

Magnetic and Structural Characteristics of Fe₂O₃ Nanostructure Synthesized in the Presence of Sour Cherry Juice

Mohammad Reza Mohammad Shafiee¹, Mahboubeh Kargar^{2,*}, Majid Ghashang¹

¹ Department of chemistry, Faculty of Sciences, Najafabad Branch, Islamic Azad University, Najafabad, Iran

² Department of physics, Faculty of Sciences, Najafabad Branch, Islamic Azad University, Najafabad, Iran; P.O

ARTICLE INFO

Article history:

Received 17 May 2016

Accepted 5 September 2016

Available online 25 September 2016

Keywords:

Sour cherry juice
Fe₂O₃ nanostructure
Green synthesis
Magnetism characterization

ABSTRACT

The nanostructures of Fe₂O₃ have been synthesized applying sour cherry juice and iron chloride as a low-cost and eco-friendly method at ambient conditions. Sour cherry juice has been used as a surfactant and the kind of surfactant had an important effect on the size and morphology of the products. The effect of sour cherry juice concentration and calcination temperature on the morphologies of Fe₂O₃ nanostructures has been investigated. The prepared nanoparticles were subjected to X-ray diffraction (XRD) analysis, field emission scanning electron microscopy (FE-SEM), and vibrating sample magnetometer (VSM) system. The powder X-ray diffraction analysis confirmed that Fe₂O₃ nanostructures are in Rhombohedral and Cubic phases. The average crystalline size estimated by the Williamson-hall method was about 13-32 nm for all samples. Various morphologies were also obtained by changing the amount of sour cherry juice. The saturation magnetization increased with the growth of crystals.

1. Introduction

The construction of nano-scale materials with the modified size, dimension, morphology, and so forth has been receiving a great deal of attention not only for their common interest, but also for many practical and technological applications [1]. Alternatively, the development of new methods for the preparation of nanomaterials which would overcome the problems caused by the present methods is of great interest. Recently, many efforts have been made to search for alternative biotechnologies and green mediums synthesis in order to develop a new method for the creation of nano-materials, as this is essential for addressing applications such as green synthesis and clean energy storage [2-11].

The use of fungus, leaf, bacteria, and plant extracts as the green media for the synthesis of

nano-materials and especially metal oxides is called the biosynthesis method. The wide ranging application of metal oxides increased the awareness towards green chemistry of these materials. The biosynthesis approach has led to a desire to develop an eco-friendly approach for the synthesis of nanocrystalline metal oxides [12-20].

Hematite (-Fe₂O₃) as one of the most important metal oxides and an n-type semiconductor has attracted much interest due to its narrow band gap of 2.1 eV, and magnetic, anti-corrosive properties, which are applicable in medical science, catalysis, pigments, photonics, water treatment, sensors, electrochemistry and magnetism [21-23].

These properties of Fe₂O₃ have led the scientists to expose various methods for the preparation of different shapes and sizes of

* Corresponding author:

E-mail: mahboubeh_kargar@yahoo.com

Fe₂O₃. As a consequence, a variety of methods have been reported for the synthesis of iron oxide nanoparticles, including sol-gel, micro-emulsion, sono-chemical, ultrasonic spray pyrolysis and microwave plasma methods [24, 25]. Some of these methods have their drawbacks as they mainly involve several steps, and are usually time consuming, costly, and toxic [26]. To overcome these problems, biosynthesis as a green synthesis method for preparation of Fe₂O₃ nanoparticles has been reported applying plants such as Camellia sinensis leaves and curcuma and tea leaf extract. These green syntheses are simple and viable alternatives to chemical and physical methods [27, 28].

In the present work, we expanded the green biosynthesis of Fe₂O₃ nanoparticles by the use of sour cherry juice for the first time as the stabilizer and capping agent to control the crystal growth for synthesis of Fe₂O₃ nanocrystalline using co-precipitation method. The method is cost-effective and non-toxic, and generally leads to the formation of crystalline nanostructures with a collection of shapes. Furthermore, the effect of various amounts of sour cherry juice and different calcination temperatures on morphology, crystal-size, and magnetic properties of the samples is investigated.

2. Materials and methods

2.1. Physical measurements

Phase identification the as-precipitated and heat treated samples was carried out by X-ray diffraction (XRD) method with a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu-K radiation. Field emission scanning electron

microscope (FE-SEM) images were obtained on HITACHI S-4160. The magnetic measurements were performed by a Lake Shore 7300 vibrating sample magnetometer (VSM) system. The size of the particle was calculated with the help of Williamson-Hall plot.

2.2. Synthesis of Fe₂O₃ particles

Ferric chloride hexahydrate was purchased from Merck Company and used without further purification. Fe₂O₃ nanostructures were prepared by the following experimental progression: two different solutions were prepared. Solution A: a solution of 20 mmol of FeCl₃. 6H₂O was dissolved in 200 mL of aqueous ethanol 50% (v/v). Solution B: a mixture of various amounts (100, 150, and 200 mL) of sour cherry juice with 20 mL of aqueous ammonia. Solution B was added drop wise into e solution A. The obtained mixture was stirred at room temperature for 15 min. The resultant black precipitates were filtered, washed with distilled water and pure ethanol and dried at room temperature. Moreover, the experiment was carried out by using 100, 150 and 200 mL of sour cherry juice under the same conditions, respectively. The precipitates were then heated slowly up to 600 °C in an electric furnace using alumina crucibles and maintained at the mentioned stable temperature for 2h. For investigating the calcination temperature, the sample that was synthesized with 100 mL of sour cherry juice was heated at 500 and 700 °C. For comparison, a blank sample was prepared by 100mL of water and then heated in 600 °C for 2h. After calcination, the obtained Fe₂O₃ products were stored in an airtight container for further analysis. All samples have been shown on Table 1.

Table 1. The properties of all samples.

Sample No.	Amount of Sour cherry Juice (mL)	Temperatu Calcination	Crystal size (nm)	Morphology
1	100	500	13	Nano-rod and Cube-shape
2	100	600	14	Agglomerated nano-rod and c
3	150	600	19	Nano-rod
4	200	600	21	Agglomeration
5	100	700	32	Agglomerated nanoparticle
6	-	600	210	-

3. Results and discussion

The XRD patterns of Fe₂O₃ nanoparticles prepared with various amounts of sour cherry juice and calcined at different temperatures are shown in Figures 1, 2, and 3.

All the XRD peaks could easily be indexed to rhombohedral Fe₂O₃ (space group R-3C) with lattice parameters $a = b = 5.03 \text{ \AA}$, $c = 13.7370 \text{ \AA}$, $\text{Alpha} = 55.20^\circ$ (JCPDS 013-034) and cubic Fe₂O₃ (space group L-3a) with lattice parameters $a = 9.4040 \text{ \AA}$, $\text{Alpha} = 90^\circ$ (JCPDS 039-0238).

The XRD peaks of Fe₂O₃ blank sample are indexed to rhombohedral Fe₂O₃ (space group R-3C) with lattice parameters $a = b = 5.03 \text{ \AA}$, $c = 13.7370 \text{ \AA}$, $\text{Alpha} = 90^\circ$ (JCPDS-013-0534).

By using the slope of the Williamson-Hall plot [29] based on the powder diffraction peak broadening the crystalline size of Fe₂O₃ nanoparticles was evaluated and the result is summarized in Table 1. Surprisingly, crystals have grown completely and their size has increased by increasing the amount of sour cherry juice due to the presence of hydrogen bonding [30]. Undoubtedly, the more the increase of the calcination temperature, the more the growth of sample crystalline size will be. The particle size of Fe₂O₃ decreased by adding the sour cherry juice in comparison with a blank sample since sour cherry juice act as a surfactant.

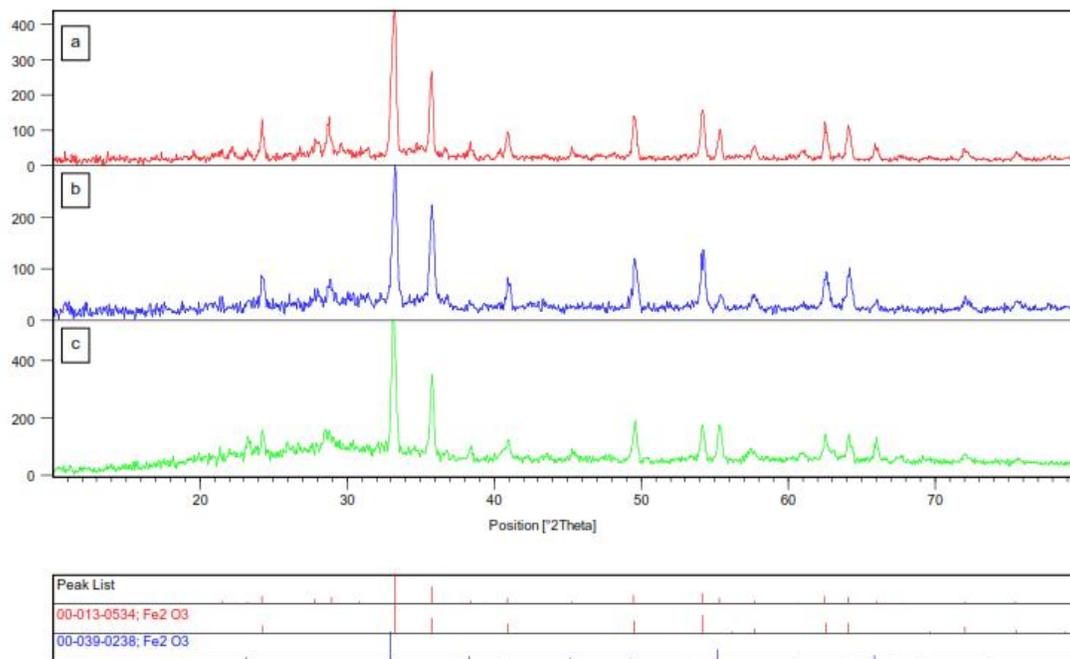


Fig. 1. XRD patterns of Fe₂O₃ particles synthesized at different calcination temperature: (a) 500°C, (b) 600°C, and (c) 700°C.

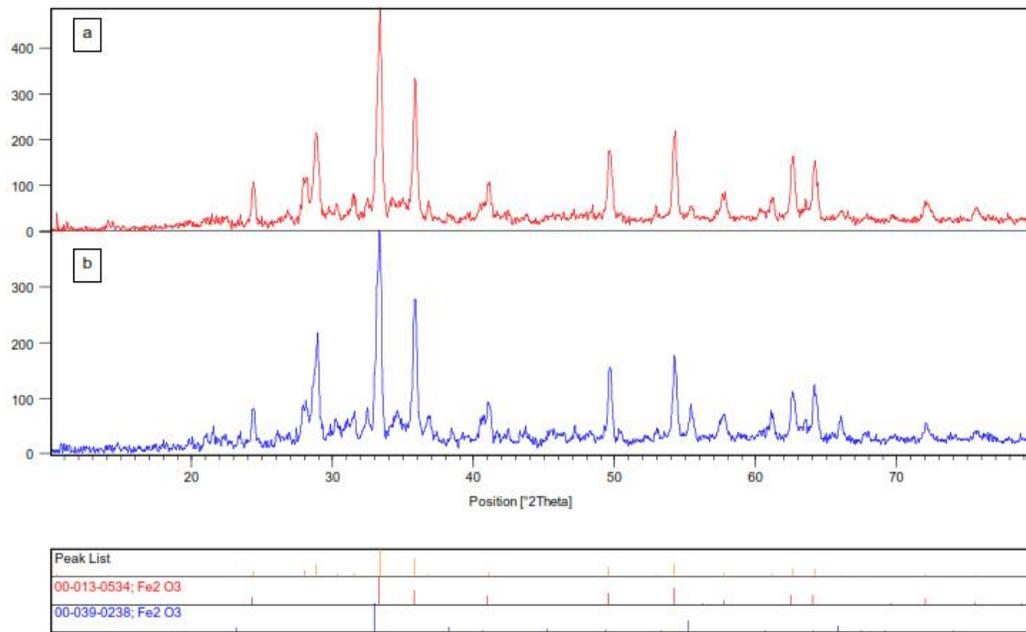


Fig. 2. XRD patterns of Fe_2O_3 particles synthesized using (a) 150 mL and (b) 200 mL of sour cherry juice.

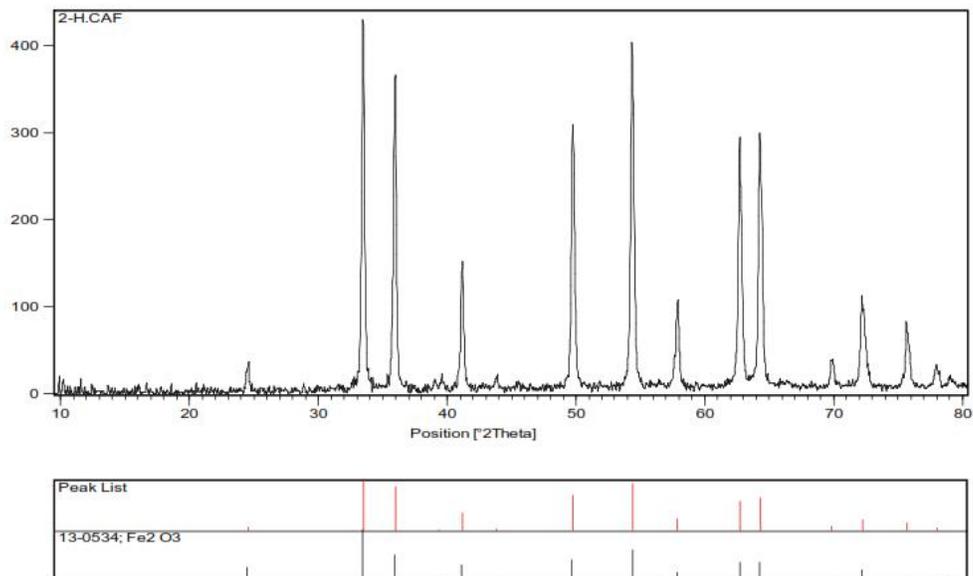


Fig. 3. XRD patterns of Fe_2O_3 particles synthesized without sour cherry juice in 600 °C.

The morphological investigation of the as-prepared samples was done using FE-SEM technique. The FE-SEM images of the as-prepared Fe_2O_3 nano-structures using 100 mL of sour cherry juice and calcined at different temperatures of 500, 600 and 700 °C are shown in Figure 4. It was revealed that the use of 100 mL of sour cherry juice and a calcination temperature of 500 °C would lead to the formation of mixtures of morphology, including nano-rods and nano-cubes of Fe_2O_3 samples (Figures 4a and 4b). The bundles of nano-rods have a wide range in length and diameter. Straight threads, with a minimum diameter of 100-150 nm, grow radially from the nucleation points on the surface of the aggregated nanoparticles.

With increasing the calcination temperature to 600 °C, a break on the nano-rods aggregation has occurred (Figures 4c and 4d). By enhancing the calcination temperature to 700 °C, the formation of nano-rods disappears and the amount of agglomerated particles has increased (Figure 4e and 4f).

In this regard, we used sour cherry juice as a cheap and available surfactant. Moreover, anthocyanin as the major component of sour cherry is most likely responsible for uniform shapes and sizes of the confirmed nanoparticles [31]. The existence of the relatively resistant benzene rings in sour cherry is a distinct advantage to prevent agglomeration due to the high-temperature heating of powders. Schematic diagram (Figure 5) illustrates the effect of antioxidants in sour cherry juice.

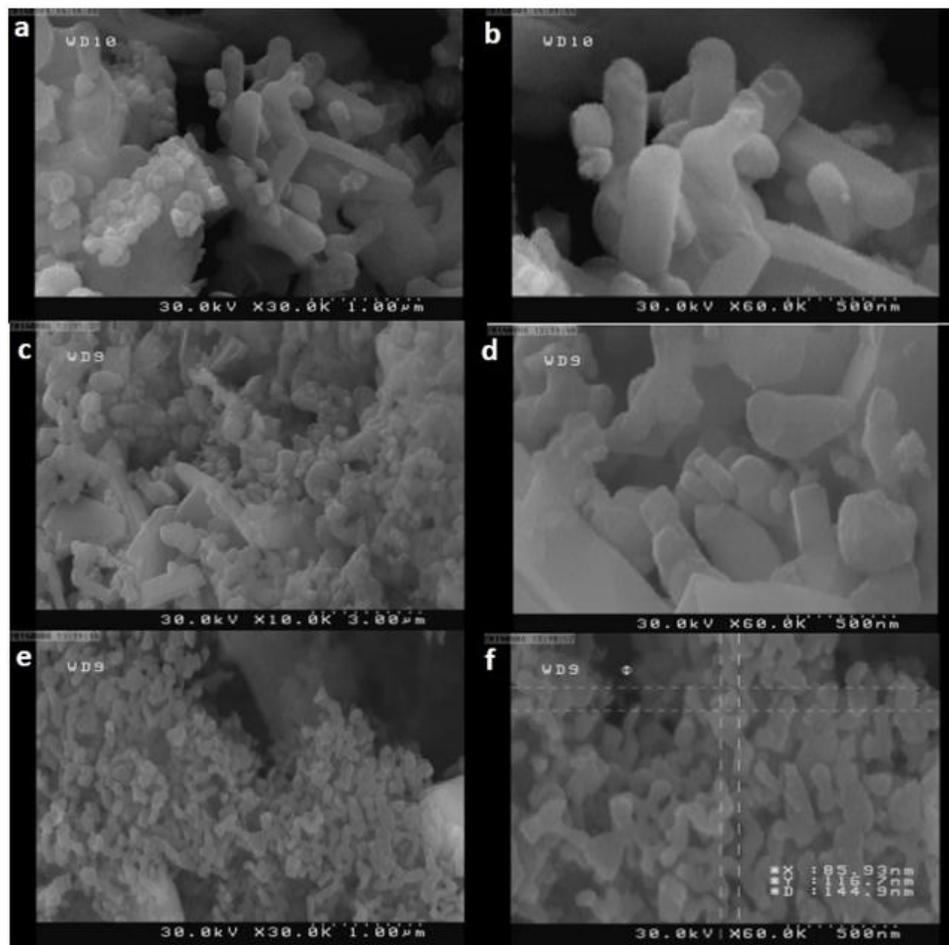


Fig. 4. SEM images of Fe_2O_3 particles calcinated at (a) and (b) 500°C, (c) and (d) 600°C, (e) and (f) 700°C.

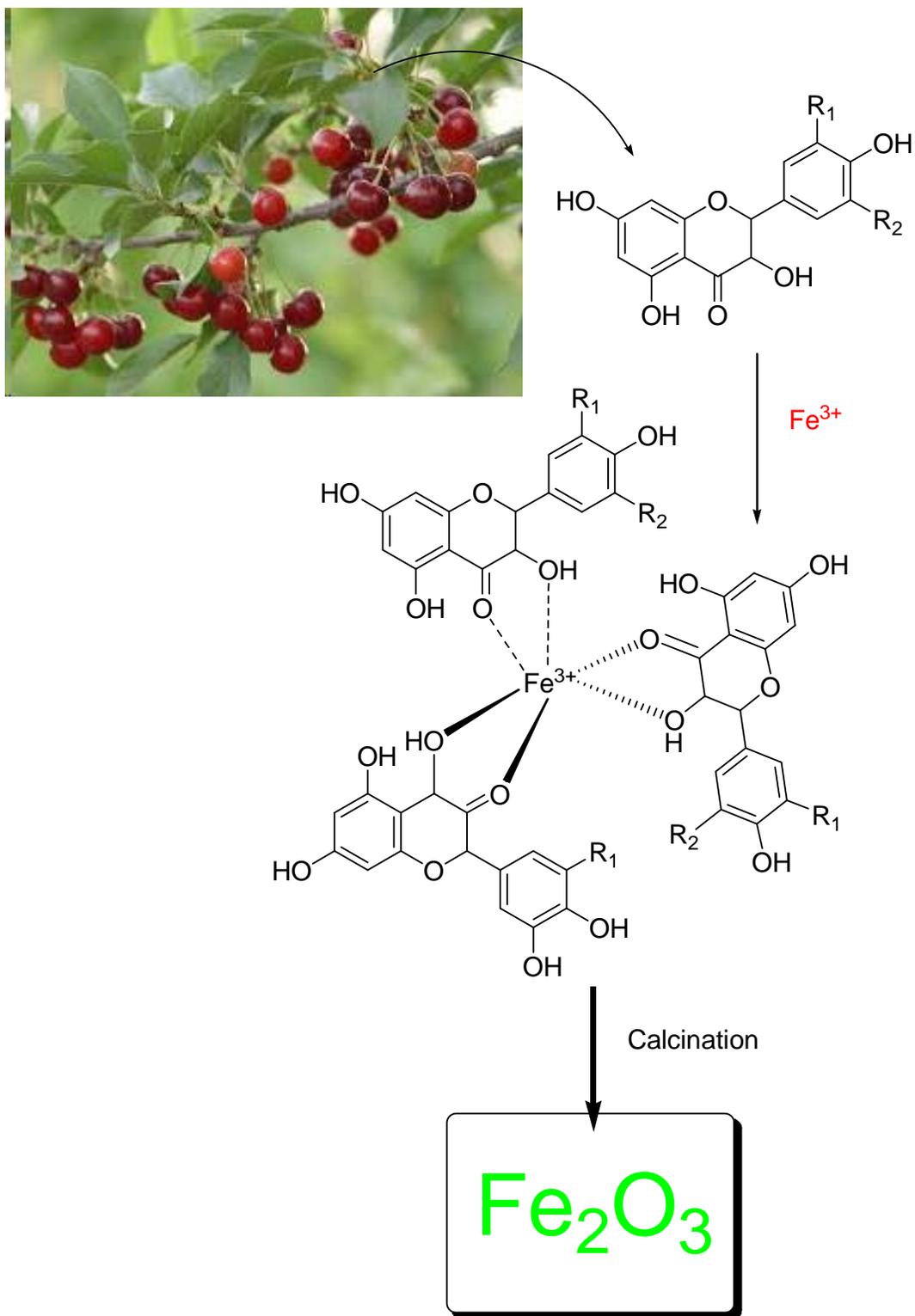


Fig. 5. Effect of antioxidants (or phenolic) from sour cherry juice in synthesis of Fe_2O_3 nanoparticles.

For further investigation, the effect of concentration of the surfactant was studied by changing the amount of sour cherry juice from 100, 150 and 200 mL in the other Fe_2O_3 samples. It can be seen in FE-SEM images (Figure. 6) that the Fe_2O_3 nanoparticles are synthesized in the presence of sour cherry juice. Figures 6a and 6b, which include 150 mL sour cherry juice, show that the nano-rods have grown non-uniformly. In Figures 6c and 6d, by raising the molar ratio to 50 mL, agglomerated particles are obtained. By enhancing the amount of sour cherry juice to 200 mL, heterogeneous particles are produced. Clearly, the agglomeration processes take place between the Fe_2O_3 nanoparticles capped by anthocyanin molecules in sour cherry juice

thanks to the presence of hydrogen bonding.

It is found that the size and shape of nanoparticles are affected by many preparation parameters, such as the initial materials, the type of utilized surfactant, the annealing time, and so forth. According to Table 2 and Figure 7, the magnetic property of all samples of Fe_2O_3 nanoparticles has been considered. Through increasing the calcination temperature, the saturation magnetization (M_s) has increased and the coercivity field (H_c) has decreased. By enhancing the amount of sour cherry juice, the saturation magnetization (M_s) has risen and the coercivity field (H_c) has dropped off in lieu of 200 ml of sour cherry juice.

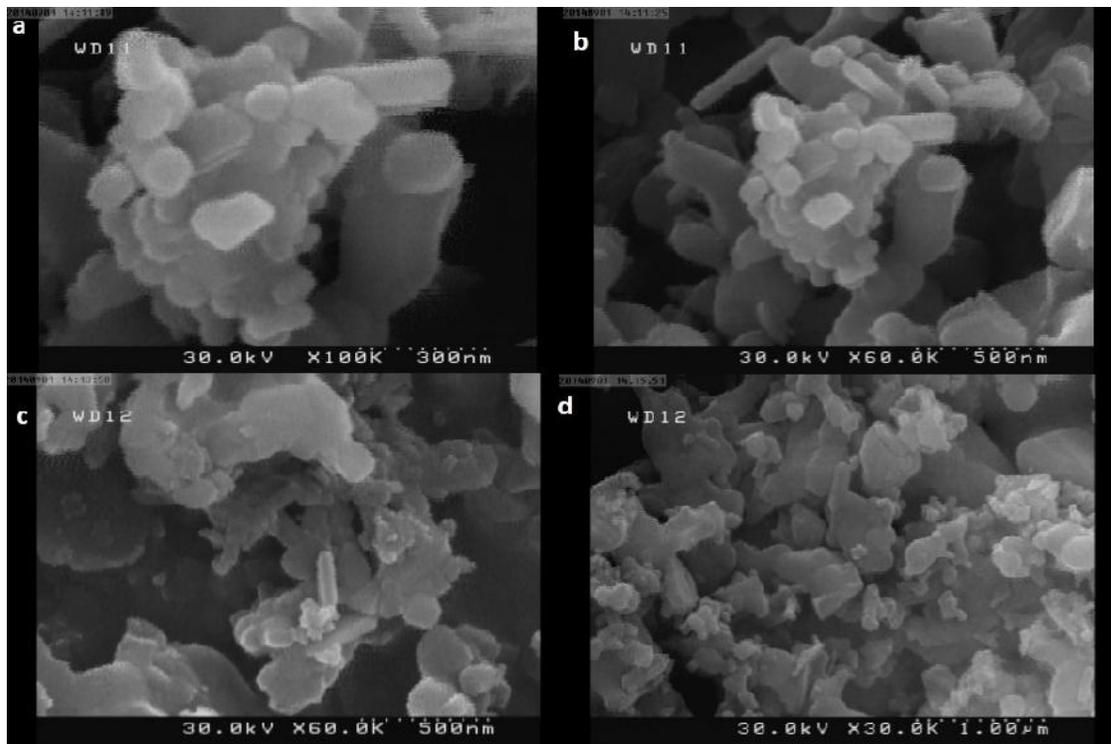
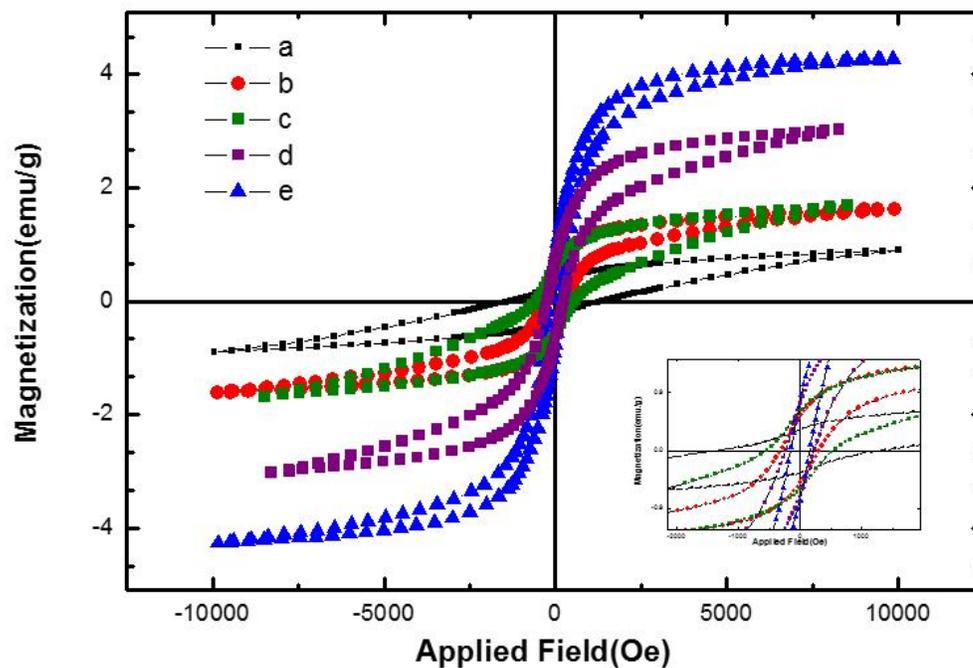


Fig. 6. SEM images of Fe_2O_3 particles synthesized using (a) and (b) 150 mL; (c) and (d) 200 mL of sour cherry juice.

Table 2. The magnetic properties of all samples.

Sample No.	Amount of Sourcherry Juice (mL)	Temperature of Calcination ($^{\circ}\text{C}$)	(Emu/g) M_s	M_r (emu/g)	S_q	H_c (loop) (Oe)
1	100	500	0.90	0.54	0.60	1090
2	100	600	1.61	1.04	0.65	313
3	150	600	1.69	1.04	0.62	581
4	200	600	3.02	2.45	0.81	246
5	100	700	4.26	3.45	0.80	171

**Fig. 7.** VSM of Fe_2O_3 particles: (a) Sample1, (b) sample2, (c) sample3, (d) sample4, and (e) sample5.

In order to have a comparison between the sizes of the as-prepared samples and to understand the effect of the crystal size, concentration was done on the coercivity field and statistical analysis was performed from the XRD and VSM analysis to obtain information about the crystal size distribution of the samples

and the results are shown in Figure 8. It was revealed that the crystal diameters are in the range of 13 -32 nm.

In comparison with the XRD results, clearly, the coercivity field has decreased with the enhancing of the crystal size, which is in accordance with the Cullity theory [32].

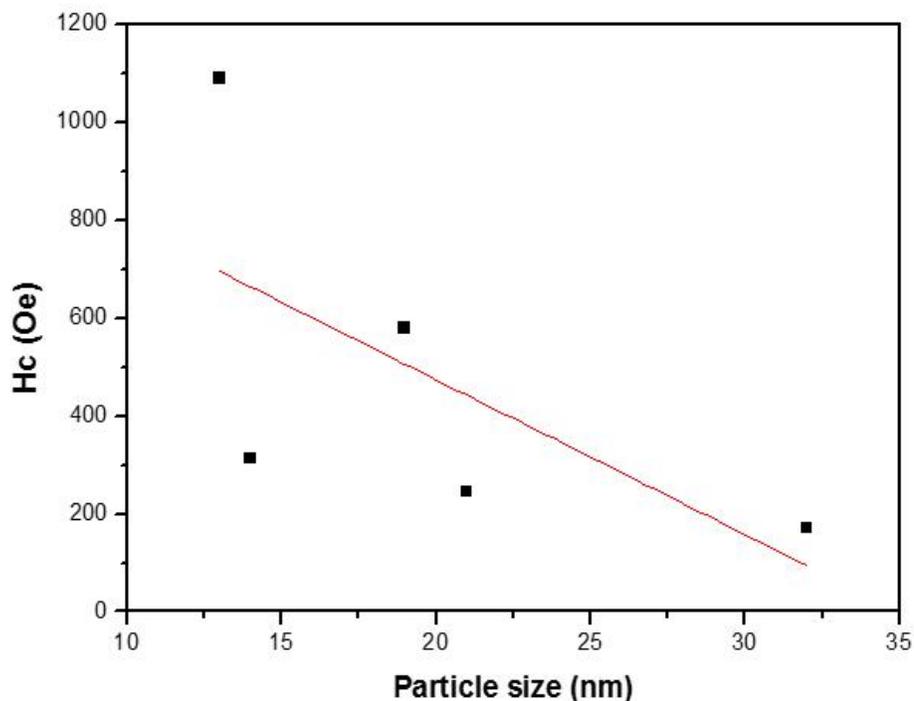


Fig. 8. Investigation of crystal size on the Coercivity Field (Hc).

4. Conclusions

Fe₂O₃ nanostructures with various morphologies have been successfully prepared via a co-precipitation method with iron chloride. The use of sour cherry juice as surfactant was the novelty of this work and it was found that the kind of surfactant had an important effect on the size and morphology of the products. The qualities of the method, nanometer scale were formed by reasonable and low-price in a normal atmosphere in which green synthesis. The XRD results showed that Fe₂O₃ powders were formed with crystalline sizes around 13-32 nm, and that the coercivity field (Hc) decreased with the growth of crystals.

References

- [1] K.J. Klabunde, R.M. Richards, *Nanoscale Materials in Chemistry*, 2nd ed., John Wiley & Sons, New Jersey, 2009.
- [2] A. Quarta, R.D. Corato, L. Manna, S. Argentiere, R. Cingolani, G. Barbarella, T. Pellegrino, "Multifunctional nanostructures based on inorganic nanoparticles and oligothiophenes and their exploitation for cellular studies", *J. Am. Chem. Soc.*, Vol. 130, pp. 10545-10555.
- [3] P. Sun, H. Zhang, C. Liu, J. Fang, M. Wang, J. Chen, J. Zhang, C. Mao, S. Xu, S. Langmuir, "Preparation and characterization of Fe₃O₄/CdTe magnetic/fluorescent nanocomposites and their applications in immuno-labeling and fluorescent imaging of cancer cells", *Langmuir*, Vol. 26, 2009, pp. 1278-1284.
- [4] W.C. Law, K.T. Yong, I. Roy, G.X. Xu, H. Ding, Z.H. Bergey, P.N.J. Prasad, "Optically and magnetically doped organically modified silica nanoparticles as efficient magnetically guided biomarkers for two-photon imaging of live cancer cells", *J. Phys. Chem. C*, Vol. 112, 2008, pp. 7972-7977.
- [5] S.A. Corr, Y.P. Rakovich, Y.K. Gun'ko, "Multifunctional magnetic-fluorescent nanocomposites for biomedical

- applications”, *Nanoscale Res. Lett.*, Vol. 3, 2008, pp. 87-104.
- [6] R. He, X. You, J. Shao, F. Gao, B. Pan, D. Cui, “Core/shell fluorescent magnetic silica-coated composite nanoparticles for bioconjugation”, *Nanotechnol.*, Vol. 18, 2007, pp. 315601-315608.
- [7] M. Jr. Bruchez, M. Moronne, P. Gin, S. Weiss, A.P. Alivisatos, “Semiconductor nanocrystals as fluorescent biological labels”, *J. Sci.*, Vol. 281, 1998, pp. 2013-2016.
- [8] N. Kohler, C. Sun, J. Wang, M. Zhang, “Methotrexate-modified superparamagnetic nanoparticles and their intracellular uptake into human cancer cells”, *Langmuir*, Vol. 21, 2005, pp. 8858-8864.
- [9] M.R. Mohammad Shafiee, M. Ghashang, A. Fazlinia, “Preparation of 1,4-dihydropyridine derivatives using perchloric acid adsorbed on magnetic Fe₃O₄ nanoparticles coated with silica”, *Curr. Nanosci.*, Vol. 9, 2013, pp. 197-201.
- [10] M. Dehbashi, M. Aliahmad, M.R. Mohammad Shafiee, M. Ghashang, “Nickel doped SnO₂ nanoparticles: Preparation and evaluation of their catalytic activity in the synthesis of 1-amidoalkyl-2-naphtholes”, *Synth. React. Inorg. Met. Org. Chem.*, Vol. 43, 2013, pp. 1301-1306.
- [11] M. Ghashang, “Preparation and application of barium sulfate nanoparticles in the synthesis of 2,4,5-triaryl and N-aryl(alkyl)-2,4,5-triaryl imidazoles”, *Curr. Org. Synth.*, Vol. 9, 2012, pp. 727-732.
- [12] K.C. Bhainsa, S.F.D. Souza, “Extracellular biosynthesis of silver nanoparticles using the fungus *aspergillus fumigates*”, *Coll. Surf. B: Biointerfaces*, Vol. 47, 2006, p. 160.
- [13] I. Willner, B. Basnar, B. Willner, “Nanoparticle–enzyme hybrid systems for nanobiotechnology”, *J. FEBS*, Vol. 274, 2007, pp. 302-309.
- [14] N. Saifuddin, Fig.C.W. Wong, A.A.N.E. Yasumira, “Rapid biosynthesis of silver nanoparticles using culture supernatant of bacteria with microwave irradiation”, *J. Chem.*, Vol. 6, 2009, p. 61.
- [15] J.L. Gardea-Torresdey, J.G. Parsons, E. Gomez, J. Peralta-Videa, H.E. Troiani, P. Santiago, M. Jose Yacaman, “Formation and growth of Au nanoparticles inside live alfalfa plants”, *Nano Lett.*, Vol. 2, 2002, pp. 397-401.
- [16] J.L. Gardea-Torresdey, J.G. Parsons, E. Gomez, J. Peralta-Videa, H.E. Troiani, M. Jose-Yacaman, “Alfalfa sprouts: a natural source for the synthesis of silver nanoparticles”, *Langmuir*, Vol. 12, 2003, pp. 1357-1361.
- [17] J. Huang, Q. Li, D. Sun, Y. Lu, Y. Su, X. Yang, H. Wang, Y. Wang, W. Shao, N. He, J. Hong, C. Chen, “Biosynthesis of silver and gold nanoparticles by novel sundried *Cinnamomum camphora* leaf”, *Nanobiotechnol.*, Vol. 18, 2007, 18, 105104.
- [18] S.S. Shankar, A. Rai, A. Ahmad, M. Sastry, “Rapid synthesis of Au, Ag, and bimetallic Au core-Ag shell nanoparticles using Neem (*Azadirachta indica*) leaf broth”, *J. Colloid Interface Sci.*, Vol. 275, 2004, pp. 496-502.
- [19] B. Ankamwar, D. Chinmay, A. Absar, S. Murali, “Biosynthesis of gold and silver nanoparticles using *emblica officinalis* fruit extract, their phase transfer and transmetallation in an organic solution”, *J. Nanosci. Nanotechnol.*, Vol. 10, 2005, pp. 1665-1671.
- [20] S.S. Shankar, A. Rai, B. Ankamwar, A. Singh, A. Ahmad, M. Sastry, “Biological synthesis of triangular gold nanoprisms”, *Nat. Matter.*, Vol. 3, 2004, pp. 482-488.
- [21] N.D. Kandpal, N. Sah, R. Ioshali, R.; Joshi, J. Prasad, “Co-precipitation method of synthesis and characterization of iron oxid nanoparticles”, *J. Sci. Ind. Res.*, Vol. 73, 2014, pp. 87-90.
- [22] R.M. Cornell, U. Schwertmann, *The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses*, VCH Publisher, New York, 1996.
- [23] S. Bagheri, K.G. Chandrappa, A.H. Sharifah Bee, “Generation of Hematite Nanoparticles via Sol-Gel Method”, *Res. J. Chem. Sci.*, Vol. 3, 2013, pp. 62-68.
- [24] J. Grabis, G. Heidenmane, D. Rasmene, “Preparation of Fe₃O₄ and -Fe₂O₃ Nanoparticles by Liquid and Gas Phase Processes”, *J. Mater. Sci.*, Vol. 14, 2008, pp. 292-295.
- [25] E. Darezeshki, F. Bakhtiari, M. Alizadeh, A. Behradvakylabad, M. Ranjbar, “Direct thermal decomposition synthesis and characterization of hematite (-Fe₂O₃)

- nanoparticles”, *Mater. Sci. Semicond. Process*, Vol. 15, 2012, pp. 91–97.
- [26] P.P. Sarangi, B. Naik, N.N. Ghosh, “Low temperature synthesis of single-phase γ - Fe_2O_3 nano-powders by using simple but novel chemical methods”, *Powder Technol.*, Vol. 192, 2008, pp. 245–249.
- [27] M. Alagiri, A.H. Sharifah Bee, “Green synthesis of γ - Fe_2O_3 nanoparticles for photocatalytic application”, *J. Mater. Sci. Mater. Electron*, Vol. 25, 2014, pp. 3572-3577.
- [28] B. Ahmmad, K. Leonard, Md. Shariful Islam, J. Kurawaki, M. Muruganandham, T. Ohkubo, Y. Kuroda, “Green synthesis of mesoporous hematite (γ - Fe_2O_3) nanoparticles and their photocatalytic activity”, *Adv. Powder Technol.*, Vol. 24, 2013, pp. 160–167.
- [29] A. Khorsand Zak, W.H.A. Majid, M.E. Abrishami, R. Yousefi, “X-ray analysis of ZnO nanoparticles by Williamson-Hall and size-strain plot methods”, *Solid State Sci.*, Vol. 13, 2011, pp. 251-256.
- [30] F.Tavakoli, M. Salavati-Niasari, D. Ghanbari, K. Saberyan, S.M. Hosseinpour-Mashkani, “Application of glucose as a green capping agent and reductant to fabricate CuI micro/nanostructures”, *J. Mater. Res. Bull.*, Vol. 49, 2014, pp. 14-20.
- [31] L. Kaume, L.R. Howard, L. Devareddy, “The Blackberry Fruit: A Review on Its Composition and Chemistry, Metabolism and Bioavailability, and Health Benefits”, *J. Agric. Food Chem.*, Vol. 60, 2012, pp. 5716-5727.
- [32] B. D. Cullity, C. D. Graham, *Introduction to magnetic materials*, Second Edition John Wiley & Sons, New Jersey, 2009.