DOI: 10.6060/ivkkt.20186109-10.5861a

СИНТЕЗ МАГНИТНЫХ НАНОЧАСТИЦ ИЗ ОТРАБОТАННЫХ ТРАВИЛЬНЫХ РАСТВОРОВ В НАСЫЩЕННОМ РАСТВОРЕ ГИДРОКСИДА КАЛЬЦИЯ

Ву Суан Минь, Ле Тхи Тху Ха, Фам Тхи Лан, Фам Хонг Нам, Ле Тхи Май Хыонг, Ле Чонг Лы, Нгуен Туан Зинг

Ву Суан Минь, Фам Тхи Лан

Институт тропической технологии вьетнамской академии наук и технологий, ул. Хоанг Куок Вьет, 18, Ханой, Вьетнам, 100000
E-mail: xuanminh1987@gmail.com, pham_lan@mail.ru

Ле Тхи Тху Ха, Ле Чонг Лы, Нгуен Туан Зинг*

Высший университет по науке и технологии Вьетнамской Академии наук и технологий, ул. Хоанг Куок Вьет, 18, Ханой, Вьетнам, 100000
Институт тропической технологии Вьетнамской Академии наук и технологий, ул. Хоанг Куок Вьет, 18, Ханой, Вьетнам, 100000
E-mail: hapurewater@yahoo.com, ltlu@itt.vast.vn, ndung@itt.vast.vn*

Фам Хонг Нам

Институт материаловедения Вьетнамской Академии наук и технологий, ул. Хоанг Куок Вьет, 18, Ханой, Вьетнам, 100000
E-mail: namph.ims@gmail.com

Ле Тхи Май Хыонг*

Институт технологии радиоактивных и редких элементов (Институт по атомной энергии), ул. Ланг Ха, 48, Ханой, Вьетнам, 100000
E-mail: huonghvc@gmail.com*

Отработанный травильный раствор считается опасным отходом из-за его очень высокой кислотности и высокой концентрации металлов, а обычный метод нейтрализации образует избыточное количество осадка, что представляет собой серьезную проблему, связанную с удалением стока и риском загрязнения подземных вод. Таким образом, требуется регенерация отработанного травильного раствора. Были предприняты различные исследования для отработанного травильного раствора, но они обычно являются дорогостоящими и приводят к получению различных солей или оксидов (или гидроксидов) железа, которые имеют ограниченную ценность. В настоящем исследовании мы изучаем потенциал использования отработанного травильного раствора в качестве предшественника железа для синтеза магнитных наночастиц. При этом наночастицы Fe_3O_4 были получены с помощью окисления-осаждения из отработанных хлоридов железа в водном насыщенном растворе гидроксида кальция при комнатной температуре, в воздухе и при подходящей скорости вращения. Результаты FT-IR, XRD и TEM показали, что монодисперсные частицы Fe_3O_4 в диапазоне размеров 10-25 нм были получены с высоким уровнем кристалличности. Площадь поверхности BET составляла около 46 м^2/г. Полученные Fe_3O_4 наночастицы проявили суперпарамагнитное свойство с относительно высокой намагниченностью насыщения, M_s = 73 Гс·см^3/г. Проведенный здесь синтез магнитных наночастиц даст новую возможность более эффективно утилизовать отработанные травильные растворы.

Ключевые слова: отработанный травильный раствор, магнитные наночастицы, окисление-осаждение, гидроксид кальция

SYNTHESIS OF MAGNETIC NANOPARTICLES FROM SPENT PICKING LIQUORS IN AQUEOUS SATURATED SOLUTION OF CALCIUM HYDROXIDE

Minh X. Vu, Ha T. T. Le, Lan T. Pham, Nam H. Pham, Huong T. M. Le, Lu T. Le, Dung T. Nguyen

Minh X. Vu, Lan T. Pham

Institute for Tropical Technology, Vietnam Academy of Science and Technology, Hoang Quoc Viet, 18, Cau Giay, Hanoi, Vietnam
E-mail: xuanminh1987@gmail.com, pham_lan@mail.ru

Ha T. T. Le, Lu T. Le, Dung T. Nguyen *

Graduate University of Science and Technology, Vietnam Academy of Science and Technology, Hoang Quoc Viet, 18, Cau Giay, Hanoi, Vietnam

Institute for Tropical Technology, Vietnam Academy of Science and Technology, Hoang Quoc Viet, 18, Cau Giay, Hanoi, Vietnam

E-mail: hapurewater@yahoo.com, ltlu@itt.vast.vn, ndung@itt.vast.vn *

Nam H. Pham

Institute of Materials Science, Vietnam Academy of Science and Technology, Hoang Quoc Viet, 18, Cau Giay, Hanoi, Vietnam
E-mail: namph.ims@gmail.com

Huong T. M. Le*

Institute for Technology of Radioactive and Rare Elements, Lang Ha, 48, Dong Da, Hanoi, Vietnam
E-mail: huonghvc@gmail.com*

Spent pickling liquor 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 as iron precursor for the synthesis of magnetic nanoparticles. Here, Fe_3O_4 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_3O_4 nanoparticles in the size range of 10-25 nm were obtained, with a high level of crystallinity. The BET surface area was about 46 $m^2 g^{-1}$. The synthesized Fe_3O_4 nanoparticles exhibited the superparamagnetic behavior with relatively high saturation magnetization, M_s = 73 emu/g. The synthesis procedure of magnetic nanoparticles revealed here will provide a new possibility for spent pickling liquors recovery more effectively.

Key words: spent pickling liquor, magnetic nanoparticles, oxidation-precipitation, calcium hydroxide

Для цитирования:
Ву Суан Минь, Ле Ха Тхи Тху, Фам Лан Тхи, Фам Хонг Нам, Ле Тхи Май Хыонг, Ле Чонг Лы, Нгуен Зинг Туан Синтез магнитных наночастиц из отработанных травильных растворов в насыщенном растворе гидроксида кальция. *Изв. вузов. Химия и хим. технология*. 2018. Т. 61. Вып. 9-10. С. 59–63

For citation:
Vu Minh X., Le Ha T. T., Pham Lan T., Pham Nam H., Le Huong T. M., Le Lu T. Nguyen Dung T. Synthesis of magnetic nanoparticles from spent picking liquors in aqueous saturated solution of calcium hydroxide. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2018. V. 61. N 9-10. P. 59–63

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 steelsare 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 orderto 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], crystalisation [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(Fe_3O_4) particles gained more attractive attention due to their potential applications in various fields, such as ferrofluids, 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 asmicroemulsions [11], coprecipitation [12, 13], hydrothermalreactions [14, 15], *etc*. Among these, chemical coprecipitation 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 Fe_3O_4 from spent chloride pickling liquor by ultrasonic-assistedchemical coprecipitation [16]. In their study, sodium perchlorate ($NaClO_4$) wasused to adjust the molar ratio of Fe(III) and Fe(II) to 2:1, and coprecipitationreaction was carried out at 75 °C in an ultrasound bath. Acontinuous and homogeneous ultrasonic irradiation of frequency 40 kHz has been provided all over the solutions. The Fe_3O_4 particles obtained of 13-23 nm diameter and exhibited paramagnetic behavior, with saturation magnetization of 67.77 emu/g.

In this study, we report a simple approach for synthesis of Fe_3O_4 supermagnetic 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 areawas also determined and magnetic property was characterized by Vibrating Sample Magnetometer.

EXPERIMENTAL

Samples of chloride pickling liquors (pH ~0.1, total iron 151.2 g L^{-1}, trace amounts of other heavy metals, e.g. Mn 26.7 mg L^{-1}, Cr 16.9 mg L^{-1} and Cu 9.3 mg L^{-1}) was collected from Hoa-Phat Steel Factory, Vietnam. Oxidation-precipitation reaction was caried out at room temperature in a beaker containing 600 mL of saturated $Ca(OH)_2$ solution (pH ~14) 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 abtain the black precipitate of the Fe_3O_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 choise the optimized value, in accordance with the saturation magnetization (Ms) of the samples. Ms was measured at room temperature using a vibrating sample magnetometer (VSM, DMS 800, Quantum Design, Inc.). The chemical and crystalline structure of Fe_3O_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 Fe_3O_4 nanoparticles was determined by physical adsorption of nitrogen gasusing Micromeritics TriStar 3000 apparatus.

RESULTS AND DISCUSSION

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

The values of the saturationmagnetization (Ms) were strongly influenced by the rotation condition, the maximum Ms 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 coprecipitated 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+}.

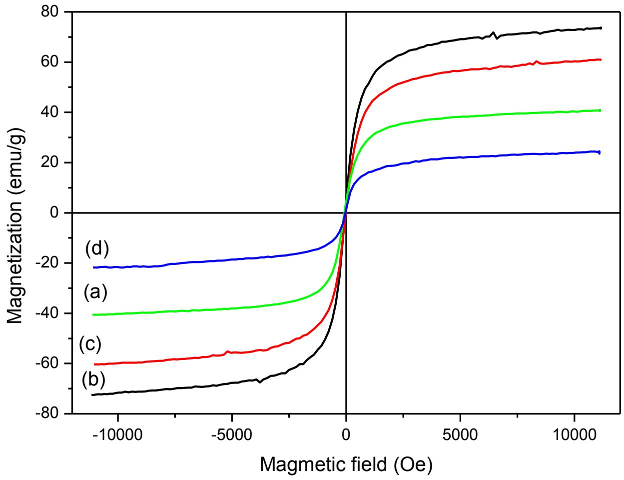

Fig. 1. Magnetic properties of the magnetite nanoparticles synthesized with rotation speed of (a) 200; (b) 400; (c) 600 and (d) 800 rpm
Рис. 1. Магнитные свойства наночастиц магнетита, синтезированных с частотой вращения (a) 200; (b) 400; (c) 600 и (d) 800 об/мин

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 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 cm^{-1} can be attributed respectively to the stretching and bending vibrations of –OH groups on the surface of nanoparticles.

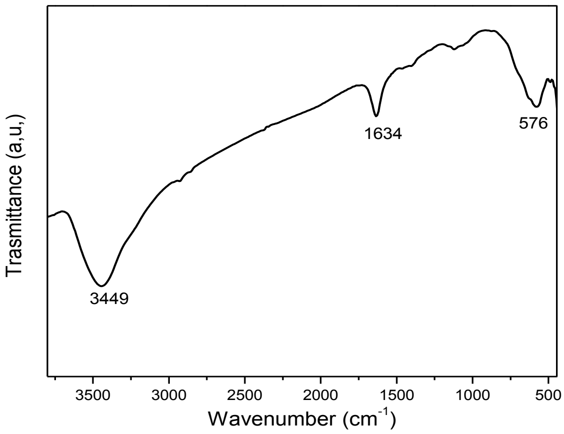

Fig. 2. FT-IR spectrum of magnetite nanoparticles synthesized with 400 rpm
Рис. 2. FT-IR-спектр наночастиц магнетита, синтезированных с 400 об/мин

The diffraction peaks observed at 30.2 °, 35.5 °, 43.3 °, 53.7 °, 57.2 ° and 62.9 ° on the XRD pattern were corresponding to the (220), (311), (400), (422), (511) and (440) crystal planes of a pure Fe_3O_4 with a spinel structure [20]. The absence of characteristic diffraction peaks at (113), (210), (213) and (210) of maghemite and hematite [21], indicating that there is no other iron compounds in the synthesized magnetite.

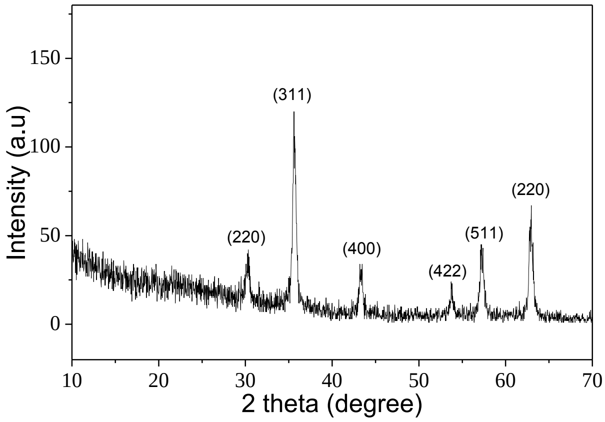

Fig. 3. XRD pattern of magnetite nanoparticles synthesized with 400 rpm
Рис. 3. XRD наночастиц магнетита, синтезированных с 400 об/мин

The morphology of synthesized Fe_3O_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.

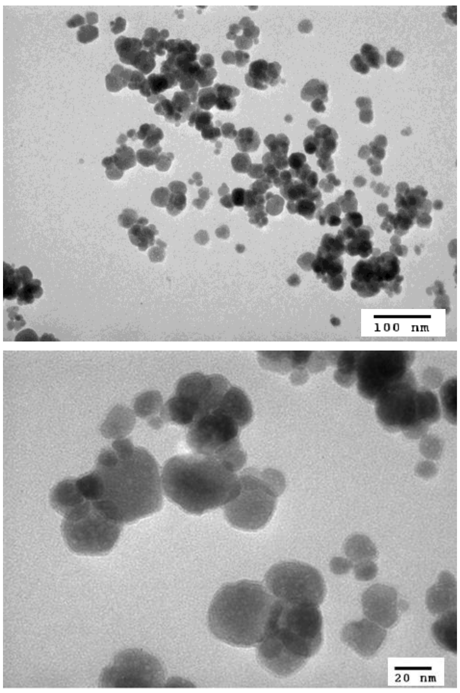

Fig. 4. TEM images of Fe_3O_4
Рис. 4. TEM-изображения Fe_3O_4

Synthesized Fe_3O_4 particles were measured on specific surface areaand then compared with the samples prepared from pure iron (II) salts. The results showed that samples from the pickling solution had a specific surface area of approximately 45 m^2 g^{-1}, nearly double the sample from pure iron (II) salt – 24 m^2 g^{-1}. This proves that some impurities in the pickling solution such as Mn, C ... help to develop the surface.

CONCLUSIONS

The magnetic nanoparticles are successfully synthesized from 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 10-25 nm, exhibit superparamagnetic behavior with saturation magnetization, Ms = 73 emu/g. The specific surface area of Fe_3O_4 nanoparticles was about 46 m^2g^{-1}.

ACKNOWLEDGMENTS

The authors would like to acknowledge the financial supports from Vietnam Academy of Science and Technology under grant VAST07.04/17-18.

Л И Т Е Р А Т У Р А

R E F E R E N C E S

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 sulphatewaste 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 sulphateheptahydrate: 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 Fe3O4 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., Drygała A., Hawełek L., Łukowiec D.** Structure and optical properties of Fe_3O_4 nanoparticles synthesized by coprecipitation method with different organic modifiers. *Materials Characterization.* 2017. V. 131. P. 148-156. DOI: 10.1016/ /j.matchar.2017.06.034.
13. **Nabiyouni G., Julaee M., Ghanbari D., Aliabadi P.C., Safaie N.** Room temperature synthesis and magnetic property studies of Fe3O4 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_3O_4 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 nanosized 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_3O_4 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_3O_4 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_3O_4 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.

Поступила в редакцию 09.07.2018
Принята к опубликованию 05.09.2018

Received 09.07.2018
Accepted 05.09.2018