The optimization of natural resources of local indonesian materials to synthesize magnetic and magnetic hybrid particles via chemical ablation, co-precipitation, and hydrothermal route process

S Arjo¹, M N Hidayat¹, N Suminten¹, B Nurjanati², and S Husain³
¹Department of Physics Education, Universitas Muhammadiyah Prof. Dr. HAMKA, Jakarta, Indonesia
²Department of Physics, Faculty of Mathematics and Natural Sciences, IPB University, Bogor, Indonesia
³Department of Physics, Faculty of Mathematics and Natural Sciences, Lambung Mangkurat University, Banjar Baru, Indonesia

*Corresponding author:s.arjo@uhamka.ac.id

Abstract: The magnetic nano-particle synthesized from natural iron sand had been successfully done. Generally, this natural iron sand is a kind of natural waste in Indonesia that has not been optimally used. This research is expected to explain the utilization of Indonesian local natural iron sand as an advanced magnetic material resource. Therefore the reader of this article can develop it for further application. Magnetic particles are a material that is very promising in supporting developments of science and technology. One of them is the development in medical fields. Most previous researchers carried out the magnetic synthesis of particles using chemicals as precursors. In this study, the researchers would like to report how to synthesize magnetic particles using local natural iron sand. The applied method consisted of three steps, namely chemical ablation, co-precipitation, and hydrothermal method. The results of this research showed that Zn-dopped magnetic particles in Quasi-spherical structures become hollow-microsphere morphological structures even though they had not been perfected yet. The Zn-dopped treatment broadens the frequency wave absorptions and magnetism properties. The Zn-dopped ion had stronger magnetic properties than that of organic factor effects from C-dot that theoretically can decrease the magnetic properties. This article briefly describes the synthesis mechanism of magnetic material from natural iron sand as material resources to substitute highly expensive mainstream chemical material. However, this study still needs to be deeply investigated to produce the optimum scientific application.

Keywords: Developmental Synthesis, Iron Sand, Magnetic Natural Resource, Magnetic Particles
1. Introduction

Magnetic particles are materials that have fine magnetization properties with ferromagnetism, paramagnetism, and diamagnetism characteristics. The ferromagnetism and paramagnetism are very attractive characteristics to the magnetic field. The diamagnetic has a repellant characteristic. Generally, magnetic particles can be obtained from two main material resources, natural and artificial. Natural resources are natural minerals such as iron ores [1–3] and iron sand [4–7] while the artificial resources incorporate the chemical salts that contain metallic elements from rare earth elements [8–10].

In Indonesia, the iron ore and iron sand have not been explored optimally since they are only used as exported raw materials [11]. However, the researchers have recently started to develop them as promising science materials through syntheses. The magnetic particles are Fe₃O₄, (α,γ)-Fe₂O₃ respectively called Magnetite, Hematite, and Maghemite [12]. All of them are the potential to be developed in many applications. The researchers tried to deeply evolve this field, especially the magnetic particle synthesis derived from natural minerals. The urgencies of this research were the exploration of natural local iron sand resources (magnetic particle sources) and a local orange peel (carbon sources) as science and technological advanced supports. This was crucial to do because it aimed to decline the dependence of synthetic mineral sources that tend to be more expensive.

Indonesia is a country that is formed by the unity of many archipelago islands from Sabang to Merauke. It has a lot of natural resources, such as natural iron sand. Next, Pelabuhan Ratu, one of the littorals in Indonesia, has a lot of these raw materials. The natural iron sand contains compound minerals like Hematite (α-Fe₂O₃), Maghemite (γ-Fe₂O₃), and Magnetite (Fe₃O₄). Fe₃O₄ compound has fine magnetization properties than other compounds. Lately, more researchers have been developing Fe₃O₄ particles for science and technology specialists. Another application is biomedical, such as biosensor [13–15], photodynamic therapy of cancer cells [16,17], bioimaging, labeling, tracking system of cells, or DNA [18,19], and the army military system [20]. Based on this information, it can be said that magnetic particles are the potential to be used as multifunctional material in many applications.

A method that has been developed to synthesize natural iron sand to be magnetic particles is co-precipitation. Beside synthesizing magnetic particles using commercial chemical-magnetic particle precursors, the co-precipitation and hydrothermal can be used instead.

Furthermore, to increase their application performance, the Fe₃O₄ has to be fabricated into nanosize [21]. Next, to synthesize magnetic particles from nature iron sand, chemical ablation or chemical reduction, co-precipitation [22], or hydrothermal [23] methods can be used. Fe₃O₄ particle sizes have been controlled at the synthesized moment using polymer [24] and pH control [25,26]. The precursor generally used to synthesize is the chemical compound salt. The ferrous (Fe²⁺) and ferric (Fe³⁺) of Fe₂Cl, FeNO₃, and FeSO₄ can be applied as the precursors in iron particle synthesis. In this work, the researcher used natural iron sand to synthesize the magnetite particles and core-shell system with C-dot using chemical ablation, co-precipitate, and hydrothermal methods. The C-dot particles were synthesized from the Indonesian local lemon. In this research, natural materials were synthesized, especially natural ferruginous sand to be developed materials with additional hydrothermal methods which made it different from the previous research.

2. Materials and methods

2.1 Materials

Hydrochloride Acid (HCl, Fajar Kimia, online store), Ammonium hydroxide (NH₄OH, Setiaguna Chemical Store, Bogor, Indonesia), zinc acetate dihydrate (Zn(CH₃CO₂)₂·2H₂O, Setiaguna Chemical Store, Bogor, Indonesia), Deionized water (DI) was used without further purification.
2.2 The Magnetic and Magnetic Hybrid Particles Synthesis
The experimental procedure of the magnetic and magnetic hybrid system was synthesized using the chemical ablation, co-precipitation, and hydrothermal process respectively. The typical-experimental procedure mechanism (chemical ablations process, natural iron sand) was extracted using a permanent magnet. Furthermore, 5 grams of iron sand was added to the HCl solution for 24 hours. Then, the solution became a precursor of magnetite particles. The precursor was placed in 50 ml and 5 ml beaker glasses. After that, 1M of NH₄OH solution was added into the precursor solution slowly and stirred at 120°C on a hotplate. The pH solution was controlled by pH paper and adjusted at 9. A black product was magnetically separated (using a permanent magnet) and washed using DI water and ethanol replacements to neutral pH. Furthermore, the step was applied to the hydrothermal method. The black product was added 50 ml DI water and/or Lemon juice (source C-dot) for coating the core-shell system and transferred to Teflon-line stainless steel autoclave and heated at 200 °C for 4 hours. The result was ultrasonicated using a bath treatment for 30 minutes, then it was dried out at 90 °C on a hotplate to dehydrate. The Zn-dopped magnetite as the precursor solution was transferred into a beaker glass of 100 ml and added Zn(CH₃COO)₂·2H₂O while it was stirred for 30 minutes. The process of the magnetic particle synthesis mechanism is defined in Figure 1.

Figure 1. The Schematic of Magnetic Particles Synthesis from Natural Iron Sand

3. Results and discussion
3.1 Optical Properties
The magnetic sand used was taken from natural sources. The FTIR characterization was used as the molecular group analysis. Next, Spectrophotometer Uv-Vis and fluorescence characterization were utilized as excitation and emission optical properties characteristic. The optical properties of Fe₃O₄ particles and core-shell systems using C-dot were shown in Figure 1 via FTIR characterization. The characterization was shown on the molecular and chemical bonds. The magnetic bond had a wavenumber of 694 and 345.2 cm⁻¹ with a structure of Fe-O and O-H bonds that widened the vibration and vibration stretching state respectively[25–27]. The symmetric and asymmetric stretching characteristics of C-H were shown at 2804 and 3009 cm⁻¹ properly corresponded to sp³ of the ZnFe₂O₄@C sample [28]. The C-H characteristic was shown at a wavenumber of 3150 cm⁻¹ of sp², Fe₃O₄, and ZnFe₂O₄@C samples[28].

The double-bond characteristic of C (C=C) was the most addictive stretching vibrational, as they corresponded with Fe₃O₄@C and ZnFe₂O₄@C samples [28][16]. It indicated the carbon characteristic of C-dot[29]. The magnetic bond characteristic was signed via wavenumber 694 cm⁻¹ corresponding with Fe-O, Fe₃O₄@C, and ZnFe₂O₄@C that had a wider absorbed area of Fe₃O₄ origin sample. It was the width area of Fe₃O₄@C and ZnFe₂O₄@C i.e 534 – 950 and 520 – 950 cm⁻¹ respectively. The ZnFe₂O₄@C had higher optical absorptions corresponded to C=C and Fe-O [28].
The optical properties of a core-shell system of magnetic particles were characterized by spectrophotometer UV-Vis and Fluorescence for excitation and emission processes respectively. The excitation process was shown in Figure 2, the optical absorption peak maximum site on the ultraviolet region i.e at 295, 302, and 305 nm corresponding with Fe₃O₄, Fe₃O₄@C, and ZnFe₂O₄ respectively. It displays a situation of peak absorption shifting to a visible region due to the particle's size and n-π* transition of C-dot [30] whereas the optical defect was shown in Fe₃O₄@C and ZnFe₂O₄ since it is not the same as the morphology and particle’s size. The particle’s size that is smaller has the capacity as a larger surface adsorb in C-dot particles, in this case, as shown in ZnFe₂O₄[30] by FTIR and absorbance characteristic shown at Figure 2 and 3.
The fluorescence spectra in Figure 2 illustrates an absorption peak shifting to the blue region. The emission of samples was indicated as an energy transition from higher to lower energy levels with previously experienced excitation process. The fluorescence spectra of Fe$_3$O$_4$ had a blue emission at 490 nm whereas the emission of Fe$_3$O$_4$@C and ZnFe$_2$O$_4$ particles has green-blue emissions at 505 nm. The emission shift was likely due to the quantum size affected by the particle size difference [31]. The emission shift of fluorescence spectra can be seen according to Figure 4.
The synthesis of magnetic particles from natural iron sand was done by chemical ablation, co-precipitation, and hydrothermal route process. The treatment in this research (i.e. hybrid magnetic particle system) employed the C-dot. The C-dot had been synthesized from local Indonesian lemon juice. As a result, the hybrid magnetic particles had been synthesized from local Indonesian natural resources. A morphological structure through SEM visualization showed a quasi-spherical structure of magnetic particle with a particle size of 125 nm which was included in the microsize category. Figure 5a shows how magnetic particles were formed by a quasi-spherical structure that has not been perfected yet since it was still in the form of piled clumps. This case can be caused by treatment processes. Some articles reported that the additional PEG (polyethylene glycol) polymer can decrease the clotting process in the synthesis of the particles [32]. In Figure 4b, Zn-dopped Fe$_3$O$_4$ affected the hollow-submicron sphere on the magnetic particle surface [33]. The size of the hollow submicron spheres was 50 nm. On the other hand, these hollow-submicron spheres had not been perfectly formed and it was only for a few percent. This was possibly affected by the additional uncertainty concentration of Zn ion [33,34]. To have a maximum result, it is necessary to make a different additional concentration of Zn Ion for the next research. However, C-dot affected the morphological covering. The visualization image of magnetic particles can be seen in Figure 5.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{The Visualization of Magnetic Hybrid Particles Synthesized from Natural Iron Sand via Chemical Ablation, Co-precipitation, and Hydrothermal Route Process. a) Fe$_3$O$_4$, b) Fe$_3$O$_4$@C-dot, c) ZnFe$_2$O$_4$@C-dot particles}
\end{figure}
3.2 Magnetic Properties
The magnetic properties from natural iron sand were synthesized by chemical ablation, co-precipitation, and hydrothermal route processes while the magnetic and magnetic hybrid particles have magnetization properties. Therefore, the magnetic and magnetic hybrid particles via VSM analysis at room temperature with an applied magnetic field from -30k to 30k shown that they had different magnetizations. Figure 5 shows that Zn-dopped Fe3O4 had a higher value of magnetic saturation (Ms) characteristic than that of other values [28]. This research showed that the additional Zn2+ metal ion could increase the magnetic property performance of the ZnFe2O4@C-dot magnetic particle. Although the additional carbon had been done correctly, it still can decrease the magnetic saturation properties[29].

Then, the additional Zn2+ ion composition is the most influential component of the magnetic saturation value [35]. This had been proven by the absorption value of the metal bonds shown by the FTIR data so that it was necessary to have an intensive study about Zn2+ ion on the magnetic particles. Specifically, the magnetic saturation produced by the magnetic and magnetic hybrid particles was Fe3O4 with a value of 60 emu/g. The investigation found that C-dot can decline the magnetic properties as shown by Fe3O4@C-dot. However, C-dot widened the absorption of frequency waves which illustrated the strong and weak the magnetic-field of the used external tester. It can be concluded that the value of the x-axis $\rightarrow 0$. It showed that all particles had the same magnetic momentum.

In this research, the additional organic factor can decline the magnetism properties. On the other hand, using the right metal ion substitution can raise magnetism properties. Next, the characteristic of the magnetic saturation value properties of the magnetic particle can visually be seen in Figure 6.

This research specifically showed a synthesis process of a magnetic particle of natural iron sand gradually using the combination of some methods. Surprisingly, this combined method gave positive impacts to magnetic properties even though it did not give a perfect effect on the morphological side. For further research, it is necessary to give more evaluation of the hydrothermal reaction in various temperatures. Some references state that temperature changes on the hydrothermal method could control the size and morphology [36–39].
4. Conclusion
Magnetic and hybrid magnetic particles had been successfully synthesized through chemical ablation, co-precipitation, and hydrothermal route process using local natural iron sand as magnetic particle sources. The morphological, optical, and magnetic properties showed a quasi-spherical structure and formed a hollow-submicron spheres subduction effect of Zn ions. The optical properties of C-dot were given when a frequency wave absorption was broad although it had lower magnetism. The Zn-dopped increased optical absorption and magnetical properties.

References
[1] Jalil Z, Rahwanto A, Mulana F and Handoko E 2019 Synthesis of nano-hematite (Fe2O3) extracted from natural iron ore prepared by mechanical alloying method AIP Conf. Proc.2151
[2] Husain S, Irfansyah M, Haryanti N H, Suryajaya S, Arjo S and Maddu A 2019 Synthesis and characterization of Fe3O4 magnetic nanoparticles from iron ore J. Phys. Conf. Ser.1242
[3] Darezereshki E, khodadadi Darban M, Abdollahy M and jamshidi A 2018 Synthesis of magnetite nanoparticles from iron ore tailings using a novel reduction-precipitation method J. Alloys Compd.749 336–43
[4] Rahmawati R, Taufiq A, Sunaryono S, Fuad A, Yuliarto B, Suyatman S and Kurniadi D 2018 Synthesis of Magnetite (Fe3O4) Nanoparticles from Iron sand by Coprecipitation-Ultrasonic Irradiation Methods J. Mater. Environ. Sci.9 155–60
[5] Rahmawati R, Permana M G, Harison B, Nugraha, Yuliarto B, Suyatman and Kurniadi D 2017 Optimization of Frequency and Stirring Rate for Synthesis of Magnetite (Fe3O4) Nanoparticles by Using Coprecipitation- Ultrasonic Irradiation Methods Procedia Eng.170 55–9
[6] Maulinda, Zein I and Jalil Z 2019 Identification of Magnetite Material (Fe3O4) Based on Natural Materials as Catalyst for Industrial Raw Material Application J. Phys. Conf. Ser.1232
[7] Taufiq A, Saputro R E, Sunaryono, Hidayat N, Hidayat A, Mufti N, Diantoro M, Patriati A, Mujamilah, Putra E G R and Nur H 2017 Fabrication of Magnetite Nanoparticles Dispersed in Olive Oil and Their Structural and Magnetic Investigations IOP Conf. Ser. Mater. Sci. Eng.202
[8] Gul S, Khan S B, Rehman I U, Khan M A and Khan M I 2019 A Comprehensive Review of Magnetic Nanomaterials Modern Day Theranostics Front. Mater.6 1–15
[9] Rashid H, Mansoor M A, Haider B, Nasir R, Abd Hamid S B and Abdulrahman A 2020 Synthesis and characterization of magnetite nano particles with high selectivity using in-situ precipitation method Sep. Sci. Technol.55 1207–15
[10] Schwaminger S P, Syhr C and Berensmeier S 2020 Controlled synthesis of magnetic iron oxide nanoparticles: Magnetite or maghemite? Crystals10
[11] Sayuti M, Ibrahim A, Yusuf M and Putra R 2018 Development of Aceh iron sand to produce pig iron: Studies on hardness properties MATEC Web Conf.204 1–7
[12] Dar M I and Shivashankar S A 2014 Single crystalline magnetite, maghemite, and hematite nanoparticles with rich coercivity RSC Adv.4 4105–13
[13] Kundu M, Bhardwaj H, Pandey M K, Krishnan P, Kotnala R K and Sumana G 2019 Development of electrochemical biosensor based on CNT–Fe 3 O 4 nanocomposite to determine formaldehyde adulteration in orange juice J. Food Sci. Technol.56 1829–40
[14] Sanaeifar N, Rabiee M, Abdulrahim A, Taherii M, Vashaei D and Tayebi L 2017 A novel electrochemical biosensor based on Fe3O4 nanoparticles-polyvinyl alcohol composite for sensitive detection of glucose Anal. Biochem.519 19–26
[15] Zhang W, Li X, Zou R, Wu H, Shi H, Yu S and Liu Y 2015 Multifunctional glucose biosensors from Fe3O4 nanoparticles modified chitosan/graphene nanocomposites Sci. Rep.5 1–9
[16] Palanisamy S and Wang Y M 2019 Superparamagnetic iron oxide nanoparticulate system: Synthesis, targeting, drug delivery and therapy in cancer Dalt. Trans. 48 9490–515
[17] Zhao C, Song X, Jin W, Wu F, Zhang Q, Zhang M, Zhou N and Shen J 2019 Image-guided cancer therapy using aptamer-functionalized cross-linked magnetic-responsive Fe 3 O 4 @carbon nanoparticles Anal. Chim. Acta 1056 108–16
[18] Kasten A, Grüttnner C, Kühn J P, Bader R, Pasold J and Frerich B 2014 Comparative in vitro study on magnetic iron oxide nanoparticles for mri tracking of adipose tissue-derived progenitor cells PLoS One 9
[19] Lu M, Cheng X, Jiang J, Li T T, Zhang Z, Tsauo C, Liu Y and Wang Z 2018 Dual-modal photoacoustic and magnetic resonance tracking of tendon stem cells with PLGA/iron oxide microparticles in vitro PLoS One 13 1–13
[20] Li B, Weng X, Wu G, Zhang Y, Lv X and Gu G 2017 Synthesis of Fe3O4/polyaniline/nanocomposites by in-situ method and their electromagnetic absorbing properties J. Saudi Chem. Soc. 21 466–72
[21] Li Q, Kartikowati C W, Horie S, Ogi T, Iwaki T and Okuyama K 2017 Correlation between particle size / domain structure and magnetic properties of highly crystalline Fe 3 O 4 nanoparticles Sci. Rep. 1–4
[22] Yazdani F and Seddigh M 2016 SC Mater. Chem. Phys.
[23] Lei W, Liu Y, Si X, Xu J, Du W, Yang J, Zhou T and Lin J 2017 Synthesis and magnetic properties of octahedral Fe3O4 via a one-pot hydrothermal route Phys. Lett. Sect. A Gen. At. Solid State Phys. 381 314–8
[24] Sun X, Zheng C, Zhang F, Yang Y, Wu G, Yu A and Guan N 2009 Size-controlled synthesis of magnetite (Fe3O4) nanoparticles coated with glucose and gluconic acid from a single Fe(III) precursor by a sucrose bifunctional hydrothermal method J. Phys. Chem. C 113 16002–8
[25] Jiang X, Guan Q, Feng M, Wang M, Yan N, Wang M, Xu L and Gui Z 2019 Preparation and pH controlled release of Fe3O4/anthocyanin magnetic biocomposites Polymers (Basel). 11 1–14
[26] Yusoff A H M, Salimi M N and Jamlos M F 2017 Synthesis and characterization of biocompatible Fe3O4 nanoparticles at different pH AIP Conf. Proc. 1835 1–5
[27] Ramadan W, Kareem M, Hannoyer B and Saha S 2011 Effect of pH on the structural and magnetic properties of magnetite nanoparticles synthesised by co-precipitation Adv. Mater. Res. 324 129–32
[28] Liu J, Bin Y and Matsuo M 2012 Magnetic behavior of Zn-doped Fe 3 O 4 nanoparticles estimated in terms of crystal domain size J. Phys. Chem. C 116 134–43
[29] Guo Y, Zhang L, Liu X, Li B, Tang D, Liu W and Qin W 2016 Synthesis of magnetic core-shell carbon dot@MFe2O4 (M = Mn, Zn and Cu) hybrid materials and their catalytic properties J. Mater. Chem. A 4 4044–55
[30] Gude V, Das A, Chatterjee T and Mandal P K 2016 Molecular origin of photoluminescence of carbon dots: Aggregation-induced orange-red emission Phys. Chem. Chem. Phys. 18 28274–80
[31] He M, Zhang J, Wang H, Kong Y, Xiao Y and Xu W 2018 Material and Optical Properties of Fluorescent Carbon Quantum Dots Fabricated from Lemon Juice via Hydrothermal Reaction Nanoscale Res. Lett. 13
[32] Liu B, Wang Y, Zhang M and Zhang H 2016 Initiator systems effect on particle coagulation and particle size distribution in one-step emulsion polymerization of styrene Polymers (Basel). 8 1–14
[33] Sang Nguyen X, Zhang G and Yang X 2017 Mesocrystalline Zn-Doped Fe3O4 Hollow Submicrospheres: Formation Mechanism and Enhanced Photo-Fenton Catalytic Performance ACS Appl. Mater. & Interfaces 9 8900–9
[34] Cen H and Nan Z 2018 Monodisperse Zn-doped Fe3O4 formation and photo-Fenton activity for degradation of rhodamine B in water J. Phys. Chem. Solids121 1–7
[35] Mameli V, Musinu A, Ardu A, Ennas G, Peddis D, Niznansky D, Sangregorio C, Innocenti C, Thanh N T K and Cannas C 2016 Studying the effect of Zn-substitution on the magnetic and hyperthermic properties of cobalt ferrite nanoparticles Nanoscale8 10124–37
[36] Latham K G, Ferguson A and Donne S W 2019 Influence of ammonium salts and temperature on the yield, morphology and chemical structure of hydrothermally carbonized saccharides SN Appl. Sci.1 1–13
[37] He G, Yang W, Zheng W, Gong L, Wang X, An Y and Tian M 2019 Facile controlled synthesis of Ag3PO4 with various morphologies for enhanced photocatalytic oxygen evolution from water splitting RSC Adv.9 18222–31
[38] Andrade A B, Ferreira N S and Valerio M E G 2017 Particle size effects on structural and optical properties of BaF2 nanoparticles RSC Adv.7 26839–48
[39] Zulkifli Z A, Razak K A and Rahman W N W A 2018 The effect of reaction temperature on the particle size of bismuth oxide nanoparticles synthesized via hydrothermal method AIP Conf. Proc.1958

Acknowledgments
This study was funded by internal grants from Muhammadiyah Prof. DR. Hamka University. As for the involvement of outside institute, is to contribute to leasing services.