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Biosynthesis of Magnetite (Fe_3O_4) Nanostructures using *Vernonia Amygdalina* Leaves Extract

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Abstract: An eco-friendly biosynthesis route was employed to synthesize magnetite nanostructures using *Vernonia amygdalina* leaves extract as a reducing and chelating agent and ferric nitrate nonahydrate precursor at ambient conditions. The desired phase formation and crystal structure of the synthesized nanostructures were in cubic face-centered as confirmed by X-ray diffraction analysis. Morphological properties were studied by scanning electron micrograph, and it showed that nanostructures were synthesized. Ultra-violate visible spectrometer was used to study the optical properties, and ultra-violate visible analysis revealed that spectral absorption band occurred at about 396 nm, which is a characteristic feature of iron oxide. From the Fourier-transform infrared spectrometer analyses of functional groups, the appearance of peaks at 561 cm^{-1} and 461 cm^{-1} also corroborate the formation of Fe_3O_4 nanostructures.

Keywords: biosynthesis; nanostructures; *Vernonia amygdalina;* magnetite.

1. Introduction

Iron exists in more than a dozen of oxidation states in nature [1]. The commonly known iron oxides hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), and magnetite (Fe_3O_4) are promising candidates for various technological applications due to their polymorphism involving temperature-dependent phase transition [2]. As a result of its hydrophilic and biocompatibility properties, Fe_3O_4 has received enormous attention for various applications such as wastewater treatment, pigment, magnetic resonance imaging, and biomedical applications [3-6]. However, due to its thermodynamic instability, there is a limitation in the technological applications of Fe_3O_4 [7]. Fe_3O_4 possesses an inverse spinel structure with the Fe^{3+} ions distributed randomly between octahedral and tetrahedral sites and the Fe^{2+} ions occupying the octahedral sites [6].

Now a day, several synthetic methods such as co-precipitation [7-9], thermal decomposition [3], hydrothermal [5, 10, 11], sol-gel [12], micro-emulsion [13], sonochemical synthesis [14], microwave combustion [15] and biological synthesis [1, 16] have been employed to produce Fe_3O_4 nanostructures. Among these, nanostructures' biosynthesis is an alternative compared to conventional methods since it is non-toxic, eco-friendly, and can control the size and shape of synthesized nanoparticles [17, 18]. For instance, magnetite iron oxide nanoparticles were successfully synthesized using an aqueous extract of spent tea waste as a reducing agent [19]. Similarly, magnetic iron oxide nanoparticles with an average crystallite size of 18 nm were synthesized from *Sargassum muticum* aqueous extract as a

reducing agent [20]. Nano-sized iron particles were also successfully synthesized using leaf extract of Mint (*Mentha spicata L.)* plant [21]. In the present study, we used *Vernonia amygdalina* (*V. amygdalina)* leaves aqueous extract to successfully synthesize magnetite nanostructures.

V. amygdalina is a small shrub, three-five meters tall, mostly distributed in tropical Africa [22-24]. The plant is commonly called *bitter leaf* due to its bitter taste [23]. *V. amygdalina ('Grawa'* in Amharic, Ethiopia) is known for its high production, adaptability, and its ability to improve the soil fertility for better crop production [25]. In the rural highlands of Ethiopia, the water extract of *V. amygdalina* leaves serves as a tonic drink for the prevention of stomach-ache. It exhibits excellent antioxidant property [24], and this has been reported in an attempt to synthesize NiO nanoparticles [26].

2. Materials and Methods

2.1. Materials.

Analytical grade reagents such as ferric nitrate nonahydrate ($Fe(NO_3)_3$•$9H_2O$, 97% purity) were used in this experiment. Fresh, matured, and healthy *V. amygdalina* leaves were gathered from Debre Birhan town, North Shoa, Ethiopia. Taxonomically authenticated *V. amygdalina* leaves were thoroughly washed with tap water followed by distilled water for removing unwanted impurities such as dust and scum. The leaves were dried at room temperature for a couple of weeks, cut into small pieces, and kept in a tight plastic bag till the experiment.

2.2. Methods.

Weighed 10 gm of the dried leaves were added into 200 mL of deionized water and boiled at 80 ℃ for about 60 minutes to obtain the aqueous extract (Figure 1a). After cooling down to room temperature, it was filtered using Whatman No.1 filter paper, and the filtrate was stored in a refrigerator at 4 ℃ for further experiments. On the other hand, 0.1M solution of Fe $(NO_3)_3$•$9H_2O$ was prepared by dissolving 4 g of Fe $(NO_3)_3$•$9H_2O$ salts in 100 mL deionized water while stirring for about 15 minutes (Figure 1b).

In a typical experiment, *V. amygdalina* plant leaves extract was added to the 0.1M Fe $(NO_3)_3$•$9H_2O$ solution in 1:2 ratios by volume until the mixture reaches light black in color.

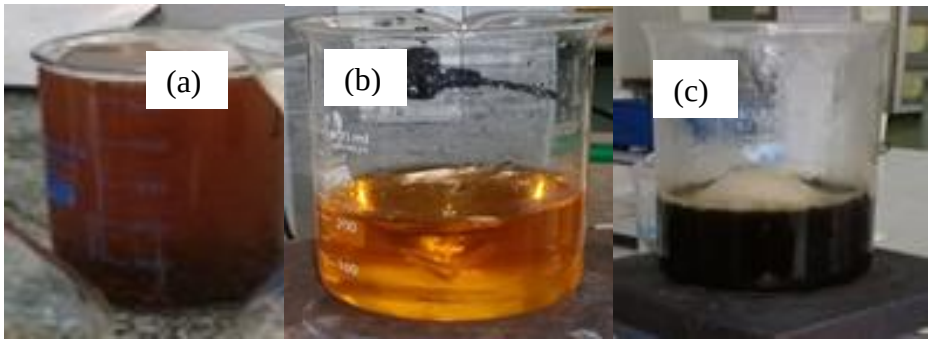

Figure 1. Synthesis procedure of Fe_3O_4 nanostructures. (**a**) *V. amygdalina* extract; (**b**) precursor solution; (**c**) *V. amygdalina* extract + precursor solution.

The resulting mixture was continuously stirred for about 30 min at 50 ℃ until the solution changes from light black to brownish-black color, revealing the formation of iron

oxide nanostructures (Figure 1c). The solution was then cooled down to room temperature and centrifuged at 3000 rpm for 10 minutes three times, and the precipitates were collected on a Petri dish and oven-dried at 100 °C. Finally, the nanopowder was collected and calcined in an air furnace at 450 °C for 6 hours to get the black iron oxide nanostructures.

3. Results and Discussion

Morphological studies of the biosynthesized Fe_3O_4 nanostructures were confirmed by an X-ray diffractometer (XRD) (Bruker D8 ADVANCED Diffractometer). The XRD patterns of all randomly oriented powder specimen were recorded in the 10° to 80° with 2θ angles using CuKα (λ = 0.15064 nm) whose operating voltage is 40 kV and current of 30 mA with a step size of 0.02°. The XRD peaks for the sample at 18.5°, 30.36°, 35.76°, 43.47°, 53.81°, 57.50°, 63.16°, 66.23°, 71.52°, 74.75°, and 75.77° with the miller indices (111), (220), (311), (400), (422), (511), (440), (531), (442), (620) and (533), respectively, were well matched with JCPDS no. 00-900-5841 and confirmed that the Fe_3O_4 nanostructures were in a face-centered cubic structure. The average crystallite size (D) of Fe_3O_4 is determined from the prominent diffraction peaks at (311) using Scherer's equation to be 5 nm.

$$D = \frac{0.9\lambda}{\beta \cos\theta}, \qquad (1)$$

where 'D' is the crystallite size,' k' is the shape factor = 0.9, 'λ' = 0.15406 nm is the x-ray wavelength, 'β' is the full width broadening at half maximum intensity (FWHM) in radians, and 'θ' is the Bragg diffraction angle in radians. Powder XRD patterns of the as-synthesized Fe_3O_4 nanostructures are matched with the standard XRD file of Fe_3O_4, as shown in Figure 2.

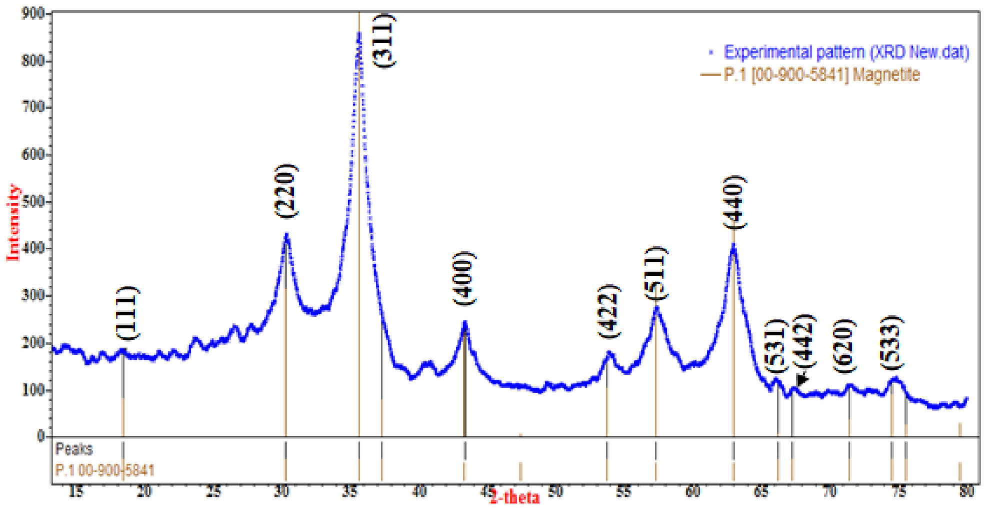

Figure 2. XRD patterns of Fe_3O_4 nanostructures synthesized using *V. amygdalina* leaves extract.

The presence of functional groups responsible for the reduction and stabilization of the Fe_3O_4 nanostructures was confirmed by Fourier transform infrared (FTIR) spectrometer [27]. For FTIR spectral analysis, the as-synthesized powder of Fe_3O_4 was mixed with KBr to prepare pellets that suit the Perkin Elmer 65 instrument, and values were recorded in the wavenumber range of 400−4000 cm^{-1}. Figure 3a shows the FTIR spectrum of *V. amygdalina* plant leaves extract, and the broad absorption band from 3626 cm^{-1}−3175 cm^{-1} is related to the O−H bond stretching of the phenolic group; the peak at 2082 cm^{-1} is related to the C-H bending, and the

peak 1638 cm^{-1} is related to the N−H bending [2, 28]. Figure 3b shows the FTIR spectrum of the as-synthesized iron oxide nanopowder. The broadband at 3394 cm^{-1} and 1627 cm^{-1} corresponds to the –OH stretching and bending vibration of water molecules, respectively [7, 15]. The peak at 2916 cm^{-1} corresponds to C−H stretching vibration, and the band at 1394 cm^{-1} indicates C−O bending vibration mode [15]. The peaks at about 561 cm^{-1} and 461 cm^{-1} are due to the Fe-O bond and confirm the formation of spinel-type Fe_3O_4 [7, 15].

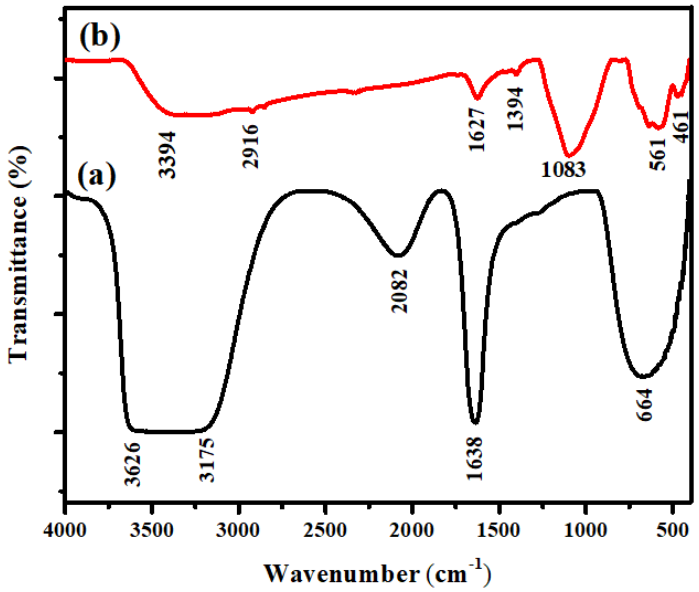

Figure 3. FTIR spectrum of (**a**) *V. amygdalina* leaves extract; (**b**) synthesized Fe_3O_4 nanostructures.

The synthesized nanostructures were characterized using a UV−Visible (UV−Vis) spectrophotometer working at a wavelength range of 200−900 nm to study the optical properties.

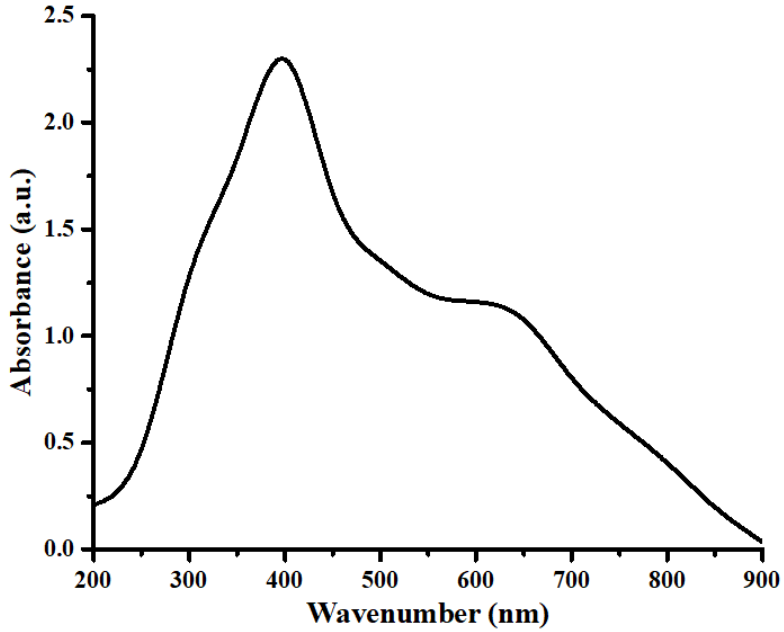

Figure 4. UV−Vis absorption spectra of Fe_3O_4 nanostructures.

The absorption in the visible range of the electromagnetic spectrum affects the perceived color of the chemicals involved. The UV−Visible spectrum of Fe_3O_4 nanostructures synthesized by the extract of *V. amygdalina* leaves is shown in Figure 4. The UV−Vis

spectroscopic study shows the plasmonic resonance property resulting from electronic transitions of molecules and confirmed the reduction of metal ions and formation of Fe_3O_4 nanostructures with a sharp peak at 396 nm [20].

Scanning electron micrograph (SEM) image of the synthesized Fe_3O_4 nanostructures was recorded using JSM−IT 300 LV. The morphology of the as-synthesized Fe_3O_4 using *V. amygdalina* plant extract looks like flakes, as shown in Figure 5. Although XRD analysis shows a face-centered cubic structure, SEM observation does not confirm the cubic structure, which implies that optimization of the work is significant.

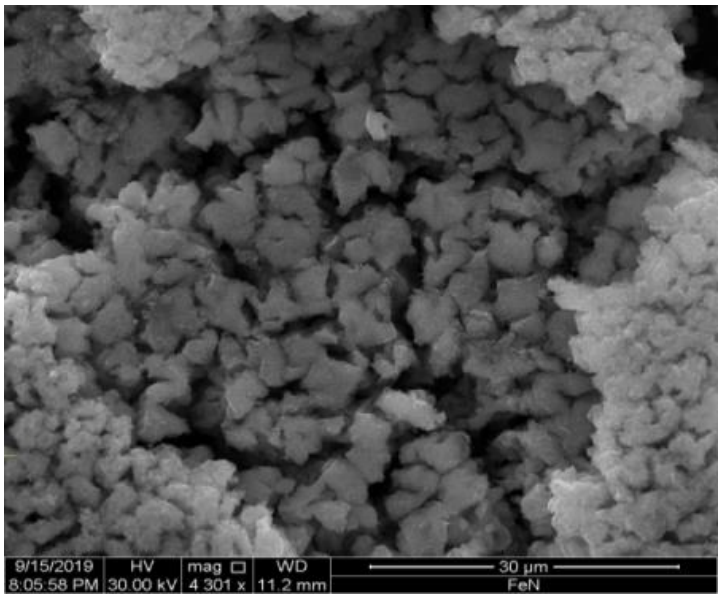

Figure 5. SEM images of Fe_3O_4 nanostructures.

4. Conclusions

Fe_3O_4 nanostructures were successfully synthesized using leaves extract of *V. amygdalina* as reducing and chelating agents at ambient temperature and pressure conditions. Powder XRD patterns revealed the formation of a cubic-face-centered spinel structure. FTIR peaks at 561 cm^{-1} and 461 cm^{-1} also support the formation of Fe_3O_4 nanostructures. The UV−Vis spectral absorption band at 396 nm is characteristic of the iron oxide, further affirming Fe_3O_4 nanostructures' formation. SEM image analysis showed that magnetite (Fe_3O_4) nanostructures were successfully synthesized.

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Conflicts of Interest

The author declares no conflict of interest.

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