

# Synthesis of magnetic nanoparticles from FeCl<sub>2</sub> solution and spent pickling liquor in aqueous saturated lime solution

Le Thi Mai Huong<sup>1</sup>, Nguyen Van Tien<sup>1</sup>, Vu Xuan Minh<sup>2</sup>, Le Trong Lu<sup>2</sup>, Nguyen Tuan Dung<sup>2</sup>

<sup>1</sup> Institute for Technology of Radioactive and Rare Elements, 48, Lang Ha, Dong Da, Hanoi, Vietnam

<sup>2</sup> Institute for Tropical technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam

E-mail: huonghvc@gmail.com

## Abstract

Spent pickling liquor containing almost FeCl<sub>2</sub> is a considered hazardous waste because of its very high level of acidity and high metal concentration, and the conventional neutralization method regenerates an excessive quantity of sludge that poses a serious problem concerning to the landfill disposal and risk of ground water contamination. Therefore, recovery of spent pickling liquor is necessary. Several approaches have been investigated for spent pickling liquor recovery, but they are generally costly and lead to produce various iron salts or oxides which have a limited value. In the present study, we explore the potential of using spent pickling liquor and FeCl<sub>2</sub> solution as iron precursor for the synthesis of magnetic nanoparticles. Here, Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared easily by oxidation-precipitation from spent hydrochloride acid pickling liquors in aqueous saturated solution of calcium hydroxide at room temperature, in the air, and under suitable speed of rotation. The FT-IR, XRD and TEM results shown that monodisperse Fe<sub>3</sub>O<sub>4</sub> nanoparticles in the size range of 10-40 nm were obtained, with a high level of crystalline. The BET surface area of particles from spent pickling liquor was about 46 m<sup>2</sup>g<sup>-1</sup>, and from FeCl<sub>2</sub> salt was about 24 m<sup>2</sup>g<sup>-1</sup>. The synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles exhibited the super paramagnetic behavior with relatively high saturation magnetization, from spent pickling liquor about Ms=73 emu g<sup>-1</sup> and from FeCl<sub>2</sub> salt was higher, about 83 emu g<sup>-1</sup>. The tested adsorbed capacity of As (V) of particles from spent pickling liquor was about 90 mg As/g Fe<sub>3</sub>O<sub>4</sub>, and from FeCl<sub>2</sub> salt was about 42 mg As/g Fe<sub>3</sub>O<sub>4</sub>. This proves that some impurities in the pickling solution such as Mn, C ... help to develop the surface and adsorption capacity.

**Key words:** *spent pickling liquor, FeCl<sub>2</sub> salt, magnetic nanoparticles, oxidation-precipitation, and calcium hydroxide.*

## I. INTRODUCTION

Pickling is an important stage for surface treatment in the metal processing industries. It is the cleaning process by strong acids to remove impurities, such as stains, inorganic

contaminants and rust from ferrous metals, copper, precious metals and aluminum alloys. Carbon steels are often pickled in hydrochloric or sulfuric acids which are called pickling liquor. Through the usage the pickle liquors were gradually contaminated with dissolved metals. As the metal concentration increases, the free acid concentration decreases and pickling efficiency drop, the spent pickling liquor must be discarded [1]. A considerable amount of waste generated by the metal pickling industries is identified as an environmentally hazardous waste because of its very high level of acidity and also high metal concentration [2]. Until now, the most economical method for treatment of spent pickling liquor is the neutralization with lime or some other cheap alkaline agent. This conventional method regenerates an excessive quantity of sludge that poses a serious problem concerning to the landfill disposal and risk of ground water contamination [3]. Therefore, recovery of spent pickling liquor is necessary, in order to reduce the steel processing cost and also the risk of environment pollution.

Several approaches and methodologies have been investigated for recovery of acid and metal from the ferrous chloride-bearing spent HCl pickling liquor, such as anion exchange [4], solvent extraction [5], pyrohydrolysis [6], crystallization [7], membrane distillation [8,9], microwave-hydrothermal processes [10], *etc...* Generally, these methods are costly and lead to produce various iron salts, iron oxides which have a limited value.

Among the different types of iron oxides, magnetite ( $\text{Fe}_3\text{O}_4$ ) particles gained more attractive attention due to their potential applications in various fields, such as ferro fluids, catalysts, environment, high-density magnetic recording media and medical diagnosis. Many technologies have been investigated for synthesis of magnetic nanoparticles during the last few years, such as micro emulsions [11], co-precipitation [12,13], hydrothermal reactions [14,15], *etc.* ... Among these, chemical co-precipitation of ferrous and ferric ions by base is the most frequently used method.

Spent pickling liquor containing a large amount of iron salts can be used as precursor for the fabrication of magnetic nanoparticles. Recently, Bing Tang et al. demonstrated the synthesis procedure to obtain the  $\text{Fe}_3\text{O}_4$  from spent chloride pickling liquor by ultrasonic-assisted chemical co-precipitation [16]. In their study, sodium perchlorate ( $\text{NaClO}_4$ ) was used to adjust the molar ratio of Fe(III) and Fe(II) to 2:1, and co-precipitation reaction was carried out at  $75^\circ\text{C}$  in an ultrasound bath. Continuous and homogeneous ultrasonic irradiation of frequency 40 kHz has been provided all over the solutions. The  $\text{Fe}_3\text{O}_4$  particles obtained of 13–23nm diameter and exhibited paramagnetic behavior, with saturation magnetization of  $67.77 \text{ emug}^{-1}$ .

In this study, we report a simple approach for synthesis of  $\text{Fe}_3\text{O}_4$  super magnetic nanoparticles via chemical oxidation-precipitation in aqueous saturated solution of calcium

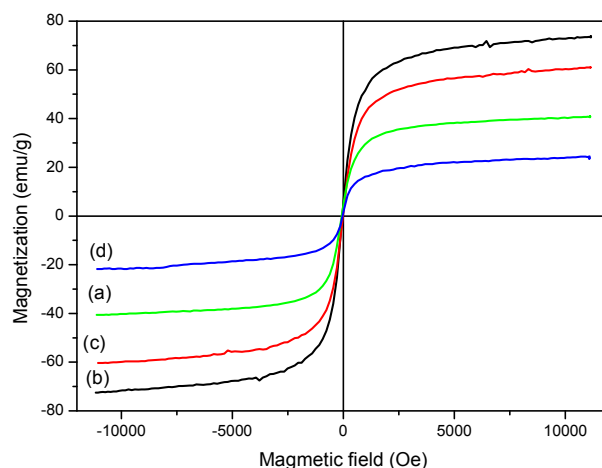
hydroxide, at room temperature. The chemical and crystalline structure of synthesized nanomaterials was examined by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction, the morphology was observed by TEM, BET surface area was also determined and magnetic property was characterized by Vibrating Sample Magnetometer.

## **II. EXPERIMENTAL**

Samples of chloride pickling liquors (pH  $\sim$ 0.1, total iron  $151.2 \text{ g L}^{-1}$ , trace amounts of other heavy metals, e.g. Mn  $26.7 \text{ mg L}^{-1}$ , Cr  $16.9 \text{ mg L}^{-1}$  and Cu  $9.3 \text{ mg L}^{-1}$ ) was collected from Hoa-Phat Steel Factory, Vietnam. Samples of  $\text{FeCl}_2$  solution was prepared from chemical  $\text{FeCl}_2$  salt made China with pH  $\sim$ 0.1. Oxidation-precipitation reaction was carried out at room temperature in a beaker containing 600 mL of saturated  $\text{Ca(OH)}_2$  solution (pH  $\sim$ 12) under vigorously stirring in the air. 4.5 mL SPL was added drop-wise into the solution within 2 min. Reaction mixture was further stirred for 30 min to obtain the black precipitate of the  $\text{Fe}_3\text{O}_4$  which was separated from solution by an external magnet, then washed with distilled water until pH reached 7. The rotation speed was changed from 200 to 800 rpm to choose the optimized value, in accordance with the saturation magnetization ( $M_s$ ) of the samples.  $M_s$  was measured at room temperature using a vibrating sample magnetometer (VSM, DMS 800, Quantum Design, Inc.). The chemical and crystalline structure of  $\text{Fe}_3\text{O}_4$  was examined by Fourier transform infrared spectra (Nicolet iS10 FT-IR Spectrometer) and X-ray powder diffraction pattern (Siemens/Bruker D5005 X-ray diffractometer). Transmission electron microscopy images were obtained by the JEM 1010 TEM in order to investigate the morphology of the samples. The specific surface area of  $\text{Fe}_3\text{O}_4$  nanoparticles was determined by physical adsorption of nitrogen gas using Micromeritics TriStar 3000 apparatus.

## **III. RESULTS AND DISCUSSION**

The hysteresis loops of the samples synthesized with different rotation speed were presented in Fig.1, all they showed the super paramagnetic behavior when the remanence and the coercivity are close to zero [17].



**Fig. 1.** Magnetic properties of the magnetite nanoparticles synthesized with rotation speed of (a) 200; (b) 400; (c) 600 and (d) 800 rpm.

The values of the saturation magnetization ( $M_s$ ) were strongly influenced by the rotation condition, the maximum  $M_s$  was obtained 73 emu/g in the case applied the speed 400 rpm. In the waste chloride pickling liquor at pH close to zero, iron exists as the ferrous ions ( $Fe^{2+}$ ). When it was added to the saturated  $Ca(OH)_2$  solution,  $Fe^{2+}$  ion oxidized partially to  $Fe^{3+}$  by oxygen dissolved in the solution, then  $Fe^{2+}$  and  $Fe^{3+}$  were co-precipitated to form magnetite particles. Rotation speed during the synthesis reaction may affect on the oxidation level and thus on the stoichiometric ratio  $Fe^{3+}/Fe^{2+}$ .

The magnetic particles synthesized with rotation speed of 400 rpm were characterized by FT-IR spectroscopy and X-ray diffraction methods as shown in Fig.2 and Fig.3.

The FT-IR spectrum shows clearly the characteristic absorption band at  $576\text{ cm}^{-1}$  attributed to the stretching vibration of the Fe–O bond of  $Fe_3O_4$  [18,19]. Additional, the broad bands at around 3449 and  $1634\text{ cm}^{-1}$  can be attributed respectively to the stretching and bending vibrations of –OH groups on the surface of nanoparticles.

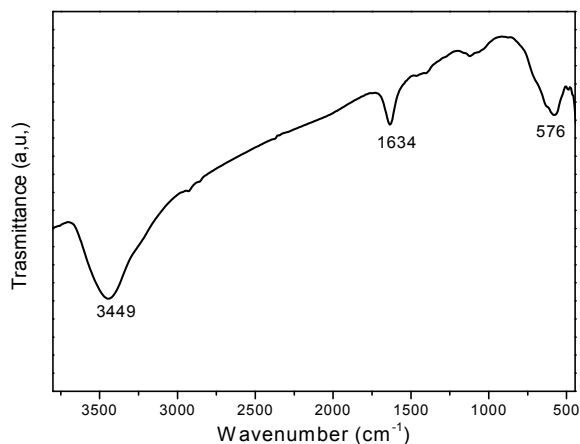


Fig. 2. FT-IR spectrum of magnetite nanoparticles synthesized with 400 rpm.

The diffraction peaks observed at  $30.2^\circ$ ,  $35.5^\circ$ ,  $43.3^\circ$ ,  $53.7^\circ$ ,  $57.2^\circ$  and  $62.9^\circ$  on the XRD pattern were corresponding to the (220), (311), (400), (422), (511) and (440) crystal planes of a pure  $\text{Fe}_3\text{O}_4$  with a spinel structure [20]. The absence of characteristic diffraction peaks at (113), (210), (213) and (210) of magnetite and hematite [21], indicating that there is no other iron compounds in the synthesized magnetite.

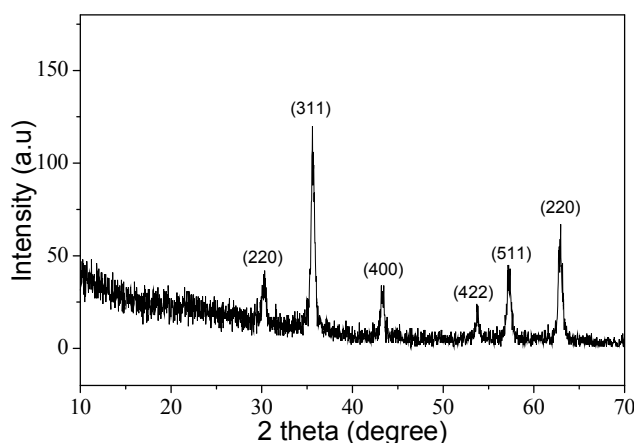


Fig. 3. XRD pattern of magnetite nanoparticles synthesized with 400 rpm.

The morphology of synthesized  $\text{Fe}_3\text{O}_4$  particles was analyzed by TEM as shown in Fig. 4. From the TEM images we can observe that the monodisperse magnetite nanoparticles were successfully synthesized from spent pickling liquor, with size in the range of 10-25 nm.

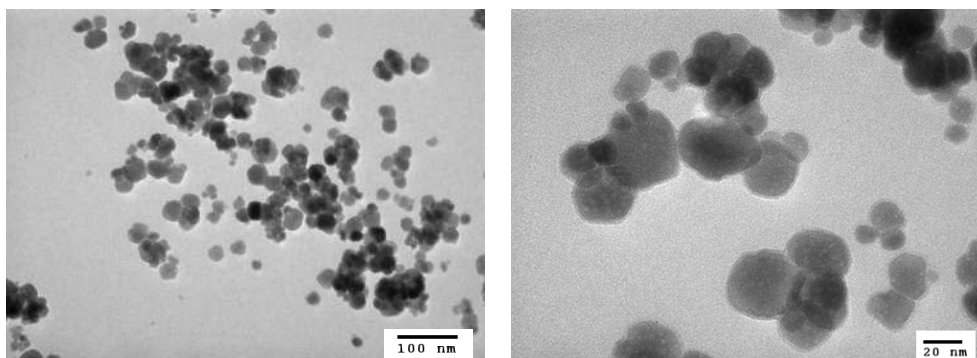


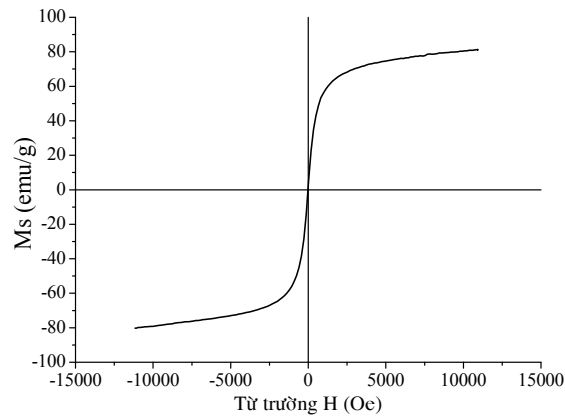
Fig. 4. TEM images of  $\text{Fe}_3\text{O}_4$

Synthesized  $\text{Fe}_3\text{O}_4$  particles from pure iron (II) salts were measured magnetic properties (Ms), were characterized by FT-IR, XRAY and observed by SEM. Results were shown in Fig. 5, 6,7 and 8.

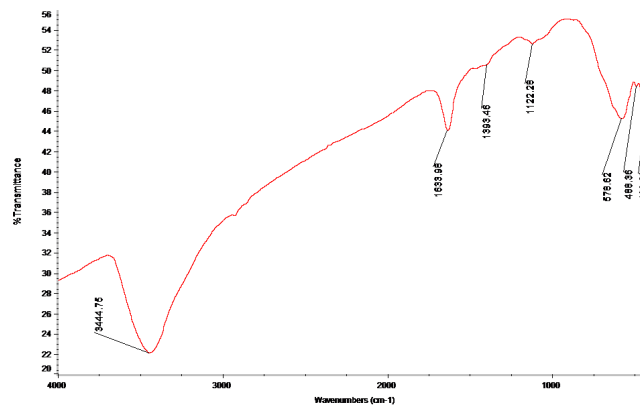
The synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles exhibited the super paramagnetic behavior with relatively high saturation magnetization, from spent pickling liquor about  $M_s=73 \text{ emu g}^{-1}$  and from  $\text{FeCl}_2$  salt was higher, about  $83 \text{ emu g}^{-1}$ .

Results of FT-IR, XRAY are the same as for samples from the pickling solution

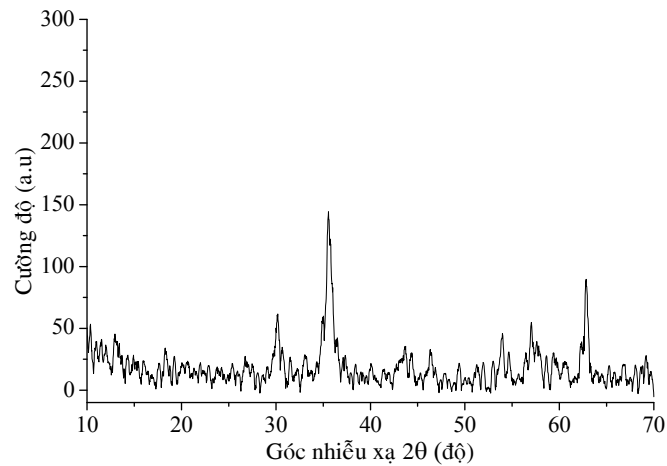
The results BET showed that samples from the pickling solution had a specific surface area (S) of approximately  $45 \text{ m}^2 \text{ g}^{-1}$ , nearly double the sample from pure iron (II) salt -  $24 \text{ m}^2 \text{ g}^{-1}$ .



**Fig. 5.** Magnetic properties of the magnetite nanoparticles synthesized from  $\text{FeCl}_2$  salt



**Fig. 6.** FT-IR spectrum of magnetite nanoparticles synthesized from  $\text{FeCl}_2$  salt



**Fig. 7.** XRD pattern of magnetite nanoparticles synthesized from  $\text{FeCl}_2$  salt

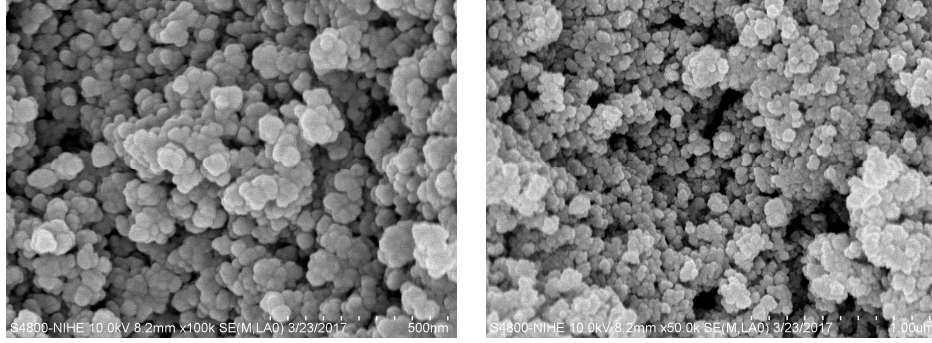


Fig. 8. SEM images of  $Fe_3O_4$  synthesized from  $FeCl_2$  salt

*Adsorption Test of  $Fe_3O_4$  samples made from the pickling solution and from pure iron (II) salts*

To test the adsorption capacity of the above samples were conducted experiments with ion As (V) from solution  $H_3AsO_4$  with concentration 100 mg/L . The experiments were carried out in room temperature conditions, the volume of solution 100 ml, the mass of adsorbent 0,5 g, pH = 5. Adsorption time was 3 hours and the concentration of adsorbed solutions is checked by standard AAS method. The adsorbed capacity results of samples are shown in Table 1. The Adsorbed capacity of As of particles from spent pickling liquor was about 90 mg As/g  $Fe_3O_4$ , and from  $FeCl_2$  salt was about 42 mg As/g  $Fe_3O_4$  (table 1). This proves that some impurities in the pickling solution such as Mn, C ... help to develop the surface and adsorption capacity.

Table 1: The absorbed capacity of As (V) of  $Fe_3O_4$  particles

Sample	S ( $m^2/g$ )	mgAs (V)/g $Fe_3O_4$
$Fe_3O_4$ from $FeCl_2$ salt	24	40
$Fe_3O_4$ from spent pickling liquor	45	90

#### IV. CONCLUSIONS

The magnetic nanoparticles are successfully synthesized from  $FeCl_2$  salts and waste pickling liquor in aqueous saturated solution of calcium hydroxide; the process is easily realized at room temperature in the air. The obtained monodisperse particles present the single phase magnetite ( $Fe_3O_4$ ) with a size range of 10-45 nm, exhibit super paramagnetic behavior with saturation magnetization, from spent pickling liquor about  $M_s=73 \text{ emu g}^{-1}$  and from  $FeCl_2$  salt was higher, about  $83 \text{ emu g}^{-1}$ . a specific surface area (S) of approximately  $45 \text{ m}^2 \text{ g}^{-1}$ , nearly double the sample from pure iron (II) salt -  $24 \text{ m}^2 \text{ g}^{-1}$ . The test adsorbed capacity of As of particles from spent pickling liquor was about 90 mg As/g  $Fe_3O_4$ , and from  $FeCl_2$  salt was about 42 mg As/g  $Fe_3O_4$ . This proves that some impurities in the pickling solution such as Mn, C ... help to develop the surface and adsorption capacity.

## REFERENCES

1. **Devi A., Singhal A., Gupta R.** A review on spent pickling liquor, *Int. J. of Environ. Sci.* 2013. V.4. P. 284-295. DOI:10.6088/ijes.2013040300007.
2. **Rogener F., Sartor M., Ban A., Bucholoh D. Reichardt T.** Metal recovery from spent stainless steel pickling solution. *Res. Conserv. Recycl.* 2012. V. 60. P. 72–77. DOI: 10.1016/j.resconrec.2011.11.010.
3. **Ozdemir T., Oztin C., Kincal N.S.** Treatment of waste pickling liquors: process synthesis and economic analysis. *Chem. Eng. Comm.* 2006. V. 193. P. 548–563. DOI: 10.1080/00986440500192238.
4. **Csicsovszki G., Kekesi T., T.I. Torok T.I.** Selective recovery of Zn and Fe from spent pickling solutions by the combination of anion exchange and membrane electrowinning techniques. *Hydrometallurgy.* 2005. V. 77. P 19–28. DOI: 10.1016/j.hydromet.2004.10.020.
5. **Agrawal A., Kumari S., Ray B.C., Sahu K.K.** Extraction of acid and iron values from sulphate waste pickle liquor of a steel industry by solvent extraction route. *Hydrometallurgy.* 2007. V. 88. P. 58–66. DOI: 10.1016/j.hydromet.2007.04.001.
6. **Barhold F., Engelhardt W.** United States Patent N 6375915. 2002.
7. **Shaikh L., Pandit A., Ranade V.** Crystallisation of ferrous sulphate heptahydrate: experiments and modeling. *Can. J. Chem. Eng.* 2013. V. 91. P. 47–54. DOI: 10.1002/cjce.20695.
8. **Bernata X., Fortuny A., Stüber F., Bengoa C., Fabregat A., Font J.** Recovery of iron(III) from aqueous stream by ultra filtration. *Desalination.* 2008. V. 221. P. 413–418. DOI: 10.1016/j.desal.2007.01.100
9. **Tomaszewska M., Grypta M., Morawski A.W.** Recovery of hydrochloric acid from metal pickling solutions by membrane distillation. *Sep. Purif. Technol.* 2001. V. 22–23. P. 591–600. DOI: 10.1016/S1383-5866(00)00164-7.
10. **Ciminelli V.S.T., Dias A., Braga H.C.** Simultaneous production of impurity-free water and magnetite from steel pickling liquors by microwave-hydrothermal processing. *Hydrometallurgy.* 2006. V. 84. P. 37–42. DOI: 10.1016/j.hydromet.2006.03.058.
11. **Lu T., Wang J. H., Yin J., Wang A. Q., Wang X. D., Zhang T.** Surfactant effects on the microstructures of Fe<sub>3</sub>O<sub>4</sub> nanoparticles synthesized by microemulsion method. *Colloids and Surfaces A.* 2013. V. 436, P. 675-683. DOI: 10.1016/j.colsurfa.2013.08.004.
12. **Radoń A., Drygala A., Hawelek L., Lukowiec D.** Structure and optical properties of Fe<sub>3</sub>O<sub>4</sub> nanoparticles synthesized by co-precipitation method with different organic modifiers. *Materials Characterization.* 2017. V. 131. P. 148-156. DOI: 10.1016/j.matchar.2017.06.034.



13. **Nabiyouni G., Julaei M., Ghanbari D., Aliabadi P.C., Safaie N.** Room temperature synthesis and magnetic property studies of Fe<sub>3</sub>O<sub>4</sub> nanoparticles prepared by a simple precipitation method. *J. Ind. Eng. Chem.* 2015. V. 21. P. 599–603. DOI: 10.1016/j.jiec.2014.03.025.
14. **Zhang H., Zhu G.** One-step hydrothermal synthesis of magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles immobilized on polyamide fabric. *Appl. Surf.Sci.* 2012. V. 258. P. 4952-4959. DOI: 10.1016/j.apsusc.2012.01.127.
15. **Chen F., Gao Q., Hong G., Ni J.** Synthesis and characterization of magnetite dodecahedron nanostructure by hydrothermal method. *J. Magn. Magn. Mater.* 2008. V. 320. P. 1775–1780. DOI : 10.1016/j.jmmm.2008.02.117.
16. **Tang B., Yuan L., Shi T., Yu L., Zhu Y.** Preparation of nano-sized magnetic particles from spent pickling liquors by ultrasonic-assisted chemical co-precipitation. *J. Hazar. Mater.* 2009. V.163. P. 1173–1178. DOI: 10.1016/j.jhazmat.2008.07.095.
17. **Yan H., Zhang J., You C., Song Z., Yu B., Shen Y.** Influences of different synthesis conditions on properties of Fe<sub>3</sub>O<sub>4</sub> nanoparticles. *Mater. Chem. Phys.* 2009. V. 113. P. 46–52. DOI: 10.1016/j.matchemphys.2008.06.036.
18. **Lu W., Shen Y., Xie A., Zhang W.** Green synthesis and characterization of superparamagnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles. *J. Magn. Magn. Mater.*2010. V. 322. P. 1828-1833. DOI:10.1016/j.jmmm.2009.12.035.
19. **Petcharoen K., Sirivat A.** Synthesis and characterization of magnetite nanoparticles via the chemical co-precipitation method. *Mater. Sci. Eng. B.* 2012. V. 177. P. 421-427. DOI:10.1016/j.mseb.2012.01.003.
20. **Aslibeiki B., Kameli P., Manouchehri I., Salamati H.** Strongly interacting superspins in Fe<sub>3</sub>O<sub>4</sub> nanoparticles. *Current Appl. Phys.* 2012. V. 12. P. 812-816. DOI: 10.1016/j.cap.2011.11.012.
21. **Murbe J., Rechtenbach A., Topfer J.** Synthesis and physical characterization of magnetite nanoparticles for biomedical applications. *Mater. Chem. Phys.* 2008. V. 110. P. 426–433. DOI: 10.1016/j.matchemphys.2008.02.037.