Synthesis of Iron Oxide Nanoparticles by Using Eucalyptus Globulus Plant Extract*

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Iron oxides have attracted a great deal of attention among specialists because of their multivalent oxidation states. The \( \beta \)-iron oxide nanoparticles have been synthesized by adding a Eucalyptus globulus leaf extract into the aqueous solution of ferric chloride. The synthesized nanoparticles were characterized by Ultra Violet - Visible spectrum (UV-Vis), X-Ray diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), and Fourier Transform Infra Red spectroscopy (FT-IR). TEM and SEM image shows the nanostructures of prepared iron oxide nanoparticles. The XRD and UV-Vis spectrum confirmed the prepared iron oxide nanoparticles \( \beta \) in phase. [DOI: 10.1380/ejssnt.2014.363]

Keywords: Iron oxide; SEM; X-ray diffraction; Visible/Ultraviolet absorption spectroscopy; Nano-particles

I. INTRODUCTION

The development of nanotechnology is not only for their fundamental scientific interest, but also for offering many technological solutions. Oxides of iron are available widely in nature in different phases [1]. Additionally, iron oxides have attracted a great deal of attention among specialists because of their multivalent oxidation states [2], a large set of possible polymorphisms [3], and especially at the nano scale, their characteristic structural changes [1]. These materials have a considerable potential to be applied as sensors, in catalysis [4], as high-density magnetic recording media [5], for targeted drug delivery in clinical trials [6], and as substrates in cancer treatment methods [7]. Iron oxides are relatively inert, non-toxic, and present in living organisms [1]. Iron oxide nanoparticles play an important role in environmental remediation circles. As it removes both of organic and inorganic heavy metal pollutants from polluted water [8]. There are several chemical and physical methods available for synthesis of iron oxide nanoparticles. Those methods are used toxic or potentially hazardous as starting materials and more energy. However, it is still a big challenge to develop simple and reliable synthetic method for low-dimensional iron oxide nanostructures. The primary goal of nanotechnology is to improve simple eco-friendly method for synthesis of nanoparticles. The biomaterial such as microbes and plant extract can be used to prepare various types of nanoparticles and even nanorods. However, as some organisms are pathogens, it is risky to handle. Microorganisms need maintenance of culture and controlled conditions such as temperature, pH and other factors for growth. Sometimes, the synthesis of nanoparticles utilizing plant parts could prove advantageous over other biological processes by eliminating the elaborate process of maintaining the microbial culture. Synthesis of iron oxide nanoparticles by using plant extract has been quite limited and few works have been reported. The reports are available for synthesis of hexagonal metallic iron, amorphous iron, and \( \alpha \)-Fe\(_2\)O\(_3\) by using tea extract [9, 10] and iron nanoparticles by using Aqueous Sorghum Bran Extracts [11]. The tea extract mediated synthesized iron nanoparticles were found to be nontoxic when compared with iron nanoparticles prepared using conventional NaBH\(_4\) reduction protocols. The concentration of the tea extract in the reaction mixture plays an important role in the size and crystallinity (hexagonal metallic iron, amorphous iron, and R-FeO\(_3\)) of the synthesized iron nanoparticles [9]. In this study iron oxide nanoparticles were synthesized using a rapid, single step, and completely green biosynthetic method employing aqueous Eucalyptus globulus leaf (Family: Myrtaceae) extracts as both the reducing and capping agent. Eucalyptus globulus essential oil shows higher medicinal property and antimicrobial potential against the range of food spoiling microorganisms and it contain 1,8-cineole (45.4%), limonene (17.8%), p-cymene (9.5%), \( \gamma \)-terpinene (8.8%), \( \alpha \)-pinene (4.2%) and \( \alpha \)-terpineol (3.4%), while in the vapour, 1,8-cineole (34.6%), limonene (29.9%), p-cymene (10.5%), \( \gamma \)-terpinene (7.4%), \( \alpha \)-pinene (4.0%) and \( \alpha \)-phellandrene (2.4%) [12]. Green synthesis of iron oxide nanoparticles is being evolved as a method that would impart more stabilization of iron nanoparticles against aggregation and

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FIG. 1. Digital photograph of visible color changes, after adding the *Eucalyptus globulus* leaf extract into an aqueous Ferric chloride.

help overcome the other synthesis method so far. To the best of our knowledge, this is the first report of synthesis iron oxide nanoparticles by using *Eucalyptus globulus* leaf extract.

II. MATERIALS AND METHODS

A. Materials

Iron (III) chloride/ Ferric chloride (FeCl$_3$) analytical grade was purchased from Merck & Co. and used without further purification. Double distilled deionised (DI) water was used throughout the course of this investigation. A solution of FeCl$_3$ (0.01 M) was prepared by dissolving the solid FeCl$_3$ in DI water. The PP plant parts were freshly harvested from local agricultural land, Tamilnadu, India.

B. Preparation of *Eucalyptus globulus* leaf extract

The fresh *Eucalyptus globulus* leaf was collected and washed thoroughly to remove the adhering soil and dust and heated 100 g/L fine piece of leaves at 80°C for 30 min followed by filtering through filter paper to separate out the broth. The pH of the extract was 4.10. The extract was stored at 4°C for further experiments.

C. Synthesis of iron oxide nanoparticles

In the typical synthesis of Iron oxide, the above-prepared *Eucalyptus globulus* leaf extract was used in order to reduce and cap the Fe ions. 20 ml of the above-prepared *Eucalyptus globulus* leaf extract was dripped slowly into the aqueous solution of FeCl$_3$ with constant stirring at room temperature with normal atmosphere pressure. After adding the *Eucalyptus globulus* leaf extract into FeCl$_3$ solutions within 3 mins a visible color changes were observed, the yellow color aqueous solution of FeCl$_3$ turned to greenish black (Fig. 1).

D. Characterizations

1. UV-Visible Spectroscopy

The surface Plasmon resonances (SPR) of synthesized iron oxide nanoparticles have been studied by UV-Vis double-beam bio-spectrophotometer ELICO-BL-198 using the software SPECTRAL TREATS VERSION 2.37.4 REL-1. After the addition the *Eucalyptus globulus* leaf extract into the aqueous solution of FeCl$_3$, the solution was filled in glass cuvette of path length 10mm and UV-Vis spectral analysis has been done in the range of 300 to 700 nm. DI water was used as blank.

2. Powder X-Ray diffractometry study

The synthesized iron oxide nanoparticles were dried at 50°C to carry out the XRD studies. The diffraction pattern was recorded by SEIFFERT. RAYFLEX SOFTWARE which provides control modules for the complete range of diffractometer accessories together with the corresponding analysis software. XRD with Cu-Kα radiation ($\lambda = 1.540598$ Å).

3. Scanning electron microscopy with energy-dispersive X-ray spectroscopy

The morphology of the samples was analyzed through Quanta-200F SEM. The double side carbon tape was fixed on acetone clean polished aluminium (10 mm × 10 mm × 5 mm) piece. The samples were spread in the middle of carbon tape and pressure was applied with butter sheet and was blown to remove free particles. The samples were kept in a vacuum chamber for 1h and were loaded in SEM instrument. Inorganic metals presented with samples identified by EDS characterization.

4. Transmission electron microscopy

The samples were analyzed by TEM to determine the size and morphology of the particles. TEM analysis was done using a JEOL-JEM-2100F (FE-TEM). The samples for HR-TEM was prepared by putting one drop of the prepared solution onto standard carbon coated copper grids and drying under atmospheric air. The size and morphology of nanoparticles were examined.

5. Fourier transform infrared spectroscopy study

The prepared iron oxide nanoparticles were then subjected to FT-IR spectroscopy measurements. It was recorded by using a Thermo Scientific, Nicolet 10 using a KBr pellet technique. It was used to identify the possible biomolecules responsible for the reduction and capping of the nanoparticles, which is present in the *Eucalyptus globulus* leaf extract.

III. RESULTS AND DISCUSSIONS

In the typical synthesis of Low dimensional iron oxide nanoparticles *Eucalyptus globulus* leaf extract was added slowly into FeCl$_3$ solutions at room temperature. After adding within 3min a visible color change was observed,
that the yellow color aqueous solution of FeCl$_3$ turned to greenish black (Fig. 1). The intensity of color increased with time and dosage of plant extract (Fig. 1) it indicates the more growth of nanoparticles. The color change is the most easy and commonly used indication of the metal nanoparticles formation [13]. This procedure results is a reproducibly high yield about 83% of stable iron oxide nanoparticles. Generally, the iron oxide nanoparticles have been prepared by strong hydrolysis of iron salts at elevated temperature [14]. The plant mediated iron oxide nanoparticles was prepared at room temperature. The plant extracts contained much organic content. Hence the mechanism study of iron oxide nanoparticles formation is a little difficult. However, the organic compound, which is present in the plant extracts act as a reducing as well as capping or binding agent to form iron oxide nanoparticles.

The optical property of synthesized iron oxide nanoparticles is one of the important characteristics for evaluation of its optical and photo catalytic activity. UV-Visible absorption spectrum is the preliminary characterization to know the optical property. Figure 2 shows the UV-Vis spectrum of 100 ml of FeCl$_3$ (0.01 M) and 20 ml of *Eucalyptus globulus* leaf extract mixture. It shows an absorption maximum ($\lambda_{\text{max}}$) peak around 402 nm indicating the formation of low dimensional $\beta$-Fe$_2$O$_3$. The $\beta$-Fe$_2$O$_3$ was one of the polymorphs of iron (III) oxides discovered by Bonnevie-Svendsenat in 1956 [15]. The absorption maximum of prepared nanoparticles is quite different to $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ [16]. The UV-Vis represents the formation of $\beta$-Fe$_2$O$_3$.

The Structural characterization of the material was performed by using Powder X-Ray diffraction (XRD) analysis. Figure 3 shows the XRD pattern of Iron Oxide nanoparticles prepared by using *Eucalyptus globulus* leaf extract. All the diffraction peaks in this pattern were found to be in good agreement with JCPDF No. 089-2810, which is corresponding to $\beta$-Fe$_2$O$_3$ in rhombohedral geometry. The sample showed the major characteristic peaks for prepared crystalline metallic nanoparticles at 2$\theta$ values of 24.2, 33.1, 35.7, 40.9, 49.4, 54.1, 57.6, 62.6, and 64.0 degrees corresponding to (012), (104), (110), (113), (024), (116), (018), (214), and (300) respectively. An additional
peak observed at 2θ values of 45.5 is corresponding to (332). It might be due to the presence of trace amount of hollow \( \beta\)-Fe\(_2\)O\(_3\) nanoparticles [17]. It indicates that the prepared iron oxide nanoparticles are well crystalline \( \beta\)-Fe\(_2\)O\(_3\).

The prepared iron oxide nanoparticles were analyzed by Scanning Electron Microscopy (SEM) with Energy-dispersive X-ray spectroscopy (EDX) to know the morphology and atomic percentages. Figure 4 shows the SEM image of \( \beta\)-Fe\(_2\)O\(_3\) nanoparticles prepared from 100 ml of 0.01 M aqueous FeCl\(_3\) solutions with 20 ml of eucalyptus leaf extract. SEM image shows the clear morphology of \( \beta\)-Fe\(_2\)O\(_3\) nanoparticles. The SEM also reveals that nanoparticles are agglomerated. Energy-dispersive X-ray spectroscopy is an analytical technique used for the elemental analysis. The EDX spectrum (Fig. 5) contains intense peaks of Cl and C in addition to Fe and O. The Cl signals must be originating from FeCl\(_3\) precursors used in the synthesis protocol. The C signals are attributed mainly to organic molecules in the Eucalyptus globulus leaf extracts. The atomic percentages obtained from EDX quantification were 48.98% of O, 8.83% of Fe, 36.77% of C and 5.42% of Cl. These values could be helpful in reflecting the atomic content on the surface and near surface regions of the NPs.

In addition, the iron oxide nanoparticles were analyzed by Transmission Electron Microscopy. Figure 6 shows the TEM image of \( \beta\)-Fe\(_2\)O\(_3\) nanoparticles prepared from 100 ml of 0.01 M aqueous FeCl\(_3\) solutions with 20 ml of eucalyptus leaf extract. TEM image reveal that the \( \beta\)-Fe\(_2\)O\(_3\) nanoparticles have the average core diameter of 100 nm and the nanoparticles are agglomerated and cluster. The aggregation may be due to a magnetic property of iron oxide nanoparticles. Iron oxide nanoparticles have a large surface to volume ratio and therefore possess high surface energies. Consequently, they tend to aggregate so as to minimize the surface energies [18].

Figure 7 shows the FT-IR spectrum of prepared iron oxide nanoparticles. It displays three strong bands around 3449 cm\(^{-1}\) (br), 1637 cm\(^{-1}\) and 544 cm\(^{-1}\). The observed bands are similar to those reported for \( \beta\)-Fe\(_2\)O\(_3\) [19]. The vibration bands are 544 cm\(^{-1}\) (Fe–O str), 1637 cm\(^{-1}\) (H\(_2\)O bending vibration) and a broad peak at 3448 cm\(^{-1}\) (H\(_2\)O str). Presence of organic molecule on the surface of iron oxide nanoparticles has the influence on the FT-IR peaks [20]. The broad peak observed around 544 cm\(^{-1}\) (Fe–O str) instead of two sharp peaks, may due to the organic molecule which was from the leaf extract on the surface of iron oxide nanoparticles. The weak band at 2076 cm\(^{-1}\) may be due to the unsaturated Nitrogen (C≡N) compounds from the leaf extract.

IV. CONCLUSIONS

In summery the present work provides a method to synthesize low dimensional \( \beta\)-iron oxide nanoparticles by using Eucalyptus globulus leaf extract. From the UV-Vis and XRD we could conclude the prepared iron oxide nanoparticles were in beta phase. The SEM and TEM image shows the nanostructure of \( \beta\)-Fe\(_2\)O\(_3\) and size of particles are measured as about 100 nm. This technique has the ability of yielding crystalline \( \beta\)-Fe\(_2\)O\(_3\).

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