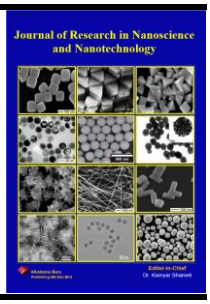
Journal of Research in
Nanoscience and Nanotechnology

Journal homepage:
http://akademiabaru.com/submit/index.php/jrnn/index
ISSN: 2773-6180



Bio-Mediated Production and Characterisation of Magnetic Nanoparticles Using Fruit Peel Extract

Mostafa Yusefi, Ong Su Yee, Kamyar Shameli *

Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia,
Jalan Sultan Yahya Petra, 54100, Kuala Lumpur, Malaysia
* Correspondence: E-mail: kamyarshameli@gmail.com; +60173443492
https://doi.org/10.37934/jrnn.1.1.5361

ABSTRACT

The overwhelming request for nanodevices and heat flow developments has led to consider magnetic Fe_3O_4 nanoparticles as a new dawn to the sophisticated nanotechnology in a sustainable manner. This research presented a facile production of Fe_3O_4 nanoparticles using co-precipitation method and the extract of *Garcinia Mangostana* fruit peel waste as a green stabilizer and capping agent. The X-ray powder diffraction (XRD) planes of the synthesized nanoparticles showed the formation of magnetite Fe_3O_4 nanoparticles with good crystallinity. Based on the image of field emission scanning electron microscope (FESEM), the diameter of the nanoparticles was estimated to be 69.14±2.87 nm as was coated by the extract. The Fe_3O_4 nanoparticles presented an acceptable magnetization value of 51.17 emu/g. From the analysis of Fourier-transform infrared spectroscopy (FTIR), the phenolic compounds and other functional groups of the extract had interactions with the Fe ions to successfully synthesize the nanoparticles. The green synthesized Fe_3O_4 nanofluids showed small hydrodynamic size of 145.80±3.14 and high zeta potential value of -30.5±1.82 mV. This study, thus, showed that the extract of *Garcinia Mangostana* fruit peel waste can serve as a bio-stabilizer and capping agent to enhance physiochemical properties and colloidal stability of the Fe_3O_4 nanofluids with an environmentally-friendly manner and low cost for modern applications.

Keywords:
Green Approach, Fruit Peel Extract, Fe_3O_4 Nanoparticles, Magnetic Nanofluids, Physicochemical Properties

Received: 13 December 2020 | **Revised: 28 December 2020** | **Accepted: 31 January 2021** | **Published: 28 February 2021**

1. Introduction

Magnetic Fe_3O_4 nanoparticles (NPs) can be considered as a smart, multifunctional and magneto-responsive nano-scaled device for a myriad of research fields. Fe_3O_4 NPs have already proven several functionalities for different modern applications such as cancer therapy, nanodrug delivery systems, magnetic hyperthermia therapy, magnetic resonance imaging, electronics cooling, biosensors,

tunable heat transfer fluids, and density separation, and ink jet printers [1-4]. The magnetic Fe_3O_4 NPs is widely synthesized by co-precipitation method [5, 6]. Co-precipitation is well-known as a facile and on-step method to produce the NPs, albeit, it has showed drawbacks such as lack of capability to control the particle size and low stability of the NPs. To overcome these disadvantages, the green stabilizers and capping agents such as plant extracts have been used to improve the physiochemical properties and colloidal stability of Fe_3O_4 NPs suspension [6]. In the biosynthesis method, the green materials as stabilizers can hydrolyze the solution of Fe ions to form ferric hydroxide and consequently reduced by biomolecules to fabric Fe_3O_4 NPs with high stability [7]. It is worth to mention that coating the bare NPs is may have high-cost with environmental-issues as chemicals are used [8]. To solve these issues, the synthesis of the NPs can be performed by an environmental friendly and low-cost approach, as the green stabilizer (for example plant extracts) with polyphenol components can be deposited into/onto the NPs to diminish particle interactions and coat the NPs [9]. Of this, Fe_3O_4 NPs containing the plant extract stabilizer can possibly display an improved water permeability, colloidal stability biocompatibility, and safety to use in numerous applications [10-12].

The plant extract has high polyphenol or flavonoid with great antibacterial actions [13]. Interestingly, the peel of fruits may have better antioxidant activity compared to the pulp [14]. In this manner, the crude extract of fruit peel wastes includes *Garcinia Mangostana* (*G.Mangostana*) [14] and mango [15] may show significantly antioxidant activities to use in biomedical applications. Many researchers, therefore, have used different plant extracts, for example *Kappaphycus Alvarezii* [16] and *Punica Granatum* peel wastes [9] to synthesize Fe_3O_4 NPs. Yet, synthesis of Fe_3O_4 NPs with the extract of *G.Mangostana* is less concerned [3]. The extract of *G.Mangostana* fruit peel waste has used to synthesize Au NPs [17] and Ag NPs [18], but it is required more investigations in production of Fe_3O_4 NPs.

In this current study, Fe_3O_4 NPs was synthesized with a facile co-precipitation method and using the extract of the *G.Mangostana* fruit peel waste as a capping agent and stabilizer. The green synthesized Fe_3O_4 NPs was evaluated by X-ray powder diffraction (XRD), field emission electron microscope (FESEM), energy dispersive X-ray spectroscopy (EDS), vibrating sample magnetometer (VSM), and Fourier-transform infrared spectroscopy (FTIR). The zeta potential value, the hydrodynamic size, and polydispersity index of the Fe_3O_4 NPs solution were also examined.

2. Materials and Methods

2.1 Materials

G.Mangostana fruit was purchased from Terengganu state in Malaysia. Iron (II) chloride tetrahydrate ($FeCl_2.4H_2O \geq 99$ %) and iron (III) chloride hexahydrate ($FeCl_3.6H_2O$, 97 %) purchased from Sigma-Aldrich provided. Sodium hydroxide (NaOH) (R&M Chemicals) was obtained from the chemical supplier. The chemicals were used without any purification process. All aqueous solutions were prepared using distilled water. All glassware used was washed and rinsed with distilled water and dried before used.

2.2 Preparation of Fe_3O_4 Nanofluids with *G.Mangostana* Fruit Peel Extract

The *G.Mangostana* fruit peel aqueous extract was produced by modification of the method in our previously published reports [9, 17]. The fruit peels were washed several times to remove dust, followed by drying at an ambient condition and it is ground to obtain the extract powder. In order to produce a pure peel extract solution, an eco-friendly water extraction method was used. For this purpose, 10 g extract powder was dissolved in 100 ml of double deionized water at an adjusted

temperature of 80 °C using the oil bath under constant stirring at 250 rpm for one hour and then filtered and stored in dark at 4 °C for further processing.

A simple co-precipitation method and the extract of *G.Mangostana* fruit peel as a stabilizing and capping agent were used to fabricate Fe_3O_4 NPs. For this aim, the extract, iron salts (Fe^{2+}/Fe^{3+}), and sodium hydroxide acted as a stabilizer, iron sources, and reducing agent, respectively. The extract solution (wt.%) was prepared as 5 g of the dried extract was mixed with 95 g of double deionized water and stirred for 15 min at an ambient condition. $FeCl_3$. $6H_2O$, 97% and $FeCl_2.4H_2O \geq 99\%$ (2:1 M) were respectively added into the extract solution. Then, 1 M of sodium hydroxide was dropwise added into the solution to adjust the pH to around 11 and stirred vigorously for another 45 min. Finally, the solution was centrifuged three times at 10,000 rpm for 15 min and the collected precipitates were oven-dried at 60°C. The sample was termed as Fe_3O_4-NPs/*G.Mangostana.*

2.2 Characterization of the green synthesized Fe_3O_4-NPs/*G.Mangostana*

The structural characteristics of the synthesized Fe_3O_4-NPs/*G.Mangostana* was analyzed by using PANalytical X'Pert PRO X-ray diffractometer with the wavelength Cu Kα radiation (λ= 0.15406nm). An applied current of 20 mA and accelerating voltage of 45 kV in the range of 2θ = 5°- 80° with the scanning rate = 2θ/min were set. The standard magnification selected is at 50 kX. FESEM was used to determine the size distribution and morphology of the selected sample by using JSM-7800F Prime Schottky FESEM equipped with the energy dispersive X-ray analyzer (EDS). The accelerating voltage of the microscope was set at 5.0 kV and the standard magnification selected at 40 kX. VSM was required to investigate the magnetic properties of the samples by using vibrating sample magnetometers Model 7400, Tokyo, Japan. Dynamic light scattering using Anton Paar instruments measured the zeta potential value and hydrodynamic sizes of the samples. The functional group of the sample was identified by using IR Tracer-100 FTIR with a wavelength range of 400–4000 cm^{-1}. Each sample was mixed with the potassium bromide (KBr) with a ratio of 1:10 to produce pellet.

3. Results and Discussion

Figure 1 depicts the schematic diagram of this study, presenting the compounds in *G.Mangostana* fruit peel aqueous extract acted as stabilizing agents and mixed with the mixture of iron chloride salts with the ratio of 2 Fe^{3+}: 1 Fe^{2+} to form Fe_3O_4-NPs. The formation of the green synthesized Fe_3O_4-NPs/*G.Mangostana* was observed through the color change of the solution from purple to black color. The attraction of the synthesized Fe_3O_4-NPs by the magnet indicated the magnetic properties of NPs.

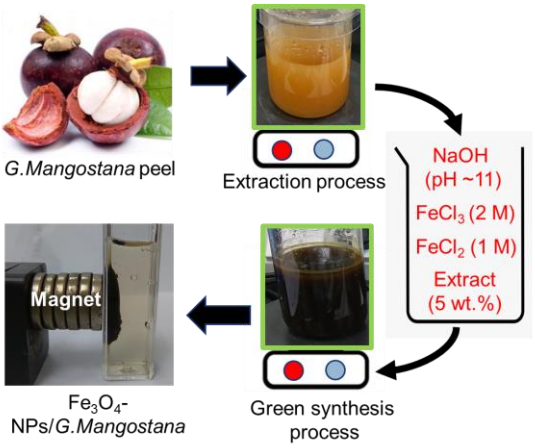


Figure 1. A schematic of Fe_3O_4-NPs/*G.Mangostana* synthesis by using the extract of *G. Mangostana* fruit peel waste (5 wt.%) as a green stabilizer and capping agent.

3.1 Identify the crystal structure of Fe_3O_4-NPs/*G.Mangostana* using X-ray diffraction (XRD)

Figure 2 shows the XRD spectra for the biosynthesized Fe_3O_4-NPs/*G.Mangostana*. From the result, all the biosynthesized NPs showed a similar pattern. The diffraction peaks were presented at 2θ = 30.44°, 35.82°, 43.47°, 53.92°, 57.45°, 63.01°, and 74.69°, which are equivalent to the (220), (311), (400), (422), (511), (440), and (533) crystal planes of the pure cubic spinel crystal structure phase of Fe_3O_4, respectively, based on literature data (JCPDS file no: 00-003-0863) [9, 12]. The Debye-Scherrer equation is used to measure the crystallite size of the synthesized Fe_3O_4 NPs [19]. Equation 1 is as shown below:

$$D_{hkl} = \frac{K\lambda}{\beta_{hkl}\cos\theta} \qquad (1)$$

Where hkl is the Miller indices of lattice planes being examined, D_{hkl} is the size of crystallite in the direction perpendicular to lattice planes, K is the crystallite-shape factor with Scherrer constant = 0.9 when there is the absence information of the crystallite-shape, λ is the wavelength of the X-rays = 0.154059 nm, β_{hkl} is the full width at half maximum (FWHM) of XRD diffraction peak in radians in 2θ scale and θ is the half diffraction angle of the peak [20]. By using the equation, the crystallite size of the strongest reflection of 35.82° (311) peak from Fe_3O_4-NPs/*G.Mangostana* was 14.39 nm, respectively. It can be determined that the peel extract will lead to an increased crystallite size of synthesized Fe_3O_4-NPs [21]. From the XRD patterns of all the samples, the purities of the crystalline were very high due to low impurity peaks.

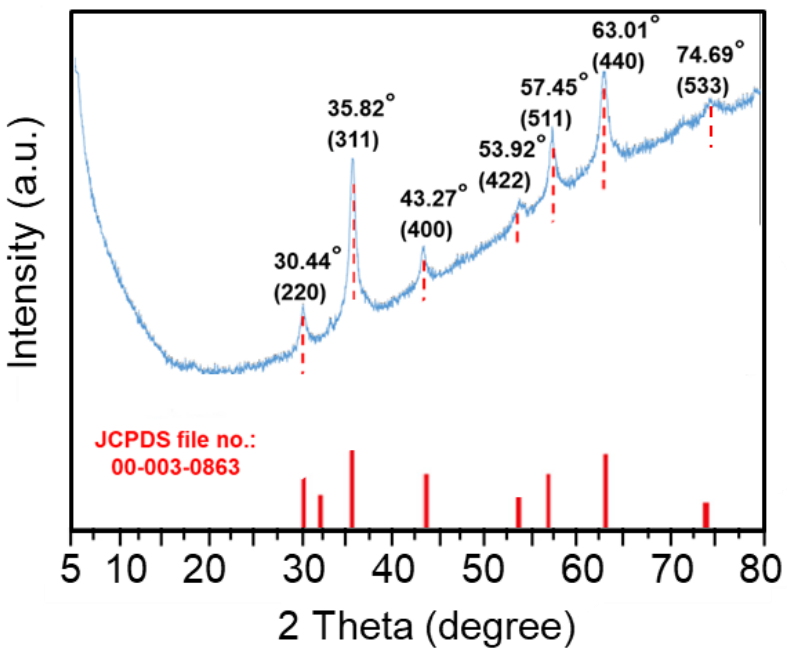


Figure 2. XRD spectra of the green synthesized Fe_3O_4-NPs/*G.Mangostana* containing 5 wt.% of the extract stabilizer.

3.2 Field Emission Scanning Electron microscopy (FESEM) and Energy Dispersive X-ray Spectroscopy (EDS) of Fe_3O_4-NPs/*G.Mangostana*

Figure 3a-c show the FESEM images, EDX and an average diameter of Fe_3O_4-NPs/*G.Mangostana* stabilized with 5 wt.% of the extract, respectively. It can be seen that the nano-sized particles are

nearly spherical shape. A low level of agglomeration was observed in the synthesized Fe_3O_4-NPs due to the strong inter-particles, Van der Waals force, and magnetic attraction among the particles. The irregular shapes were detected due to the agglomeration process [16]. Figure 3b indicates the EDX result that the elemental composition of Fe_3O_4-NPs/*G.Mangostana* was 68.45, 18.65 and 12.90 wt.% of iron (Fe), oxygen (O), and carbon (C), respectively. This proved the existence of *G.Mangostana* extract and purity of the synthesized NPs. Also, the presence of the hydroxyl groups in the peel extract may lead to agglomeration and enhance the ratio of the carbon. The histogram of NPs size distribution was plotted with 180 counts as shown in Figure 3c. The size distribution is between 20 nm and 145 nm with a mean size of 69.14 ±2.87 nm and a standard deviation of 2.31 nm. Thus, the SEM study displayed that the biosynthesized Fe_3O_4 NPs possessed nearly spherical shapes as coated with the extract stabilizer.

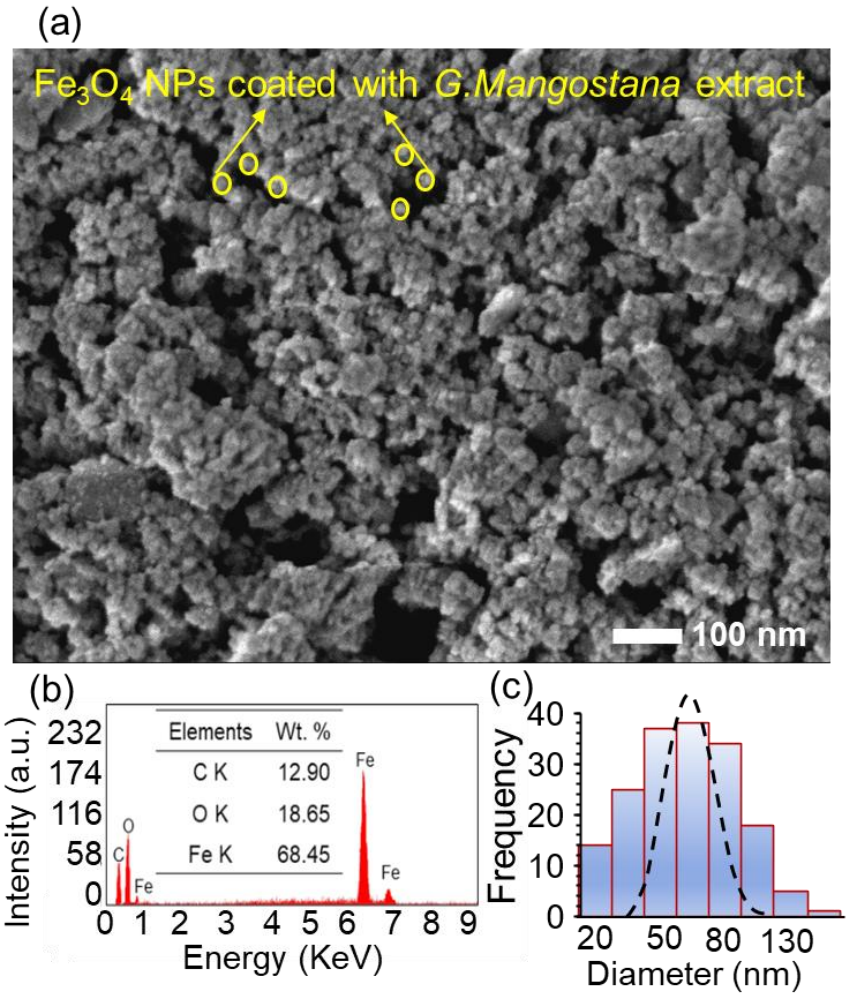


Figure 3. (A) FESEM image, (B) EDS spectra, and histogram of the green synthesized Fe_3O_4-NPs/*G.Mangostana* containing 5 wt.% of the extract stabilizer.

3.3 Vibrating-Sample Magnetometer (VSM) of Fe_3O_4-NPs/*G.Mangostana*

The VSM study of the synthesized Fe_3O_4-NPs/*G.Mangostana* is shown in Figure 4. The saturation magnetization of Fe_3O_4-NPs/*G.Mangostana* was found to be 51.17 emu/g, respectively, at room temperature. The samples with the extract showed an acceptable magnetic property, indicating the contribution of the extract stabilizer was suitable for the production of the Fe_3O_4 NPs. When the magnetic field was removed, an increase in the applied field rose the magnetic moment/mass.

Hysteresis loops occurred when the external magnetic field was applied to the NPs [22] and magnetization decreased from a plateau value to zero. The extract ratio decreased the saturation magnetization due to the non-magnetic nature of the extract as coated the magnetic NPs. It can be understood from the VSM results, the green synthesized Fe_3O_4 NPs could be used for various applications.

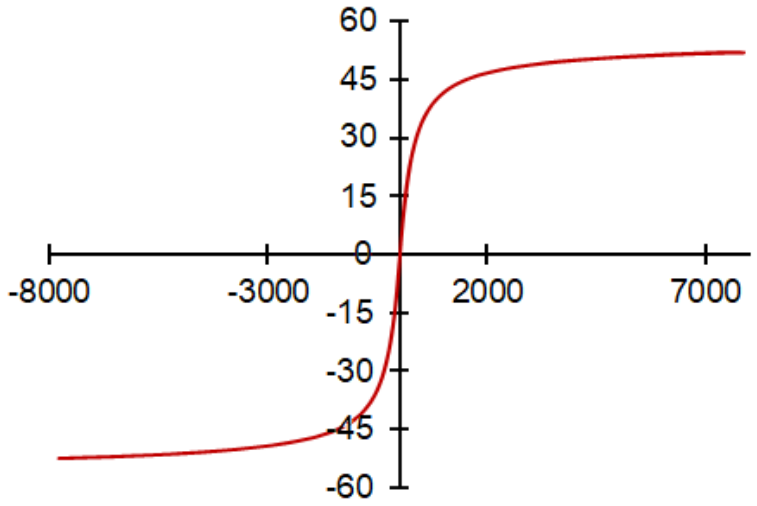


Figure 4. (A) Saturation magnetization of the green synthesized Fe_3O_4-NPs/*G.Mangostana* containing 5 wt.% of the extract stabilizer.

3.4 Measurement of zeta potential, hydrodynamic diameter and polydispersity index of Fe_3O_4-NPs/*G.Mangostana*

Table 1 shows the values of the zeta potential values, hydrodynamic size, and polydispersity index of the biosynthesized Fe_3O_4-NPs/*G.Mangostana*. The extract stabilizer favorably led to obtain the high zeta potential value and small hydrodynamic size. Fe_3O_4-NPs/*G.Mangostana* with the extract stabilizer concentration (5 wt.%) showed the zeta potential, hydrodynamic size, and polydispersity index value of -30.5±1.82 mV, 145.80±3.14 nm, and 0.24±0.07, respectively. This may show the coating of the NPs with the plant extract provided a repulsive force between the NPs [23]. Since the magnetic sample obtained the polydispersity index values below 0.7, it shows the properties of narrow particle size distribution and proved that polyphenolic molecules of the *G.Mangostana* extract may cause the nucleation of Fe_3O_4 with narrow dispersity [9].

Table 1. Zeta potential, hydrodynamic size and polydispersity index of the nanofluids of the green synthesized Fe_3O_4-NPs/*G.Mangostana* containing 5 wt.% of the extract stabilizer.

Sample	Zeta potential (mV)	Hydrodynamic size (nm)	Polydispersity index
Fe_3O_4-NPs/*G.Mangostana*	-30.5±1.82	145.80±3.14	0.24±0.07

3.5 Fourier-Transform Infrared Spectroscopy (FTIR)

Figure 5 shows FTIR spectra of Fe_3O_4-NPs/*G.Mangostana*. The C=O stretching vibration and C-O stretch could be due to the presence of the carbonyl group in the anthocyanin structure and alcohol

group, respectively. Of this, broad band between 1637 cm^{-1} could be due to C=O stretching vibration. Furthermore, the peaks in a range from 3435 cm^{-1} was assigned to the hydroxyl group, representing the O-H stretching vibration. The functional groups of O-H, C=O, and C-O could maybe indicate the presence of gartanin compound in the sample. Gartanin is a chemical compound in xanthone isolated from *G.Mangostana* fruit peel. A peak appeared at 698 cm^{-1} indicated characteristic of metal-oxygen band, which was the Fe-O stretching vibration of Fe_3O_4 NPs. These stretching vibration bands could be linked to the metal in the tetrahedral and octahedral site [24]. Thus, the FTIR results could indicate that the extract successfully served as both stabilizing and capping agents during the green synthesis process of Fe_3O_4-NPs/*G.Mangostana*.

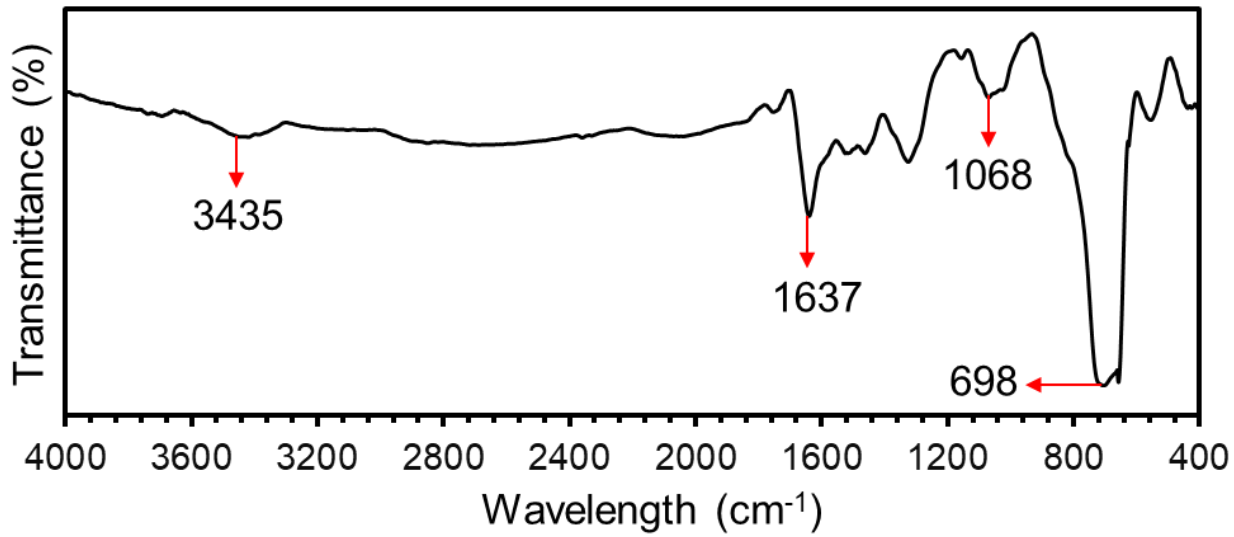


Figure 5. FTIR spectra of Fe_3O_4-NPs/*G.Mangostana* containing 5 wt.% of the extract stabilizer.

4. Conclusion

In this work, the green synthesis of magnetic Fe_3O_4 nanofluids (Fe_3O_4-NPs/*G.Mangostana*) was carried out by using 5 wt.% of a green stabilizer of *G. Mangostana* fruit peel extract. The XRD data showed that Fe_3O_4-NPs/*G.Mangostana* with high crystallinity and a pattern related to the Fe_3O_4 magnetite phase. The FESEM image of the sample displayed that the extract of *G.Mangostana* fruit peel could role as a coating agent for Fe_3O_4 NPs. The saturation magnetization value of Fe_3O_4-NPs/*G.Mangostana* was 51.17 emu/g. The FTIR data indicated that the green synthesized Fe_3O_4-NPs/*G.Mangostana* contained the spectroscopy peaks related to the iron and the extract with xanthone, carboxylic, alcohol, and aromatic groups. The solution of the synthesized nanoparticles showed good colloidal stability with zeta potential values of -30.5±1.82 mV and hydrodynamic size of 145.80±3.14 nm. In conclusion, this research introduced that the extract of *G.Mangostana* fruit peel can be used as a green stabilizer and capping agent to fabricate Fe_3O_4 NPs for potentially use in various applications.

Funding

This research was funded by Takasago Thermal Engineering Co. Ltd. grant (#4B422) from the research management center (RMC) of Universiti Teknologi Malaysia (UTM) and Malaysia-Japan International Institute of Technology (MJIIT).

Acknowledgement

Special thanks to of Universiti Teknologi Malaysia (UTM) and Malaysia-Japan International Institute of Technology (MJIIT) for supports.

References

1. Kumar, A. and S. Subudhi, Preparation, characteristics, convection and applications of magnetic nanofluids: A review. Heat and Mass Transfer, 2018. 54(2): p. 241-265. doi: 10.1007/s00231-017-2114-4.
2. Felicia, L.J., S. Vinod, and J. Philip, Recent advances in magnetorheology of ferrofluids (magnetic nanofluids)—a critical review. J. Nanofluids, 2016. 5(1): p. 1-22. doi: 10.1166/jon.2016.1203.
3. Yew YP, Shameli K, Miyake M, Khairudin NBBA, Mohamad SEB, Naiki T, Lee KX, Green biosynthesis of superparamagnetic magnetite Fe_3O_4 nanoparticles and biomedical applications in targeted anticancer drug. Arab. J. Chem. 2020;13(1):2287-2308. doi: 10.1016/j.arabjc.2018.04.013.
4. Hedayatnasab Z, Abnisa F, Daud WMAW. Review on magnetic nanoparticles for magnetic nanofluid hyperthermia application. Mater. Des. 2017;123:174-196. doi: 10.1016/j.matdes.2017.03.036.
5. Yusefi, M., K. Shameli, and A.F. Jumaat, Preparation and Properties of Magnetic Iron Oxide Nanoparticles for Biomedical Applications: A Brief Review. Journal of Advanced Research in Materials Science, 2020. 75(1): p. 10-18. doi: 10.37934/arms.75.1.1018.
6. Yusefi, M., Shameli, K., Hedayatnasab, Z., Teow. S-Y., Ismail, U.N., Azlan, A.C., Ali, R.R., Green synthesis of Fe_3O_4 nanoparticles for hyperthermia, magnetic resonance imaging and 5-fluorouracil carrier in potential colorectal cancer treatment. Res. Chem. Intermed., 2021: p. 1-20. doi: 10.1007/s11164-020-04388-1.
7. Herlekar M, Barve S, Kumar R. Plant-mediated green synthesis of iron nanoparticles. J. Nanopart., 2014;2014. doi: 10.1155/2014/140614.
8. Magro M, Vianello F. Bare iron oxide nanoparticles: Surface tunability for biomedical, sensing and environmental applications. Nanomaterials, 2019;9(11):1608. doi: 10.3390/nano9111608..
9. Yusefi M, Shameli K, Ali RR, Pang S-W, Teow S-Y. Evaluating anticancer activity of plant-mediated synthesized iron oxide nanoparticles using Punica granatum fruit peel extract. J. Mol. Struct., 2020;1204:127539. doi: 10.1016/j.molstruc.2019.127539.
10. Kallumadil, M., Tada, M., Nakagawa, T., Abe. M., Southern, P., Pankhurst, Q.A., Suitability of commercial colloids for magnetic hyperthermia. J. Magn. Magn., 2009. 321(10): p. 1509-1513. doi: 10.1016/j.jmmm.2009.02.075
11. Ogholbeyg AB, Kianvash A, Hajalilou A, Abouzari-Lotf E, Zarebkohan A. Cytotoxicity characteristics of green assisted-synthesized superparamagnetic maghemite (γ-Fe_2O_3) nanoparticles. J. Mater. Sci. Mater., Electron 2018;29(14):12135-12143. doi: 10.1007/s10854-018-9321-8.
12. Izadiyan Z, Shameli K, Miyake M, et al. Cytotoxicity assay of plant-mediated synthesized iron oxide nanoparticles using Juglans regia green husk extract. Arab. J. Chem., 2018. doi: 10.1016/j.arabjc.2018.02.019.
13. Tungmunnithum D, Thongboonyou A, Pholboon A, Yangsabai A. Flavonoids and other phenolic compounds from medicinal plants for pharmaceutical and medical aspects: An overview. Medicines, 2018;5(3):93. doi: 10.3390/medicines5030093.
14. Suttirak W, Manurakchinakorn S. In vitro antioxidant properties of mangosteen peel extract. J. Food Sci. Technol., 2014;51(12):3546-3558. doi: 10.1007/s13197-012-0887-5.
15. El-Faham S, Mohsen M, Sharaf A, Zaky A. Utilization of mango peels as a source of polyphenolic antioxidants. Curr. Sci. Int., 2016;5(04):529-542
16. Yew YP, Shameli K, Mohamad SEB, et al. Potential anticancer activity of protocatechuic acid loaded in montmorillonite/Fe_3O_4 nanocomposites stabilized by seaweed Kappaphycus alvarezii. Int. J. Pharm., 2019;572:118743. doi: 10.1016/j.ijpharm.2019.118743.
17. Xin Lee K, Shameli K, Miyake M, et al. Green synthesis of gold nanoparticles using aqueous extract of Garcinia mangostana fruit peels. J. Nanomater., 2016;2016. doi: 10.1155/2016/8489094.

18. Lee KX, Shameli K, Mohamad SE, et al. Bio-Mediated Synthesis and characterisation of silver nanocarrier, and its potent anticancer action. Nanomaterials, 2019;9(10):1423. doi: 10.3390/nano9101423
19. Holzwarth U, Gibson N. The Scherrer equation versus the'Debye-Scherrer equation'. Nat. Nanotechnol., 2011;6(9):534-534. doi: 10.1038/nnano.2011.145
20. Kroon R. Nanoscience and the Scherrer equation versus the'Scherrer-Gottingen equation'. S. Afr. J. Sci. 2013;109(5-6):01-02. doi: 10.1590/sajs.2013/a0019.
21. Lassoued, A., Dkhil, B., Gadri, A., Ammar, S. Control of the shape and size of iron oxide (α-Fe2O3) nanoparticles synthesized through the chemical precipitation method. Results Phys., 2017. 7: p. 3007-3015. doi: 10.1016/j.rinp.2017.07.066.
22. Yang J, Kim J, Lee J, et al. Inverted hysteresis loops observed in a randomly distributed cobalt nanoparticle system. Phys. Rev. B, 2008;78(9):094415. doi: 10.1103/PhysRevB.78.094415.
23. Sathishkumar G, Logeshwaran V, Sarathbabu S, et al. Green synthesis of magnetic Fe_3O_4 nanoparticles using Couroupita guianensis Aubl. fruit extract for their antibacterial and cytotoxicity activities. Artif. Cell Nanomed., 2018;46(3):589-598. doi: 10.1080/21691401.2017.1332635.
24. Testa-Anta M, Ramos-Docampo MA, Comesaña-Hermo M, Rivas-Murias B, Salgueiriño V. Raman spectroscopy to unravel the magnetic properties of iron oxide nanocrystals for bio-related applications. Nanoscale Advances., 2019;1(6):2086-2103. doi:10.1039/C9NA00064J.