Comparative Study Between Hydrothermal And Co-Precipitation Methodes For The Synthesis Of Fe_3o_4Nanoparticle

MarwaYousef Freshik[1],Fathi Mohammad Asseid[2]

1. ***Dept.of Physics Faculty of Science, Zawia University***
2. ***Dept. of Chemistry Faculty of Science, Zawia University***

Abstract:

There has been an exponential growth in the interest in developing nanoparticles scale technology for various applications, so there are several ways to prepare magnetic iron oxide, Fe_3O_4 Nanoparticles, such as Gas phase, Liquid phase, Two-phase ,Sol-gel methods , High pressure hydrothermal, and Co-precipitation Methods. In this study we will are comparing the best methods, High pressure hydrothermal and Co-precipitation Methodsfor the synthesis of Iron Oxide Nanoparticles. Iron Oxide Nanoparticles exhibit many interesting properties that can be

used in a variety of applications such as some of the applications of nanomaterials to biology or medicine is Fluorescent biological labels [1], Drug and gene delivery [2], Bio detection of pathogens [3], Probing of DNA structure [4], Detection of proteins [5], Tissue engineering [6], Tumors destruction via heating (hyperthermia)[7], Separation and purification of biological molecules and cells [8], MRI contrast enhancement [9].

The different methods of preparation of Fe_3O_4 nanoparticles .The first part of this study will summarize the basic principle of each method of nanoparticle preparation, which presents the most recent innovations and progresses during the last decade, however were not included in previous studies on the subject. Strategies for obtaining nanoparticles with controlled in vivo fate are described in the second part of this study. Treatments of nanoparticles, applied after the synthesis, are described in the next part including purification, XRD, SEM, TEM, VSM. Finally, methods to obtain labeled nanoparticles for in vitro and in vivo investigations are described in the last part of this study.

1. Introduction

Magnetite is a ferromagnetic mineral with chemical formula Fe_3O_4, one of several iron oxides and a member of the spinel group. The chemical IUPAC name is iron (II, III) oxide and the common chemical name ferrous-ferric oxide. The formula for magnetite may also be written as $FeO{\bullet}Fe_2O_3$, which is one part wustite (FeO) and one part hematite (Fe_2O_3). This refers to the different oxidation states of the iron in one

structure, not a solid solution. The Curie temperature of magnetite is 858 K (585 °C; 1,085 °F). Fe_3O_4 has inverse spinel structure, Fe^{2+}ions in octahedral sites , whereas Fe^{3+} ions are half in tetrahedral and half in octahedral sites of close-packed array of oxide ions. This makes the electrical conductivity 10^6 times that of Fe_2O_3, which is probably due to rapid valence oscillation between Fe sites.

Iron oxide nanoparticles are iron oxide particles with diameters between about 1 and 100 nanometers. The two main forms are magnetite (Fe_3O_4) and its oxidized form maghemite -Fe_2O_3). They have attracted extensive interest due to their super paramagnetic properties and their potential applications in many fields (although Co and Ni analogues are also highly magnetic materials, but they are toxic and easily oxidized). The size of these particles encountered will be the reason for the quality of the technology used to construct the nanoparticles, in addition to the fact that the nature of the use constitutes an important work in the nature of the technique used, especially in the field of optical and medical technologies. There is a wide variety of technologies that are manipulated to produce nanomaterials with varying degrees of quality, speed, and cost. All of these techniques can be included in two categories hydrothermal methods[11] and Co-precipitation Method[13].

Experimental

SYNTHESIS OF Fe_3O_4 by hydrothermal method, Hawa et al.,[11]

Materials

The chemicals used were analytical grade and used without further purification. Ferrouschloride hexahydrate (FeCl2 • 6 H2O) and ferric chloride (FeCl3) used as precursor.

Sodium hydroxide (NaOH), medium weight chitosan, hydrochloride acid (HCl), ethanol(C_2H_5OH) and acetone (CH_3COCH_3) were used in this study. Deionized water wasprocessed by Purelab Maxima ELGA (Resistance = 17.2 MI) and was used to prepare allsolutions.

2.2 Preparation of

To synthesize iron oxide nanoparticles via hydrothermal, autoclave was used in this method. 0.01 M HCl (Fischer Chemicals Ltd.) was diluted by using deionized water so that to be used along the process of SPION preparation. Next, molar ratio of 1:2:8 of Fe2+, Fe3+ and OH- (Surechem Ltd.) were used and dissolved into a 50 ml three neck flask by the as-prepared acidified deionized water. Nitrogen gas was allowed to flow through the flask for 10 minutes prior to the addition of the chemicals. To be noticed, OH- should be added with slow rate into the mixture of Fe2+and Fe3+ and was stirred thoroughly under nitrogen condition for 5 minutes. Once it is done, the mixture was poured into a 60 ml Teflon-lined autoclave and then was tightly sealed. The reactor was subsequently put into electric furnace and heated with 200 °C for 1 hour. Then, there actor was cooled to room temperature and the resulting black solid particles were obtained. The product was washed with distilled water and acetone for several times and then was dried in oven at 45 °C

SYNTHESIS OF Fe_3O_4 BY CO- PRECIPITATION USING $NH_3 \cdot H_2O$

The synthesis began with heating the reaction vessel which is previously filled with 150 ml of deionized water and degassed throughout the experiment until the temperature is reached at about 60-65^oC, the salt solution (Fe_2 and Fe_3) is immediately added into the reaction vessel and stirred vigorously. When the temperature is raised up to nearly 75-80 ^oC, the NaOH is added quickly to raise the pH of the mixture (to 9-10) . Black precipitate was observed spontaneously. Figure 3.1 shows the resulting black precipitate from the synthesis stage by co-precipitation. The mixture of product is heated and maintained at 80-85 ^oC for 30 minutes. Then the product is washed 2 times with ethanol alternatively once the product is cooled to room temperature. The black viscous product (Fe_3O_4) later dried with oven overnight to yield powder form of Fe_3O_4 nanoparticles at 50 ^oC.

The procedure of this method involves weighting 1.710g of Fe_2salt , 2.79 of Fe_3 salt, and 2.752 of OH^-, then dissolved in distilled water to form ferrous and ferric solution respectively.

Figure 1. shows the resulting black precipitate from the synthesis stage by co-precipitation.

This phase is very difficult to be observed by the naked eye unless seen under a powerful electron microscope. The resulting products comprise a majority of large magnetite particles. Co-precipitation is a facile and convenient way to synthesize iron oxides (either Fe_3O_4 or γ-Fe_2O_3) from aqueous Fe^{2+}/Fe^{3+} salt solutions by the addition of a base under inert atmosphere at room temperature or at elevated temperature. The size, shape, and composition of the magnetic nanoparticles very much depends on the type of salts used (e.g. chlorides, sulfates, nitrates), the Fe^{2+}/Fe^{3+} ratio, the reaction temperature, the pH value and ionic strength of the media [11]

Results and discussion

Characterization of Fe_3O_4 magnetic particles using various methods. The structure of Fe_3O_4 is determined by X-ray diffraction (XRD), magnetic property of Fe_3O_4 magnetic particles is evaluated using Vibrating Sample Magnetometer (VSM), and the microscopic image is determined by Scanning Electron Microscope (SEM).[10,13,14]

X-ray diffraction (XRD)

The crystallinity and structure of the iron nanoparticle can be investigated by powder X-ray diffraction. A crystal lattice is a regular three-dimensional distribution of atoms in space. These are arranged so that they form a series of parallel planes separated from one another by a distance *d*, which varies according to the nature of the material. For any crystal, planes exist in a number of different orientations - each with its own specific *d*-spacing. When a monochromatic X-ray beam with

wavelength *lambda* is projected onto a crystalline material at an angle *theta*, diffraction occurs only when the distance traveled by the rays reflected from successive planes differs by a complete number *n* of wavelengths. By varying the angle *theta*, the Bragg's Law conditions are satisfied by different *d*-spacing in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is

characteristic of the sample. Where a mixture of different phases is present, the resultantdiffractogram is formed by addition of the individual patterns[15].

Comparison the methods of synthesis, hydrothermal methods and Co-precipitation Method using XRD results (table 1) utilizing the values of 2θ angle for the samples with reference based on the intermediate plane of magnetite HKL figure 2a, The result obtained by

Table 1. Comparison of XRD results of hydrothermal and Co-precipitation Methods

co-precipitation method			hydrothermal method
Plane hkl	Value 2θ (°) (our samples)	Value 2θ (°) (Standard JCPDS: 19-0629)	Value 2θ (°) (Hawa et al)
220	30.36	30.10	30.20
311	35.71	35.42	35.40
222	37.41	37.05	37.12
400	43.47	43.05	43.36
422	53.94	53.39	53.80
511	57.51	56.94	57.04
440	63.16	62.52	62.43

There are seven groups of intermediate planes provide the main peaks in the XRD spectra obtained by co-precipitation method a 2θ angle values of the peak intensity is significant in this study was 30.36°, 35.72°, 37.41°, 43.47°, 53.95°, 57.51° and 63.17°, referring to the intermediate plane HKL magnetite crystals of (220) (311), (222), (400), (422), (511), and (440), respectively.

Another study by Hawa et al [11], the sample was prepared by hydrothermal method, the XRD of magnetite crystals supplied by the standard data spectra obtained give 2θ angle values of the peak intensity is significant obtained are angle of 30.20°, 35.40°, 37.12°, 43.36 °,53.80°, 57.04°, and 62.43° referring to the intermediate plane HKL

magnetite crystals of (220) (311), (222), (400), (422), (511), and (440), respectively figure 2c. The peaks matched very well with the standard provided (JCPDS: 19-0629), figure 2b. These results clearly indicate that the XRD values correspond to synthesized magnetite, in addition to the physical evidence such as black color of the crystallized product. These data closely match that of the magnetite standard.

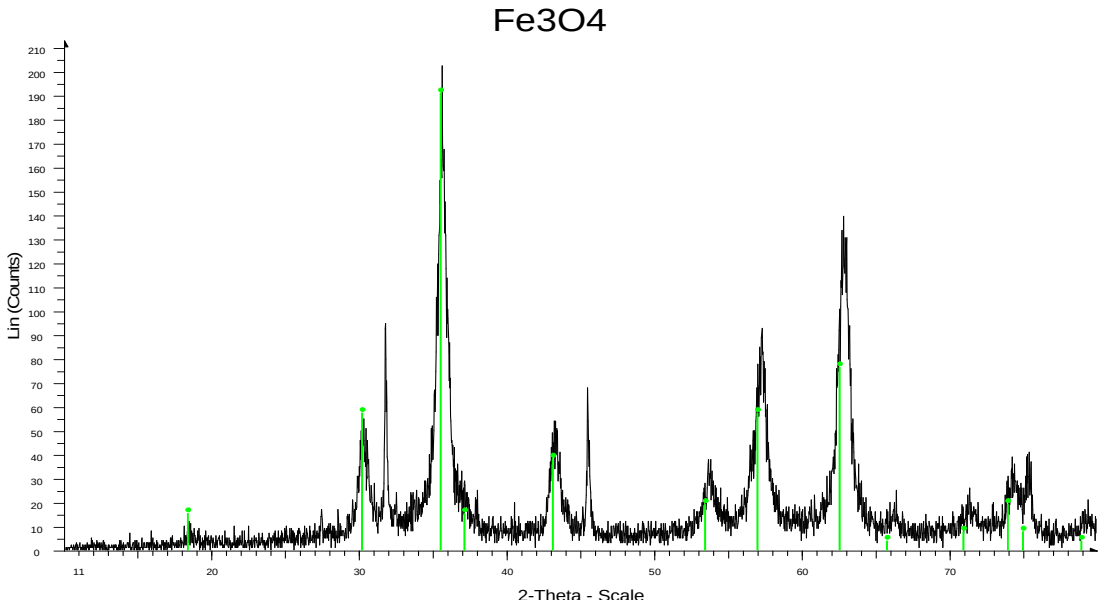
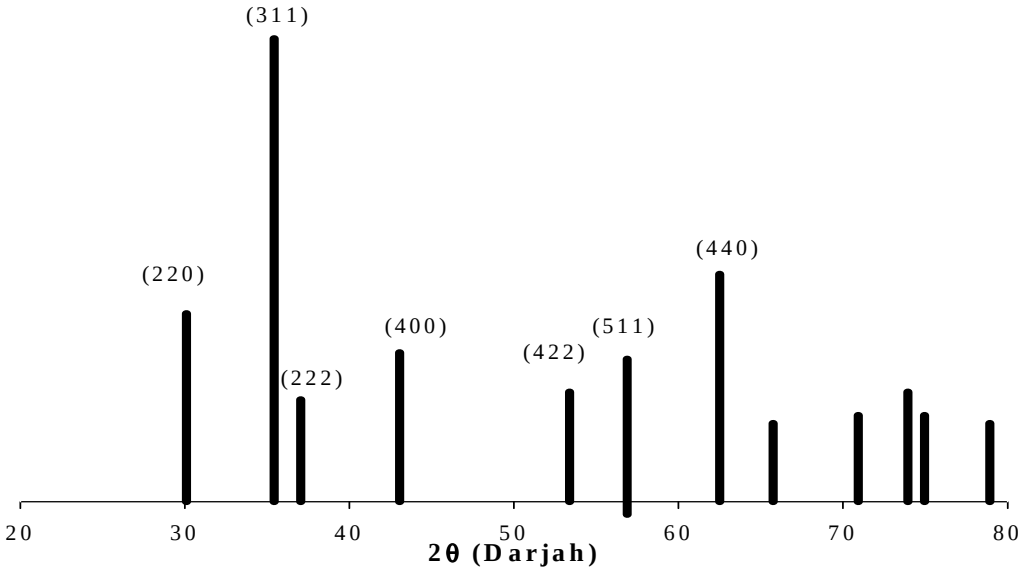


Figure 2a XRD spectra for synthesized Fe_3O_4 nanoparticles by using co-precipitation method



Degree Figure 2b XRD spectra for standard reference (JCPDS: 19-0629).2θ

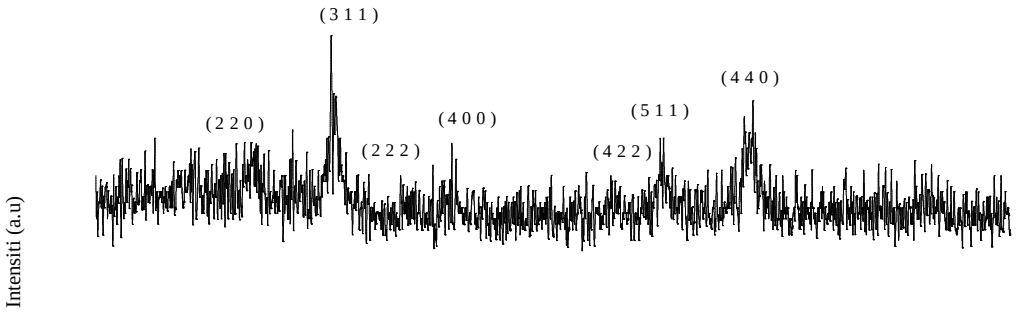


Figure 2c XRD spectra for synthesized Fe_3O_4 nanoparticles by hydrothermal method

Transmission electron microscopy (TEM):

The size and morphology of Fe_3O_4 nanoparticles was investigated by TEM and the image is shown in Figure 3a. It shows the particles produced were almost monodisperse and spherical in shape .The particles mean diameter is approximately 17.12 ± 4.65 nm for the Fe_3O_4 particles prepared by hydrothermal method which was confirmed from TEM image. We can also can observe that the magnetite nanoparticles approximately display a uniform morphology. Whilst figure 3b, a histogram shows the particles size distribution for Fe_3O_4 with most of the particles having size between 10 and 29 nm with average particle size is close to 17 nm. This classifies these particles as nanoparticles, since the size of Fe_3O_4 nanoparticles should be less than 20 nm.

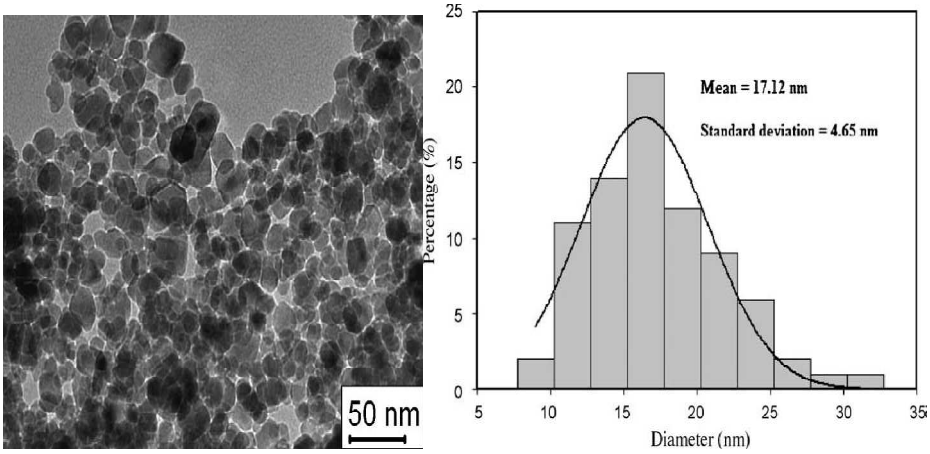


Fig. 3. TEM analysis (a) TEM photograph of iron oxide nanoparticles of the sample. (b) TEM histogram showed the range value diameter of Fe_3O_4 and its mean diameter is 17.12 ± 4.65 nm.

SCANNING ELECTRON MICROSCOPY (SEM)

The surface morphology and particle size of Fe_3O_4 are recorded by Scanning electron microscopy (SEM), which was obtained on a field emission SEM micrograph shown in Figure4. The average diameter was observed to be distributed at 100nm for the Fe_3O_4 particles prepared by co-precipitation method. The micrograph is obtained at 150 x, 5x and 7x magnification in the field of view at 7mm WD. Each sample is recorded at 20 EHT.

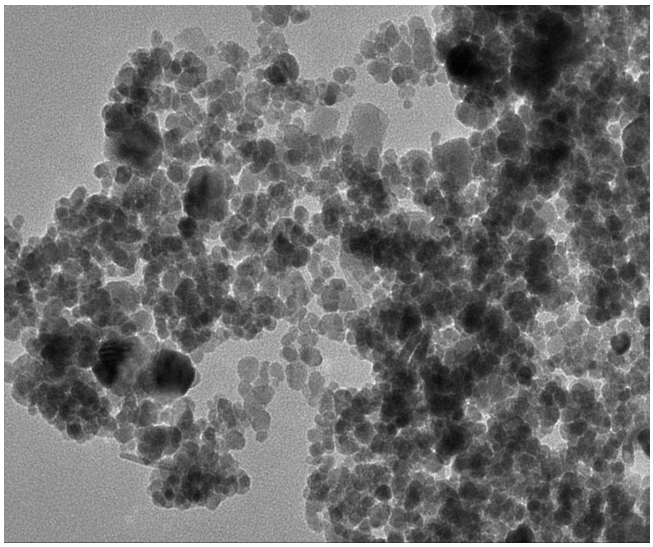


Figure 4 SEM micrograph SEM shows the average diameter observed to be distributed at 100nm for the Fe_3O_4 particles prepared by co-precipitation method

VIBRATING SAMPLES MAGNETOMETER (VSM)

Vibrating samples magnetometer (VSM) measured the magnetic properties of synthesized Fe_3O_4 nanoparticles by LakeShore 736 vibrating magnetometer operating at 298 K. The samples were vibrated at a frequency of 85 Hz to shear the magnetic flux created and a signal generated from the samples was recorded by a Gauss meter.

Examining the magnetic properties of magnetite Fe_3O_4 synthesized, branded sample magnetometer LakeShore operating at 298 K was used. A hysteresis curve in the shape of "S" has been observed as shown in figure 5. This figure also shows the magnetometer results for magnetite Fe_3O_4. For the saturation magnetization (*M*s), magnetization (*M*r), and coercivity (*H*c) values were each given a total of 54.23 $emug^{-1}$, 3.53 emug-1, and 23.40 Oe, respectively as shown in Table 2. The value of saturation magnetization obtained in this study is lower than the value of the magnetization of bulk magnetite 92 $emug^{-1}$. The difference is likely due to the lack of mass used in the preparation of magnetite sample magnetometer.

Table 2 Property acquired magnetism magnetite

saturation magnetization (Ms)	magnetization (Mr)	coercivity (Hc) values
54.23 $emug^{-1}$	3.53 $emug^{-1}$	23.40 Oe

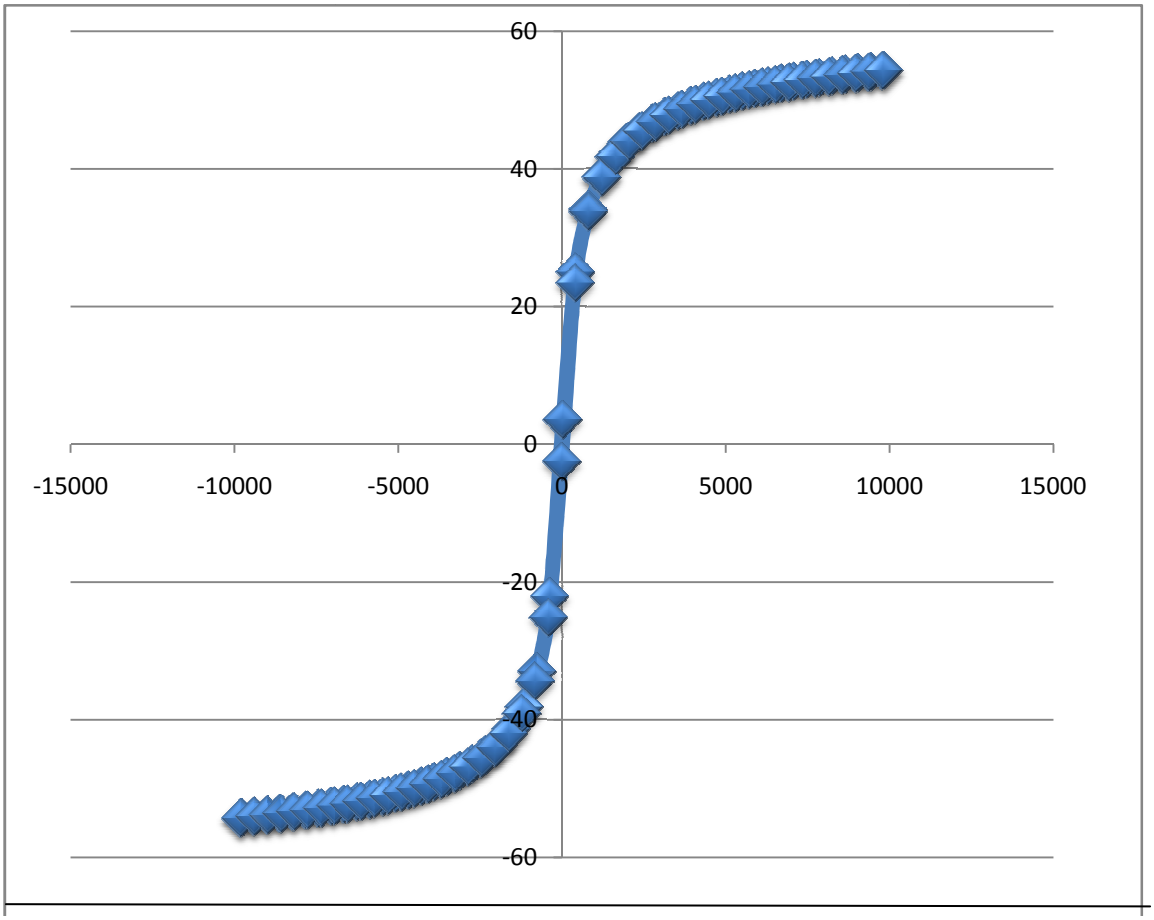


Fig.5. Magnetization curve obtained by VSM at room temperature of Fe_3O_4samples.

Table 3 Property acquired magnetism magnetite

saturation magnetization (Ms) values	magnetization (Mr)	coercivity (Hc)
57.40 $emug^{-1}$	1.86 $emug^{-1}$	26.40 Oe

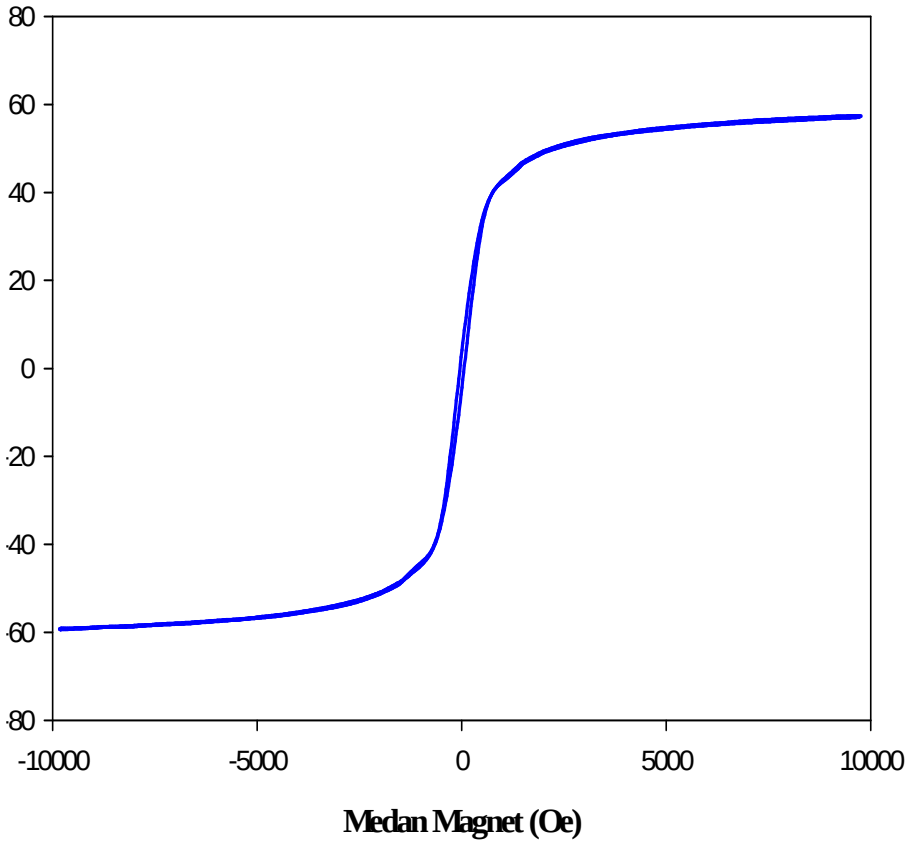


Fig 6.. Hysteresis loop obtained for Fe_3O_4 nanoparticles measured at 298 K.

CONCLUSION

Magnetite Fe_3O_4 was successfully prepared by two ways, but the co-precipitation method was the preferred method for giving the best results in terms of size, structure, and magnetic properties. The method has been found to be very simple, easy to carry on, and low in cost, it also gives a better yield than other method and without the use of organic reagents.

Results from X-ray Diffraction (XRD) proved that the phase of magnetite in the sample was present. Fe_3O_4 in this study have almost similar XRD spectra with spectra of standard data observed for magnetite. No amorphous components can be observed in the spectrum of this study and this show that the resulting magnetite has the inverse spinel crystal structure.

A Vibrating Sample Magnetometer Analysis (VSM) indicated that the outcome of the sample has super paramagnetic characteristics. A 'S' shaped hysteretic band was derived and the value of the saturated magnetization along with the coersive value which is reported to be 54.23 emu/g and 23.40 Oe. The shift of the magnetic phrase to the Ferum Oxide phrase in a smaller quantity makes the coersive value to be observed.

Scanning Electron Microscopy (SEM) was used to confirm the particle size distribution and morphology. The results indicate that the Fe_3O_4 nanoparticles produced are of well-defined crystal shape and bigger due to the recrystallization. The Fe_3O_4 crystals have the octahedral structure and the size of these octahedral can be as small as 100 nm to as large as several micrometers as in this study.

References

1- *Nishio, K.; Ikeda, M.; Gokon, N.; Tsubouchi, S.; Narimatsu, H.; Mochizuki, Y.; Sakamoto, S.; Sandhu, A.; Abe, M.; and Handa, H. Preparation of size-controlled (30–100 nm) magnetite nanoparticles for biomedical applications. J. Magn. Magn. Mater. 2007, 310, 2408–2410.*

2- *LazhenShen, Bei Li 1 and YongshengQiao , Fe3O4 Nanoparticles in Targeted Drug/Gene Delivery Systems (2018)*

3- *Zhou, Y.; Chen, M.; Zhuo, Y.; Chai, Y.; Xu, W.; and Yuan, R. In situ electrodeposited synthesis of electrochemiluminescent Ag nanoclusters as signal probe for ultrasensitive detection of Cyclin-D1 from cancer cells. Anal. Chem. 2017, 89, 6787–6793.*

4- *MeiChen, ChangjunHou, DanqunHuo, HuanbaoFa, YananZhao, and CaihongShen, sensitive electrochemical DNA biosensor based on three-dimensional nitrogen-doped graphene and Fe_3O_4 nanoparticles 2016.08.036*

5- *Xi Zhou, WenlongXu, Yan Wang, Qin Kuang, Yanfeng Shi, LubinZhong, and Qiqing Zhang, Fabrication of Cluster/Shell Fe_3O_4/Au Nanoparticles and Application in Protein Detection via a SERS Method 2010, 114, 46, 19607-19613*

6- *Cunha, S Panseri , D Iannazzo, A Piperno, A Pistone, M Fazio, A Russo, and M Marcacciand S Galvagno, Hybrid composites made of multiwall carbon nanotubes functionalized with Fe_3O_4 nanoparticles for tissue engineering applications 2012 IOP Publishing Ltd Nanotechnology, Volume 23, Number 46*

7- *Luong, D.; Sau, S.; Kesharwani, P.; Iyer, A.K. Polyvalent folate-dendrimer-coated iron oxide theranostic nanoparticles for simultaneous magnetic resonance imaging and precise cancer cell targeting. Biomacromolecules 2017, 18, 1197–1209.*

8- *Guo, J.; Filpponen, I.; Johansson, L.S.; Mohammadi, P.; Latikka, M.; Linder, M.B.; Ras, R.H.A.; Rojas, O.J. Complexes of magnetic nanoparticles with cellulose nanocrystals as regenerable, highly efficient,*

and selective platform for protein separation. Biomacromolecules 2017, 18, 898–905

9- *Ma, M.; Yan, F.; Yao, M.; Wei, Z.; Zhou, D.; Yao, H.; Zheng, H.; Chen, H.; Shi, J. Template-free synthesis of hollow/porous organosilica-Fe_3O_4 hybrid nanocapsules toward magnetic resonance imaging-guided high-intensity focused ultrasound therapy. ACS Appl. Mater. Interfaces 2016, 8, 29986–29996*

10- *Leslie Nagy, Adam Rauwerdink, Dr. Guandon Zhang, PI: Dr. John Weaver Magnetic Nanoparticle Imaging: On the Binding and Localization of Nanoparticles Using Combination Magnetic Fields Research Experience for Undergraduates Program 2008*

11- *C.Y. Hawa, F. Mohamed a, C.H. Chia a, S. Radiman a, S. Zakaria a, N.M. Huang b, and H.N. Lim . Hydrothermal synthesis of magnetite nanoparticles as MRI contrast agents. ccepted 30 January 2010 Available online 1 March 2010*

12- *Wensheng Lu, YuhuaShen, AnjianXie, and Weiqiang Zhang, Green synthesis and characterization of super paramagnetic Fe_3O_4 nanoparticles*

13- *Leslie Nagy, Adam Rauwerdink, Dr. Guandon Zhang, PI: and Dr. John Weaver Magnetic Nanoparticle Imaging: On the Binding and Localization of Nanoparticles Using Combination Magnetic Fields..Research Experience for Undergraduates Program 2008*

14- *X-Ray Diffraction. PANalytical.*

http://www.panalytical.com/index.cfm?pid=135 Accessed August 8, 2008.

15- *Vibrating Sample Magnetometer. CNSM.*

http://cnsm.kaist.ac.kr/vsm.html . Accessed July 20, 2008.