Optical and Morphology Properties of the Magnetite (Fe$_3$O$_4$) Nanoparticles Prepared by Green Method

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Abstract: Magnetite nanoparticles have been synthesized by a green method. For this process, ferric chloride hexahydrate, ferrous chloride tetrahydrate (2/1 molar ratio) solution was mixed with different amounts of carob leaves extract and NaOH solution was added to get pH(2, 5, 8 and 11) heated for 30 min at (30, 60, 80 and 100) °C. In this report, a description was introduced for the synthesis of Fe$_3$O$_4$ nanoparticles (NPs) in order to obtain the optimum (pH8, temperature and amount of extract) that have small particle size MNPs. The magnetite nanoparticles were characterized by UV–Vis absorption spectroscopy, through Field emission scanning electron microscopy (FESEM) and Atomic Force Microscope (AFM). In UV–Vis spectroscopy, the absorbance of surface plasmon resonance (SPR) of magnetite nanoparticles synthesized with different parameters, were observed a single visible peak located in the range of (290-519) nm and it was related to spherical monodisperse, peak shifts to shorter wavelength (blue shift) with change parameter. FESEM images confirm the Fe$_3$O$_4$ NPs synthesized with different parameters were spherical shaped and lower than 50 nanoscale. AFM images of magnetite nanoparticles with different parameter. It is observed that each nucleus magnetite Nanoparticles is spherical in geometry

Keywords: Fe$_3$O$_4$ Nanoparticles, Green synthesis, Surface Plasmon Resonance (SPR), FESEM, AFM.

1. Introduction
Metal nanoparticles exhibit improved properties such as plasmon resonance characteristics depending upon their size and morphologies [1]. An interesting thing about some metallic nanoparticles is that these particles show strong plasmonic properties. When light photons interact with the surface of metals, the outer free electrons of the particles form localized plasmons [2]. Plasmons are density waves of the free outer electrons. Specific wavelengths of light cause the outer electrons to oscillate. This phenomenon is called surface plasmon resonance (SPR). When these resonances occur, the intensities of absorption and scattering are much higher than those of the same particles without plasmonic properties. surface plasmon resonance (SPR) is highly dependent on particle characteristics [3]. Recently, magnetite (Fe3O4) nanoparticles received considerable attention not only in the fields of medical applications [4], including radiofrequency hyperthermia, photo magnetics, dynamic scaling, biosensors, magnetic resonance imaging (MRI) [5], medical diagnostics, cancer therapy, drug delivery, but also in the field of waste water treatment [6]. Fe$_3$O$_4$ NPs possess excellent properties that involve non-toxicity [7], biocompatibility, super paramagnetic behavior, and good magnetic susceptibility [8]. To properties of Fe$_3$O$_4$ MNPs, such as size and shape, can be altered with different synthesis methods [9] and as a result, the MNPs can be specialized for different applications. Several synthesis routes have been reported including thermal decomposition [10], co-precipitation [11], and hydrothermal synthesis [12]. Green synthesis of nanoparticles is a perfect
field of nanotechnology, which attracts great attention in the fields of medicine, pharmaceutical, electrical, technological and other science research areas [13]. Mostly the nanoparticles synthesized through different chemical and physical methods, these approaches are complicated, expensive and cause potential environmental and biological hazards. Generally, the particle size of Fe₃O₄ MNPs is affected by pH variation [14], temperature [15], and stirring rate [16] during the synthesis process. The biosynthesis (green synthesis) of iron oxide nanoparticles of different sizes and shapes has been reported using bacteria, fungi, and plant extract [17].

In this research, a magnetite nanoparticles with various parameters were synthesized using carob leaf extract through a fast and easy green method, in just 30 minutes, to obtain the optimum synthesis of magnetite, which has small particle size (shorter wavelength) and specific physiochemical characteristics such as spherical monodisperse.

2. Material
Sodium hydroxide (NaOH), carob leaf, iron (III) chloride hexahydrate (FeCl₃·6H₂O) and iron (II) chloride tetrahydrate (FeCl₂·4H₂O) were purchased from Panreac AppliChem /Barcelona, Spain. All the aqueous solutions were prepared by deionized water.

3. Methods
3.1. Synthesis of Carob Leaf Extract
Carob leaves have been obtained from trees in Baghdad, Iraq. Carob extract is used as a reducing agent, which speeds up the reaction. The leaves were washed thoroughly with distilled Water to prevent the dust particles and dried to remove the remaining water. Then dried fine-cut leaves. An extract of Carob leaves used for preparation of Fe₃O₄ NPs by putting 1.25 g of leaves in 100 mL beaker and with 50 mL of deionized water and boiling at a steady temperature of 80 °C for 5 minutes. The aqueous solution color shifted to yellow after boiling, allowing it to cool to room temperature. Then filtered to eliminate the heavy biomaterials with medium Qualitative filter paper and centrifuging at 2000 rpm for 5 minutes. At room temperature. A image of the carob leaf extract (colour yellow) is shown in Figure 1A.

3.2. Synthesis of Magnetite Nanoparticles
Fe₃O₄-NPs were synthesized by 0.53 g of FeCl₂·4H₂O and 1.44 g of FeCl₃·6H₂O (1/2 molar ratio) were dissolved in 100 mL of deionized water in a 250 mL beaker and heated at different temperature (30,60, 80 and 100)°C under mild stirring and using a magnetic stirrer. After 10 minutes, (1,5,9 and13) mL of the aqueous solution of carob leaf extract was added to the mixture, immediately the yellowish colour of the mixture changed to reddish-brown colour. Then, the prepared 0.1 M of NaOH was added drop-wise to the solution under continuous stirring, continuous add NaOH solution to get pH(2, 5,8 and 11). From the first addition of sodium hydroxide, the reddish-brown mixture changed to black suspended particles, shown in Figure 1. The solution was then stirred for 30 min under(30,60, 80 and 100)°C to completion of the reaction. The mixture has been allowed to cool down to room temperature. Magnetite nanoparticles were washed twice by centrifugation in deionized water. When prepared in the deionized water, the magnetite nanoparticles remain without any additives. For more than two weeks, the stability of retained nanoparticles in pure deionised water. Figure 2 shown the Image of synthesis Fe₃O₄ nanoparticles for four parameters (NaOH(pH)), temperature and amount of carob leaf extract ).
Figure 1. shows process of synthesizing of magnetite nanoparticles (A) image of carob leaf extract (yellow colour), (B) mixture of Fe(II) and Fe(III), (C) add extract and (D) add NaOH.

Figure 2. The image of synthesis Fe$_3$O$_4$ nanoparticles for four parameters (NaOH, temperature and amount of carob leaf extract).

4. Characterization
Fe$_3$O$_4$ NPs prepared by a green method were analyzed by UV-Vis spectroscopic analysis using the Shimadzu UV-1601 spectrophotometer. The morphology and structure of the Fe$_3$O$_4$ NPs was evaluated by a Atomic Force Microscope (AFM) and the Field Emission Scanning Electron Microscopy (FESEM).

5. Results and Discussion
UV-Vis spectroscopy is quite useful for the analysis of localized surface plasmon resonance (SPR). This device enables the absorption intensity to be established against the different wavelengths of light. Ultraviolet and visible light wavelengths can interfere with the surface electrons of the magnetite nanoparticles. The absorption peak gives data on the scale, size and shape distribution of the nanoparticles. Figure 3 shows the absorbance of surface plasmon resonance (SPR) of synthesized magnetite nanoparticles (5mL of extract mixture, different amounts of NaOH at 80°C). It observes from the Figure 3 with change NaOH absorbance curve of each (Fe$_3$O$_4$) solution that had a single visible peak that was positioned in the range of (300-519) nm and it was related to spherical monodisperse, and the peak shifts to a shorter wavelength (more the peak shifts to left) (blue shift) with the increase...
of solution NaOH at pH (2,5,8 and11) the peak shifte (317,311,308 and 306)nm .Figure 4 drew between absorbance peak position and absorbance intensity of surface plasmon resonance (SPR) of Fe₃O₄ nanoparticles with change NaOH to get the shorter wavelength which has small particales size [18] with perfect absorbance intensity .The optimum condition for synthesized magnetite nanoparticles at pH8.

![Figure 3](image3.png)

**Figure 3.** The absorbance of surface plasmon resonance (SPR) of megmetite nanoparticles synthesized (5mL of extact , different amount of NaOH and 80°C).

![Figure 4](image4.png)

**Figure 4.** Absorbance peak position and absorbance intensity of surface plasmon resonance (SPR) of megnetite nanoparticles with change NaOH.

Figure 5 showed that the temperature change with 5mL of extact and pH8 , the absorbance curve of each magnetite solution showed a single visible peak that was positioned in(290-480) range of nm and it was related to spherical of monodisperse. The SPR peak shifts to a shorter wavelength (blue shift) at (302,303,308 and 310 )nm with (30,60,80 and 100) °C . The growth of Fe₃O₄ nucleus is easier to happen when the temperature is higher than 45 °C resulting in larger size nanoparticles when the temperature is inresed than 45 °C, implying there was greater polydispersity in reactions at higher temperatures [9].The optimum condition for synthesized magnetite nanoparticles at 45°C that has shorter wavelength with perfect absorbance intensity getted in Figure 6.
Figure 5. The absorbance of surface plasmon resonance (SPR) of megmetite nanoparticles synthesized (5mL of extract, pH8 and different temperature).

Figure 6. Absorbance peak position and absorbance intensity of surface plasmon resonance (SPR) of megnetite nanoparticles with change temperature.

Change the amount of the extract could change the size of Fe$_3$O$_4$ NPs [19]. The results of the UV-Vis spectra analysis in Figure 7 showed that with change the extract absorbance curve of each Fe$_3$O$_4$ solution NPs had a singular visible peak located in the range of (290-440)nm. Figure 8 showed the change in the absorbance peak position and the absorbance intensity with the change extract as the SPR peak is affected by the extract. between 5mL of extract has peak shifts to shorter wavelengths and 13mL has high absorbance intensity, the 6 mL of extract was selected optimum condition for synthesized Fe$_3$O$_4$ nanoparticles.
Figure 7. The absorbance of surface plasmon resonance (SPR) of megnetite nanoparticles synthesized (different amount of extract, pH8 and 45°C).

Figure 8. Absorbance peak position and absorbance intensity of surface plasmon resonance (SPR) of magnetite nanoparticles with different amount of extract).

Therefore, 6 mL of extract, pH8 and 45°C were selected optimum conditions for synthesized magnetite nanoparticles which SPR peak at 305 nm.

Figure 9. Optimum absorbance of surface plasmon resonance (SPR) of magnetitennanoparticles (Fe$_3$O$_4$NPs) in blue shift region.
Table 1. shows the Optimum magnetite nanoparticles synthesized with different parameter.

| Sample | NOaH(pH) | Temperature(℃) | Amount of extract (mL) |
|--------|----------|----------------|------------------------|
| S1     | pH2      | 80             | 5                      |
| S2     | pH8      | 80             | 5                      |
| S3     | pH8      | 45             | 5                      |
| S4     | pH8      | 45             | 6                      |

Figure 10 showed FESEM image of Fe₃O₄Nps synthesized with different parameter S1, S2, S3 and S4, in the picture appears that Fe₃O₄ particles composed of small particles. The FESEM image confirms that the Fe₃O₄NPs are spherical shape and particle size of S1 about (30 to 70)nm, S2 about (28 to 65.3) nm, S3 about (26.32 to 48.28) nm and S4 about (24 to 46.52)nm.

![FESEM image of Fe₃O₄NPs](image1)

Figure 11 showed the AFM image of magnetite nanoparticles with different parameter, It is observed each nucleus magnetite Nanoparticles is spherical in geometry and the surface tension and surface energy were changed with change Fe₃O₄NPs synthesized. It is observed from Table 2 that surface roughness and root mean square (RMS) of magnetite nanoparticles increased when changed pH at S1 (pH2) to S2(pH8) then decreased when changed Temperature at S2(80°C) to S3(45°C) and decreased at S3(5 mL) to S4(6mL) when extract changed. This means decreased in particle size.
Figure 11. shows AFM image of magnetite nanoparticles with different parameters.

Table 2. Surface roughness, root mean square (RMS) and grain size of magnetite nanoparticles with different parameters.

| Sample | Surface roughness(nm) | Root mean square(nm) | Average Grain size(nm) |
|--------|------------------------|----------------------|------------------------|
| S1     | 6.39                   | 7.53                 | 50.1                   |
| S2     | 12.9                   | 15.3                 | 55.4                   |
| S3     | 6.18                   | 7.35                 | 35.8                   |
| S4     | 4.99                   | 5.75                 | 45                     |

6. Conclusions
This research assessed the synthesis of magnetite nanoparticles produced by a simple, quick and green method in a single-pot reaction. Green synthesis using carob leaf extracts with a change parameter can be an economical and efficient method for synthesizing the Fe₃O₄ NPs. The analysis indicated that the crystalline and particle size of Fe₃O₄ NPs is depended on (pH, temperature and extract amount). UV–Vis spectroscopy confirmed magnetite nanoparticles, and showed that singular visible peak located in the range of (290-519) nm and related to the spherical monodisperse, and the optimum conditions at (6 mL of extract, pH8 and 45°C) for synthesized magnetite nanoparticles which SPR peak at 305 nm. AFM and FSEM data showed that Fe₃O₄ nanoparticles have a spherical shape.
References

[1] Scholl J A, Koh A L and Dionne J A 2012 Quantum plasmon resonances of individual metallic nanoparticles Nature 483(7390) 421-427

[2] Ismail R K, Mubarak T H and Al-Haddad R M 2019 Surface Plasmon Resonance of Silver Nanoparticles: Synthesis Characterization and Applications J Biochem Tech 10(2): 62-64

[3] Ismail R K, Al-Haddad R M and Mubarak T H 2019 Time effect on the red shift of surface plasmonic resonance core-shell SiO2: Gold nanoparticles (AuNPs) In AIP Conference Proceedings Vol. 2190 No. 1 p. 020095 AIP Publishing LLC

[4] Aftabtalab A and Sadabadi H 2015 Application of magnetite (Fe3O4) nanoparticles in hexavalent chromium adsorption from aquatic solutions J Pet Environ Biotechnol 6(1) 1-6

[5] Dheyab M A, Aziz A A, Jameel M S and Noqta O A 2019 Synthesis and Coating Methods of Biocompatible Iron Oxide/Gold Nanoparticle and Nanocomposite for Biomedical Applications Chin. J. Phys. 64 305-325

[6] Vicky M, Rodney S, Ajay S and Hardik M 2010 Introduction to metallic nanoparticles J. Pharm. Biocluded Sci 2(4): 282-289

[7] Yew Y P, Shameli K, Miyake M, Khairudin N B B A, Mohamad S E B, Naiki T and Lee K X 2020 Green biosynthesis of superparamagnetic magnetite Fe3O4 nanoparticles and biomedical applications in targeted anticancer drug delivery system: A review Arabian Journal of Chemistry 13(1) pp.2287-2308

[8] Shahbazi-Gahrouei D, Setayandeh S S, Aminolrooyaei F and Shahbazi-Gahrouei S 2018 Biological effects of non-ionizing electromagnetic fields on human body and biological system: A systematic literature review J. Med. Sci. 18: 149-156

[9] Mahdavi M, Ahmad M B, Haron M J, Namvar F, Nadi B, Rahman M Z A and Amin J 2013 Synthesis surface modification and characterisation of biocompatible magnetic iron oxide nanoparticles for biomedical applications Molecules 18(7) 7533-7548

[10] Sharma G and Jeevanandam P 2013 Synthesis of self-assembled prismatic iron oxide nanoparticles by a novel thermal decomposition route RSC Adv. 3 189–200

[11] Dheyab M A, Aziz A A, Jameel M S, Noqta O A, Khanibadi P M and Mehrdel B 2020 Simple rapid stabilization method through citric acid modification for magnetite nanoparticles Scientific reports 10(1) pp.1-8

[12] Li H, Lu Z, Cheng G, Rong K, Chen F and Chen R 2015 HEPES-involved hydrothermal synthesis of Fe3O4 nanoparticles and their biological application RSC Advances 5(7) 5059-5067

[13] Gour A and Jain N K 2019 Advances in green synthesis of nanoparticles Artificial cells nanomedicine and biotechnology 47(1) pp.845-844

[14] Sun J, Zhou S, Hou P, Yang Y, Weng J, Li X and Li M 2007 Synthesis and characterization of biocompatible Fe3O4 nanoparticles Journal of biomedical materials research Part A 80(2) 333-341

[15] Mahdavi M, Ahmad M, Haron M J, Rahman M Z and Fatehi A 2011 Optimized conditions for graft copolymerization of poly(acrylamide) onto rubber wood fiber BioResources 6 5110–5120

[16] Hua C C, Zakaria S, Farahiyan R and Khong L T 2008 Size-controlled synthesis and characterization of Fe Sains Malaysiana 37(4) 389-394

[17] Veeramanikandan V, Madhu G, Pavithra V, Jaianand K and Balaji P 2017 Green synthesis characterization of iron oxide nanoparticles using leucas aspera leaf extract and evaluation of antibacterial and antioxidant studies International Journal of Agriculture Innovations and Research 6(02) pp.242-250

[18] Honary S, Ebrahimip E, Asgari-rad H and Mohamadpour F 2014 Optimization of Iron Oxide Nanoparticle Preparation for Biomedical Applications by Using Box-Behenken Design International Journal of Nanoscience and Nanotechnology 10(4) 257-261

[19] Nida M S, Ahmad L A and Akl M A 2013 New route for synthesis magnetite nanoparticles from ferrous ions and pistachio leaf extract Nanoscience and Nanotechnology 3(3) 48-51