The effect of 6 hours stirring time on natural iron sand base on magnetics Fe₃O₄ nanoparticle by sonification

A A Wibowo¹, H Sutanto¹², P Priyono¹², A N Syahida¹, F D D Irianti¹, I Alkian¹²
¹Departemen of Physics, Faculty of Science and Mathematics, Diponegoro University, Semarang-Indonesia
²Smart Materials Research Center Laboratory, Diponegoro University, Semarang-Indonesia

Corresponding author: herisutanto@live.undip.ac.id

Abstract. In this research, ferrite magnetic nanoparticles (Fe₃O₄) from natural iron sand have been synthesized by co-precipitation technique with varying stirring time and sonification process. The purpose of this study was to determine the effect of 6 hours of synthesized magnetic nanoparticles (MNPs) on the resulting crystal size. The different structures and properties of the synthesized Fe₃O₄ nanoparticles were investigated using X-Ray Diffraction (XRD), Scanning electron microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR), and Energy Dispersion X-ray (EDX), respectively. XRD and SEM produced mean crystal sizes over the range of 13.93 nm and particle sizes of 14.8 nm. The EDX test explained that the Fe₃O₄ compound was successfully formed at 6.00 KeV. FTIR showed the element content of Fe-O at 555 cm⁻¹. This study's results indicate the MNPs synthesis process at 6 hours and the sonification process can produce Fe₃O₄ nanoparticles with a minimum size at the optimal time compared to synthesis at 8 hours, 7 hours, and 5 hours.

1. Introduction
Compared to bulk forms, nanoscale materials (<100 nm diameter) have superior physical and chemical properties due to the mesoscopic effect, small object effect, quantum size effect, surface/interface effect. In this decade, MNP Fe₃O₄ has been studied intensively because of its superparamagnetic properties, high coercivity, low curie temperature. There are also additional, deficient toxic, biocompatible properties. Therefore, Fe₃O₄ MNPs generate several applications such as biosensors [1], gas sensors, contrast agents for MRI, contrast agents for PET and NIRF, hyperthermia therapy, magnetic target-drug delivery systems, microelectronic applications such as photodiodes, microwave absorbers, adsorbent for vegetables and fruits, nano-photocatalysis, lithium-ion battery, ferrofluid, magnetic printer ink, thin-film, Solar Cell, bone repair [2], bioremediation [3], cancer treatment[4], SERS application[5].

There are various ways to synthesize nano Fe₃O₄, including solvothermal [6], hydrothermal [7], sol-gel [8], electrospinning [9], microwave combustion method, photochemical [10], co-precipitation. Among the developed synthesis methods, the coprecipitation method is the simplest because it is easier to perform and requires a relatively low reaction temperature (<100°C). Controlling the shape and size of the particles can be controlled by variations in reaction temperature [11], pH at reaction time [12], and concentration of materials [13]. The co-precipitation method is a chemical process that reduces
solute to form the desired precipitate. With low operating costs and easy synthesis preparation, a co-precipitation method can still synthesize Fe₂O₃ nanoparticles.

Nanotechnology, particularly in nanoparticles, has been widely developed because of its size and very active performance. The disadvantage is that it is prone to clumping between the nanoparticles and their neighbors due to their small size and high surface energy [14,15]. The sonification process is carried out to reduce clumping to produce a homogeneous particle size and tend not to agglomerate easily. Research by Rahmawati (2017) uses a sonification process resulting in a much smaller nanoparticle size than without the sonification process [16].

Synthesis of MNPs from natural iron sand using a synthesis time of 6 hours is known to have never been carried out. Several studies conducted the synthesis of MNPs at 90 minutes by Setiadi (2016) to produce Fe₂O₃ nanoparticles with a size of 25-50nm [17], Rahmawati's research (2017) carried out the synthesis of MNPs in 30 minutes resulting in 20-25 nm of Fe₂O₃ nanoparticles. The synthesis process with a long time will make the nanoparticles stable and well homogenized [16]. Therefore, this research is focused on the synthesis of nano Fe₂O₃ with a stirring time of 6 hours using local natural iron sand. The Fe₂O₃ nanopowder formed was characterized using XRD to see its crystal structure, SEM-EDX to see the surface morphology and powder composition, and FTIR to see the presence of its molecular structure.

2. Methods

2.1. Materials
The main ingredients used in the synthesis of Fe₂O₃ nanoparticles with the co-precipitation method are natural iron sand (Kulonprogo Beach, Yogyakarta, Indonesia), 37% Chloride Acid (HCL) solution, Ammonium Hydroxide (NH₄OH) solution, and aquades.

2.2. Synthesis
The first step is the extraction of natural iron sand using permanent magnets. Natural iron sand is filtered using gauze with a certain mesh size to separate the remaining impurities. Re-extraction uses permanent magnets to obtain magnetic components. The natural iron sand is then washed and dried in the sun. To obtain Fe₂O₃ nanoparticles, the method used is co-precipitation. The decomposition of natural iron sand is dissolved with HCl at 370 rpm for 6 hours to form a black solution. The result of decomposition with HCl is then filtered with filter paper to obtain FeCl₂ and FeCl₃. Then the solution that passes through the filter is added to the NH₄OH solution. FeCl₂ and FeCl₃ solutions react chemically with NH₄OH to form a Fe₂O₃ nano, NH₄Cl, and H₂O solution. The result of the solution was then sonified for 2 hours. Then washed with distilled water to lower the pH. After that, it is dried to produce Fe₂O₃ nanoparticle powder.

2.3. Characterization
SEM-EDX measurement, SEM is a testing technique to see the surface morphology of Fe₂O₃ nanoparticles. EDX is a testing technique used to determine the composition of Fe₂O₃ nanoparticles. The tool type and series are SEM-EDX JED-2300 JEOL. To calculate the average particle size of the SEM images, ImageJ 1.52V software was used. XRD measurement XRD is one of the testing tools to determine the structure crystal of Fe₂O₃ nanoparticles. CuKα radiation was used to investigate the phase of Fe₂O₃ powder in the range of angles from 20 to 80. The tool type and series are Shimadzu 7000. The spectra obtained were compared with a standard database by Joint Committee on Powder Diffraction Standard (JCPDF 19-0629 and JCPDF 07-0007) from the International Center for Diffraction Data (ICDD). FTIR measurement, FTIR, is used to find out the bonding functional groups of Fe₂O₃ nanoparticles through their specific adsorption spectrum. The functional groups on the surface of Fe₂O₃ nanoparticles can be determined with the Perkin Elmer FTIR Spectrometer. Samples were examined in the wavenumber range between 400-4000 cm⁻¹.
3. Result and Discussion

To obtain Fe$_3$O$_4$ nanoparticles, the method used is co-precipitation with the following chemical reactions.

$$3Fe_3O_4(s) + 8HCl(l) \xrightarrow{370 \text{ rpm}} FeCl_2(l) + 2FeCl_3(l) + 3Fe_2O_3(s) + 3H_2O(l) + H_2(g) \quad (1)$$

$$FeCl_2(l) + 2FeCl_3(l) + 3Fe_2O_3(s) + 3H_2O(l) \xrightarrow{\text{filter}} FeCl_2(l) + 2FeCl_3(l) + H_2O(l) \quad (2)$$

$$FeCl_2(l) + 2FeCl_3(l) + H_2O(l) + 8NH_4OH(l) \rightarrow \text{nano-Fe}_3O_4(s) + 8NH_4Cl(l) + 5H_2O(s) \quad (3)$$

$$\text{nano-Fe}_3O_4(s) + NH_4Cl(l) + 2H_2O(l) \xrightarrow{\text{Furnace}} \text{nano-Fe}_3O_4(s) + NH_4Cl(s) + 2H_2(g) + O_2(g) \quad (4)$$

**Figure 1.** EDX Elemental composition of (a) kulonprogo beach natural iron sand (b) Fe$_3$O$_4$ nanoparticles

Figure 1(a) shows the results of EDX natural iron sand for kulonprogo beach showing the elemental composition of C, O, Mg, Al, Si, Cl, K, Ca, Ti, Fe, and Zr. Figure 1(b) shows the change in composition after natural iron sand was synthesized using the co-precipitation method. The composition contained into C, O, Al, Cl, and Fe with Al composition can be neglected because % w.t is below 0.5%.
The morphological structure of natural iron sand using SEM is shown in Figure 2; it can be seen that the synthesized Fe₃O₄ nanoparticles are still agglomerated and not homogeneous. The cause of agglomeration [18] and not homogeneous [19] is due to the presence of the element NH₄Cl, which is very strong to bind water. From calculations using ImageJ software, the measured average particle size is 14.8 nm.

![Figure 2. SEM surface morphology of Fe₃O₄ nanoparticles for 1000X magnification](image)

The XRD patterns of the synthesized Fe₃O₄ nanoparticles are shown in Figure 3. All peak characteristics are following the JCPDF database standard. Fe₃O₄ intensity peaks are seen at angles of 2θ 30.23, 35.60, 43.29, and 62.93; corresponds to the crystal plane of Fe₃O₄ with d₁₀₀ values in (2 2 0), (3 1 1), (4 0 0), and (4 4 0) respectively. These results are consistent with the XRD Fe₃O₄ pattern standard (JCPDS 19-0629 Card [14,20–22]). Meanwhile, the peak intensity of NH₄Cl can be seen at angles of 2u 22.94, 32.68, 40.30, 46.90, 52.77, 58.30, 68.43, and 77.86; corresponds to the crystal field of NH₄Cl with d₁₁₀ values at (1 0 0), (1 1 0), (1 1 1), (2 0 0), (2 1 1), (2 2 0), and (3 1 0)). Each. This result follows the peak value of the NH₄Cl XRD pattern standard (JCPDS 07-0007 Card). Through the JCPDF standard database, it can be seen that the Fe₃O₄ and NH₄Cl structures formed are cubic. The color of the powder synthesized black indicates that Fe₃O₄ nanoparticles have been formed.

![Figure 3. XRD spectrum for (a) Fe₃O₄ nanoparticles sample; (b) standard reference Fe₃O₄ (JCPDF Card 19-0629); and (c) standard reference NH₄Cl (JCPDF Card 07-0007)](image)

| Stirring time (hour) | Crystallite Size (nm) |
|---------------------|-----------------------|
| 8 hours             | 24.132 nm             |
| 7 hours             | 16.309 nm             |
| 6 hours             | 13.661 nm             |
| 5 hours             | 14.439 nm             |

![Table 1 Crystallite size at different stirrer time](image)
energy produced is greater so that the particles tend to interact with other particles and form a much larger size [23].

![Figure 4. FTIR spectrum analysis on Fe₃O₄ nanoparticles](image)

Figure 4. FTIR spectrum analysis on Fe₃O₄ nanoparticles

Figure 4. described an FTIR was used to analyze the atomic bonds of Fe₃O₄ nanoparticles. The FTIR spectrum detected in Fe₃O₄ nanoparticles is shown in Figure 2. The adsorption peaks detected were at wavenumbers 555 cm⁻¹, 1091 cm⁻¹, 1393 cm⁻¹, 1442 cm⁻¹, 1644 cm⁻¹, 1752 cm⁻¹, 2006 cm⁻¹, 2805 cm⁻¹, 3016 cm⁻¹, 3116 cm⁻¹, 3356 cm⁻¹. The single peak of adsorption observed at 555 cm⁻¹ is the Fe - O functional group bond [24], which indicates that a single-phase Fe₃O₄ bond has been formed. The adsorption peak with a wavenumber of 1091 cm⁻¹ to 3356 cm⁻¹ shows that the pattern of functional bond groups formed is NH₄Cl, following PerkinElmer's FTIR analysis shown in Figure 5.

![Figure 5. FTIR spectrum pattern on NH₄Cl](image)

Figure 5. FTIR spectrum pattern on NH₄Cl
4. Conclusion
Synthesis of natural iron sand in the Kulonprogo area (Yogyakarta, Indonesia) has been carried out using the co-precipitation method. The final result is a powder of black Fe3O4 nanoparticles with an average particle diameter of 14.8 nm, good crystallinity, and maintaining the purity of Fe3O4 particles (single-phase at wave number 555 cm⁻¹); from SEM-EDX, XRD, and FTIR analysis. The stirrer time effect indicated that 6 hours was the optimal time to produce a crystal size of 13.661 nm compared to the stirrer duration of 8 hours, 7 hours, and 5 hours.

Acknowledgement
We really appreciate the financial support for research provided by the Ministry of Research, Technology, and Higher Education (Ristekdikti) in 2020.

References
[1] Guo J-W, Lin F-P, Chang C-J, Lu C-H and Chen J-K 2020 Sensors and Actuators B: Chemical
[2] Yan Y, Zhang Y, Zuo Y, Zou Q, Li J and Li Y 2018 Mater. Lett. 212 303–6
[3] Mehta R V. 2017 Materials Science and Engineering C
[4] You L, Liu X, Fang Z, Xu Q and Zhang Q 2019 Materials Science and Engineering C 94 291–302
[5] Zhao X Y, Wang G and Hong M 2018 Mater. Chem. Phys.
[6] Fotukian S M, Barati A, Soleymani M and Alizadeh A M 2020 J. Alloys and Compounds 816
[7] Haw C Y, Mohamed F, Chia C H, Radiman S, Zakaria S, Huang N M and Lim H N 2010 Ceramics International 36 1417–22
[8] Gaba S, Rana P S, Kumar A and Pant R P 2020 J. Magn. Magn. Mater. 508
[9] Wang S, Sun Z, Yan E, Yuan J, Gao Y, Bai Y, Chen Y, Wang C, Zheng Y and Jing T 2014 Mater. Science and Engineering B: Solid-State Materials for Advanced Technology
[10] Jadhav N L, Gondhalekar K A, Doltade S B and Pinjari D V. 2018 Solar Energy
[11] Yasemin A R, Almasi Kasho M and Ramazani A 2019 Mat. Chem. Phys. 230 9–16
[12] Rani S and Varma G D 2015 Physica B: Condensed Matter 472 66–77
[13] Lin C C and Lee C Y 2020 Mat. Chem. Phys. 240 122049
[14] Ma Y, Zhou Y Y, Qi C, Sun Y, Zhang Y and Liu Y 2020 Progress in Organic Coatings 141 105538
[15] Pentcheva R, Wendler F, Meyerheim H L, Moritz W, Jedrecy N and Scheffler M 2005 Phys. Review Letters 94
[16] Rahmawati R, Permana M G, Harison B, Nugraha, Yuliarto B, Suyatman and Kurniadi D 2017 Procedia Engineering 170 55–9
[17] Setiadi E A, Sebayang P, Ginting M, Sari A Y, Kurniawan C, Saragih C S and Simamora P 2016 J. Phys.: Conf. Ser. 776 012020
[18] Besenhard M O, LaGrow A P, Hodzic A, Kriegbaum M, Panariello L, Bais G, Loizou K, Damilos S, Margarida Cruz M, Thanh N T K and Gavriilidis A 2020 Chemical Engineering Journal 399 125740
[19] Fahlepy M R, Tiwow V A and Subaer 2018 J. Phys.: Conf. Ser. 997 0–7
[20] Injumpa W, Ritprajak P and Insin N 2017 J. Magn. Magn. Mater. 427 60–6
[21] Vinh N T, Tuan L A, Vinh L K and Van Quy N 2020 Materials Science in Semiconductor Processing 118 105211
[22] Wang Y, Liu X yu, Xu X, Yang Y, Huang L hong, He Z yu, Xu Y he, Chen J ju and Feng Z sheng 2018 Materials Research Bulletin
[23] Beyaz S, Tanrisever T, Kock H and Butun V 2011 S. J. Appl. Polym. Sci. 121 2264–72
[24] Tazikeh S, Sayyad Amin J and Zendehboudi S 2020 J. Molecular Liquids 301 112254