

A Novel Approach for Synthesis Magnetite Nanoparticles at Ambient Temperature

Nidá M. Salem¹, Akl M. Awwad^{2,*}

¹Department of Plant Protection, Faculty of Agriculture, Jordan University, Amman, Jordan
²Department of Knowledge, Royal Scientific Society, El Hassan Science City, Amman, Jordan

Abstract A novel and facile approach for synthesis magnetite (Fe_3O_4) nanoparticles from ferric chloride (FeCl_3) and ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) in the presence of pistachio leaf extract at ambient temperature and atmospheric pressure. The effect of pistachio leaf extract amount in the reaction mechanism and particle size was studied. The synthesized magnetite nanoparticles were characterized by Fourier transforms infrared spectrophotometer (FT-IR), scanning electron microscopy (SEM) and X-ray diffraction (XRD). XRD analysis showed that the synthesized magnetite nanoparticles are highly crystalline and well-monodisperse with 8 nm of average diameter. The synthesized magnetite nanoparticles can be easily dispersed in aqueous media due to coated by a layer of pistachio leaf extract *in situ*. This approach provides a facile route to prepare magnetite nanoparticles.

Keywords Magnetite Nanoparticles, Pistachio Leaf Extract, One-Pot Reaction

1. Introduction

Magnetite (Fe_3O_4) nanoparticles have received much interest due to its magnetic, catalytic, magnetic recording, drug delivery, magnetic resonance imaging, cancer diagnosis and treatment, bimolecular separation, etc. Various methods for synthesis magnetite nanoparticles have been developed such as micro-emulsion method[1,2], thermal decomposition of organic iron precursors in organic solvents[3-5], co-precipitation process[6,7], sol-gel method [8], solvothermal method[9,11], hydrothermal synthesis [12,13], electrochemical synthesis [14], ultrasonic chemical co-precipitation[15,16]. These methods have many disadvantages due to the difficulty of scale up of the process, separation and purification of nanoparticles from the oil, surfactant, co-surfactant, organic solvents[17-25]. We have attempted to synthesis magnetite nanoparticles by co-precipitation of Fe^{3+} and Fe^{2+} ions without using toxic organic solvents and surfactants. In this one-pot synthesis process, magnetite nanoparticles were synthesized by co-precipitation of iron oxides in presence of pistachio leaf extract at ambient temperature and atmospheric pressure. Thereby the approach is economic, green, facile and easily to scale up.

2. Experimental Section

* Corresponding author:

akl.awwad@yahoo.com (Akl M. Awwad)

Published online at <http://journal.sapub.org/nn>

Copyright © 2013 Scientific & Academic Publishing. All Rights Reserved

2.1. Materials

Ferric chloride (FeCl_3 , Aldrich 98%), ferrous chloride tetra hydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, Aldrich 99%), pistachio leaf extract and sodium hydroxide (NaOH, Aldrich) were used for synthesis of magnetite nanoparticles without further purification as well as deionized sterile water with pH 7.0 and conductivity $1 \mu\text{S}/\text{cm}$.

2.2. Preparation of Pistachio Leaf Extract



Figure 1. A photograph shows the pistachio leaves and their extract

Freshly pistachio leaves were collected from pistachio trees planted at the campus of the Royal Scientific Society, Jordan and washed several times with distilled water to remove the dust particles and then sun dried to remove the residual moisture. The Pistachio leaves extract used for synthesis magnetite nanoparticles was prepared by placing 10 g of washed dried fine cut leaves in 250 mL glass beaker

along with 200 mL of sterile distilled water. The mixture was then boiled for 5 minutes, the color of the aqueous solution changed from watery to light yellow color, **Fig 1**. Then the extract was cooled to room temperature and filtered with Whatman No. 1 filter paper before centrifuging at 1000 rpm for 5 minutes to remove the heavy bio materials. The extract was stored at room temperature in order to be used for further experiments.

2.3. Synthesis of Magnetite Nanoparticles

100 ml of aqueous mixture containing 0.01 M ferrous chloride tetra hydrate and 0.02 M of anhydrous ferric chloride (1/2 molar ratio) was placed in a 250 mL glass beaker and stirred magnetically at room temperature and atmospheric pressure. Afterwards, 10 mL of an alkaline solution of Pistachio leaf extract (pH = 8.0) was added, the yellowish brown color of iron chlorides changed immediately to black color, indicating the formation of magnetite nanoparticles. The suspended black particles solution was purified by dispersing in sterile distilled water and centrifugation three times. The magnetite particles are divided into two parts. In the first part, the magnetite nanoparticles are remained in the sterile distilled water without any additives as prepared. The stability of magnetite suspended nanoparticles in sterile distilled water for more than four weeks. In the second part, the magnetite nanoparticles after purification were dried under vacuum. The solid sample was used for further characterization.

2.4. Characterization

Magnetite (Fe_3O_4) nanoparticles synthesized by this green method were examined by X-ray diffractometer, XRD-6000 (Shimadzu, Japan) equipped with Cu K α radiation source using Ni as filter at a setting of 30 kV/30mA. All XRD data were collected under the experimental conditions in the angular range $3^\circ \leq 2\theta \leq 50^\circ$. FT-IR spectra of Pistachio leaf extract and magnetite nanoparticles were obtained in the range $4000\text{-}400\text{ cm}^{-1}$ with IR-Prestige 21 spectrophotometer (Shimadzu, Japan) using KBr pellet method. Scanning electron microscopy (SEM) analysis of synthesized magnetite nanoparticles was done by S-4500 SEM machine (Hitachi, Japan).

3. Results and Discussion

3.1. X-ray diffraction (XRD) Studies

Analysis through X-ray diffraction was carried out to confirm the crystalline nature of the magnetite nanoparticles. The XRD pattern showed numbers of Bragg's reflections that may be indexed on the basis of the face centered cubic structure of magnetite. A comparison of our XRD spectrum with the standard XRD data for bulk magnetite (JCPDS file No. 19-0629) confirmed that the magnetite particles formed in our experiments were in the form of nanocrystals, as evidenced by the peaks at 2θ values of 18.55° , 30.81° , 36.48° ,

43.52° , 54.59° , 56.83° and 62.34° corresponding to (111), (220), (311), (222), (400), (422) and (511) Bragg's reflections, respectively, which may be indexed based on the face centered cubic (fcc) structures of magnetite. The X-ray diffraction results clearly show that the magnetite nanoparticles formed by our co-precipitation method in presence of Pistachio leaf extract are crystalline in nature. The unassigned peaks at $2\theta = 31.88^\circ$, 37.44° and 46.18° denoted by (*) in **Fig. 2** are thought to be related to crystalline and amorphous organic phases, It was found that the average size from XRD data and using Debye-Scherrer equation was approximately 8 nm. The presence of structural peaks in XRD patterns and average crystalline size around 8 nm clearly illustrates that magnetite particles synthesized by our green method were nanocrystalline in nature. The average particle size of magnetite nanoparticles synthesized by the present green method can be calculated using Debye-Scherrer equation[26].

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

Where

D is the mean diameter of nanoparticles, β is the full width at half-maximum value of XRD diffraction lines, λ is the wavelength of X-ray radiation source 0.15405 nm, θ is the half diffraction angle –Bragg angle and K is the Scherrer constant with value from 0.9 to 1. The presence of structural peaks in XRD patterns and average crystalline size calculated 8 nm clearly illustrates the magnetite nanoparticles synthesized by our green approach were nanocrystalline in nature.

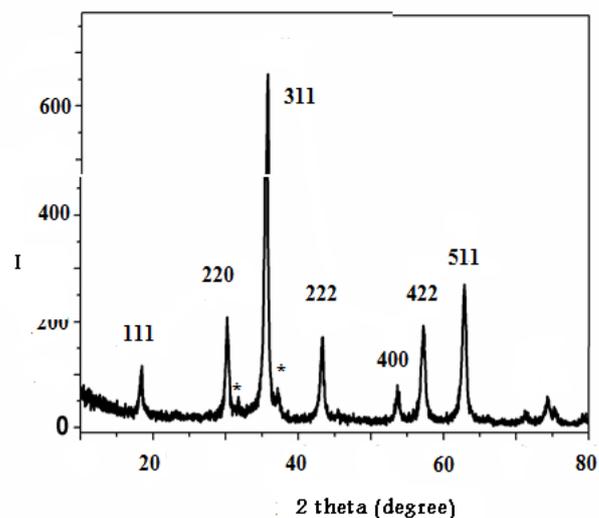


Figure 2. XRD pattern of the synthesized magnetite nanoparticles

3.2. Surface Charge and Surface Coating

The FT-IR spectra of Pistachio leaf extract is given in **Fig. 3**. A broad band between 3417 cm^{-1} is due to the N-H stretching and bending vibration of amine group NH_2 and O-H the overlapping of the stretching vibration of attributed for water and Pistachio leaf extract molecules. The peak at 2920 cm^{-1} could be assigned to the stretching vibrations of $-\text{CH}_3$ and CH_2 functional groups. The strong band at 1635

cm^{-1} and the peak at 1438 cm^{-1} are identified as the amide I and amide II, which arise due to C=O and NH stretching vibrations in the amide linkage of the protein. The peaks at 1311 cm^{-1} and 1203 cm^{-1} can be assigned to the C-O group of polyols. The peak at 1041 cm^{-1} corresponds to C-N stretching vibrations of aliphatic amines.

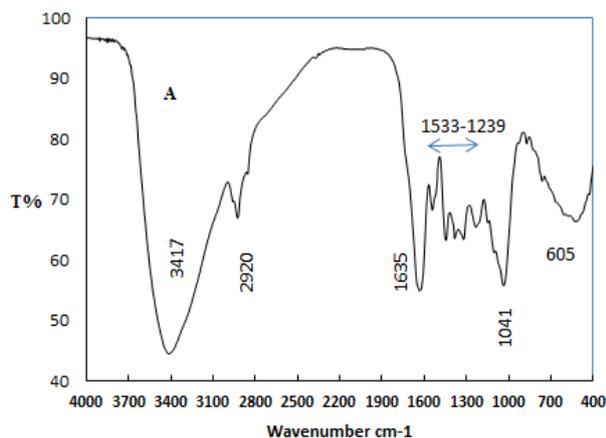


Figure 3. FT-IR spectra of pistachio leaf extract

FT-IR spectra of synthesized magnetite nanoparticles were carried out to identify the possible biomolecules responsible for capping and stabilization of nanoparticles.

Fig. 4 shows the peaks associated with magnetite nanoparticles. The peaks 3433 cm^{-1} , 1627 cm^{-1} and 1035 cm^{-1} have been assigned to the C-H stretching, O-H stretching, N-H stretching and bending vibration of amine NH_2 group in Pistachio leaf extract and the overlap of the stretching vibration of O-H. The peak at 1384 cm^{-1} and 1035 cm^{-1} are attributed to the asymmetric and symmetric stretching vibration of COO^- . The presence of magnetite nanoparticles can be seen by two absorption bands at around 584 cm^{-1} and 428 cm^{-1} which, corresponding to the Fe-O stretching band of bulk magnetite (Fe_3O_4). These results revealed that the C=O groups were bonded on the magnetite particle surface. Overall the observation confirms the presence of protein in pistachio leaf extract, which acts as a capping agent and stabilizer for magnetite nanoparticles.

Fig. 5 shows the separation and redispersing process of the capped magnetite nanoparticles. In the absence of an external magnetic field, the dispersion of the Pistachio magnetite nanoparticles was saddle black and homogenous, **Fig. 5A**. This indicates that the magnetite nanoparticles are highly soluble in water to form a stable ferrofluid suspension. When the external magnetic field was applied, the Pistachio magnetite nanoparticles were enriched leading to transparency of the dispersion, **Fig. 5B**.

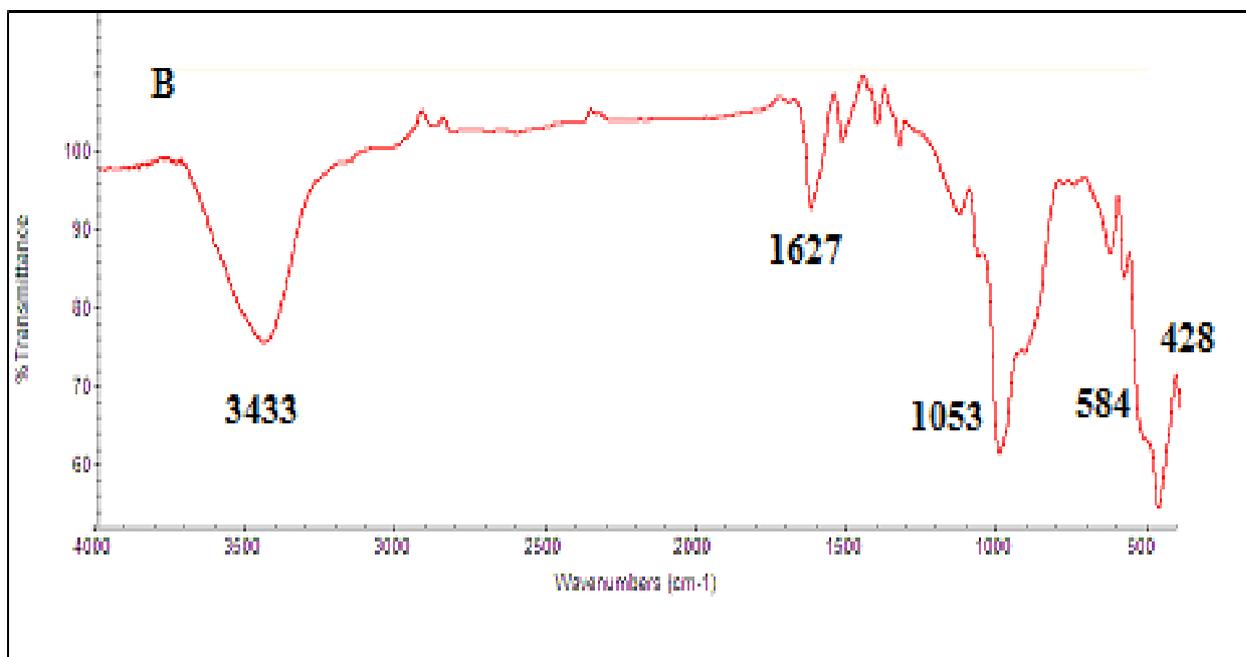


Figure 4. FT-IR spectra of synthesized magnetite nanoparticles

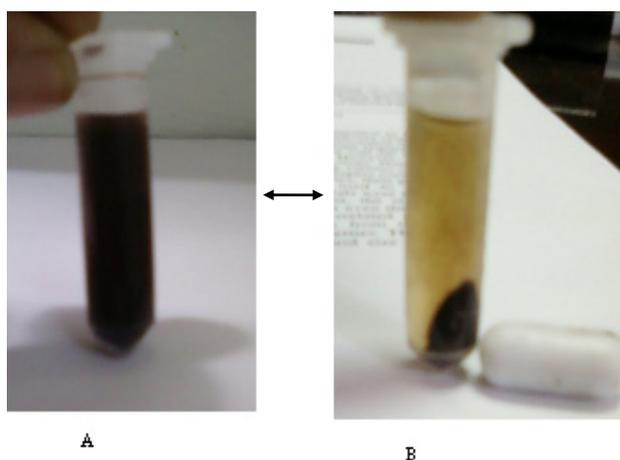


Figure 5. Photographs of the separation A to B and dispersion B to A of the pistachio magnetite nanoparticles: (A) without external magnetic field and (B) with external magnetic field

3.3. SEM Analysis of Magnetite Nanoparticles

The morphology of pistachio leaf extract stabilized magnetite nanoparticles (Fe_3O_4) have been investigated by scanning electron microscope. **Fig. 6** shows the scanning electron microscope (SEM) images of MNPs prepared by this green method in presence of Pistachio leaf extract. It can be clearly seen from SEM images that MNPs are nearly spherical with an average diameter ranges from 5-18 nm. The size and shape of the synthesized magnetite nanoparticles could be controlled by the amount of Pistachio leaf extract and the concentration of $\text{Fe}^{3+}/\text{Fe}^{2+}$. The crystalline and organic phases of pistachio leaf extract are shown in The SEM image with MNPS denoted by red circles, which acts as stabilizing agent for magnetite nanoparticles and preventing agglomeration of particles.

This research work is the first to report on using Pistachio leaf extract to synthesis monodisperse magnetite nanoparticles via co-precipitation method in the presence of Pistachio leaf extract, as illustrated in scheme 1. By changing the amount of pistachio leaf extract, the magnetite nanoparticles sizes could be adjusted from 5 ± 1.2 to 18 ± 2.2 nm.

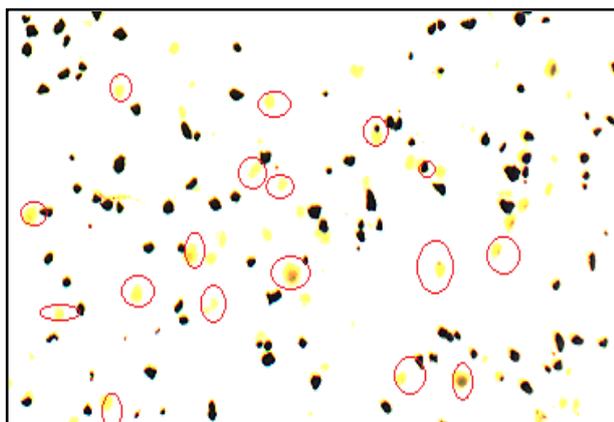
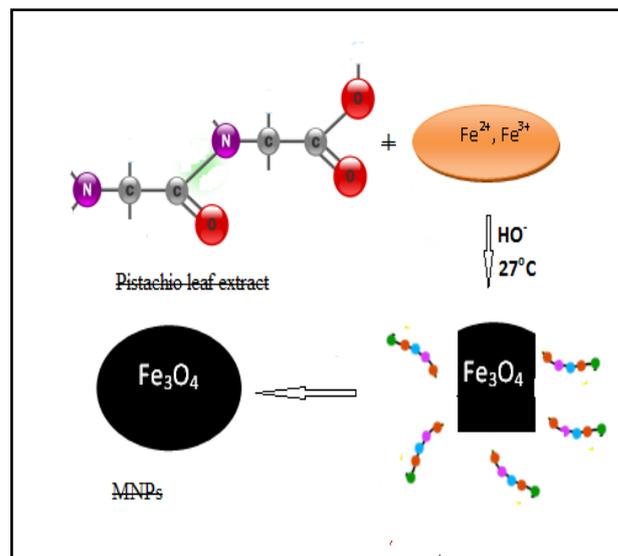


Figure 6. SEM images of synthesized magnetite nanoparticles



Scheme 1. Synthesis route of magnetite nanoparticles

4. Conclusions

A novel and simple approach for synthesis magnetite nanoparticles in one-pot reaction process at ambient temperature and atmospheric pressure. Our synthesis approach employed an environmental friendly solvent, pistachio leaf extract, as an alternative to organic solvents and surfactants. Pistachio leaf extract acts both as dispersing and stabilizing agent, which prevents the agglomeration of magnetite nanoparticles (Fe_3O_4) formed during synthesis. XRD and SEM data showed that the size and shape of the Fe_3O_4 nanoparticles could be controlled by the amount of Pistachio leaf extract and the concentration of Fe^{3+} and Fe^{2+} . The method in the present study offers several important advantageous features. First, the synthesis method is economical and environmentally friendly, because it involves inexpensive and non-toxic materials. Second, size-controlled Fe_3O_4 nanoparticles are produced easily by different amounts of Pistachio leaf extract.

ACKNOWLEDGMENTS

The authors would like to thank Abdul Hameed Shoman Fund for Support of Scientific Research (AHSFSSR), Jordan for financial support. We are also thankful to Royal Scientific Society and Jordan University, Jordan for providing all facilities to carry out this work.

REFERENCES

- [1] Liu, Z. L., Wang, X., Yao, K.L., Du, G.H., Lu, Q.H., Ding, Z.H. Tao, J., Ning, Q., Luo, X. P., Tian, D.Y., Xi, D. (2004). Synthesis of magnetite nanoparticles in W/O microemulsion. *J. Mater. Sci.* 39: 2633-2639.

- [2] Gotić M., Jurkin T., Musić S. (2007). Factors that may influence the micro-emulsion synthesis of nanosize magnetite particles. *Colloid Polym. Sci.* 285: 793-800.
- [3] Maity D., Kale S.N., Kaul-Ghanekar R., Xue J-M., Ding J. (2009). Studies of magnetite nanoparticles synthesized by thermal decomposition of iron (III) acetylacetonate in tri(ethylene glycol). *J. Magn. and Magn. Mater.* 321: 3093-3098.
- [4] Sun S.H., Zeng H. J. (2002). Size-controlled synthesis of magnetite nanoparticles. *J. Amer. Chem. Soc.* 124: 8204-8209.
- [5] Chin S.F., Pang S.C., Tan C.H. (2011). Green synthesis of magnetite nanoparticles (via thermal decomposition method) with controllable size and shape. *J. Mater. Environ. Sci.* 2: 299-302.
- [6] Pang S.C., Chin S.F., Anderson M. A. (2007). Redox equilibria of iron oxides in aqueous-based magnetite dispersions: Effect of pH and redox potential. *J. Colloid Interface Sci.* 311: 94-101.
- [7] Pang S.C., Khoh W.H., Chin S.F. (2010). Nanoparticle magnetite thin films as electrode materials for the fabrication of electrochemical capacitors. *J. Mater. Sci.* 45: 5598- 5604.
- [8] Xu J, Yang H, Fu W, Du K, Sui Y, Chen J, Zeng Y, Li M, Zou G. (2007). Preparation and magnetic properties of magnetite nanoparticles by sol-gel method. *J. Magn. Mater.* 309: 307-311.
- [9] Hou Y, Yu J, Gao S. J. (2003). Solvothermal reduction synthesis and characterization of superparamagnetic magnetite nanoparticles. *Mater. Chem.* 13: 1983-1987.
- [10] Ou P., Xu G., Xu C., Zhang Y., Hou X., Han G. (2010). Synthesis and characterization of magnetite nanoparticles by a simple solvothermal method. *Mater. Sci., Poland.* 28: 817-822.
- [11] Wang J., Yao M., Xu G., Cui P., Zhao J. (2009). Synthesis of monodisperse monocrystals of high crystallinity magnetite through solvothermal process. *Mater. Chem. Phys.* 113: 6-9.
- [12] Mizutani N., Iwasaki T., Watano S., Yanagida T., Tanaka T., Kawai T. (2008). Effect of ferrous/ferric ions molar ratio on reaction mechanism for hydrothermal synthesis of magnetite nanoparticles. *Bull. Mater. Sci.* 51: 713-717.
- [13] Hu F., Li Z., Tu C., Gao M. J. (2007). Preparation of magnetite nanocrystals with surface reactive moieties by one-pot reaction. *J. Colloid Inter. Sc.* 311: 469-474
- [14] Cabrera L., Gutierrez S., Menendez N., Morales M.P., Herrasti, P. (2008). Magnetite nanoparticles: Electrochemical synthesis and characterization. *Electrochimica Acta* 53: 3436-3441.
- [15] Wu S., Sun A., Zhai F., Wang J., Xu W., Zhang Q., Volinsky A.A. (2011). Fe₃O₄ magnetic nanoparticles synthesis from tailing by ultrasonic chemical co-precipitation. *Mater. Lett.* 65: 1882-1884.
- [16] Cheng J.P., Ma R., Shi D., Liu F., Zhang X.B. (2011). Rapid growth of magnetite nanoplates by ultrasonic irradiation at low temperature. *Ultrason. Sonochem.* 18: 1038-1042.
- [17] Basavaiah K., Rao A. V. P. (2012). Synthesis of polystyrenesulfonic stabilized magnetite nanoparticles. *Chem. Sci. Trans.* 1: 382-386.
- [18] Wang Y., Zhu Z., Xu F., Wei X. (2012). One-pot reaction to synthesize superparamagnetic iron oxide nanoparticles by adding phenol as reducing agent and stabilizer. *J. Nanopart. Res.* 14: 755-761.
- [19] Wen X., Yang J., He Y., Gu Z. (2008). Preparation of monodisperse magnetite nanoparticles under mild conditions. *Current Applied Physics* 8: 535-541.
- [20] Marinescu G., Patron L., Culita D.C., Neagoe C., Lepadat C.I., Balint I., Bessais L., Cizmas C.B. (2006). Synthesis of magnetite nanoparticles in the presence of aminoacids. *J. Nanopart. Res.* 8: 1045-1051.
- [21] Nyirő-kósa I., Rečník A., Pósfai M. (2012). Novel methods for the synthesis of magnetite nanoparticles with special morphologies and textured assemblages. *J. Nanopart. Res.* 14: 1150-1159.
- [22] Cai W., Wan J. (2007). Facile synthesis of superparamagnetic nanoparticles in liquid polyols. *J. Colloid Interface Sci.* 305: 366-370.
- [23] Guin D., Manorama S.V. (2008). Room temperature synthesis of monodispersed iron oxide nanoparticles. *Mater. Lett.* 62: 3139-3142.
- [24] Yang C., Yan H. (2012). Green and facile approach for synthesis of magnetite nanoparticles with tunable sizes and morphologies. *Mater. Lett.* 73: 129-132.
- [25] Pang S. C., Khoh W.H., Chin S.F. (2011). Synthesis and characterization of magnetite/carbon nanocomposite thin films for electrochemical applications. *J. Mater. Sci. Technol.* 27: 873-879.
- [26] Vidhu V.K., Aromal S. A., Philip D. (2011). Green synthesis of silver nanoparticles using *Macroty lomauniflorum*. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy.* 83: 392-397.