

Synthesis and Characterization of Magnetites Obtained from Mechanically and Sonochemically Assisted Co-precipitation and Reverse Co-precipitation Methods

Triastuti Sulistyarningsih, Sri Juari Santosa, Dwi Siswanta, and Bambang Rusdiarso

Abstract—It has been examined the physical and chemical properties of magnetite synthesized mechanically and sonochemically by co-precipitation and reverse co-precipitation methods. Ammonia solution was used as precipitating agent to adjust the pH of the suspension to reach 11. Characterization of the synthesized magnetites was conducted using the Fourier Transform Infrared Spectroscopy (FTIR), the X-ray diffraction (XRD), Scanning electron microscopy (SEM), and Vibrating Sample Magnetometer (VSM). The characterization results showed that the crystallinity of magnetites synthesized by the ordinary mechanically assisted co-precipitation was higher than that of magnetites synthesized by mechanically assisted reverse-co-precipitation. The involvement of sonochemical treatment instead of mechanical treatment gave smaller and more homogeneous crystal size. The morphology of magnetites was spherical and agglomerated with homogeneous size distribution.

Index Terms—Magnetite, mechanically, sonochemically, synthesis.

I. INTRODUCTION

Magnetite or ferrous ferrite (FeO , Fe_2O_3 or Fe_3O_4) is an iron oxide which has an inverse spinel structure with Fe(III) ions distributed randomly between octahedral and tetrahedral sites, and Fe(II) ions in octahedral sites [1]. Magnetite is highly preferred for many applications such as drug carrier [2], drug release [3], cancer therapy [4], a proton exchange membrane [5] and the heavy metal adsorbent [6]. Main advantage of using magnetic adsorbent is that the magnetic adsorbent is nontoxic and can be reused and easily separated from the solution by an external magnet [7]. Hence, an efficient, economic, scalable and non-toxic synthesis of Fe_3O_4 began to grow rapidly.

For most applications of magnetite, require the magnetite nanoparticles to be of uniform size, shape and well dispersed in a solvent. The main factor that affects many interesting properties is the particle size. The size and shape of magnetite particles are generally controlled by synthesis method. There are several techniques that have been used for the synthesis of

magnetite, which including co-precipitation of ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions by an alkali, usually NaOH solution [8], [9], hydrothermal reaction [10], oxidative co-precipitation [11], reduction reaction with α -D-glucose as the reductant [12] and precipitation from partially reduced ferric chlorida aqueous solutions [13].

The co-precipitation process includes several stages : nucleation, growth and secondary process such as agglomeration, attrition, and breakage [14]. The particles obtained with a convention co-precipitation process are relatively larger with a broad size distribution, because it is difficult to avoid the nucleation during the subsequent growth of nuclei [14]. In the other side, sonochemical technology starting developed for preparation of magnetite because the ultrasonic irradiation can decreases the particles sizes of magnetite. In present work, it has been conducted the synthesis of magnetites by mechanically and sonochemically assisted co-precipitation and reverse co-precipitation methods using ammonia solution as precipitating agent and then comparing the results of the synthesis products. The physical and chemical properties of the synthesized magnetites were examined by means of Fourier Transform Infrared Spectroscopy (FTIR), the X-ray diffraction (XRD), Scanning electron microscopy (SEM), and Vibrating Sample Magnetometer (VSM).

II. PROCEDURE

A. Reagent

In this work, all chemicals such as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and NH_4OH (25%, w/w) were of analytical reagent grade from Merck (Germany) and used without further purification.

B. Synthesis of Magnetite

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (molar ratio $\text{Fe}^{3+}:\text{Fe}^{2+} = 1.5:1$) were dissolved in 25 ml distilled water. A NH_4OH (3,5 M) solution was added dropwise into the mixed $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution at 50°C under stirring to increase pH until 11. After 3 h aging, the products were collected by external magnet, washed with distilled water to neutral pH and then dried at 60°C to obtain mechanical magnetite nanoparticles (MMco) [15]. For reverse co-precipitation method, the mixed $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution was added dropwise into NH_4OH solution and this product was termed as MMrco. For sonochemically method, the reaction between $\text{Fe}^{3+}/\text{Fe}^{2+}$ with NH_4OH was done in ultrasonic batch (Branson 3210) and the aging time was 1h. The products are called UMco and UMrco.

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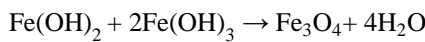
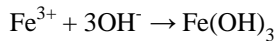
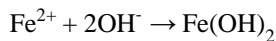
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C. Characterization of Materials

The magnetites were first characterized for the functional groups by FT-IR. FT-IR spectra were recorded using a Shimadzu FTIR-820 IPC in the transmission mode in spectroscopic grade KBr pellets. XRD patterns of samples to study the crystalline structure were recorded using a Shimadzu XRD-6000 diffractometer with Ni-filtered Cu K α radiation ($\lambda = 0.15406$ nm) at voltage 40 kV and current 30 mA. Every sample was scanned in steps of 0.02° (2θ) in the range from 0° to 70° with a count time of 4 s per step. The magnetic properties of the as-synthesized nanopowder magnetites were analyzed by Vibrating Sample Magnetometer (VSM) tipe OXFORD VSM 1.2H. The morphology of samples was viewed by scanning electron microscopy (SEM) using a JSM-6360 instrument.

III. RESULT AND DISCUSSION

Synthesis of magnetite is done in two methods that is co-precipitation (co) and reverse co-precipitation (rco). Co-precipitation is the simplest method and the most economical and efficient way to get the magnetite particles. In ordinary co-precipitation, a solution of Fe $^{2+}$ /Fe $^{3+}$ was titrated using an alkaline solution 3, 5N NH $_4$ OH to pH 11, while on the reverse-co-precipitation method, NH $_4$ OH solution was titrated using a mixed solution of Fe $^{2+}$ /Fe $^{3+}$. Both methods were done mechanically and sonochemically. The mechanic treatment was done using a magnetic stirrer barr and hot plate stirrer, while the sonochemical treatment was performed in an ultrasonic batch. Instead of NaOH, NH $_4$ OH solution was employed in this study as precipitating agent in order to obtain magnetite with better crystallinity and smaller size [14]. The formation of magnetite began to form at pH 9 and as predicted from the Pourbaix diagram [9] the formation of magnetite would be complete at pH 11. According to Pourbaix diagram, Fe $_3$ O $_4$ precipitates as a stable phase in highly basic aqueous media where the precipitated Fe $_3$ O $_4$ nanoparticles acquire negative charges on their surface. The co-precipitation reaction is represented by eq.:



A. Characterization by FTIR

FTIR characterization results for the mechanically and sonochemically assisted co-precipitation and reverse co-precipitation methods yield clear absorption bands at wavelengths of 586 and 524 cm $^{-1}$ which show the vibration of strain Fe-O tetrahedral and 393; 378; 339; 354 cm $^{-1}$ which correspond to strain of Fe-O octahedral of Fe $_3$ O $_4$ (Fig. 1(A)). In addition, there are a weak absorption bands at wave number 1627, 1635 and around 3400 cm $^{-1}$ which are the stretching vibration of OH groups on the surface of the magnetite indicating that the crystallization process was complete [16], [8]. But with the obvious appear of -OH groups on UMco shows that Fe(OH) $_2$, Fe(OH) $_3$ and FeOOH formed as a result of hydrolisation on the surface of Fe $_3$ O $_4$ [12].

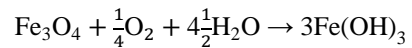
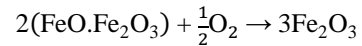
B. Characterization by XRD

Structures of magnetite crystal were characterized using XRD. Diffractogram XRD magnetite synthesis results shown in Fig. 1B. The resulted diffractogram shows six peaks corresponding to the standard data for Fe $_3$ O $_4$ (JCPDS no. 89.0691). The characteristic diffraction peaks of the synthesized magnetites seen in $2\theta = 30.27^\circ$, 35.68° , 43.30° , 57.21° , 62.90° and 74.51° which are the reflection (220), (311), (400), (511), (440) and (533). Diffractogram peaks at d311 ($2\theta = 35.68^\circ$) which were high and sharp observed on magnetite synthesized by co-precipitation. This indicates a higher crystallinity of magnetite synthesized by co-precipitation method rather than reverse-co-precipitation. Based on the XRD data, the size of the magnetite crystals can be estimated using the Debye-Scherrer equation [15]:

$$d = \frac{K\lambda}{\beta \cos\theta}$$

where d is the crystal size (nm), K is a constant Sherrer (0.89), λ is the wavelength of X-rays (0.15418 nm), β is the peak FWHM (Full Width at a Half Maximum) the strongest peak (d311) (radians), θ is the Bragg diffraction angle (radians). The average size distribution of magnetite crystals synthesized by the Debye-Scherrer equation presented in Table I.

In addition to 6 peaks corresponding to the peaks of magnetite, there is one peak in $2\theta = 32^\circ$ which is the peak of ϵ -Fe $_2$ O $_3$ [17]. This shows that the synthesized magnetite do not have high purity because synthesis conditions not under N $_2$ gas. In highly alkaline media, Pourbaix diagram indicates that other phases such as FeO $_4^{2-}$, Fe $_2$ O $_3$, Fe(OH) $_3$ and HFeO $_2^-$ are possible to form in this condition. In addition, magnetite can be seen as a combination of FeO and Fe $_2$ O $_3$. When synthesized not under conditions of N $_2$ gas, FeO can be oxidized to Fe $_2$ O $_3$ or Fe(OH) $_3$ according to the following reaction equation [9]:



That oxidation reaction explain why synthesis of magnetite in alkaline media in air has been always abandoned to avoid the formation of phase-impure Fe $_3$ O $_4$.

TABLE I: THE AVERAGE SIZE DISTRIBUTION OF MAGNETITE CRYSTALS SYNTHESIZED

sample	2θ (degree)	θ (radian)	FWHM (β) (radian)	Crystal size average (nm)
MMco	35.56	0.310	0.01112	15.6
UMco	35.70	0.316	0.01044	14.6
MMrco	35.68	0.311	0.01142	13.3
UMrco	35.53	0.311	0.01394	10.9

Based on calculation results (Table I), the crystal size of the magnetite which synthesized by reverse co-precipitation method smaller than that by the ordinary co-precipitation. In addition, magnetites synthesized by sonochemical treatment have crystal sizes smaller than using mechanical treatment. However, based on the high and sharp peaks in the XRD pattern, it is seen that crystallinity of particles synthesized by co-precipitation higher than that reverse co-precipitation (Fig. 1).

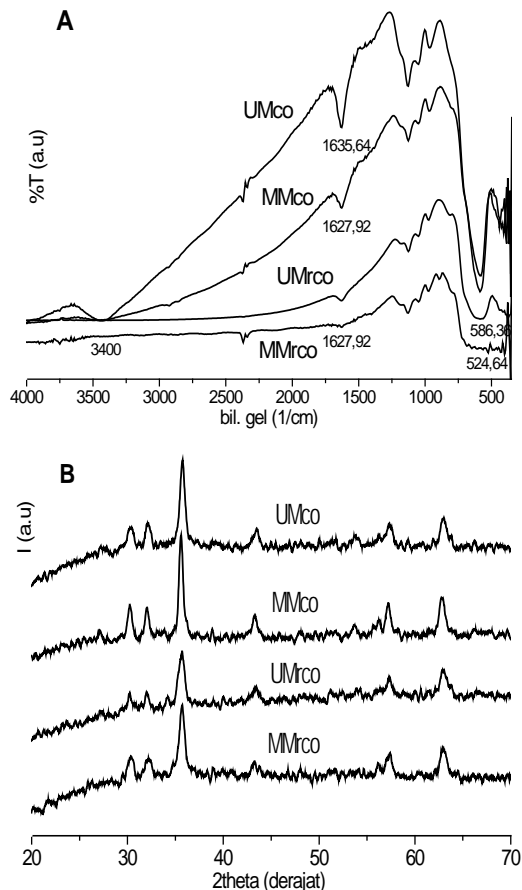


Fig. 1. FTIR spectra (A) and XRD patterns (B) of the magnetite.

C. Magnetic Properties

Magnetic properties were measured at room temperature using a VSM (Fig. 2). The results of measurements of the specific saturation magnetization (M_s) of the two samples of magnetite, MMco and UMco, yielded the value M_s of UMco (73.6 emu/g) that was higher than MMco (65.2 emu/g). This is likely due to a more homogeneous particle UMco and purity higher than MMco. So although UMco give smaller particle size, but it produces higher magnetic properties than MMco. This result can be explained by their agglomeration and size characteristics. Previous result by Thapa *et al.* [18] attributed the increase in the magnetization of magnetite with the decrease of particle size to the decrease in the oxygen content in the magnetite samples and the subsequent increase of $[\text{Fe}^{2+}]$ in the magnetite lattice, which is the main cause of magnetic character of magnetite nanoparticles. Ma and Liu [19] related the decrease in magnetic properties with increasing size of Fe_3O_4 nanoparticles to the agglomeration of particles, which is caused by the hydrophobic interaction between them.

D. Morphology of Magnetite

Fig. 3 gives the SEM image of the prepared magnetite via co-precipitation method. Based on SEM micrographs (Fig. 3(a) and 3(b)) it seen that the morphology of magnetites is spherical and agglomerated with homogeneous size distribution. The magnetite which was synthesized sonochemically showed smaller particle size than mechanically synthesized magnetite. It is proved that the sonochemical method can reduce the size of the magnetite particles. Ultrasound irradiation may locally produce extremely-high temperatures (>5000 K) and pressures (>20 MPa) during acoustic cavitation, providing enough energy

for generation of crystal nuclei. This is favorable to significantly accelerating the nucleation of magnetite particles [15]. Agglomeration formed by hydrophobic interactions between nanoparticles of magnetite nanoparticles.

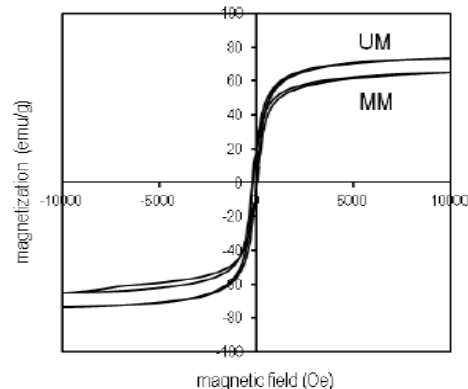


Fig. 2. Hysteresis loops of magnetite.

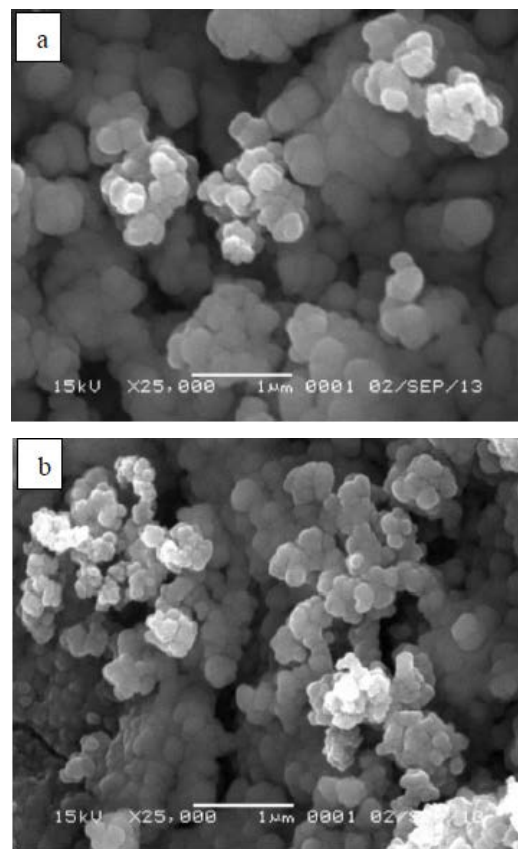


Fig. 3. SEM image of (a) the mechanically and (b) sonochemically magnetite.

IV. CONCLUSION

Magnetite could be synthesized by mechanically or sonochemically assisted co-precipitation and reverse co-precipitation methods. This both methods yielded magnetite particles with small and homogenous size but magnetites synthesized by sonochemical treatment have crystal sizes smaller than using mechanical treatment. In this study, the magnetite was synthesized with no protecting gas N_2 and could be easily done.

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