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ORIGINAL ARTICLE

Green Synthesis of Magnetite Nanoparticles (Fe_3O_4) Using Propolis Extract

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KEYWORDS

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ABSTRACT: The magnetite nanoparticles have currently received considerable attention for their high biocompatibility, non-toxicity, and specific magnetic properties in various fields, particularly in the removal of environmental pollutants. The present study was to facilitate the production of Fe_3O_4 nanoparticles (NPs) as an environmentally friendly method via green synthesis. For this purpose, the Fe_3O_4 NPs were synthesized via coprecipitation (CPT) using the divalent (II) and trivalent (III) iron solutions and the propolis extract in the presence of the nitrogen (N_2) gas. To characterize the synthesized NPs, the Fourier transform infrared (FTIR) mapping, the field emission scanning electron microscopy (FE-SEM), the X-ray diffraction (XRD), and the vibrating-sample magnetometry (VSM) were implemented. The obtained results from XRD analysis confirmed the production of high pure Fe_3O_4 crystals. The SEM micrographes of the synthesid Fe_3O_4 NPs revealed that their average diameter was 24 nm. The magnetic evaluationsed showed that the Fe_3O_4 NPs were in the superparamagnetic state with a saturation magnetization (M_s) of 12.6 emu g^{-1}. This study demonstrated the appropriate physicochemical properties of the Fe_3O_4 NPs stabilized by the green synthesis using the propolis extract, which could be thus a suitable and practical alternative as well as an environmentally friendly one in preference to chemical substances.

INTRODUCTION

The green synthesis of materials and nanomaterials is of assistance to expand the environmentally friendly ones through modifying and controlling their production process in an effective and efficient manner. In this line, the green method of synthesis is typically considered necessary to avoid the generation of harmful byproducts by the development of reliable, sustainable, and environmentally friendly techniques[1]. Among different types of metals and metal oxide nanoparticles (NPs), the iron oxides have been up to now the most prominent [2-4]. Moreover, various types of iron oxide NPs, such as the hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), and magnetite (Fe_3O_4) ones have been documented with many applications due to their morphological properties[5].

The Fe_3O_4 NPs have been widely investigated among the magnetic materials, because of their unique chemical and physical properties, including superparamagnetism, low curie temperature, coercivity, and high magnetic sensitivity[6-9]. The Fe_3O_4 NPs have been synthesized by various methods, such as coprecipitation (CPT) [6, 10, 11], the sol-gel process [12, 13], sonochemical synthesis[14], hydrothermal synthesis [15], pyrolysis [16, 17], microemulsion [18-20], and electrodeposition [21,

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22].

The co-precipitation method is one of the oldest methods of making nanoparticles, which was first used by Khalafala for the synthesis of magnetite nanoparticles. The advantage of this method is that it is cheap and not time-consuming, and it is also possible to make a large amount of nanoparticles in a small reaction volume[23]. The main reason for using the co-precipitation method in this study is the main advantage of the co-precipitation method, that is, the very high quality of the nanomaterials produced in this method. Among the different synthesis methods, the chemical co-precipitation method is one of the multi-purpose techniques, which is one of the most promising methods due to its simplicity and productivity, which is widely used due to its simplicity and the need for less dangerous materials and processes[24].

Generally, two types of classification have been proposed for the green synthesis of the Fe_3O_4 NPs. In the first method, some bioligical agents such as microorganisms, e.g., algae, bacteria, and fungi are utilized, and in the second method, some agents with reducing and stabilizing properties, like plant extracts, are used [25-28]. Between the proposed methods, the second method is introduced with better stability and greater compatibility as well as large-scale Fe_3O_4 NP production, as a relatively simple and easy process [29].

Besides, the disadvantages of physical and chemical synthesis include need to high temperature, utilizing of the toxic reducing agents, and stabilizing agents that can bring damaging effects to both humans and animals [30, 31]. On the other hand, the advantages of the green synthesis methods compared to different chemical procedures, are cost-effectiveness, no need for high temperature and high energy, absence of harmful chemicals, and compatibility with the environment [32]. Among the advantages of green synthesis of nanoparticles, we can mention the reduction of environmental effects and increase of biocompatibility due to insignificant pollution, low cost, safety for the environment and human health. Another advantage of using plant materials for the synthesis of nanoparticles is the absorption mechanism of metal ions by plants and understanding the possible mechanism of formation of metal nanoparticles in plants. The disadvantages of chemical and physical methods for the synthesis of nanoparticles are the use of regenerating and stabilizing substances with high radiation and high concentration, which are harmful to the environment and human health. In addition, the biological synthesis of nanoparticles is a one-step bioremediation method, and less energy is consumed for environmentally friendly synthesis. For example, green techniques eliminate the use of expensive chemicals, use less energy, and produce environmentally friendly products and products. Accordingly, green nanobiotechnology is a promising alternative route for the synthesis of biocompatible stable nanoparticles[33, 34].

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In the green synthesis of Fe_3O_4 NPs, some compounds such as saponins, alkaloids, phenols, tannins, organic acids, flavonoids, and vitamins act as regenerating agents through reaction with the iron precursors, and then produce the Fe_3O_4 NPs [35]. The green synthesis based on biological precursors also depends on various reaction parameters, i.e., pressure, temperature, pH, and solvent conditions[36]. In the biogenic synthesis of the metal NPs, they are usually synthesized using plant extracts, algae, bacteria, and fungi along with their biological compounds/metabolites, viz., proteins and lipids [37-40]. In this study, propolis was thus exploited to synthesis the Fe_3O_4 NPs. The Fe_3O_4 NPs have been thus far synthesized using plant extracts, such as soya bean (Glycine max) [41], the elkhorn sea moss (*Kappaphycus alvarezii*) [42], *Syzygium cumini* seed [43], *Euphorbia peplus* Linn leaf [44], *Garcinia mangostana* fruit peel [45], sawdust carbon [46], *Chromolaena odorata* root [47], *Zanthoxylum armatum* DC [48], the caricature-plant (*Graptophyllum pictum*) [49], green tea [50], and *Anthemis pseudocotula* [51].

The propolis is a resin-like mixture collected by honey bees from the buds and bark of plants. After being

transferred to the hive, such bees make some changes on it and then combine it with their saliva and wax secretions, to seal and fill the hive cracks. Propolis has a complex chemical composition and its constituents greatly differ in various regions, mainly due to the diverse plant sources that bees feed on, as well as geographical and weather conditions. The main and active components of propolis are wax, balsam, essential oils (10%), pollen (5%), flavonoids, and phenolcarboxylic acids [52]. It has been proven that propolis, as a natural product, has many biological benefits, including antioxidant, anti-inflammatory, antimicrobial, anti-parasitic, and anti-cancer properties[53-56]. For example, flavonoids (such as galangin) and phenolcarboxylic acids (e.g., diphenylhydroxycinnamic acid) are natural compounds (as antibiotics) with antimicrobial properties. The propolis has been thus applied in traditional medicine worldwide in the treatment of various diseases [57]. The antioxidant properties of propolis are largely attributed to the presence of flavonoids, which are present in the form of sugar-bound derivatives. Chrysin, also known as 5,7-dehydroxyflavone, is a flavone found in honey, propolis, and other plant sources. Generally, propolis contains more chrysin than honey. Quercetin is another member of the flavonoid group of polyphenols, found in various products, including many fruits, grains, vegetables, honey, and propolis. As well, quercetin glycosides constitute the major part of flavonoids in propolis. Caffeic acid or 3,4-dihydroxy-cinnamic acid from polyphenolic derivatives is the other active component whose antioxidant, anti-inflammatory, anti-cancer, and antiviral properties have been well established and found naturally in a choice of plants. Caffeic acid in the form of caffeic acid phetyl ester is another active ingredient in propolis [58]. As evidenced in previous scientific reports, the propolis extract has been used for the synthesis of selenium [59, 60], silver[59], gold [61], titanium [62], copper [63], and zinc oxide [64]. The present study was to synthesize and identify the Fe_3O_4 NPs using the propolis extract. The Fe_3O_4 NPs were evaluated through the XRD to determine the sample phases and the average particle size of the dried powders, the FTIR spectroscopy, and the Fe-SEM. Moreover, magnetization evaluations were performed accomplished at room temperature up to a maximum magnetic field (H) of 900 Tesla, by means of the homemade vibrating-sample magnetometry (VSM) device and magnetic parameters like specific saturation magnetization (M_s).

MATERIALS AND METHODS

Materials

The propolis used in this study was prepared from the Alamut region, Qazvin, Iran. Iron (II) chloride tetrahydrate ($FeCl_2.4H_2O \geq 99\%$) and iron (III) chloride hexahydrate ($FeCl_3.6H_2O$, 97%) were also purchased from Sigma-Aldrich Co. (the United States). As well, sodium hydroxide (NaOH) pellets obtained from Merck & Co. Inc. (Germany). All aqueous solutions were made using distilled water (DW). Moreover, all glassware and other equipment employed in this experiment were washed with DW and dried before use.

Propolis extract preparation

For the extract preparation, 10 g of raw propolis was extracted with 100 ml of 80% (v/v) ethanol for 24 h at room temperature. The extract was then centrifuged, and the supernatant was filtered using a 0.45 μm membrane filter to remove any impurities. The samples were kept under 4^{o}C until analysis. The collected propolis samples were also kept desiccated in the dark for further analysis [65-67].

Test for tannin compounds

Phenolic compounds such as tannins, flavonoids and phenolic acids are present in large quantities in plants. In order to determine the presence of phenolic compounds in propolis extract, a ferric ion reduction test was performed. According to the studies done, by adding iron chloride solution to the extract, the color changes rapidly to black[68-70].

In this experiment, $FeCl_3$ solution was added to the propolis extract and then the color change was observed.

Fe_3O_4 nanocomposite synthesis

To prepare the Fe_3O_4 NPs, the divalent (II) and trivalent (III) iron salts (2.25 and 8.48 g, respectively) were

dissolved in 400 ml of DW for 1 h at 80°C, under severe mechanical mixing conditions and exposed to the N_2 gas. Afterward, 40 ml of the propolis extract was added to the solution and the pH was adjusted to about 11 using two normal sodium hydroxide solutions, and a black precipitate was formed. The stirring of the solution continued for 30 min. Then, the stirring was stopped, and the precipitate was separated from the solution by the use of a magnet. To separate the soluble materials, the washing process was repeated several times with DW, and the obtained powder was dried in a vacuum dryer at a temperature of 50°C for 8 h (Figure 1).

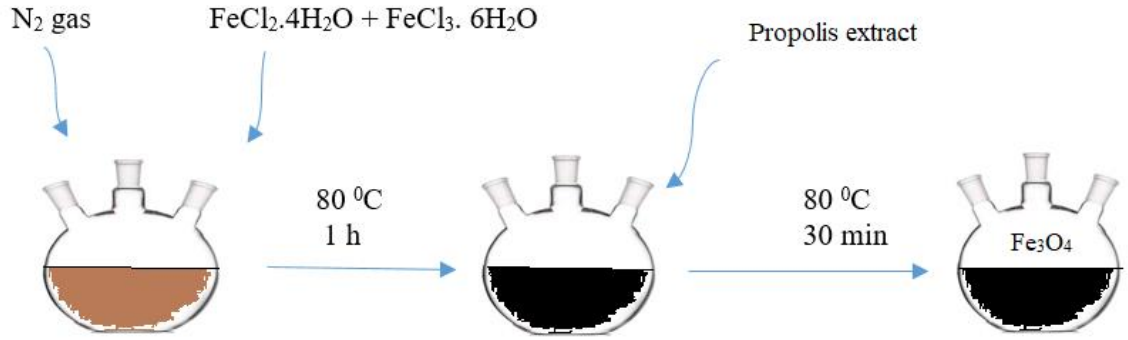

Figure 1. The schematic of the green synthesis of Fe_3O_4 NPs.

Characterization of Fe_3O_4 NPs

XRD

The synthesized Fe_3O_4 NPs were characterized by an XRD instrument (Philips, PW1730, the Netherlands) to investigate the phases and the crystal structures.

VSM

A VSM device was utilized to verify the magnetic properties of the Fe_3O_4 NPs based on the hysteresis curves to determine the coercive field as well as the hysteresis and saturation magnetism. The magnetic properties of the powder were then investigated using the VSM device (Meghnatis Kavir Kashan Co., Model: BKFB, Iran). The measurements were also made at room temperature with a magnetic field in the range of -10,000 to 10,000 Tesla.

FTIR spectroscopy

An FTIR spectrometer (Model: Thermo Scientific Nicolet, the United States) was recruited to find more information about the chemical bonds between the Fe_3O_4 core and the organic surface coating.

FE-SEM

The morphological analysis of the Fe_3O_4 NPs was obtained by an FE-SEM device (Model: XL30, Philips, the Netherlands) equipped with an X-ray dispersive spectrometer (EDS).

RESULTS AND DISCUSSION

The XRD image of the NPs and its comparison with the standard card (01-088-0315, Fe_3O_4) PDF Number 2 showed that the pure Fe_3O_4 crystals were well synthesized and no other phases existed (Figure 2). As well, the XRD outcomes revealed that 2θ = 32.093, 35.693, 45.743, 56.943, 62.893, and 75.643, as the highest curve peaks, were related to Fe_3O_4. Based on the peaks obtained and the width of the peak at half maximum height of the average particle size, 14.86 nm was calculated using the Scherer equation [71] as follows:

$$D = K\lambda = \beta \cos\theta$$

where D is the equivalent of the particle average core diameter, β denotes the full width at half maximum (in radians) of the highest intensity powder diffraction reflection, λ shows the incident X-ray wavelength, K represents the grain shape factor (K=0.9), and θ indicates the corresponding diffraction angle.

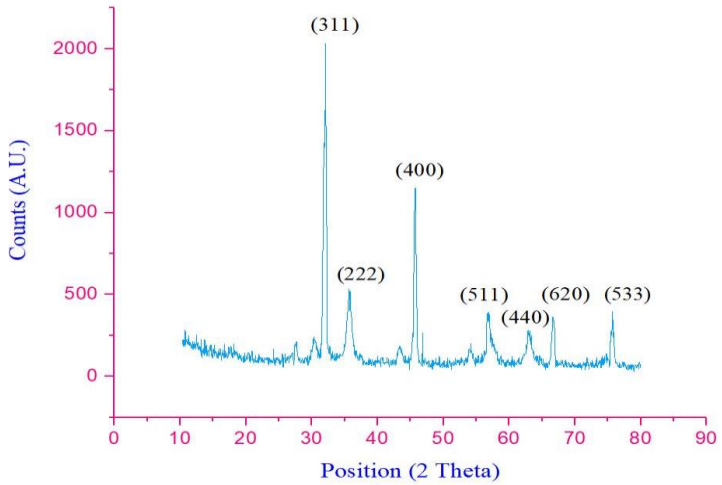

Figure 2. XRD patterns of the products obtained with green synthesis using the propolis extract.

The magnetic behavior of the Fe_3O_4 NPs sample evaluated by the VSM at room temperature is depicted in Figure 3. Accordingly, the absence of residuals indicated that the particles were in the superparamagnetic phase, and the Fe_3O_4 NPs reached saturation at 12.6 (emu g^{-1}). Moreover, the Fe_3O_4 magnetic properties of were evaluated by the VSM device (in the range of -10000 to 10000 Oe). The saturation magnetic value for the Fe_3O_4 NPs was further observed to be 12.6 emu g^{-1}, which was lower compared to that reported for Fe_3O_4 NPs in the related literature (between 70 and 80 emu g^{-1}) [72, 73]. Moreover, it confirmed the less ferromagnetic behavior of this nanocomposite compared to magnetic Fe_3O_4 NPs. The numerical values of saturation magnetism obtained in synthesized Fe_3O_4 nanoparticles are influenced by their structure, such as surface effects, morphology, size, crystallinity. These factors are strongly related to each other and are influenced by the size and geometric shape of NPs[74-76]. Therefore, the numbers obtained in the chemical synthesis and green synthesis methods depend on the mentioned factors.

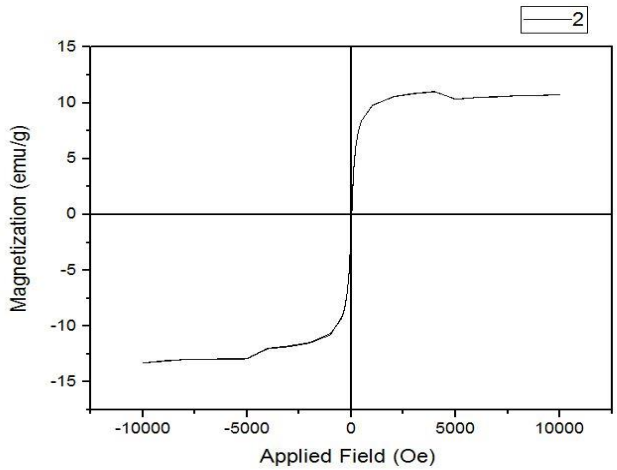

Figure 3. Magnetization curves of Fe_3O_4 NPs using the propolis extract at optimal reaction conditions.

The FTIR diagram of the Fe_3O_4 NPs is displayed in Figure 4. The typical range of the IR absorption in terms of the wave number was 400 to 4000 cm^{-1}. The position of the peaks thus depended on the nature of the bonds. These spectra provided valuable information about the chemical structure of the molecules, due to the presence of polyphenols on the surface of the Fe_3O_4 NPs and the degree of reduction of their surface magnetism. The peaks appearing at 3421.67 and 2923.45 cm^{-1} were attributed to the hydroxyl (OH) functional groups,

following the OH absorption of the Fe_3O_4 NPs. The peak seen at 2367.07 additionally corresponded to the C=O functional group, at the frequency of 1623.70 cm^{-1}. These bands were also known as the characteristic bands of the methylene (CH_2) groups, which implied a successful ligand exchange. Besides, the peak observed at the frequency of 1568.29 was associated with the double amine functional groups. The IR spectrum at low wavelengths (≤ 700 cm^{-1}) further showed the Fe-O bonds. Therefore, the peaks at 569.37 and 427.55 cm^{-1} matched the Fe-O and confirmed the Fe^{2+} and Fe^{3+} presence, thereby validating that Fe_3O_4 NPs were trapped in the molecules. The bands at 1623.70 and 3421.67cm^{-1} respectively suggested the presence of flavonoids and OH stretching, which indicated the presence of polyphenols. These flavonoids and polyphenols could thus contribute to the preparation of the Fe_3O_4 NPs.

Figure 5 shows the microstructure of the Fe_3O_4 NPs synthesized with the propolis extract at a scale of 200 nm with a magnification of 140.00 KX. This micrographe clearly revealed that the synthesized Fe_3O_4 NPs had a spherical surface and an average size of about 24 nm.

To verify the strength of the magnetic core, the powder of the Fe_3O_4 NPs produced by the green method of synthesis was exposed to a hard magnet, and it was observed that the synthesized Fe_3O_4 NPs were strongly attracted to the magnet, indicating their magnetic properties. As clearly seen, Fe_3O_4 NPs exhibited a higher magnetic response due to the presence of strong magnetism in the core of the Fe_3O_4 NPs.

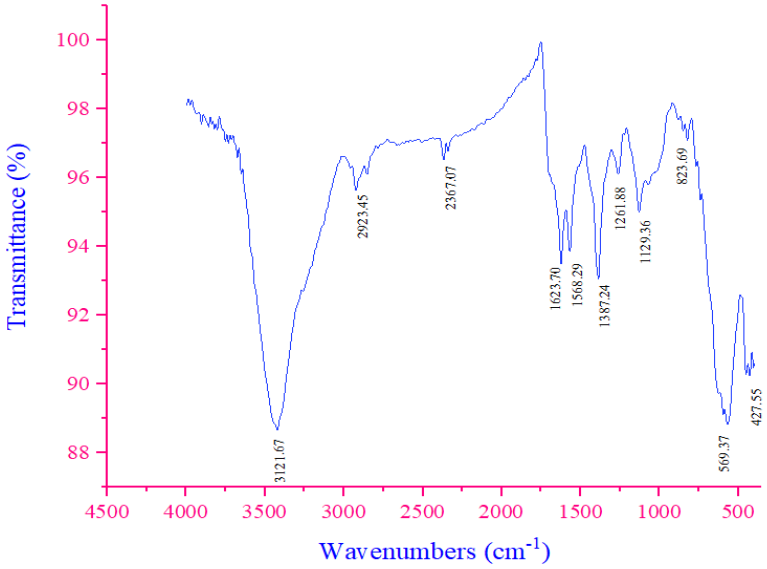

Figure 4. FTIR spectra of Fe_3O_4 NPs synthesized using the propolis extract at optimal reaction conditions.

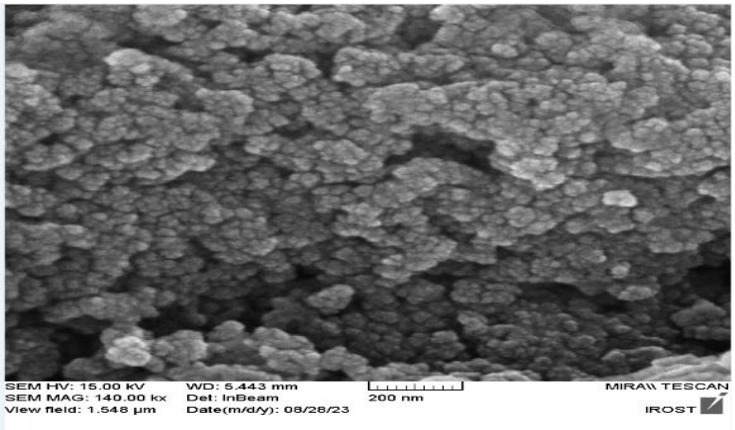

Figure 5. FESEM micrographe of Fe_3O_4 NPs green synthesized at optimal reaction conditions.

Assay of tannin compounds

To determine the presence of phenolic compounds in propolis extract, the ferric ion reduction test was performed. In this study, 5 cc of $FeCl_3$ solution (30 mM) was added to 10 cc of propolis extract, and the color change from brown to black was observed, which indicates the presence of tannins.

CONCLUSIONS

The feasibility of Fe_3O_4 NPs green synthesis using the propolis extract was investigated in the present study. As one of the advantages of making such Fe_3O_4 NPs with the given extract was the use of environmentally friendly materials, the FTIR, XRD, and FE-SEM outcomes showed that the production of the Fe_3O_4 NPs by the green method of synthesis with the propolis extract was well fixed. The superparamagnetic Fe_3O_4 NPs were also synthesized using CPT together with NaOH as a precipitating agent. The size of the Fe_3O_4 NPs was also measured in the range of 24-34 nm and their saturation magnetism was measured to be 12.6 emu gr^{-1}. The peak appearing at 569.37 cm^{-1} ultimately confirmed the vibrational bond of Fe-O in Fe_3O_4 NPs. To synthesize the Fe_3O_4 NPs in this study, the propolis extract as a completely natural and herbal substance that is easily applicable thanks to its simplicity and compatibility with the environment was applied instead of the ammonium (NH_4^+) solution, which is chemical and very hazardous to the human society and the environment.

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Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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