Characterization of magnetite (Fe$_3$O$_4$) minerals from natural iron sand of Bonto Kanang Village Takalar for ink powder (toner) application

M R Fahley$^1$, V A Tiwow$^1$ and Subaer$^1$

$^1$Department of Physics, Faculty of Mathematics and Natural Sciences, State University of Makassar, Jl. Daeng Tata Raya, Makassar 90224, Indonesia

E-mail: muhrizalfahley@gmail.com

Abstract. This research is about magnetite’s characterization (Fe$_3$O$_4$) from natural iron sands of Bonto Kanang Village, District of Takalar for ink powder (toner) application. This study aims to determine the process parameters to obtain magnetite of high purity degree and to observe its physical characteristics as a supporting toner material which synthesized through co-precipitation method. The iron sand was first separated by the magnetic technique and dissolved into HCl solution before conducting the precipitation process. Precipitation was done by dripping ammonium hydroxide (NH$_4$OH). The precipitated powder was dried at 100°C, and then calcined at 400°C. The purity degree and magnetite mineral grain size were analyzed by XRD and SEM-EDS. The EDS elemental test before and after precipitation showed an increase of iron oxide composition from 66.70% to 87.76%. Diffractogram of XRD before and after precipitation showed Fe$_3$O$_4$ compounds with magnetite phase of 59% and 98%, respectively. The crystal structure iron sand powder structure before and after precipitation is cubic with each lattice parameters a = b = c = 8.384971 Å, V = 589.528423 Å$^3$ and a = b = c = 8.386829 Å and V = 589.920291 Å$^3$ when angle α = β = γ = 90°. SEM images (using SE and HV 20kV) showed inhomogeneous magnetite morphology. The magnetite phase percentage that obtained based on the XRD analysis gives information that magnetite precipitation has been successfully performed with high degree of purity. The material obtained can be applied as a support toner material.

1. Introduction

South Sulawesi province has the abundance of iron sands as in the District of Takalar [1]. Iron sand deposits contain magnetic minerals such as maghemite ($\gamma$-Fe$_2$O$_3$) [2], hematite (α-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) [3]. The content of minerals in the iron sand is very potential as industrial materials. Mineral magnetite can be used as a biomedical application [4], diagnose including MRI (Magnetic Resonance Imaging) [5, 6], cell separation [7], drug delivery system [8-10] antibacterial activity [11], protein separation [12], hyperthermia [13-15], as magnetic catalyst on a magnesium based hydrogen storage material [16], and manufacture of ink powder (toner) [17].

Toner is a composite powder that contains a polymer, pigment, magnetite (Fe$_3$O$_4$), and additives which are used for electrophotography printing and photocopying processes. One of the most important ingredients of toner supporters is magnetite minerals because this it acts as a provider the tribocharging property for toner particles [17]. Therefore, the presence of magnetite minerals (Fe$_3$O$_4$) is needed as a toner support material.
Various methods have been reported to synthesize Fe₃O₄ among others is chemical reduction [18], sol-gel [19], electrochemical [20], flow injection [21], solvothermal [22], hydrothermal [23], microwave-assisted [24], polyol method [25], co-precipitation [26] etc. In this research, the method that used is co-precipitation method, where the parameters to be optimized are the duration of heating, grinding duration, extraction and calcination process. The use of co-precipitation methods is currently the most widespread concern because the process is simple, easy and cheap [27].

In this research the characterization of micro structure of natural iron sand in Bonto Kanang Village Takalar is done in Microstructure Laboratory of Physics Department of FMIPA UNM by using SEM-EDS (Scanning Electron Microscopy-Energy Dispersive Spectroscopy) to know morphology and composition of mineral compound and to know crystal structure, phase of Fe₃O₄ compounds and crystal size through XRD (X-Ray Diffraction) measurement data by using Debye Scherrer analysis.

2. Experimental Method
The main material used in this research is the iron sand of Bonto Kanang Village, Takalar District taken at some point randomly. In the first stages, iron sand was separated by the magnetic technique using a permanent magnet. Subsequently, the sample was crushed for 6 hours then tested using XRD and SEM-EDS methods to examine its the crystal structure, phases, morphological conditions and composition of the compound in the iron sand.

The separation result was weighed by a ratio of 25 grams of iron sand and 150 millilitres of HCl while stirred and heated to a temperature of 100°C using a magnetic stirrer at 350 rpm in 1 hour. Precipitation was done by dripping ammonium hydroxide (NH₄OH), dissolved to pH 6 and forming the precipitated reaction:

\[2\text{FeCl}_3 + 3\text{H}_2\text{O} + 6\text{NH}_4\text{OH} \rightarrow 2\text{Fe(OH)}_3 + 6\text{NH}_4\text{Cl} + 3\text{H}_2\text{O}\]

The precipitated powder washed with H₂O and dried in the memmert oven at 100°C for 19 hours, the reaction:

\[2\text{Fe(OH)}_3 + 6\text{NH}_4\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{FeOOH} + 6\text{NH}_4\text{Cl} + 5\text{H}_2\text{O}\]

Furthermore, precipitated powder was calcined at 400°C with heated time for 1 hour.

Characterization was used XRD (X-Ray Diffractometer) Rigaku MiniFlex II method with PDXL2 software to find out the crystal structure, compound phase and crystal size used Deybe Scherrer analysis and SEM-EDS (Scanning Electron Microscopy- Energy Dispersive Spectroscopy) Tescan Vega 3SB to know the morphology and composition of the compound.

3. Results and Discussion
The result of EDS spectrum test of iron sand can be seen in figure 1; these spectrums show the compound composition in the iron sand is an iron oxide especially ferrous oxide (FeO).

![Figure 1](image-url)
### Table 1. Result of EDS spectrum before synthesis.

| Element      | Unn.C | Norm.C | Atom.C | Compound norm.C | Comp.C | Error (3 sigma) |
|--------------|-------|--------|--------|-----------------|--------|-----------------|
| Sodium       | 1.02  | 1.19   | 1.57   | Na₂O            | 1.61   | 0.37            |
| Magnesium    | 1.85  | 2.17   | 2.70   | MgO             | 3.60   | 0.46            |
| Aluminium    | 2.38  | 2.79   | 3.13   | Al₂O₃           | 5.27   | 0.48            |
| Silicon      | 2.40  | 2.81   | 3.02   | SiO₂            | 6.01   | 0.43            |
| Phosphorus   | 0.31  | 0.37   | 0.36   | P₂O₅            | 0.85   | 0.14            |
| Potassium    | 0.14  | 0.16   | 0.12   | K₂O             | 0.19   | 0.11            |
| Calcium      | 0.83  | 0.97   | 0.73   | CaO             | 1.36   | 0.19            |
| Titanium     | 7.38  | 8.64   | 5.46   | TiO₂            | 14.42  | 0.77            |
| Iron         | 44.25 | 51.85  | 28.05  | FeO             | 66.70  | 3.73            |
| Oxygen       | 24.79 | 29.05  | 54.87  |                 | 0.00   | 9.98            |
| **Total**    | 85.34 | 100.00 | 100.00 |                 |        |                 |

The result of EDS analysis above shows the iron oxide compound (FeO) is major compound present in the sample. After synthesis, FeO composition content was higher than before synthesis 66.60% increased to 87.76 wt.%. This result had been accordance with previous studies when iron sand contains the dominant FeO compounds [18]. The impurity compounds present decreased composition content that is TiO₂ 14.42 wt.% to 9.95 wt.%, SiO₂ 6.01 wt.% to 0.56 wt.%, Al₂O₃ 5.27 wt.% to 0.95 wt.%. The presence of iron oxide or ferrous oxide (FeO) compounds in iron sand samples is according to the theory. Because basically iron sand deposits contain iron oxide compounds is magnetic. Also, the formed of Fe₃O₄ compounds expected in this research, that is reaction result between FeO (reduced) and ferric oxide Fe₂O₃ (oxidized) or FeO + Fe₂O₃ → Fe₃O₄, so the presence FeO is required as the dominant compound in the sample.

### Table 2. Result of EDS spectrum after synthesis.

| Element      | Unn.C | Norm.C | Atom.C | Compound norm.C | Comp.C | Error (3 sigma) |
|--------------|-------|--------|--------|-----------------|--------|-----------------|
| Titanium     | 6.20  | 5.97   | 4.25   | TiO₂            | 9.95   | 0.90            |
| Iron         | 70.92 | 68.21  | 41.69  | FeO             | 87.76  | 6.44            |
| Oxygen       | 25.56 | 24.58  | 52.44  |                 | 0.00   | 19.63           |
| Magnesium    | 0.49  | 0.47   | 0.66   | MgO             | 0.78   | 0.33            |
| Aluminium    | 0.52  | 0.50   | 0.64   | Al₂O₃           | 0.95   | 0.30            |
| Silicon      | 0.27  | 0.26   | 0.32   | SiO₂            | 0.56   | 0.20            |
| **Total**    | 103.97| 100.00 | 100.00 |                 |        |                 |

The presence of iron oxide or ferrous oxide (FeO) compounds in iron sand samples is according to the theory. Because basically iron sand deposits contain iron oxide compounds is magnetic. Also, the formed of Fe₃O₄ compounds expected in this research, that is reaction result between FeO (reduced) and ferric oxide Fe₂O₃ (oxidized) or FeO + Fe₂O₃ → Fe₃O₄, so the presence FeO is required as the dominant compound in the sample.

Diffractogram of XRD iron sand to present is shown in figure 2. It can be seen that material have dominant composition compound is Fe₂O₃ with magnetite phase. Figure 2 (a) shows the pattern of iron sand diffraction before sample passes through the precipitation stage. XRD analyzed result showed that magnetite phase emerged with composition level 59%, then followed by impurities that Al₂O₃ and CrO₃ respectively 11% and 30%. The crystal structure is cubic with lattice parameters a = b = c = 8.384971 Å where V = 589.528423 Å³ with angle α = β = γ = 90°. The crystal size was analyzed using Deybe Scherrer equation [28] by taking the highest peak in figure 2 (a). Obtained Fe₂O₃ crystals size before synthesis is 6.39244803 nm.

Figure 2 (b) shows the XRD diffractogram after passing through the precipitation process. From the analyzed results obtained Fe₂O₃ compounds with magnetite phase increased purity from 59% to 98% and ε-Fe₂O₃ impurities 1.7%. The results of the Fe₂O₃ purity study were reported previously by
Zulkarnain et al. 2014 [36], with purity levels obtained 85.80% using mechanical milling method. That means the co-precipitation method performed in this research is far superior compared the mechanical milling method if reviewed based on the purity level. The identification of Fe$_3$O$_4$ with high purity levels had been previously reported [18, 25, 31] and the results obtained in this research is close to perfect purity.

![Diffractogram XRD from mineral Fe$_3$O$_4$](image)

**Figure 2.** Diffractogram XRD from mineral Fe$_3$O$_4$ (a) before precipitation and (b) after precipitation.

The crystal structure sample after precipitation is cubic with lattice parameters $a = b = c = 8.386829$ Å and $V = 589.920291$ Å$^3$ with angle $\alpha = \beta = \gamma = 90^\circ$. The parameters obtained were similar with research result by Chaki et al, 2015, Setiadi et al, 2016, Puspitaningrum et al, 2017 [18, 29, 30]. The
maximum intensity value was obtained is \( I \) (cps) = 7120 at bragg angle \( 2\theta = 35.497^\circ \), which is reflected at the maximum peak (311) [10, 31-35] and corresponds to (JCPDS card No. 19-629) [37, 38].

The crystal size \( Fe_3O_4 \) was obtained based on Debye Scherrer analysis [39]. The results of the analysis obtained in this study was appropriate with previous research [18] where the crystal size obtained was 7.20 nm. In this research, the magnetite crystal size of natural iron sand of Bonto Kanang Village Takalar was found 5.57994062 nm.

SEM investigations were conducted to identify the morphological conditions and homogeneity of the iron sand sample. SEM images of the \( Fe_3O_4 \) mineral is shows in figure 3.

![SEM images of iron sand](image)

**Figure 3.** Morphology of iron sand (a, b) before precipitation and (c, d) after precipitation.

Figure 3 (a), (b) and (c), (d) each shows the morphological condition of iron powder before and after precipitation at 20 \( \mu \)m and 2 \( \mu \)m respectively. Based on SEM image using SE and HV detector 20 kV, it is seen that morphological conditions of iron sand appeared inhomogenous because of clumps. These visible clump is an agglomeration of tiny particles formed by scouring and calcination processes.

4. **Conclusions**
Characterization of mineral magnetite of natural iron sand of Bonto Kanang Village Takalar was successfully by co-precipitation method. The results of this study indicated that based on EDS spectrum analysis the composition content of FeO compound increased from 66.70 wt.% to 87.76 wt.%. While the result of XRD diffractogram before and after precipitation showed that iron sand successfully obtained high purity level from 59% to 98%. The purity level obtained is greatly influenced by the process parameters which is conducted in the research that is optimization during the precipitation process, drying the precipitation result at 100°C for 19 hours, and the optimum calcination time is 1 hour.
where the calcination temperature is constant 400°C. The results obtained from this research has been accordance with the results of research previously reported and can be applied as a support toner.

Acknowledgements

Acknowledgments for the financial support from Ministry of Research, Technology, and Higher Education (Kemristekdikti) the Republic of Indonesia through Student Creativity Program (PKM) 2017 and the operator of Microstructural Laboratory of Physics Department FMIPA UNM on behalf Syamsidar D and Kharisma Noor Affifah so this research can be done properly.

References

[1] Aly S H and Takdir T 2011 J. Transportasi 11 123
[2] Jarzewska M, Kościńska M and Białopiotrowicz T 2017 Journal of Physics: Conf. Series 885 012007.
[3] Kurniawan C, Eko A S, Ayu Y S, Sihite P T A, Ginting M, Simamora P and Sebayang P 2017 Mater. Sci. Eng. Conf. Series 202 012051
[4] Mishra A 2014 Int. J. Mech. Eng. Robot. 3 410
[5] Phillips M A, Gran M L and Peppas N A 2010 Targeted nano delivery of drugs and diagnostics, nano today, tom 5, p. 143 – 159
[6] Lee J H, Jun Y W, Yeon S I, Shin J S and Cheon J 2006 Angew. Chem. Int. Edn 45 8160-2
[7] Jing Y et al 2007 Biotechnol. Bioeng. 96 1139–54
[8] Neuberger T, Schöpf B, Hofmann H, Hofmann M and Von Rechenberg B 2005 J. Magn. Magn. Mater. 293 483–96
[9] Bucak S, Yavuztürk B and Sezer A D 2012 Recent Advances in Novel Drug Carrier Systems ed A D Sezer (Rijeka: InTech)
[10] Xuan N P, Tan P, Tuyet N P, Thi T N and Thi V T T 2016 Adv. Nat. Sci.: Nanosci. Nanotechnology, 7 045010
[11] Inbaraj B S, Tsai T-Y and Chen B-H 2012 Sci. Technol. Adv. Mater. 13 015002
[12] Gu H, Xu K, Xu C and Xu B 2006 Chem. Commun. 9 941
[13] Ito A et al. 2003 Cancer Sci. 94 308
[14] Spiers K, Cashion J and Gross K 2003 Key Eng. Mater. Bioceram. 213 254
[15] Múzquiz-Ramos E M, Guerrero-Chávez V, Macías-Martínez B I, López-Badillo C M and García-Cerda L A 2015 Ceram. Int. 41 397
[16] Huang Z G, Guo Z P, Calka A, Wexler D, Lukey C dan Liu H K 2006 J. Alloy. Compd. 422
[17] Ataeefard M, Ghasemi E and Ebadi M 2014 Sci. World J. 2014 706367
[18] Chaki S H, Tasmira J M, Chaudhary M D, Tailor J P and Deshpande M P 2015 Adv. Nat. Sci: Nanotechnol. 6 035009
[19] Xu J, Yang H, Fu W, Du K, Sui Y, Chen J, Zeng Y, Li M and Zou G 2007 J. Magn. Magn. Mater. 309 307
[20] Cabrera L, Gutierrez S, Menendez N, Morales P and Herrasti P 2008 Electrochim. Acta. 53 3436
[21] Alvarez S, Muhammed M and Zagorodni A 2006 Chem. Eng. Sci. 61 4625
[22] Liu M and Kim K 2009 Mater. Lett. 63 428
[23] Zhang J, Chen Y, Wang N and Shi W 2008 J. Cryst. Growth 310 5453
[24] Hong Y, Pan T and Li Z 2006 J. Magn. Magn. Mater. 303 60
[25] Vega-Chacón J, Picasso G, Avilés-Félix L and Jafellici J M 2016 Adv. Nat.: Nanotechnol. 7 015014
[26] Venkatesan M, Nawka S, Pillai S and Coey D 2003 J. Appl. Phys. 93 8023
[27] Shen L, Qiao Y., Guo Y, Tan J 2012 Tianjin University 39 737
[28] Mai T T T, Le P T H, Pham H N, Do H M and Phuc X 2014 Adv. Nat. Sci: Nanosci. Nanotechnol. 5 045007
[29] Setiadi E A, Sebayang P, Ginting M, Sari A Y, Kurniawan C, Saragih C S and Simamora P 2016 J. Phys: Conf. Series 776 012020
[30] Puspitaningrum A, Taufiq A, Hidayat A, Sunaryono, Hidayat N and Samian 2017 *Materials Science and Engineering: Conf. Series* **202** 012054

[31] Cuenca J A, Bugler K, Taylor S, Morgan D, Williams P, Bauer J and Porch A 2016 *J. Phys.: Condens. Matter* **28** 106002

[32] Fahmiati, Nuryono and Suyanta 2017 *Materials Science and Engineering: Conf. Series* **172** 012020

[33] Guan B, Ding D, LeFan W J and Xiong R 2017 *Mater. Res. Express* **4** 056103

[34] Kurniawan C, Eko A S, Ayu Y S, Sihite P T A, Ginting M, Simamora P and Sebayang P 2017 *Materials Science and Engineering: Conf. Series* **202** 012051

[35] Yusmaniar, Adi W A, Taryana Y, Muzaki R 2017 *Materials Science and Engineering: Conf. Series* **196** 012033

[36] Jalil Z, Sari E N, Ismail A B and Handoko E 2014 *Indones. J. Appl. Phys.* **4** 1

[37] Rahmawati R, Melati A, Taufiq A, Sunaryono, Diantoro M, Yuliarto B, Suyatman S, Nugraha N and Kurniadi D 2017 *Materials Science and Engineering: Conf. Series* **202** 012013

[38] Khashan, Dagher S, Omari S A and Tit N *Mater. Res. Express* **4** 055701

[39] Chaki S, Deshpande M, Chaudhary M and Mahato K 2013 *Adv. Sci. Eng. Med.* **5** 285