

Synthesis and characterization of maghemite nanopowders by chemical precipitation method

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Abstract In this study, nanoparticles of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) with a mean particle size of 9 nm have been prepared by chemical precipitation method through one step. According to the high-resolution X-ray diffraction result, the as-synthesized iron oxide nanoparticles were $\gamma\text{-Fe}_2\text{O}_3$. The particle size of the maghemite nanoparticles was below 20 nm confirmed by transmission electron microscopy image. The particle shape was almost a sphere confirmed by transmission electron microscope.

Keywords Iron oxide nanoparticles · Maghemite · Chemical precipitation

Background

Iron oxides exist in different forms in nature, magnetite, maghemite, and hematite [1]. Maghemite is ferrimagnetic at room temperature but maghemite nanoparticles smaller than 10 nm are superparamagnetic at room temperature, maghemite is unstable at high temperatures, and loses its susceptibility with time [2, 3].

Among the researchers working in the field of nanotechnology, magnetic nanoparticles have attracted intense experimental activities because of their potential applications in a numerous different industries such as storage of information [4], ferrofluid [5], audio and video recording [6], bioprocess [7] gas sensor [8–13], refrigeration systems [14], information storage [15], medical applications [16], magnetic resonance imaging [17], catalyst [18, 19], magnetooptic [20], and removal of heavy metals [38, 39].

We have various chemistry methods for iron oxide nanoparticles preparation, including gas phase methods (reduction, hydrolysis, disproportionation, oxidation, or other reactions to precipitate solid products from the gas phase), that depend on thermal decomposition [21], liquid phase methods, two-phase methods, sol–gel methods, high-pressure hydrothermal methods [22], various methods have been reported for the synthesis of maghemite nanoparticles, such as co-precipitation [23–25], sol–gel synthesis [26–28], micro emulsion [29], flow injection synthesis [30], hydrothermal synthesis [31, 32], flame spray pyrolysis [33], decomposition of organic precursors at high temperatures, and the oxidation of magnetite nanoparticles [31, 34].

Among various chemical methods for synthesis of different types of metal oxides, co-precipitation process has several advantages over other methods including, good homogeneity, low cost, high purity of product and not requiring organic solvents and heat treatment. Recently, co-precipitation method has been developed for preparation of magnetite nanoparticles using metallorganic precursors. In this paper, we report the synthesis and characterization of the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles by a chemical co-precipitation technique of ferric and ferrous ions. In this method, unlike previous methods of producing maghemite nanoparticles, we do not need expensive equipments, organic solvents and Hydrochloric acid which

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is a corrosive substance in the industry and create corrosion in equipment. Also, production time, compared with the previous method is faster and has the ability to produce on an industrial scale.

Methods

To prepare Iron oxide nanoparticles, especially maghemite ($\gamma\text{-Fe}_2\text{O}_3$), ferric chloride (FeCl_3 , 99 %), ferrous chloride tetra hydrate ($\text{FeCl}_2\cdot 4\text{H}_2\text{O}$, 98 %), hydrochloric acid (HCl , 37 %), ammonium hydroxide (NH_4OH , 25–30 % of ammonia), de-ionized water, and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 99.93 %) were used in the experiments. All the reagents used were of analytical grade. The synthesis was as follows:

FeCl_3 and $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ were dissolved in a 2 M hydrochloric acid to form a solution with the concentration of 1 M for FeCl_3 and 2 M for $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$. The $\text{NH}_3\cdot \text{H}_2\text{O}$ solution (0.8 M) was dropped to this solution with vigorous stirring at room temperature for 80 min. The final pH was 8.7.

FeCl_3 and $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ were dissolved in a de-ionized water to form a solution with the concentration of 1 M for FeCl_3 and 2 M for $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$. The $\text{NH}_3\cdot \text{H}_2\text{O}$ solution (0.8 M) was dropped to this solution with vigorous stirring at room temperature for 40 min. The final pH was 8.3.

The brown precipitate was then collected by filtration and rinsed three times with deionized water and ethanol. Finally, the washed precipitate was dried at room temperature.

The crystallographic structure of the as-synthesized iron oxide nanoparticles was characterized by high-resolution XRD analysis (Philips, X, pert-MPD) using $\text{Cu K}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation and the crystallite size was estimated using Scherrer's formula.

IR spectra were recorded on a Bruker tensor 27 FTIR spectrometer with RTDLATGS detector, in the range of $400\text{--}4,000 \text{ cm}^{-1}$ with a spectral resolution of 4 cm^{-1} in transmittance mode. The surface morphology of the powders was observed by the TEM (CM-120 PW6031/10). The magnetic properties of the as-synthesized nanopowders were analyzed by a vibrating sample magnetometer (VSM), in the Development Center of Kashan University (Kashan, Iran).

Results and discussion

The crystalline structure of the nanoparticles was characterized by X-ray diffraction (XRD, PHILIPS, X'pert-MPD system) using $\text{Cu K}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation and the crystallite size was estimated using Scherrer's formula. The results of analysis material by X-ray diffraction are shown in Fig. 1, which can be indexed as the primitive cubic system by comparison with data from $\gamma\text{-Fe}_2\text{O}_3$ (JCPDS No. 39-1346) [28]. The diffraction peaks at $2\theta = 18.30^\circ$, 30.20° , 35.45° , 43.32° , 53.81° , 57.22° , 62.98° , 74.54° , correspond to (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0) and (5 3 3), respectively. No impurity peak indicates that the product is pure. According to the

Fig. 1 X-ray diffraction patterns of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles by chemical precipitation method at room temperature

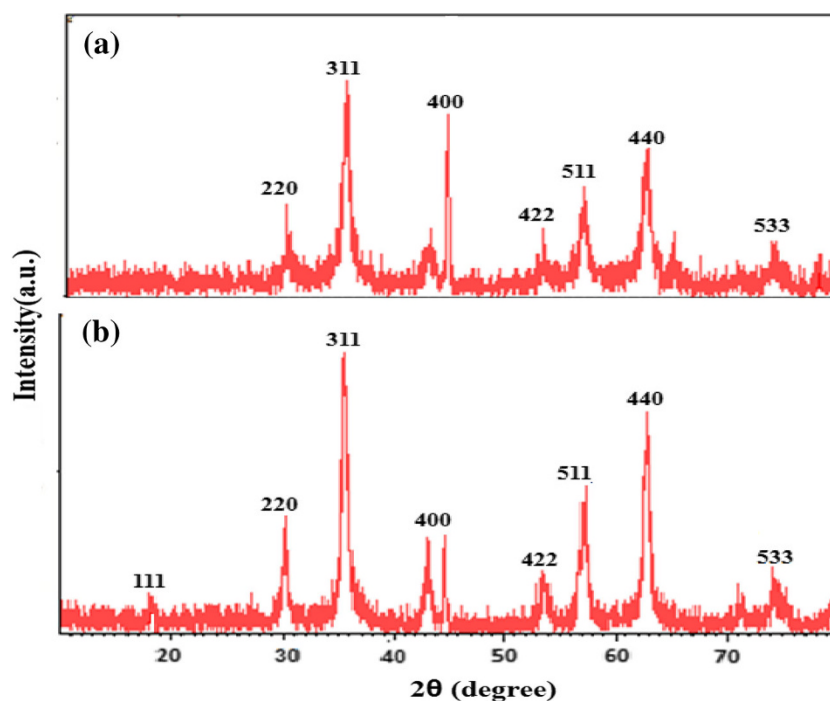


Fig. 2 FT-infrared spectra of γ -Fe₂O₃ nanoparticles performed by 200 mg KBr

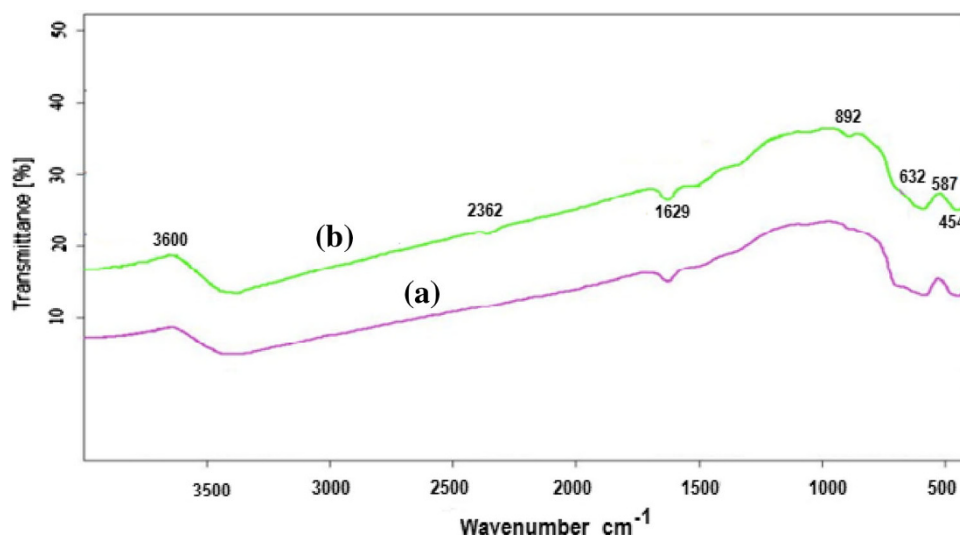
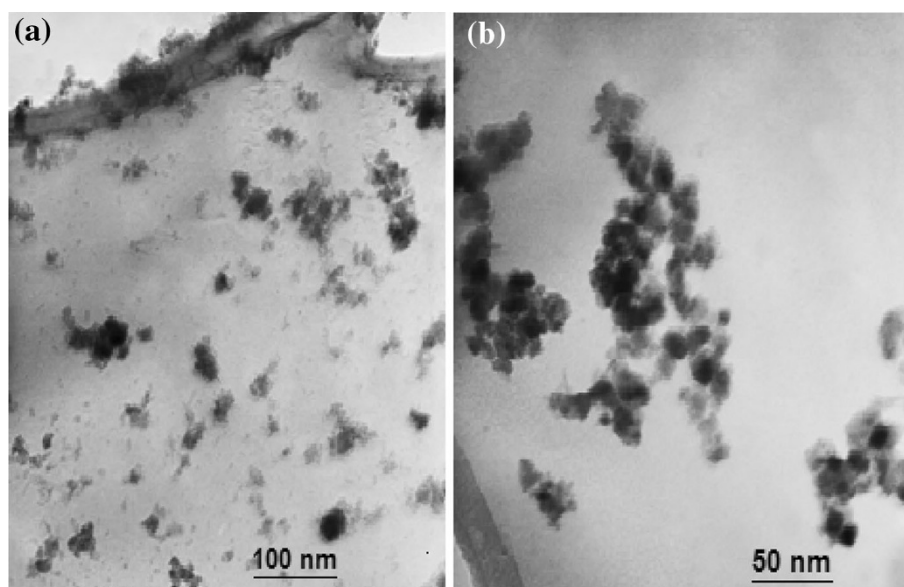


Fig. 3 TEM images of γ -Fe₂O₃ nanoparticles for **a** the sample that 2 M hydrochloric acid was used in process and **b** the sample that deionized water was used in process



Scherrer's equation, the average crystallite size of the product was calculated to be about 8–12 nm.

Figure 2 shows the FTIR spectrum of the sample, the absorption peak at 587 cm⁻¹ identified vibration of γ Fe-O [35, 36], and the other peaks at pure maghemite are 454, 632, 795, 892 cm⁻¹. The two absorption peaks at 3,170 and 3,408 cm⁻¹ arising from the O–H group stretching band and the absorption peak at 1,629 cm⁻¹ correspond to hydroxyl group (O–H) of water [34]. There is a tiny dip in the spectra at 2,362 cm⁻¹ due to the presence of atmospheric CO₂ [35]. The FTIR spectra show no impurities such as chloride and ammonium groups in the sample.

The size and shape of maghemite nanoparticles were investigated using TEM device. Figure 3 shows the TEM

images and distribution curve of maghemite nanoparticles for (a) the sample that 2 M hydrochloric acid was used in process and (b) is for the sample that deionized water was used in process. Figure 4 shows the distribution of iron oxide nanoparticles for the sample (a) and sample (b). The results show that the size of nanoparticles is decreased, and their homogeneity is increased using deionized water in process in comparison with the process that 2 M hydrochloric acid was used. The shape of nanoparticles was spherical and the average size of them was 8 nm for first sample and 12 nm for second sample.

Figure 5 shows a magnetization hysteresis loop for the prepared γ -Fe₂O₃ nanoparticle powder at room temperature. The values of saturation magnetization and coercivity



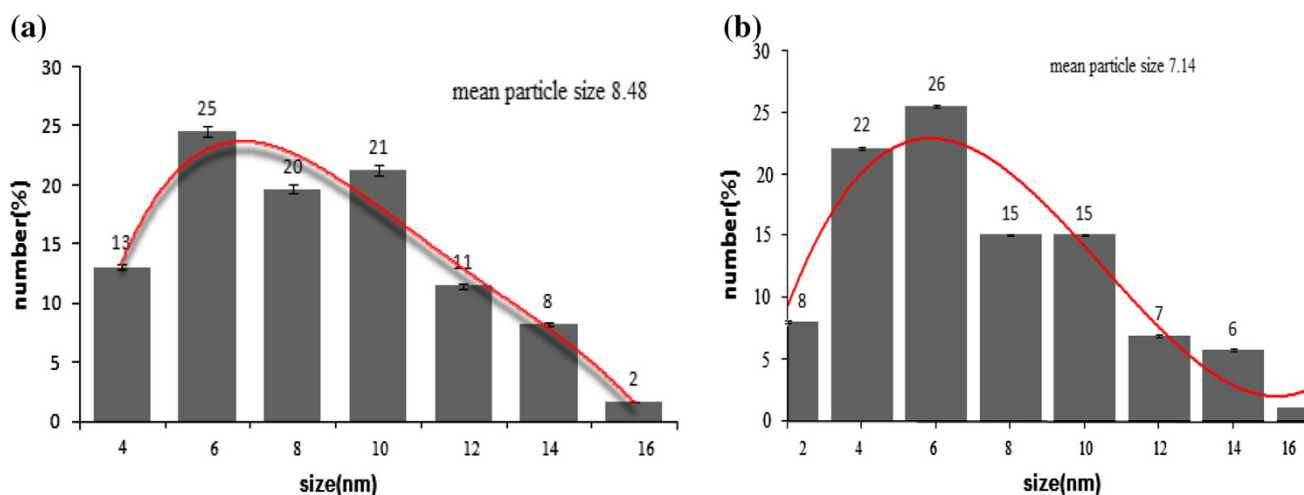


Fig. 4 Particle size distributions measured from TEM images for **a** the sample that 2 M hydrochloric acid was used in process and **b** the sample that deionized water was used in process

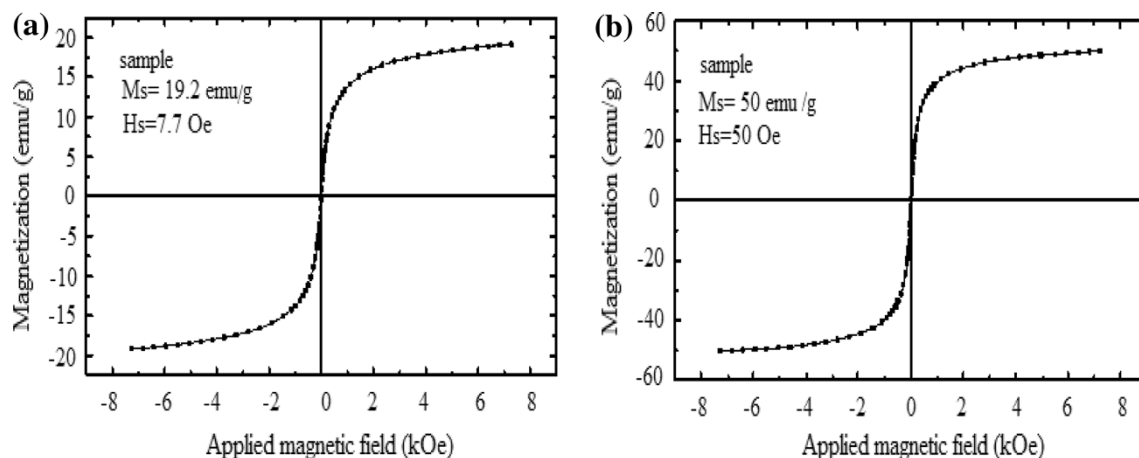


Fig. 5 Magnetization hysteresis loop for as-prepared powder

were $M_s = 19.2 \text{ emu g}^{-1}$, $H_s = 7.7 \text{ Oe}$ for first sample and were $M_s = 50 \text{ emu g}^{-1}$, $H_s = 50 \text{ Oe}$ for second sample. By increasing saturation magnetization factor, the size of the nanoparticle is decreased [37].

Conclusions

In summary, $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles have been prepared by chemical precipitation method at room temperature. The procedure in the present study offers very important advantageous features for preparation of maghemite nanoparticles. The synthetic process is economical, able to control the size of nanoparticles and production scale up and do not need heating stage and complex equipment. The XRD patterns indicated that as-synthesized iron oxide nanoparticles were maghemite. According to

the TEM image, the particle size was around 9 nm, and particle shape was almost a sphere. The saturation magnetization of the iron oxide nanopowders was 50 emu g^{-1} .

Conflict of interest The authors declare that they have no competing interests.

Author contribution MS proposed the study, carried out the experiments, performed the statistical analysis, revised, drafted manuscript, and financially supported the project. NG helped to revised, draft the manuscript. HM carried out the experiments and to draft the manuscript and MMM carried out the experiments and to draft the manuscript. All authors read and approved the final manuscript.

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References

- Cornell, R.M., Schwertmann, U.: The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses, 2nd edn. Wiley, Weinheim (2003)
- Ray, I., Chakraborty, S., Chowdhury, A., Majumdar, S., Prakash, A., Pyare, R., Sen, A.: Room temperature synthesis of γ -Fe₂O₃ by sonochemical route and its response towards butane. *Sens. Actuators B* **130**, 882–888 (2008)
- Neuberger, T., Schopf, B., Hofmann, H., Hofmann, M., von Rechenberg, B.: Superparamagnetic nanoparticles for biomedical applications: possibilities and limitations of a new drug delivery system. *J. Magn. Magn. Mater.* **293**(1), 483–496 (2005)
- Enslin, J., Gütlich, P., Klinger, R., Meisel, W., Jachow, H., Schwab, E.: Magnetic pigments for recording media. *Hyperfine Interact.* **111**(1–4), 143–150 (1998)
- Büscher, K., Helm, C.A., Gross, C., Glöckl, G., Romanus, E., Weitschies, W.: *Langmuir* **20**, 2435 (2004)
- Kiemle, P., Wiese, J., Buxbaum, G.: Process for the production of iron oxides epitaxially coated with cobalt, the coated oxides and their use. US Patent No. 652214
- Pope, N.M., Alsop, R.C., Chang, Y.A., Smith, A.K.: Evaluation of magnetic alginate beads as a solid support for positive selection of CD34 + cells. *J. Biomed. Mater. Res.* **28**, 449–457 (1994)
- Jing, Z., Wang, Y., Wu, S.: *Sens. Actuator B* **113**, 177 (2006)
- Liao, M., Chen, D.: Preparation and characterization of a novel magnetic nano-adsorbent. *J. Mater. Chem.* **12**, 3654–3659 (2002)
- Jing, Z., Wu, S.: Synthesis, characterization and gas sensing properties of undoped and Co-doped-Fe₂O₃-based gas sensors. *Mater. Lett.* **60**, 952–956 (2006)
- Liu, Y., Zhu, W., Tan, O.K., Shen, Y.: Structural and gas sensing properties of ultrafine Fe₂O₃ prepared by plasma enhanced chemical vapor deposition. *Mater. Sci. Eng. B* **47**, 171–176 (1997)
- Lim, I.S., Jang, G.E., Kim, C.K., Yoon, D.H.: Fabrication and gas sensing characteristics of pure and Pt-doped-Fe₂O₃ thin film. *Sens. Actuators B* **77**, 215–220 (2001)
- Wang, J., Tong, M., Wang, X., Ma, Y., Liu, D., Wu, J., Gao, D., Du, G.: Preparation of H₂ and LPG gas sensor. *Sens. Actuators B* **84**, 95–97 (2002)
- Mørup, S., Tronc, E.: Superparamagnetic relaxation of weakly interacting particles. *Phys. Rev. Lett.* **72**, 3278 (1994)
- Sinha, A., Chakraborty, J., Rao, V.: Process for preparing nano-sized acicular magnetic maghemite phase iron oxide particles. European Patent EP1559118
- Nagano, H., Machida, Y., Iwata, M., Imada, T., Noguchi, Y., Matsumoto, A., Nagai, T.: Preparation of magnetic granules containing bleomycin and its evaluation using model esophageal cancer. *Int. J. Pharm.* **147**, 119–125 (1997)
- Billotey, C., Wilhelm, C., Devaud, M., Bacrij, C., Bittoun, J., Gazeau, F.: Medical cell internalization of anionic maghemite nanoparticles: quantitative effect on magnetic resonance imaging. *Magn. Reson. Med.* **49**, 646–654 (2003)
- Rostovshchikova, T.N., Kiseleva, O.I., Smirnov, V.V., Maksimov, Y.V., Suzdalev, I.P., Prusakov, V.E., Tsodikov, M.V., Ikorskii, V.N.: Catalytic conversions of chloroolefines over iron oxide nanoparticles 3. Electronic and magnetic properties of γ -Fe₂O₃ nanoparticles immobilized on different silicas. *Russ. Chem. Bull. Int.* **55**, 1768–1774 (2006)
- Dutta, A.K., Maji, S.K., Adhikary, B.: γ -Fe₂O₃ nanoparticles: an easily recoverable effective photo-catalyst for the degradation of rose bengal and methylene blue dyes in the waste-water treatment plant. *Mater. Res. Bull.* **49**, 28–34 (2014)
- Ortega, D., Garitaonandia, J.S., Barrera-Solano, C., Ramírez-del-Solar, M., Blanco, E., Domínguez, M.: γ -Fe₂O₃/SiO₂ nanocomposites for magneto-optical applications: nanostructural and magnetic properties. *J. Non-Cryst. Solids* **352**, 2801–2810 (2006)
- Pierson, H.O.: Handbook of Chemical Vapor Deposition: Principles, Technology, and Applications. William Andrew Inc (1999)
- Teja, A.S., Koh, P.Y.: Synthesis: properties, and applications of magnetic iron oxide nanoparticles. *Prog. Cryst. Growth Charact. Mater.* **55**, 22–45 (2009)
- Lee, S.J., Jeong, J.R., Shin, S.C., Kim, J.C., Kim, J.D.: Impedance spectra of field-aligned CF02 needle-shape powders. *J. Magn. Magn. Mater.* **282**, 147 (2004)
- Darezereshki, E.: Synthesis of maghemite (γ -Fe₂O₃) nanoparticles by wet chemical method at room temperature. *Mater. Lett.* **64**, 1471–1472 (2010)
- Layek, S., Pandey, A., Pandey, A., Verma, H.C.: Synthesis of γ -Fe₂O₃ nanoparticles with crystallographic and magnetic texture. *Int. J. Eng. Sci. Technol.* **2**(8), 33–39 (2010)
- da Costa, G.M., De Grave, E., de Bakker, P.M.A., Vandenberghe, R.E.: Synthesis and characterization of some iron oxides by sol-gel method. *J. Solid State Chem.* **113**, 405–412 (1994)
- Cui, H., Ren, W.: Low temperature and size controlled synthesis of monodispersed γ -Fe₂O₃ nanoparticles by an epoxide assisted sol-gel route. *J. Sol Gel Sci. Technol.* **47**, 81–84 (2008)
- Cui, H., Liu, Y., Ren, W.: Structure switch between α -Fe₂O₃, γ -Fe₂O₃ and Fe₃O₄ during the large scale and low temperature sol-gel synthesis of nearly monodispersed iron oxide nanoparticles. *Adv. Powder Technol.* **24**, 93–97 (2013)
- Chin, A.B., Yaacob, I.I.: Synthesis and characterization of magnetic iron oxide nanoparticles via w/o microemulsion and Massart's procedure. *J. Mater. Process. Technol.* **191**, 235–237 (2007)
- Alvarez, G.S., Muhammed, M., Zagorodni, A.A.: Novel flow injection synthesis of iron oxide nanoparticles with narrow size distribution. *Chem. Eng. Sci.* **61**, 4625–4633 (2006)
- Liu, T., Guo, L., Tao, Y.: Synthesis and interfacial structure of nanoparticles γ -Fe₂O₃ coated with surfactant DBS and CTAB. *Nanostruct. Mater.* **11**, 487–492 (1999)
- Islam, M.S., Kurawaki, J., Kusumoto, Y., Abdulla-Al-Mamuna, M., Bin Mukhlis, M.Z.: Hydrothermal novel synthesis of neck-structured hyperthermia-suitable magnetic (Fe₃O₄, γ -Fe₂O₃ and α -Fe₂O₃) nanoparticles. *J. Sci. Res.* **4**(1), 99–107 (2012)
- Strobel, R., Pratsinis, S.E.: Direct synthesis of maghemite, magnetite and wustite nanoparticles by flame spray pyrolysis. *Adv. Powder Tech.* **20**, 190 (2009)
- Cao, S.-W., Zhu, Y.-J., Zeng, Y.-P.: Formation of γ -Fe₂O₃ hierarchical nanostructures at 500 °C in a high magnetic field. *J. Magn. Magn. Mater.* **321**, 3057–3060 (2009)
- Chakrabarti, S., Ganguli, D., Chaudhuri, S.: Optical properties of γ -Fe₂O₃ nanoparticles dispersed on sol-gel silica spheres. *J. Physica. E* **24**, 333 (2004)
- Haw, C.Y., Mohamed, F., Chia, C.H., Radiman, S., Zakaria, S., Huang, N.M., Lim, H.N.: Hydrothermal synthesis of magnetite nanoparticles as MRI contrast agents. *Ceram. Int.* **36**(4), 1417–1422 (2010)
- Lee, Y., Jun, K., Park, J., Potdar, H., Chikate, R.: A simple chemical route for the synthesis of γ -Fe₂O₃ nanoparticles dispersed in organic solvents via an iron-hydroxy oleate precursor. *J. Ind. Eng. Chem.* **14**, 38–44 (2008)
- Tuutijarvi, T., Vahala, R., Sillanpaa, M., Chen, G.: Maghemite nanoparticles for As(V) removal: desorption characteristics and adsorbent recovery. *Environ. Technol.* **33**(16), 1927–1936 (2012)
- Akhbarizadeh, R., Shayestefar, M.R., Darezereshki, E.: Competitive removal of metals from wastewater by maghemite nanoparticles: a comparison between simulated wastewater and AMD. *Mine. Water Environ.* **33**, 89–96 (2014)

