific and technological importance [3]

Iron oxide nanoparticle have found its applications as contrast agents for Magnetic Resonance Imaging (MRI), drug carriers for target specific drug delivery, therapeutic agents for hyperthermia based cancer treatments and magnetic sensing probes for in-vitro diagnostics (IVD) [6]. It has also been used as an effective material to remediate large quantities of organic contaminants in the environment due to its magnetic and catalytic properties, low toxicity, and relatively low cost [7]. Iron oxides exist in many forms in nature namely magnetite (Fe3O4), maghemite (γ-Fe2O3) and hematite (α-Fe2O3) [8].

Iron oxide nanoparticles have been synthesized using various physical and chemical methods like Co-Precipitation, Thermal Decomposition, Microemulsion, Hydro-thermal synthesis, Sonochemical synthesis, Microwave method etc [9]. In recent years, the biosynthesis of nanoparticles employing actinomycetes [11], bacteria [12], fungus [13], plants [14], viruses [15], and yeast [16] has been considered a more environmentally safe and cost-effective alternative [17]. Plant extracts are particularly promising since they contain a potent array of antioxidants such as polyphenols, reducing sugars, nitrogenous bases, and amino acids, which can reduce metal ions in a metal salt solution, are freely available, cheap, and offer simplicity of use and scalability [18].

Cinnamon (Cinnamomum zeylanicum, and Cinnamon cassia), the eternal tree of tropical medicine, belongs to the Lauraceae family (Figure 1) [19]. It has been reported to possess various pharmacological activities such as antioxidant,[20] anti-inflammatory,[21] antidiabetic, [22] antimicrobial, [23] anticancer, [24] lipid-lowering, [25] neurological disorders treatment, [26] and cardiovascular -disease-lowering properties [27].

Figure 1: *Cinnamomum zeylanicum* (Cinnamon)

The phytoconstituents embedded within cinnamon contain functional groups such as aldehyde and hydroxyl units that provide synergistic chemical reduction power for the production and stabilization of nanoparticles in a singular green process [25]. Herein we report a green methodology for the preparation and characterization of iron oxide nanoparticles using cinnamon (*Cinnamomum zeylanicum*) powder extract.

2. Experimental

Instrumentation

The powder X-ray diffraction (PXRD) patterns were recorded using Rigaku rotating anode RU-H3R X-ray diffractometer as well as Bruker D8 high resolution diffractometer employing Cu-K radiation. Scanning electron microscopy (SEM) observations were carried out on a Zeiss Leo 982 instrument operated at 4kV. The absorption spectra were recorded on a Perkin Elmer UV-Visible Spectrophotometer Lambda 25 model. pH was recorded using Digital pH meter Systronics.

Preparation of Plant Extract

About 10 g of Cinnamon powder was boiled in 100 mL MilliQ water in Erlenmeyer flask at 60°C for 2h. After boiling, the mixture was cooled and filtered. Filtrate was collected and stored at 4°C for further experiments.

Synthesis of Iron Nanoparticles

In the process of preparation of iron nanoparticles 0.1 M aqueous of $FeCl_3$ solution and *Cinnamomum zeylanicum* powder extract, were used as precursor and reducing agent, respectively. The aqueous solution of 0.1 M $FeCl_3$ and *Cinnamomum zeylanicum* powder aqueous extract were mixed in a clean sterilized flask in 1:1 proportion (v/v) with constant stirring at room temperature for 30 mins. After the addition of the extract to the salt solution, instantaneous color change was observed. The reaction mixture was centrifuged at 10,000 rpm for 15 min. The supernatant was kept separately and the pellets were repeatedly washed with MilliQ water and ethanol and were further dried. The morphology and particle size of the synthesized iron nanoparticles was characterised by using UV-Vis absorbance spectroscopy, Scanning electron microscopy (SEM) and X-ray diffraction (XRD).

3. Results and Discussion

Color and pH change

Figure 2: Formation of Iron oxide nanoparticle; Color change from yellow to intense brown on addition of *Cinnamomum zeylanicum* powder extract to 0.1 M aqueous of $FeCl_3$ solution.

Addition of *Cinnamon zeylanicum* powder extract to 0.1 M ferric (III) chloride produced an instantaneous color change in the solution from yellow to intense brown, indicating the formation of iron-containing nanoparticles (Figure 2). Generally, the iron oxide nanoparticles have been prepared by strong hydrolysis of iron salts at elevated temperature. The plant mediated iron oxide nanoparticles was prepared at room temperature. On adding ferric chloride solution to the cinnamon extract, a change in pH was observed. The pH of *Cinnamon zeylanicum* extract changed from high acidic, 6.18 to low acidic 2.24.

Chemical constituents of Cinnamon zeylanicum for nanoparticle synthesis: Cinnamon primarily contains vital oils and other derivatives, such as cinnamaldehyde (1), cinnamic acid (2), and cinnamyl acetate (3) and eugenol (4), in combination with carbohydrates (starch and polysaccharides) (Figure 3). The presence of a wide range of essential oils, such as, L-borneol, caryophyllene oxide, b-caryophyllene, L-bornyl acetate, E-nerolidol, α-cubebene, α-terpineol, terpinolene, and α-thujene has also been reported. On analysis of the cinnamon bark it was found out that it contains 65.00 to 80.00% of cinnamaldehyde [22]. It can therefore be concluded that cinnamaldehyde plays a primarily important role in the formation of iron oxide nanoparticles.

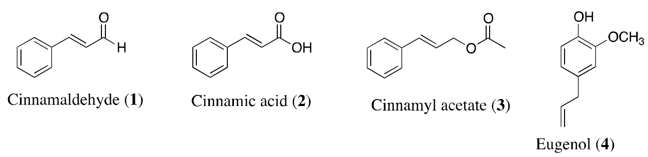

Figure 3: Chemical constituents of cinnamon.

Formation mechanism of nanoparticle

It is known that during the formation of nanoparticles, initial reduction of the metal ions leads to the formation of nucleation centers. These centres with additional metal ions incorporate neighboring nucleation sites, leading to the formation of nanoparticles. The small adjacent nanoparticles spontaneously coalesce into particles of a larger size which is accompanied by an increase in the thermodynamic stability of nanoparticles. Plant extract material is rich in compounds of different nature such as those of flavonoids, terpenoids, and many other phenolic intermediates which brings about the bioreduction of metal salt solutions and also improves particle stability. Additionally, they simultaneously act as reducing agents and capping agents.

A plausible formation mechanism of iron oxide is schematically presented in Scheme 1. We propose that ferric chloride hydrolyzes to form octahedral aqua complex of iron (III), Fe(H2O)6, and releases H+ ions. The complex instantaneously decomposes into several soluble low-molecular- weight species such as [Fe(OH2)(OH)]2+, [Fe(OH2)4(OH)2]+ via deprotonation of coordinated water molecule [22]. Next, the hydrolyzed iron species forms a complex with cinnamaldehyde. The hydrophobic part of cinnamaldehye then aggregates as shown in Scheme 1. Ferric hydroxide [Fe(OH)2]+is reduced by cinnamaldehyde of the cinnamon extract forming primary particles (Fe_2O_3) of several nanometer with organic coating. The primary particles aggregate into agglomerates in order to lower the energy associated with the large surface area to volume ratio which is further aggravated by the low surface charge. The cinnamaldehyde molecules get oxidized to cinnamic acid.

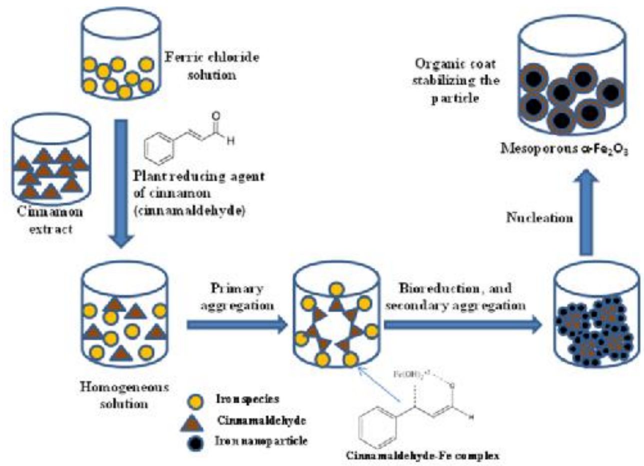

Figure 4: Plausible mechanism for the formation of hematite (α-Fe_2O_3) nanoparticles.

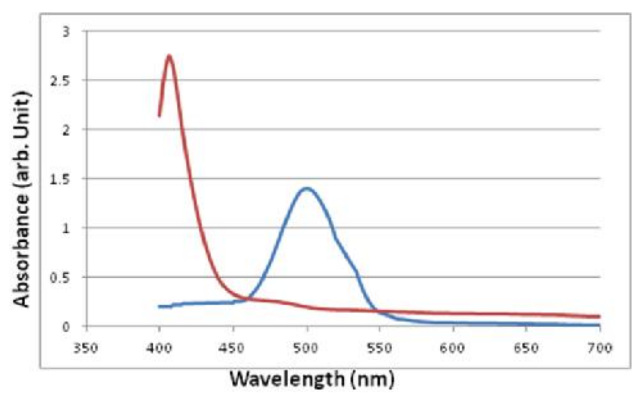

Figure 5: UV-Vis spectra of α-Fe_2O_3 (BLUE) and 0.1 M Ferric chloride solution (RED

Ultraviolet-visible spectroscopy (UV-Vis) refers to absorption spectroscopy in the UV-Visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. The bioreduction of Fe^{+3} in aqueous solutions was monitored by periodic sampling of aliquots of the mixture and subsequently measuring UV–Vis spectra. UV-Vis spectral analysis was done at the range of 300-700 nm and the absorption peak at 502 nm was observed due to the excitation of surface plasmon vibrations in the iron nanoparticles as shown in **Figure 4**. This can be assigned to the intrinsic band gap absorption of α-Fe_2O_3 due to the e-transitions from the valence band to the conduction band.

XRD Analysis of FeNPs

The nature and phase composition of FeNPs were identified by X-ray powder diffractometer with Bragg's angle ranging from 10° to 70°. Presence of diffraction peaks in XRD spectra of the sample at 2θ = 24.1°, 33.1°, 35.6°, 40.8°, 49.4°, 54.0°, 57.5° were in good agreement with the corresponding (012), (104), (110), (113), (024), (116) and (018) diffraction planes of hematite α-Fe_2O_3 (PDF Number 33-0664) (**Figure 5**).

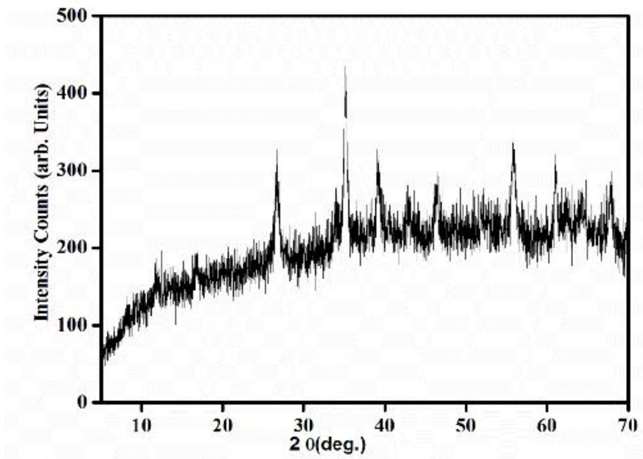

Figure 5: XRD pattern of FeNPs synthesized using *Cinnamon* extract.

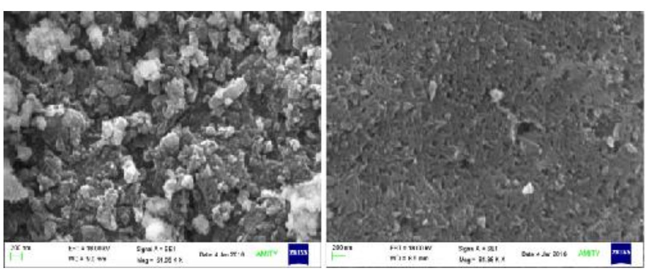

Figure 6: SEM image of FeNPs synthesized using *Cinnamon* extract.

4. Conclusion

Due to the rich biodiversity of plants, the green world has potential for the synthesis of noble metal nanoparticles. We successfully prepared αFe_2O_3 nanoparticles using cinnamon extract as the reducing and capping agent. This rapid, simple and "green" biosynthesis of iron nanoparticles is attractive as it is an alternative to chemical synthesis protocols, environmentally safe, and can produce iron nanoparticles of utility for nanotechnology applications.

5. Acknowledgements

The authors gratefully acknowledge University of Delhi for awarding the Innovation Project 2015-2016 grant.

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