Functional Group and Magnetic Properties of Fe₃O₄ Ferrofluids: The Impact of Dispersion Agent Composition

Ahmad Taufiq¹, Rosy Eko Saputro¹, Sunaryono¹, Yuanita Amalia Hariyanto¹, Nurul Hidayat¹, Arif Hidayat¹, Nandang Mufti¹, Hendra Susanto², Mujamilah³

¹Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5 Malang 65145, Indonesia
²Department of Biology, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5 Malang 65145, Indonesia
³Centre for Science and Technology of Advanced Materials, National Nuclear Energy Agency of Indonesia, Tangerang 15314, Indonesia

*Corresponding author’s email: ahmad.taufiq.fmipa@um.ac.id

Abstract. This work was aimed to identify the functional group and magnetic properties of the Fe₃O₄ ferrofluids coated by oleic acid regarding different compositions of olive oil as a dispersing agent. The results of the x-ray diffraction (XRD) data presented that the phase of the samples was a Fe₃O₄ phase, which was identified based on the diffraction peaks with highest peak at 35.6° with the particle size of 8.8 nm. The results of the Fourier transform infrared (FTIR) characterization on the ferrofluids showed those functional groups representing the existence of magnetic and dispersing agent particles. Based on the data analysis of the magnetization data, the composition of the dispersing agent influenced the saturation magnetization with the highest value of approximately 18 emu/gram. Therefore, the prepared ferrofluids in this work open a potency to be applied in various fields, such as for an antibacterial agent.

Keywords: Ferrofluid, Fe₃O₄, iron sand, dispersing agent, magnetization.

1. Introduction

In general, ferrofluid can be defined as a colloidal suspension consisting of magnetic nanoparticles which dispersed in a carrier liquid [1]. Ferrofluid is classified as a unique engineering material since it could maintain its liquid characteristics in a magnetic field and its particles would not be separated from the dispersant [2]. Therefore, in developing specific applications, ferrofluid has several advantages and opens new potential applications in various fields.

In the previous work, the development of ferrofluid using surfactant oleic acid was done by using different synthesis methods with the purpose to achieve the stable magnetic particle in nanometric size, one of them is the co-precipitation method [3]. However, some drawbacks were still found in some research above, namely the large size of the ferrofluid magnetic particle of 20 nm [4], and the agglomeration phenomenon that hampers the monodispersed particles, as well as its low durability of around one month [5]. Such disadvantages influence the magnetic properties of the ferrofluid since the superparamagnetic properties are not sustainable. Therefore, it is imperative to find out an alternative method for preparing the stable magnetic ferrofluids-based.
In order to control the stability of the ferrofluids is by selecting and controlling surfactants and dispersing agents of the fluids. In our previous work, the ferrofluids were successfully synthesized by selecting TMAH as a surfactant and controlling H$_2$O composition as a dispersing agent [6]. However, the stability of the ferrofluids was not appropriately achieved due to the presence of the aggregations and clusters. Therefore, selecting a suitable surfactant and controlling dispersing agent composition become an essential thing to be developed. Based on the above explanation, we developed the preparation of magnetic nanoparticles–based ferrofluids coated by a surfactant using oleic acid. Furthermore, in order to control the stability of the ferrofluid, we varied the composition of olive oil as a dispersing agent. To complete our study, the crystal structure, morphology, magnetic properties, and their correlation were also investigated in this work.

2. Materials and Methods

The natural sand from Banyuwangi, Indonesia was rinsed using distilled water and then sifted to obtain completely smooth sand. The natural sand was then separated using a strong permanent magnet to obtain the Fe$_3$O$_4$ powder. Subsequently, the separated Fe$_3$O$_4$ powder was reacted with HCl at room temperature while stirred. The results were then filtered to be then titrated with NH$_4$OH while being stirred continuously using a magnetic stirrer. Black sediment was then formed following the titration process. Next, the sediment was washed using distilled water with up to pH = 7 and then separated from the distilled water using a permanent magnet. To produce ferrofluids, the first step taken was preparing the Fe$_3$O$_4$ as a filler with 20% of the ferrofluid mass. It was performed based on the ratio of olive oil as a dispersion agent to oleic acid with a constant volume. Three variations of olive oil volumes were used to produce the samples coded by C, B, and A. C refers to the sample with a 2:1 ratio of oleic acid-olive oil content. B refers to the sample with a 2:1.4 ratio of oleic acid-olive oil content, and A refers to the sample with a 2:0.6 ratio of oleic acid-olive oil content. After weighing, the Fe$_3$O$_4$ was heated on a hotplate magnetic stirrer while still being stirred. Such heating aimed to produce highly homogeneous particles.

Characterizations were performed using the first instrument, i.e. XRD, to identify the composition of phase, crystal structure, and lattice parameter of the sample. The characterization was employed by an X’Pert Pro. XRD was utilized. Meanwhile, we applied an FTIR (Shimadzu) to investigate the functional group of the ferrofluids. Magnetic characterization was done to identify the magnetic properties of the samples using a vibrating sample magnetometer (VSM).

3. Results and Discussion

The XRD data and refinement analysis for the Fe$_3$O$_4$ powder performed through Rietica software are presented in Figure 1. The FTIR spectra of the three Fe$_3$O$_4$ ferrofluid samples are shown in Figure 2. Meanwhile, the results of the VSM characterization of the three Fe$_3$O$_4$ ferrofluid samples are shown in Figure 3.

The process of refinement utilized data models from the database with a code of AMCSD 0002763. The results of refinement showed the values of $R_p = 18.78$; $R_{wp} = 25.83$, and chi-square of 1.11. The particle size was then known to be 8.8 nm. Also, the highest peak was identified to be at the angle of 35.65° with an $hkl$ of (311) and a lattice parameter of 8.37 Å. The previous reports confirm such results; even the obtained particle size was smaller than those reported previously [7].

Based on Figure 2, two magnetite tapes representing the existence of magnetite (Fe-O) were found at 590.22 and 603.72 cm$^{-1}$. Such results are in accordance with the studies reported previously [8]. Also, four tapes that related to the vibration from carboxyl group (COO\(^{-}\)) were found at 1417.68, 1435.04, 1523.76, and 1591.27 cm$^{-1}$. Besides, the vibrations of C-H bond also emerged at 1118.71 cm$^{-1}$ [9], CH$_2$ bond at 2854.65 and 2929.87 cm$^{-1}$ [10], CH$_3$ bond at 3464.15 cm$^{-1}$, and C=C bond at 1377.17 cm$^{-1}$ [9]. The overall vibrations of carboxyl group and C-H bond in the sample showed the existence of oleic acid that successfully bonded with the magnetic nanoparticles.
Subsequently, the presence of olive oil functional group was also essential as a dispersion medium. Two tapes represented the vibrations of the olive oil conjugation bond were found at 2729.27, 2752.42, 3645.15, 3672.47, and 3834.49 cm\(^{-1}\). Furthermore, there was also a vibration on a tape at 1743.65 cm\(^{-1}\), which resulted from the ester carbonyl bond (C=O). The ester bond (C=O) was represented by a bond showing the olive oil saturation at 3005.10 and 1170.79 cm\(^{-1}\). Such results are in agreement with the previous research [11]. The mentioned vibrations revealed that olive oil had been successfully bond with the magnetic-oleic acid nanoparticle system.

The magnetization data (Figure 3) showed that the sample C with a 2:1 ratio of oleic acid-olive oil compositions had the highest saturation magnetization value of approximately 18 emu/gram, followed by the sample B with a 2:1.4 ratio of oleic acid-olive oil compositions having the saturation magnetization value of approximately 15 emu/gram. Meanwhile, the sample A with a 2:0.6 ratio of oleic acid-olive oil compositions had a relatively low magnetization value of approximately 10 emu/gram. The results obtained from the three samples that were already coated by oleic acid already had superparamagnetic properties, but still far from the required value of magnetization for bulk, namely 90 emu/gram [12]. Such a decline could occur when the size of the ferrofluid magnetic particle is below 25 nm [13]. Besides, the uniformity of magnetic nanoparticle size is determined by its chelation with the support of the oleic acid coating that could stabilize the magnetic particle. The oleic acid that covered the magnetic particle surface could reduce the surface activity and contact of the particle [14].
Based on the figure, it also can be seen that the B sample had an optimum composition. An aggregation was found on the A sample that influenced its magnetic response. Therefore, the magnetization data of such two samples seemed low. In the meantime, a reduction from the maximum condition was found in the C sample. It was due to the transition from the optimum condition to unstable condition because the C composition exceeded the effective composition, namely the B sample composition [15]. Furthermore, the coercivity field ($H_c$), remanent magnetization ($M_r$), and saturation magnetization ($M_s$) of all the obtained data are presented as follow.
According to the data in Table 1, the average value of the external magnetic field, in which the remanent magnetization occurred, was 0.016 T. The remanent magnetization of the A until C samples declined. Such decline was possible since the magnetic nanoparticles that acted as filler in A sample experienced an aggregation so that its remanent magnetization was relatively high, i.e. 0.006 emu/gram [16]. The remanent magnetization was reduced on the B and C samples as an impact of the oleic acid that was able to coat the magnetic nanoparticle so that the aggregation could be minimized. Theoretically, an increasing remanent magnetization is caused by an aggregation of magnetic nanoparticles. Based on the data above, it could be confirmed that the use of oleic acid could increase a magnetic response and also minimize the aggregation causing the declining value of remanent magnetization [17].

Table 1. \( H_c, M_r, \) and \( M_s \) values of the three samples through magnetization data analysis

| Sample | \( H_c \) (T) | \( M_r \) (emu/gram) | \( M_s \) (emu/gram) |
|-------|-------------|----------------------|----------------------|
| A     | 0.0157      | 0.0073               | 10.140               |
| B     | 0.0163      | 0.0038               | 17.805               |
| C     | 0.0166      | 0.0039               | 14.811               |

Table 2. Particle sizes and magnetic moment of the samples through magnetization data analysis

| Sample | Particle Size (nm) | Magnetic Moment (J/T) | Magnetic Moment (µB) |
|-------|--------------------|-----------------------|----------------------|
| A     | 8.37               | 7.35 \times 10^{-19}  | 79,235               |
| B     | 8.43               | 9.17 \times 10^{-19}  | 98,878               |
| C     | 8.41               | 9.08 \times 10^{-19}  | 97,908               |

In this study, the particle size was also obtained from the magnetization data as presented in Table 2. Based on the table, the particle sizes for the two samples are small and suitable to be called as superparamagnetic [18]. The magnetic characterization was only performed on the sample that is in a liquid form and not purely \( \text{Fe}_3\text{O}_4 \) particles. The TEM characterization was done by using a bright-field mode in order to recognize the surface morphology of the sample since it allows a larger observable diameter compared with the dark-field mode on VSM characterization [19].

Another factor that is still relevant to the declining particle size is the nanoparticle of which surface and volume ratio is higher than its surface and bulk ratio. Such high comparison caused the decrease of the crystal transitional symmetry on the ferrofluid surface layer so that a magnetization was not found in this area [20]. Besides, the strong interaction between the \( \text{Fe}_3\text{O}_4 \) filler and surfactant oleic acid cause an irregular spin that resulted in a magnetically dead layer [21]. However, theoretically, the three samples above already had suitable results calculated from the Equation (1) [22].

\[
D = \left( \frac{18k_B T}{\pi} \frac{\chi_i}{\rho M_s} \right)^{1/3}
\]  

where \( \rho \) is the density of \( \text{Fe}_3\text{O}_4 \), \( \chi_i \) is initial susceptibility, \( M_s \) was explained above, \( T \) is the room temperature, and \( k_B \) is Stefann Boltzmann’s constant which is equal \( 1.38 \times 10^{-23} \) J/K. The higher the saturation magnetization value of the sample, the larger the particle size, to the extent that the sample is in a single domain condition [23]. The magnetic nanoparticle that is categorized as having a single domain should fulfill some criteria, namely having a size below the critical size (25 nm) [24]. Such result is in line with a previous study [25]. Besides the particle size, the magnetic moment of a sample is also important to be studied. Based on the calculation of the obtained data, the values of the magnetic moment are shown in Table 2.
Table 2 shows that the magnetic moment of the two samples are in line accordance with magnetic moment value of the Fe₃O₄ nanoparticle shown in the previous research [26]. Theoretically, when characterized using Equation 2, the value of the magnetic moment was in the same direction as the cubic equation of the particle size and saturation magnetization. Hence, a large particle size and saturation magnetization of a sample shall increase the magnetic moment that could be obtained. In relation to the magnetic moment, the previous research results showed that the magnetic moment of ferrofluid Fe₃O₄ was ranged between 30,000 to 70,000 µB [26]. When compared to this research data, the magnetic moment value in this research is relatively large. This indicates that the sample has been made entirely superparamagnetic with a good magnetic response. The influence of the dispersion medium on sample magnetic moment value also need to be calculated. It is because the medium influences the filler stability inside it. The utilization of olive oil was proven to stabilize filler better than the other dispersion medium such as kerosene and chloroform. It is based on the review of ferrofluid magnetic moment value with kerosene dispersion medium and chloroform whose magnetic moment value ranged between 10,000 to 20,000 µB [27].
Figure 5. Hysteresis curve of the three Fe₃O₄ ferrofluid samples fitted with Langevin equation with susceptibility

Based on the hysteresis curves as shown in Figures 4 and 5, the magnetization data was fitted using two different Langevin equations. In Figure 4, the hysteresis curve was fitted using a general Langevin equation on Equation (2). Meanwhile, the data for Figure 5 was fitted with a modified Langevin equation with susceptibility on Equation (3) [28].

\[ M = M_s \left( \cot h \left( \frac{\mu H}{k_B T} \right) - \frac{k_B T}{\mu H} \right) \]  

where \( M \) is the magnetization, \( H \) is the magnetic field and the other quantities have been described above. When noted in Figures 4 and 5, the generated fitting curve looks different, even though they are derived from the same equation. Susceptibility was the factor influencing those differences. In physics, susceptibility in the magnetic context indicates the magnetism level of an object for magnetization, in which it is highly affected by the mineral and iron oxide content of a material [29]. Mathematically, the material susceptibility (\( \chi \)) in general fulfills the Equation 4 [30].

\[ M = \chi H \]
Since the magnetization and magnetic field in international system of units has the same unit that is ampere per meter (A/m) then the magnetic susceptibility is gradient on Equation 4. In this research, the main material used was Fe$_3$O$_4$. However, every sample has different iron oxide contents, which were caused by the filler variation performed on the sample preparation stage. In relation to theory, for the entire Figure 4 the susceptibility on the modified Langevin was ignored, while for the whole Figure 5 the susceptibility on each sample was included in refinement parameter. Thus, theoretically, the obtained fitting results also have results closer to the Fe$_3$O$_4$ susceptibility. Based on the fitting analysis, Equation 3 with is more satisfied in fitting analysis for the magnetization data.

The susceptibility values of the samples are 55.43, 61.32, and 59.32 for the respective A, B, and C. Based on the data, it suggests that the sample having the highest susceptibility is sample C, this fulfills the theoretical requirement declared on Equation 4 when the second sample has the highest magnetisation when compared to others, which is 17.805 emu/gram. Furthermore, the third and smallest sample is the first sample. A logical linkage can be made to sample B which has the best stability and a good magnetic response as well, however generally the three samples that have been made have fulfilled the theoretical aspects and showed appropriate results with the theoretical review aforementioned. Previous studies concern the magnetic susceptibility quantitatively, however some discuss it qualitatively. When compared to the previous studies, this research has a good appropriateness, that the greater the magnetization of material saturation will result in increased susceptibility [31]. Therefore, filler variation has an important role in generating a stable ferrofluid with controllable susceptibility. Based on the above discussions, the prepared magnetic nanoparticles in the ferrofluids exposed a potency to be functionalized such as for an antibacterial agent and other aspects.

4. Conclusion
A synthesis of the Fe$_3$O$_4$ particle as a ferrofluid filler with surfactant oleic acid dispersed in olive oil has successfully been performed. The magnetic nanoparticle has a particle size of 8.8 nm sized particles. The XRD data analysis confirmed such results well. Based on the XRD pattern, it can be identified that the sample has a Fe$_3$O$_4$ phase and is already representative to be applied as ferrofluid filler. Furthermore, the prepared ferrofluids had the functional groups representing the existence of magnetic and dispersing agent particles. According to the magnetics characterization, the C sample with a ratio of oleic acid-olive oil composition of 2:1 presented the largest magnetization value, and the use of oleic acid could improve the magnetic response of the samples.

Acknowledgment
We would like to thank KEMENRISTEKDIKTI RI for providing “PDUPT” for AT.

References
[1] R. Olaru, A. Arcire, C. Petrescu, and M.-M. Mihai, “Study of the magnetic force delivered by an actuator with nonlinear ferrofluid and permanent magnets,” IEEJ Trans. Electr. Electron. Eng., vol. 12, no. 1, pp. 24–30, 2017.
[2] D. Ramimoghadam, S. Bagheri, and S. B. A. Hamid, “In-situ precipitation of ultra-stable nano-magnetite slurry,” J. Magn. Magn. Mater., vol. 379, pp. 74–79, 2015.
[3] A. Taufiq, S. Pratapa, and M. Zainuri, “Various Magnetic Properties of Magnetite Nanoparticles Synthesized from Iron-Sands by Coprecipitation Method at Room Temperature,” in Materials Science Forum, 2015, vol. 827, pp. 229–234.
[4] X. Chen, M. G. Organ, and W. J. Pietro, “One-pot Synthesis of Size Controllable Amine-Functionalized Core-Shell Magnetic Nanoparticles for Use in Microfluidic Flow Separators,” J Nanosci Adv Tech, vol. 1, no. 3, pp. 25–31, 2016.
[5] V. Patsula, M. Moskvin, S. Dutz, and D. Horák, “Size-dependent magnetic properties of iron oxide nanoparticles,” J. Phys. Chem. Solids, vol. 88, pp. 24–30, 2016.
[6] A. Taufiq et al., “Studies on Nanostructure and Magnetic Behaviors of Mn-Doped Black Iron Oxide Magnetic Fluids Synthesized from Iron Sand,” Nano, vol. 12, no. 09, p. 1750110, Aug.
etic interactions between

[7] R. Govindaraj, R. Mythili, and G. Amarendra, “Stability and magnetic interactions between magnetite nanoparticles dispersed in zeolite as studied using Mössbauer spectroscopy,” J. Magn. Magn. Mater., vol. 418, pp. 248–252, 2016.

[8] S. Bhattacharya, K. Jenamoni, and S. Nayar, “Stability of biomimetic ferrofluids established by a systematic study using microwave irradiation at defined wattages,” J. Magn. Magn. Mater., vol. 324, no. 20, pp. 3261–3266, 2012.

[9] J. Dhimal, S. Bandgar, K. Zipare, and G. Shahane, “Fe 3 O 4 ferrofluid nanoparticles: synthesis and rheological behavior,” Int J Mater Chem Phys, vol. 1, pp. 141–145, 2015.

[10] M. S. Darwish, “Effect of carriers on heating efficiency of oleic acid-stabilized magnetite nanoparticles,” J. Mol. Liq., vol. 231, pp. 80–85, 2017.

[11] F. Laachari, H. Maâtaoui, F. Ei Bergadi, A. Boukir, and S. K. Ibnsouda, “Improvement of a lipolytic activity assay protocol to increase the efficiency of the lipases activity measurement and validation by infrared spectroscopy,” Afr. J. Biotechnol., vol. 14, 2015.

[12] O. V. Minaeva et al., “Comparative study of cytotoxicity of ferromagnetic nanoparticles and magnetitecontaining polyelectrolyte microcapsules,” in Journal of Physics: Conference Series, 2017, vol. 784, p. 012038.

[13] A. A. Galhoum, M. G. Mahfouz, N. M. Gomaa, T. Vincent, and E. Guibal, “Chemical modifications of chitosan nano-based magnetic particles for enhanced uranyl sorption,” Hydrometallurgy, 2016.

[14] M. A. Fontecha-Cámara, C. Moreno-Castilla, M. V. López-Ramón, and M. A. Álvarez, “Mixed iron oxides as Fenton catalysts for gallic acid removal from aqueous solutions,” Appl. Catal. B Environ., vol. 196, pp. 207–215, 2016.

[15] N. Di Maggio et al., “Rapid and efficient magnetization of mesenchymal stem cells by dendrimer-functionalized magnetic nanoparticles,” Nanomed., vol. 11, no. 12, pp. 1519–1534, 2016.

[16] S. Qin and Q. Xu, “Room temperature ferromagnetism in N 4 plasma treated graphene oxide,” J. Alloys Compd., vol. 692, pp. 332–338, 2017.

[17] S. Jovanović, M. Spreitzer, M. Tramšek, Z. Trontelj, and D. Suvorov, “Effect of oleic acid concentration on the physicochemical properties of cobalt ferrite nanoparticles,” J. Phys. Chem. C, vol. 118, no. 25, pp. 13844–13856, 2014.

[18] H. Shokrollahi, “Structure, synthetic methods, magnetic properties and biomedical applications of ferrofluids,” Mater. Sci. Eng. C, vol. 33, no. 5, pp. 2476–2487, 2013.

[19] K. Y. Yoon et al., “Control of magnetite primary particle size in aqueous dispersions of nanoclusters for high magnetic susceptibilities,” J. Colloid Interface Sci., vol. 462, pp. 359–367, 2016.

[20] B. Aslibeiki, G. Varvaro, D. Peddis, and P. Kameli, “Particle size, spin wave and surface effects on magnetic properties of MgFe 2 O 4 nanoparticles,” J. Magn. Magn. Mater., vol. 422, pp. 7–12, 2017.

[21] J. Wu, L. Pei, S. Xuan, Q. Yan, and X. Gong, “Particle size dependent rheological property in magnetic fluid,” J. Magn. Magn. Mater., vol. 408, pp. 18–25, 2016.

[22] Z. L. Liu, Y. J. Liu, K. L. Yao, Z. H. Ding, J. Tao, and X. Wang, “Synthesis and magnetic properties of Fe 3 O 4 nanoparticles,” J. Mater. Synth. Process., vol. 10, no. 2, pp. 83–87, 2002.

[23] M. Houshiar, F. Zebhi, Z. J. Razi, A. Alidoust, and Z. Askari, “Synthesis of cobalt ferrite (CoFe 2 O 4) nanoparticles using combustion, coprecipitation, and precipitation methods: a comparison study of size, structural, and magnetic properties,” J. Magn. Magn. Mater., vol. 371, pp. 43–48, 2014.

[24] J. Carrey, B. Mehdaoui, and M. Respaud, “Simple models for dynamic hysteresis loop calculations of magnetic single-domain nanoparticles: Application to magnetic hyperthermia optimization,” J. Appl. Phys., vol. 109, no. 8, p. 083921, 2011.

[25] S. A. Maboudi, S. A. Shojaosadati, and A. Arpanaei, “Synthesis and characterization of multilayered nanobiohybrid magnetic particles for biomedical applications,” Mater. Des., vol.
[26] S. V. Dyachenko, M. A. Vaseshenkova, K. D. Martinson, I. A. Cherepkova, and A. I. Zhernovoi, “Synthesis and properties of magnetic fluids produced on the basis of magnetite particles,” *Russ. J. Appl. Chem.*, vol. 89, no. 5, pp. 690–696, 2016.

[27] M. T. López-López, J. D. G. Durán, A. V. Delgado, and F. González-Caballero, “Stability and magnetic characterization of oleate-covered magnetite ferrofluids in different nonpolar carriers,” *J. Colloid Interface Sci.*, vol. 291, no. 1, pp. 144–151, 2005.

[28] N. Rezaei, M. H. Ehsani, M. Aghazadeh, and I. Karimzadeh, “An Investigation on Magnetic-Interacting Fe3O4 Nanoparticles Prepared by Electrochemical Synthesis Method,” *J. Supercond. Nov. Magn.*, vol. 31, no. 7, pp. 2139–2147, 2018.

[29] B. D. Cullity and C. D. Graham, *Introduction to magnetic materials*. John Wiley & Sons, 2011.

[30] M. Sheikholeslami and H. B. Rokni, “Simulation of nanofluid heat transfer in presence of magnetic field: a review,” *Int. J. Heat Mass Transf.*, vol. 115, pp. 1203–1233, 2017.

[31] C. Fei et al., “Synthesis and magnetic properties of hard magnetic (CoFe2O4)–soft magnetic (Fe3O4) nano-composite ceramics by SPS technology,” *J. Magn. Magn. Mater.*, vol. 323, no. 13, pp. 1811–1816, 2011.