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THE EFFECT OF PH VARIATIONS ON MAGNETIC PROPERTIES OF MAGNETITE SYNTHESIZED FROM IRON SAND

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INTISARI

Mineral magnetit telah berhasil disintesis dari pasir besi menggunakan metode ko-presipitasi dengan variasi tingkat keasaman larutan/pH. Pasir besi tersebut diperoleh dari Pantai Selatan Yogyakarta. Pasir besi dipisahkan menggunakan magnet permanen untuk mendapatkan mineral yang bersifat magnetik yang digunakan sebagai bahan utama. Bahan magnetik dihaluskan menggunakan *ball mill* hingga ukuran ≤ 74, tujuan untuk mempercepat reaksi pelarutan dan mengurangi bahan non-magnetik yang masih terbawa. Pelarutan menggunakan HCl 37% pada temperatur 80 ^{O}C. Reaksi menghasilkan larutan yang terdiri dari $FeCl_2$ dan $FeCl_3$, yang disebut sebagai larutan induk. Ammonium hidroksida (NH4OH) 20% ditambahkan ke dalam larutan induk untuk mendapatkan endapan besi oksida. Proses presipitasi tergantung pada pH larutan, sehingga pH larutan diatur dengan menggunakan variasi penambahan volume NH_4OH. Rasio volume antara larutan induk dan NH_4OH ditentukan yaitu A (2: 1), B (1: 1), C (1: 2) dan D (1: 3). Hasil pencampuran kedua larutan tersebut degan variasi volume menghasilkan larutan dengan berbagai tingkat pH masing-masing yaitu 5, 8, 10 dan 11. Serbuk hitam segera terbentuk selama proses reaksi berlangsung. Serbuk dianalisis menggunakan XRD. Sifat magnetik diukur menggunakan *vibrating sample magnetometers* (VSM) dan TEM untuk mengamati ukuran partikel. Hasil pengujian XRD tersebut ditemukan bahwa serbuk hitam tersebut adalah magnetit pada larutan dengan tingkat pH ≥ 8. Sifat magnetik menunjukkan bahwa Ms (saturasi magnetisasi) adalah 43 emu/gr dan Gambar TEM menunjukkan bahwa ukuran partikel terkecil 26 nm ditemukan pada larutan B dengan tingkat pH 8. Hasil tersebut menunjukan bahwa nanopartikel magnetik (MNPs) dengan sifat superparamagnetik dapat disintesis dari pasir besi.

Kata Kunci: magnetit, pasir besi, sintesis, pH, superparamagnetik.

ABSTRACT

Magnetite has been successfully synthesized from iron sand using co-precipitation method with variations of pH levels. The iron sand was obtained from South Coast of Yogyakarta. The iron sand was separated using a permanent magnetic bar to obtain the magnetic mineral, which is used as raw material. The raw material was ball milled to reduce the particle size down to ≤ 74 μm. It was then dissolved and stirred in HCl 37% at 80 ^{o}C for 3 hours. The reaction yielded a solution consisting of $FeCl_2$ and $FeCl_{3,}$ which is called as a master solution. Ammonium hydroxide (NH_4OH) 20% was added to the master solution to obtain Fe-oxide precipitation. The precipitation process depended on the pH of the solution, so the pH of the solution was arranged using variations of NH_4OH contents. The volume ratios of the master solution and NH_4OH were A (2:1), B (1:1), C (1:2) and D (1:3), they were designated as samples A, B, C and D, respectively. Those various compositions yielded solutions with various pH levels, i.e. 5, 8, 10 and 11, respectively. The black powder precipitation was immediately formed during the reaction. The powders were analyzed using XRD. The magnetic properties were measured using vibrating sample magnetometer (VSM). TEM was used to observe the particle size. From the XRD, it was found that magnetite compound was found on the

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solution with pH level ≥ 8. Magnetic properties test show that Ms (saturation magnetization) is 43 emu/gr found on the solution with pH level of 8. TEM images show that the smallest particle size found on the solution B with pH level of 8. Magnetic Nanoparticles (MNPs) with superparamagnetic properties can be synthesized from iron sand.

Keywords: magnetite, iron sand, synthesis, pH, superparamagnetic.

INTRODUCTION

Nano magnetic technology has been being developed very fast. Nano magnetic materials are used in many applications such as compact disc, hard disc drive, Magnetic Random Access Memory, etc. As a super-paramagnetic material, magnetic nanoparticles materials (MNPs) is also used in medical applications such as drug delivery, contrast agent, Magnetic Resonance Spectroscopy (MRS) and Magnetic Resonance Imaging (MRI) (Iida *et al*, 2007). Iron sand is available in Indonesia in huge amount, especially in South Coast of Java Island which is potentially mined (Bronto, 2007; Tekmira, 2011). The main contents of the iron sand are tetanomagnetic minerals, including magnetite, hematite, titaniferrous, limonite and ilmenite (Yulianto, *et al*, 2003; Yulianto, 2009; Putra *etal*, 2008; Anshori *et al*, 2011). In the South Coast of Yogyakarta, the deposits areas of the iron sand spread from Parangtritis Coast in Bantul to Glagah Coast in Kulonprogo. The iron sand is also found in Cilacap Coast,Central of Java, which contains Fe_3O_4, Fe_2O_3,$FeO.TiO_2$. It has been reported that the iron sand from South Coast of Bantul Yogyakarta contains Fe_3O_4 and Fe_2O_3 (Rusianto, *et al*, 2012).Several methods of producing nano magnetic materials have been reported in literature such as co-precipitation, micro emulsion, thermal decomposition, solvothermal, sonochemical, microwave-assisted, chemical vapour deposition (Faraji, 2010). Angelia*et al* (2006) reported that nano magnetite (Fe_3O_4) had been synthesized from iron sand using co-precipitation with polyetilene glycol (PEG-1000) as the template. The volume ratios of the starting solution and PEG were (1:1), (1:2) and (1:4). It was found that the particle size decreased from 10.9 nm to 7.5 nm. In 2007, Iida *et al* found that various size of nanomagnetic particles of Fe_3O_4had been successfully synthesized using controlled hydrolysis in an aqueous solution containing ferrous and ferric salts with various ratios of 1,6-hexanediamine as a base. The other method of synthesis of nano scale magnetic iron oxide is sonochemical synthesis which has been reported by Theerdhala*et al* (2008). With this method, they have successfully produced ultrafine (< 10 nm) of magnetic iron oxide nanoparticles.

One of the simple wet methods in magnetite synthesis is co-precipitation through dissolving iron sand in HCl precursor and followed by precipitation with NH_4OH addition. However, the amount and ratio of fero and feri chloride results is difficult to predict. The addition of NH_4OH into the solution, will produce of precipitation of Fe_3O_4. Addition of NH_4OH will also influence the pH level of the solution. This current research aims to investigate the effect of pH variations on magnetic properties of magnetite synthesized from iron sand. The iron sand was obtained from South Coast of Yogyakarta. The effect on the magnetite particle size and properties are also investigated.

METHODOLOGY

The iron sand was separated using a permanent magnetic bar to attractthe magnetic mineral, whichwas used as raw material.The raw material was ball milled to reduce the particle size down to ≤ 74 μm. It was then dissolved and stirred in HCl 37% at temperature 80 ^oC for 3 hours. The reaction yielded a solution consisting of $FeCl_2$ and $FeCl_3$ called as a master solution. Ammonium hydroxide (NH_4OH)

20% was added to the master solution to obtain Fe-oxide precipitation. The precipitation process depended on the pH of the solution, so the pH of the solution was arranged using variations of NH_4OH contents. The volume ratiosof the master solution and NH_4OH were (2:1), (1:1), (1:2) and (1:3), and they were designated as samples A, B, C and D, respectively. Those various compositions yielded solutions with various pH levels of 5, 8, 10 and 11 respectively. Black powder precipitation was immediately formed during the reaction. The black powders were analyzed using XRD (*XRD diffractometer Shimadzu XRD-6000)* with radiation of Cu-Kα (λ=1.54056 Å). The magnetic properties (magnetic saturation/Ms, remanent magnetism/Mr, and coercivity field/Hc)were measured using Vibrating Sample Magnetometer (VSM) according to ASTM A977/A977M - 07 Standard Test Method for Magnetic Properties of High-Coercivity Permanent Magnet Materials Using Hysteresigraphs. The type of VSM equipment was OXFORD 1.2H with the measurement range from -1 to +1 tesla. Transmission Electron Microscope (TEM) (JEOL JEM-1400) was used to observe the nano magnetic particle.

DISCUSSIONS

Figure 1 shows the XRD plots of samples A, B, C and D, with volume ratios of the master solution and NH_4OH of (2:1), (1:1), (1:2) and (1:3), respectively. It can be seen in Figure 1 that the main peaks in samples B, C and D have d-spacings of 2.53 Å, 2.97 Å, 2.01 Å, 1.62 Å and 1.48 Å with (h k l) indexes of (3 1 1), (2 2 0), (4 4 0), (5 1 1) and (4 0 0), respectively.

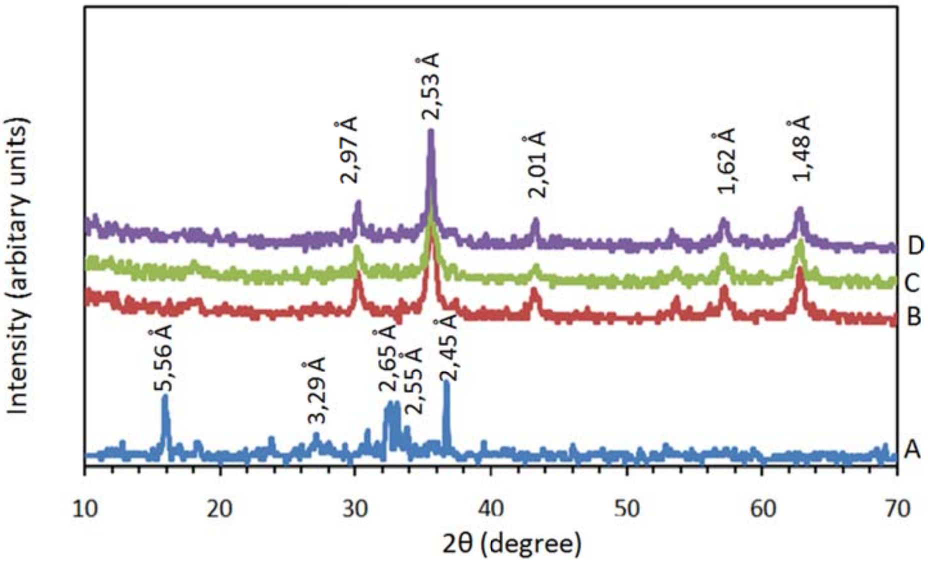

Figure 1. XRD plots of samples A, B, C dan D.

These d-spacings well correspond to d-spacings of magnetite (JCPDS card No. 19-629). However, there were no peaks or d-spacings of sample A that correspond to magnetite d-spacings. Several peaks in sample A match with d-spacings of goethite compound (α-FeO(OH) (JCPDS card no. 29-713) (Bakoyannakis, 2003). The maximum peak of sample A occurs at 2-theta (2θ) of = 36.70^o (d = 2.45 Å). Several possible Fe-oxides that can be formed in the reaction between Fe^{2+}/Fe^{3+} and OH^- (at various pH levels) as follows:

Gothite is formed with the following reaction:

$$Fe^{3+} + 3OH^- \rightarrow FeO(OH) + H_2O$$

Hematite compound is the result of the following reaction:

$$Fe^{3+} + 6OH^- \rightarrow Fe_2O_3 + 3H_2O$$

Magnetite compound is the result of the following reaction:

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow Fe_3O_4 + 4H_2O$$

At low pH level (pH = ± 4.5), Fe_2O_3 particles are formed through two transformation steps from $Fe(OH)_3$to FeOOH, and from FeOOH to Fe_2O_3. In this current research, FeOOH compound occurs at sample A where the pH level of the solution is low (pH = 5). In the synthesis of samples B, C, and D showed the precipitation of magnetite immediately formed when the master solution was reacted with ammonium hydroxide (NH4OH), according to the following reaction:

$$FeCl_{2(l)} + 2FeCl_{3(l)} + H_2O_{(l)} + 8NH_4OH_{(l)} \rightarrow Fe_3O_{4(s)} + 8NH_4Cl_{(l)} + 5H_2O_{(l)}$$

Figure 2. Black precipitation attracted by a permanent magnet.

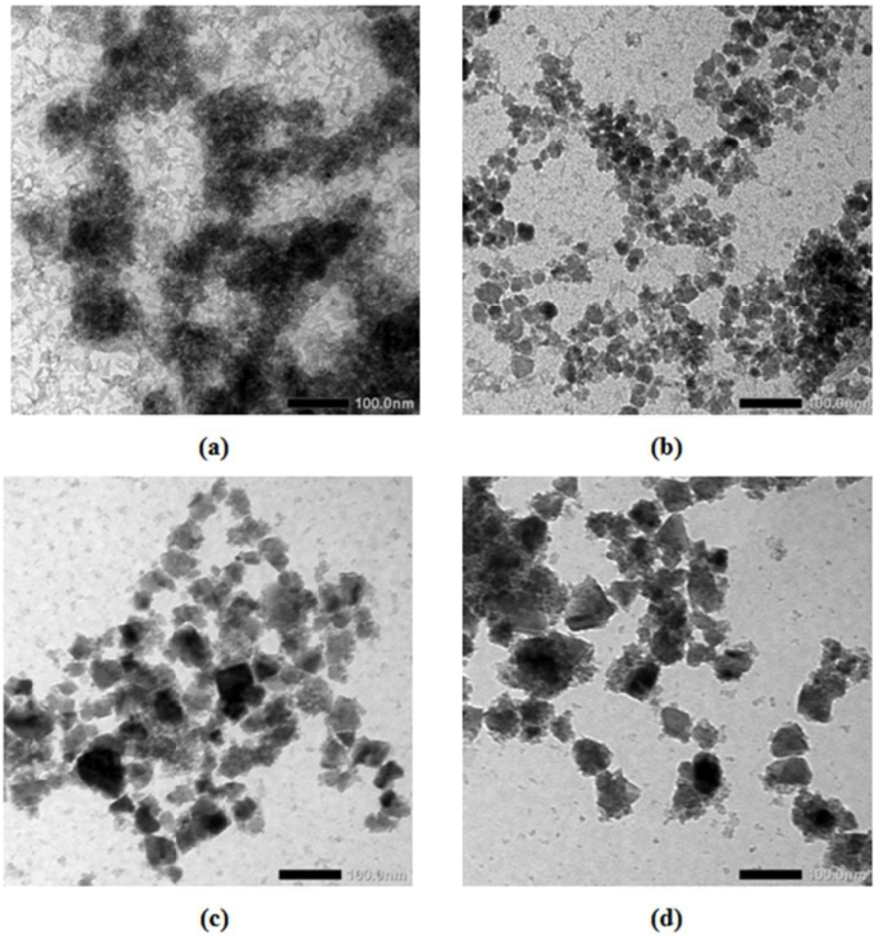

Figure 3. TEM micrograph of the synthesis results, a) sample A; b) sample B; c) sample C and d) sample D.

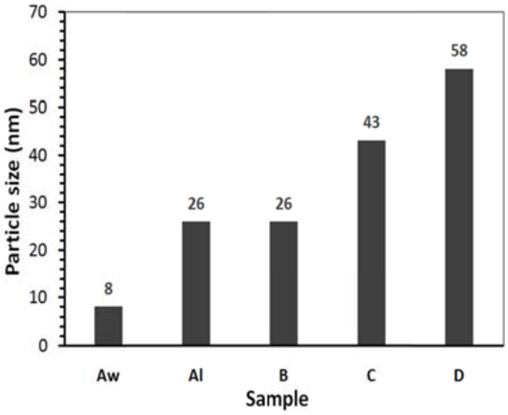

Figure 4. Particle size of the reaction results, (Aw and Al are average width and length of particle sample A, respectively); B, C, and D are average particle size of samples B, C and D, respectively.

The reaction product was in the form of black and jelly precipitation. This precipitation was washed using distillated water for several times until the water was clear in color and reaching the pH = 7. It can be seen in Figure 2 that when the precipitation was placed into a glass test tube and a permanent magnet was touching outside wall of the glass, the precipitation was then attracted by the permanent magnet.

Figure 3 (a, b, c, and d) shows TEM micrographs of the synthesis results of samples A, B, C and D, respectively. Sample A, which is goethite compound has elongated particle shape. While samples B, C, and D are magnetite compound have almost spherical shape as shown in Figure 3 (b, c, and d).

Figure 4 indicates that the particle size increases with increasing amount of NH_4OH of the mixtures. Sample B, C and D where the volume ratios of the master solution and NH_4OH are (1:1), (1:2), and (1:3) yielding nano magnetic particle sizes of 26 nm, 43 nm, and 58 nm, respectively. While the particle size of sample A with the volume ratio of the master solution and NH_4OH of (2:1) seems to be elongated bar with average size of (8 nm x 26 nm).

The synthesis results on samples B, C, and D are magnetite as shownin Figure1, but from the results of the TEM observation showed different particle sizes.The particles size increases with increasing pH of the solution. The increasing of particles size can be explained by recourse mechanisms of crystal growth. As shown in Figure 5, Tartaj *et al* (2003) mentioned that there are three typical mechanism of formation of uniform particles in solution. The first mechanism is single

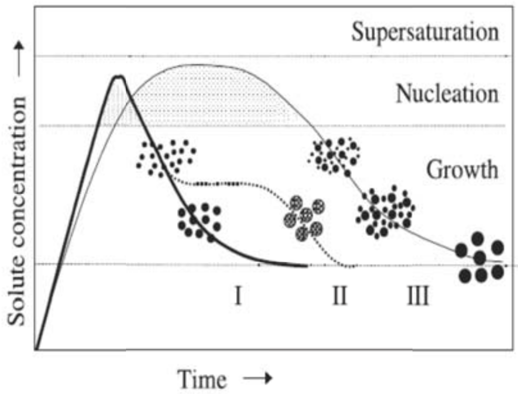

Figure 5. Mechanism of formation of uniform particles in solution: curve I: single nucleation and uniform growth by diffusion; curve II: nucleation, growth and aggregation of smaller subunits; curve III: multiple nucleation events and growth (Tartaj, *et al*, 2003)

nucleation and followed by uniform growth by diffusion. Secondly, uniform particles are formed through nucleation, growth and the aggregation of smaller sub-units. Third, uniform particles can be attained via multiple nucleation and growth.

As shown in Figure 6 and 7, the synthesis results indicate that the sample B with a volume ratio of the master solution and NH_4OH of (1:1) has a saturation magnetization of 43 emu/gr. In addition, the samples of raw material, B, C, and D have hysteresis curves with small coercivity field but they have high saturation magnetization indicating superparamagnetic characteristic. Where, Superparamagnetic material is intrinsically non-magnetic but can be easily magnetized in the appearance of an external magnetic field (Farajiet *al*, 2010). The particle in nanometer size with the appearance of superparamagnetic is known as magnetic nanoparticles (MNPs).The sample A (goethite), however, has very low saturation magnetization (Ms = 0.3 emu/gr) and it can be classified as paramagnetic material. The superparamagnetic of sample B have higher saturation magnetization compared samples C and D, they are 43 emu/gr, 31 emu/gr, and 32 emu/gr, respectively. The high saturation magnetization can be explained by particles size, that smaller particle size with superparamagnetic property with presence of a single magnetic domain than a big particle size. The big particles size can be appearance of multiple magnetic domains.

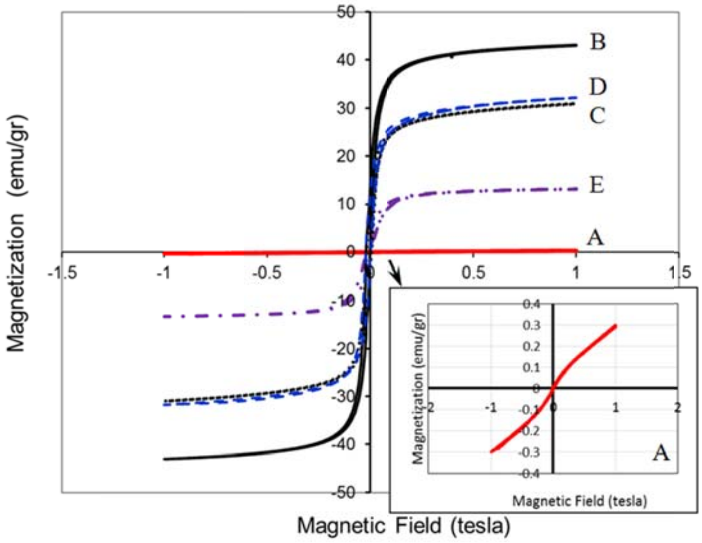

Figure 6. Hysteresis curves of samples with volume ratios between master solution (($FeCl_{2(l)}$ + $FeCl_{3(l)}$) and $NH_4OH_{(l)}$ 20%) of A (2:1), B (1:1), C (1:2) and D (1:3). Sample E is hysteresis curve of the iron sand. Inset = enlargement of sample A.

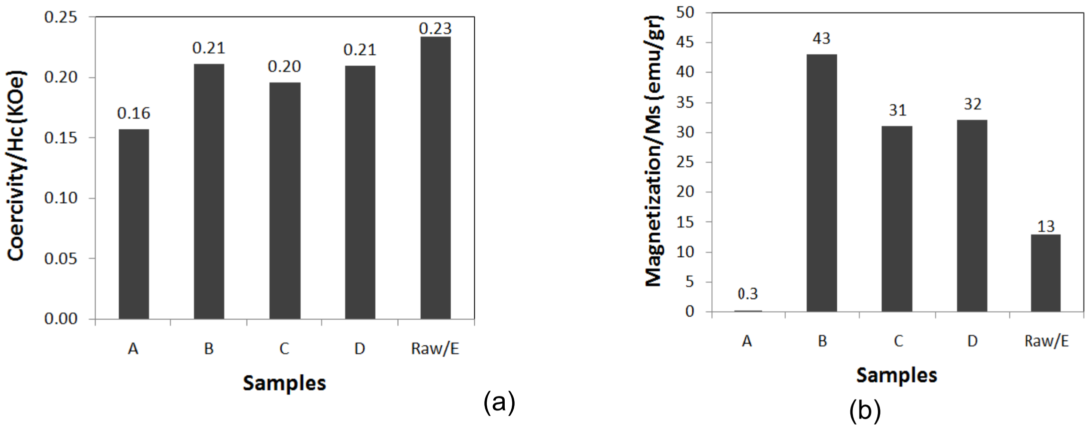

Figure 7. (a) Coercivity/Hc and (b) Magnetic saturation/Ms of samples with volume ratios between master solution (($FeCl_{2(l)}$ + $FeCl_{3(l)}$) : $NH_4OH_{(l)}$ 20%) of A (2:1), B (1:1), C (1:2) and D (1:3). Raw/E is iron sand sample.

CONCLUSION

Nano magnetite compound as superparamegnetic material has been successfully synthesized from iron sand from South Coast of Yogyakarta using co-precipitation method. The synthesis process is influenced by pH level of the solution. The results of magnetic properties testing show that the highest Ms of 43 emu/gr is achieved when the pH of the process is 8. The smallest particle size of 26 nm of the magnetite is attained on sample B (volume ratio between master solution ($FeCL_2$+$FeCl_3$) and NH_4OH = 1:1) and can be classified as Magnetic Nanoparticles (MNPs).

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