Green Synthesis of Iron Nanoparticles from Long coriander (*Eryngium foetidum*) Leaves Aqueous Extract

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***Abstract**: Green synthesis method is becoming more popular as an economical, energy-efficient, low cost and environment-friendly way of synthesis of iron nanoparticles (FeNPs). In this study, the aqueous extract of Long coriander (Eryngium foetidum) leaves was used as reducing and stabilizing agents in the synthesis of FeNPs. The aqueous extract of Long coriander (Eryngium foetidum) leaves can reduce from* Fe^{3+} *into iron nanoparticle* (Fe^0) *at room temperature. The green synthesized iron nanoparticles were characterized by Scanning Electron Microscope (SEM) analysis, Energy Dispersive X-Ray (EDX) analysis, X-ray diffraction (XRD) analysis, Fourier transforms infrared (FTIR) spectroscopy analysis and UV-Visible (UV-Vis) spectroscopy analysis. The particles were identified as being on the nanoscale by SEM images and their surface morphology was revealed to be a spherical shape with a particle size range between 30-50 nm. The elemental composition of synthesized iron nanoparticles was detected by EDX spectroscopy analysis, which also revealed that the nanoparticles are primarily present in metal form. The XRD spectrum observed the crystal structure of the synthesized FeNPs and which have crystalline in nature with a size of around 43.30 nm. The FTIR spectrum exhibited different characteristic bands, which indicated the different functional groups of the active components in synthesized FeNPs. The UV-Visible observed the absorption peaks at the 250-295 nm region due to the excitation of surface plasmon vibrations of the FeNPs and the maximum peak was shown at 272 nm. The green synthesis method from synthesized FeNPs can be applied for a wide range of industrial applications.*

***Keywords:** Green-synthesis, Environment-friendly, Iron nanoparticles, Long coriander, Room temperature*

1. Introduction

Nanotechnology is one of the most rapidly increasing technologies of new development with a wide range of practical applications (Mareedu, Poiba and Vangalapati, 2020). Nanotechnology is the study of manipulating and using matter through chemical or physical techniques to produce materials with certain properties that have various applications (Subhankari and Nayak, 2013; Modi et al., 2022). It produces small structures as well as mechanized technologies that can manage the structure of materials thoroughly and cheaply. Nanomaterials have structural components and a sample of the material that is of nanometric size. The most important factor contributing to the widespread use of these nanomaterials is their high surface area-to-volume ratio (Narayanan and Sakthivel, 2010; Samarawickrama et al., 2021). The field of study of nanotechnology is rapidly expanding and it is anticipated to have wide-ranging applications in all areas of science and technology, including material science, material processing technology, mechanics, electronics, medicine, energy and aeronautics, plastics and textiles. Its wide-ranging social impact is thought to constitute a powerful incentive for a second industrial revolution (Mahmud and Nabi, 2017; Heera and Shanmugam, 2015).

Nanomaterials can be divided into three stages such as nanoemulsions, nanoclays and nanoparticles. The most fundamental part of nanomaterials is nanoparticles. Nanoparticles are made from carbon, metal, metal oxides or organic material. They can also be categorized as carbon-based nanoparticles, metal nanoparticles, semiconductor nanoparticles, polymeric nanoparticles and lipid-based nanoparticles. The nanoparticles exhibit distinct and unique physical and chemical properties at the nano-scale compared to their corresponding particles at higher scales (Saleem and Zaidi, 2020; Thiyagarajan et al., 2020). Furthermore, nanoparticles have attracted a lot of interest because of their unique chemical and physical characteristics, which make them useful in a variety of fields including medicine, chemistry, the environment, energy, agriculture, information and communication, heavy industry, and consumer goods (Thiyagarajan et al., 2020; Amjad et al., 2021).

The chemical and physical processes were frequently used to create nanoparticles and they are suitable for the creation of nanoparticles of different sizes and shapes. Chemical reduction, microemulsion, and electrochemical thermal breakdown are three chemical processes used to make nanoparticles. Similar to that, pulse laser, ball milling, chemical vapour deposition, microwave irradiation and gamma radiation are physical processes used to create nanoparticles. These technologies require extreme circumstances such as high temperature and high pressure, resulting in hefty upfront costs (Dhingra et al., 2010; Tyagi et al., 2021). Hence, there is an increasing need to discover toxic-free, highly effective, non-expensive and environmentally friendly synthesis methods of nanoparticles. Thus, the field of green nanotechnology came into the nanoparticle synthesis procedure (Senapati et al., 2005; Rai et al., 2021). Green synthesis is a function that uses natural extract from plant materials such as leaves, flowers, and seeds to replace the reducing agent (Da'na, Taha and Afkar, 2018; Shankar et al., 2004). The green synthesis of nanoparticles does not require high pressure, energy and temperature conditions and toxic chemicals. This method is the most suitable method for synthesizing metal nanoparticles using plant component extracts (Saranya, Vijayarani and Pavithra, 2017; Wang, Zhao and Tan, 2008).

Iron nanoparticles (FeNPs) have been used for this study as iron metal which is a non-toxic, easily produced, eco-friendly and less expensive metal nanoparticle type. FeNPs are used in medical, waste-water treatment, coatings and textile applications, etc. (Saif, Tahir and Chen, 2016; Silalahi et al., 2021). The iron nanoparticles (FeNPs) were created using a green synthesis method employing an aqueous extract of long coriander leaves (*Eryngium foetidum*) as the reducing agent. The long coriander (*Eryngium foetidum*) plant is native to South America and is grown in low wetlands in Sri Lanka. It is found on grassland or cultivated as a plant in home gardens. It is also used for snakebite in Ayurveda medicine and some individuals grow the plants near their homes because they believe they are effective snake repellents and especially for cobras. (Silalahi et al., 2021; Paul, Seaforth and Tikasingh , 2011). The synthesized FeNPs were characterized by using Scanning Electron Microscope (SEM) analysis, Energy Dispersive X-Ray (EDX) analysis, X-ray diffraction (XRD) analysis and UV-Visible Spectroscopy (UV-Vis) analysis.

2. Materials and Methods

A. Collection of the Plant and Chemical Materials

Fresh long coriander (*Eryngium foetidum*) leaves (Figure 1) were collected from a village area in Matugama, Sri Lanka. Ferric chloride hexahydrate ($FeCl_3.6H_2O$) under the SRL (Indian) brand was used as the source of iron (Fe), which was obtained from a local chemical supplier in Sri Lanka. The experiment used analytically graded chemicals which could be utilized without any additional purification.

B. Preparation Method of Aqueous Extract of the Long coriander (Eryngium foetidum) Leaves

The collected leaves were washed several times using water to remove the dust and other particulate matter. The clean leaves were shade dried for a few days and finely crushed using a mortar and pestle. To make the plant extract, the crushed leaves from 20 g were mixed with 200 ml distilled water (MLR-1:10) and the mixture was heated at 70 ºC for 60 minutes. The mixture is then brought to room temperature and filtered. For further studies, the extract was kept at 16 ºC temperature.

Figure 1. Long coriander (*Eryngium foetidum*) leaves

C. Synthesis Process of Iron Nanoparticles

The long coriander (*Eryngium foetidum*) leaves extract was mixed with 0.1M of ferric chloride ($FeCl_3.6H_2O$) solution in a volume ratio of 1:2 at room temperature. The resultant mixture was stirred using a magnetic stirrer at 300 rpm for 60 minutes and the formation of an intense black-coloured solution confirmed the synthesis of iron nanoparticles. The mixture was centrifuged at 6000 rpm for 15 minutes and separated the FeNPs to precipitate (the process was done by 2 or 3 times) The supernatant was discarded and a dialysis membrane was used to dialyze pellets 2-3 times with distilled water. Eventually, the FeNPs were dried at 50°C in a vacuum oven and stored in a seal-tight container for further use.

D. Characterization Process of Iron Nanoparticles

1). SEM and EDX characterization:

The surface morphology and structure of synthesized iron nanoparticles were examined using scanning electron microscopy (SEM) analysis (Carl Zeiss eco 18 Research, Germany). Images of samples were recorded at different magnifications using an operating voltage of 10 kV. Information on the elemental composition of synthesized iron nanoparticles was determined by Energy Dispersive X-Ray (EDX) analysis (EDAX element detector, USA) attached to the SEM.

2). XRD Characterization:

X-ray diffraction analysis of Iron nanoparticles was conducted using Rigaku Ultima IV X-Ray Diffraction Spectrometer with Cu Kα radiation source (λ= 0.154 nm) and operated at 40 kV/30 mA. The diffraction pattern was obtained at the diffraction angle 2θ in the range of 10°– 60° at a scan speed of 2°/min. Crystallite size was calculated using the Scherrer Equation of $CS= K\lambda/\beta \cos \theta$, where CS is the crystallite size, constant K = 0.94, $\lambda = 1.5406\times10^{-9}$, β = Full width at half maximum (FWHM) (β=FWHM × π/180) and Cosθ=Bragg angle (Shobha, Moses and Ananda, 2014).

3). FTIR characterization:

Fourier transforms infrared spectroscopy was used to characterise functional group analysis of the sample. This characterization for used the Thermo Scientific Nicolet IS5-ATR (Attenuated Total Reflectance) FTIR spectrometer. The IS5-ATR type FTIR consisted of a single bounce diamond crystal allowing the collection of the IR spectrum directly from the sample. The iron nanoparticles sample was placed directly on the ATR diamond crystal and pressure was applied by lowering the tip of the pressure clamp using a ratchet-type clutch mechanism. The FTIR spectrum of the iron nanoparticles sample was measured in the range of 400 to 4000 cm^{-1} in transmission mode.

4). UV-Vis Characterization:

UV-visible absorption spectroscopy was employed to analyse the optical properties of the synthesized iron nanoparticles. A Thermo scientific genesis 10S series type UV Visible spectrophotometer was used to analyse the absorbency spectrum in the wavelength of 200-800 nm.

3. Results and Discussion

A. Visual Inspection of Iron Nanoparticle Formation

0.1M Ferric Chloride ($FeCl_3 \cdot 6H_2O$) aqueous solution (Figure 2) was mixed with the aqueous extract of long coriander (*Eryngium foetidum*) leaves (Figure 3), which was used to synthesize FeNPs. The colour of the mixture (0.1 M Ferric Chloride solution with aqueous extract of long coriander leaves) changed from reddish-brown to dark black at room temperature. Figure 4 shows the successfully synthesized FeNPs solution. Figure 5 illustrates the successful separation of iron nanoparticle powder from the nanoparticle solution after the centrifuged and drying procedures.

Figure 2. 0.1M Ferric chloride solution

Figure 3. Aqueous extract of long coriander leaves

Figure 4. Synthesized Iron nanoparticles solution

Figure 5. Synthesized iron nanoparticles powder

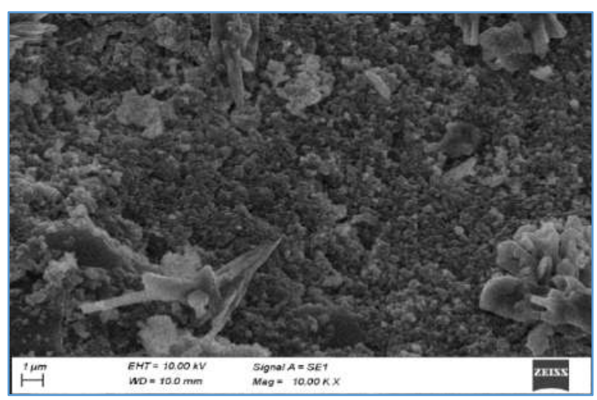

Figure 6. SEM image of synthesized iron nanoparticles at 10 kx times magnification

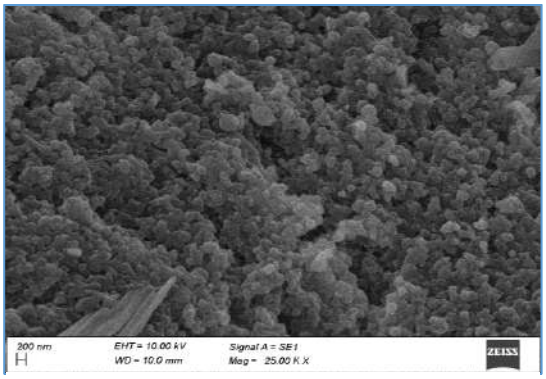

Figure 7. SEM image of synthesized iron nanoparticles at 25 kx times magnification

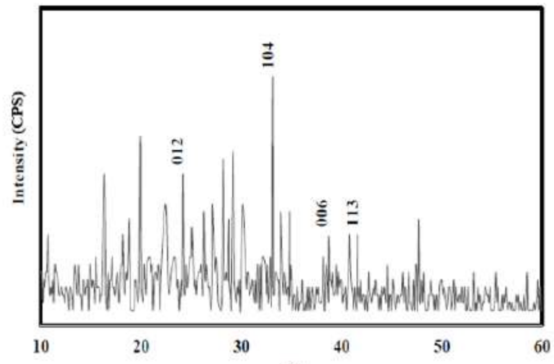

Figure 9. XRD spectrum of synthesized iron nanoparticles

B. SEM and EDX Analysis of Iron Nanoparticles

The SEM images of synthesized iron nanoparticles were provided with a 10 kx times magnification (Figure 6) and 25 kx times magnification (Figure 7). It indicates that nanoparticles formed are agglomerated due to their adhesive nature having a morphology of spherical shapes appearance with the particle size range between 30-50 nm. The EDX analysis determined the elemental composition of FeNPs that were synthesized using the aqueous extract of long coriander leaves as a reducing agent. The EDX diagram is shown in Figure 8. EDX qualification gives atomic percentages of 9.82% of iron, 44.77% of carbon, 41.71% of oxygen, 0.68% of phosphorous, 0.97% of sulphur, 1.02% of potassium and 1.03% of calcium.

C. XRD analysis of Iron Nanoparticles

The XRD spectrum of synthesized iron nanoparticles which were extracted using long coriander leaves is depicted in Figure 9. The XRD spectra display prominent peaks of 24.14°, 33.14°, 39.28° and 40.86° corresponding to the phase planes of 012, 104, 006 and 113. These values have established the characteristics of the crystalline metallic iron phase. Characteristics peak for iron nanoparticles have been observed at $2\theta = 33.14°$ (Figure 9). This broadened diffraction peak suggested that the resultant nanoparticles are crystalline in nature with a size around 43.30 nm as calculated by the Scherrer equation.

D. FTIR spectrum analysis of iron nanoparticles

Figure 10 shows the FTIR spectrum of the synthesized FeNPs using long coriander leaves aqueous extract as the reducing agent. The spectrum peak at 3302 cm^{-1} corresponds to the O-H group of intermolecular bonded stretching in alcohol (Da'na, Taha and Afkar, 2018). The spectrum broad peak at 1622 cm^{-1} was attributed to the carbonyl group (C=O) (Majumdar, Bag and Maity, 2013). The presence of a broad peak at 1539 cm^{-1} was attributed to the alkene group (C=C) (Madivoli et al., 2019). The formation of FeNP is characterized by a spectrum peak at 612 cm^{-1} which corresponds to the stretching of Fe-O bonds of iron oxide (Kumar et al., 2014).

E. UV Visible absorption analysis of iron nanoparticles

The UV Visible spectra of the long coriander leaf extract from the green synthesis of FeNps in aqueous solutions were measured. The UV Visible spectral analysis was done within the 200-800 nm range and observed the absorption peaks at the 250-295 nm region due to the excitation of surface plasmon vibrations in the iron nanoparticles. The maximum peak was observed at 272 nm, which is identical to the characteristics UV visible spectrum of iron nanoparticles and it was recorded (Pattanayak and Nayak, 2013). The room temperature UV Visible absorption spectrum of the FeNPs nanoparticles is shown in Figure 11.

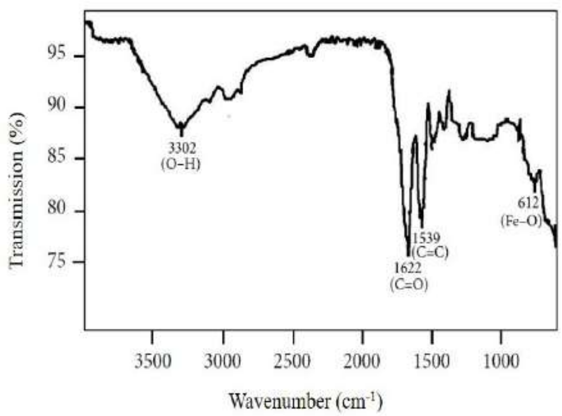

Figure 10. FTIR spectrum of the synthesized iron nanoparticles

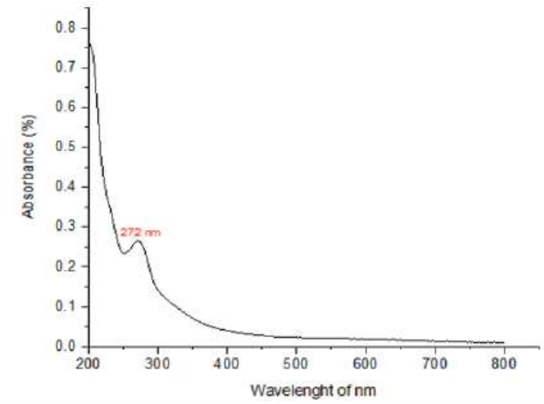

Figure 11. UV Visible spectrum of synthesized iron nanoparticles

4. Conclusion

Long coriander (Eryngium foetidum) Leaf Extract was utilized as a reducing and stabilizing agent for the synthesis of iron nanoparticles (FeNPs). Multiple characterization procedures such as SEM, EDX, XRD, FTIR and UV-Vis were employed to confirm the formation of FeNPs. The SEM imaging reveals that FeNPs tend to aggregate into spherical shapes appearance with a particle size range between 30-50 nm. The EDX analysis showed the presence of elemental iron and indicated that the nanoparticles are essentially present in metal form. The characteristic crystalline metallic iron phase of synthesized FeNPs was identified using the XRD spectrum and crystallite size around the size of 43.30 nm. The FTIR spectroscopy measurement was carried out to identify the possible functional groups like O-H, carbonyl (C=O) and alkene (C=C) in different peaks. The FTIR spectrum characteristic peak at 612 cm^{-1} indicated the stretching of Fe-O bonds of iron oxide. Using the UV-Vis spectral analysis, the absorption peaks were observed at the 250-295 nm region and the maximum peak was observed at 272 nm, which is identical to the characteristics of the UV visible spectrum of synthesized FeNPs. These results verify that the aqueous extract of long coriander (*Eryngium foetidum*) leaves can be used to synthesise iron nanoparticles as a reducing agent. The green synthesis method is a natural, fast, eco-friendly and cost-effective method of synthesis of metal nanoparticles.

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