

Original article

Synthesis of Magnetite Nanoparticles Using Reverse Co-precipitation Method With NH₄OH as Precipitating Agent and Its Stability Test at Various pH

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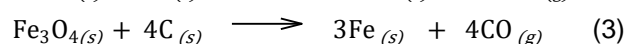
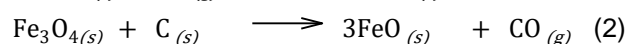
Abstract

In this study, the synthesis of magnetite was carried out through the reversed co-precipitation method with ammonium hydroxide (NH₄OH) as precipitating agent. The aim of the study was to obtain the most appropriate moles ratio of Fe(III) and Fe(II) in obtaining the best characteristics of magnetite, considering that Fe(II) was easily oxidized to Fe(III). Characterization of synthesized magnetite was performed using a Fourier Transform Infrared (FTIR) spectrophotometer and X-Ray Diffraction (XRD). The results showed that the moles ratio of Fe(III) and Fe(II) that produced magnetite with high yield, FTIR spectra absorption and diffractogram peaks with high intensity was magnetite synthesized using a ratio of Fe(III) and Fe(II)= 1.5: 1. Yield of magnetite synthesized in this condition was 81%. Based on the stability test, magnetite was stable at pH 2-10.

INTRODUCTION

In recent years, the adsorption process using magnetite compounds and modified magnetite (Fe₃O₄) compounds has been developed. Applications of magnetite compounds include metal adsorption (Muniroh et al., 2019; Rahmayanti et al., 2016a; Rahmayanti et al., 2016b; Rahmayanti et al., 2019, Rahmayanti, 2020), and dye adsorption (Latifah et al. al., 2020; Liu et al., 2019; Rahmayanti et al., 2020; Putri et al., 2020). Magnetite compounds or modified magnetite compounds can adsorb the target compound, if an external magnetic field was applied, the adsorbent can be separated from the solution rapidly. Furthermore, the adsorbate can be separated using a solvent or without a solvent. Magnetite was widely used because it was a semiconductor compound that has a small particle size, low toxicity, and was paramagnetic in nature (Jingjing et al., 2011).

Magnetite was known as black iron oxide or ferrous ferrite, which was the ferrous metal oxide with the strongest magnetic properties. In an oxidizing atmosphere, magnetite can be oxidized to maghemite or hematite according to the reaction presented in equation 1. Meanwhile, in a reducing atmosphere, magnetite can be reduced to wustite or iron as shown in equations 2 and 3 (Petrova et al., 2011).

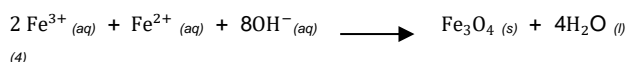


The magnetite surface contains hydroxyl groups which were protonated at a pH below pH_{PZC} magnetite and deprotonated at a pH above pH_{PZC} magnetite. The condition of pH with the same group concentration and on the surface was called the point of zero charge (PZC). Generally, it was at pH

8-9 for all iron oxides (Schwertmann, 2008). The characteristic pH_{PZC} value for each metal oxide in the aqueous medium. Several pH_{PZC} data for iron oxide have been reported in some literature and for magnetite, it ranges from 3.8 - 9.9.

At room temperature, the pH_{PZC} magnetite was assumed to be about 6.4. The pH_{PZC} value for magnetite depends on the synthesis temperature, the synthesis method used and the conditions at the time of measurement. In general, the pH_{PZC} will vary according to the particle concentration/ionic strength of the media. The magnetic field that surrounds the magnetite particles in acidic and alkaline conditions far from the pH_{PZC} of the magnetite can prevent the clumping of the particles due to the repulsion of the electric bilayer that approaches the particles due to the similarity of charges.

Understanding of the magnetite synthesis reaction process and controlling several reaction parameters were required to obtain magnetite of the desired size, shape and properties of magnetite. The magnetite synthesis reaction was shown in equation 4.



The stoichiometric reaction of equation 4 showed that magnetite can be synthesized maximally by maintaining the mole ratio = 2:1 at pH conditions 9-14 (El-Kharraq et al. 2011). In an environment that was not free of oxygen, Fe(II) solution was easily oxidized to Fe(III) so that it was not easy to maintain the mole ratio = 2:1 in the system. The excess of Fe(III) in the system can allow the formation of hematite (α -Fe₂O₃) and goethite (α -FeOOH) and consequently the resulting magnetite was not optimal. This study performed an optimization of the comparison conditions of Fe(III) and Fe(II) in the synthesis of magnetite to obtain magnetite with the best yield and characteristics. The stability of magnetite was studied in the pH range 1-10.

MATERIALS AND METHODS

The equipment used includes: a set of standard laboratory glassware, vacuum pump, 4800 Thermolyne oven/furnace, BP 110 Sartorius analytical balance, desiccator, Orion 920A pH meter, shaker (Osk), Fourier Transform Infrared (FTIR) spectrophotometer, Shimadzu -8201 PC, and X-Ray Diffraction (XRD) Shimadzu model XRD-6000. The chemicals used in this study were aquabides and analytical grade materials made by

E. Merck, namely: iron (II) sulfate heptahydrate (FeSO₄·7H₂O), iron (III) chloride hexahydrate (FeCl₃·6H₂O), ammonium hydroxide (NH₄OH).

Fe(III) (FeCl₃·6H₂O) solution was mixed with Fe(II) (FeSO₄·7H₂O) solution with variations in the ratio of each mole = 2:1; 1.75:1; 1,5:1; 1,1:1. Next, the mixture of Fe(III) and Fe(II) solutions was added dropwise into the NH₄OH 3.5 M while stirring using a magnetic stirrer at 60°C for 60 minutes. The reaction product was filtered with a buchner filter and dried in an oven for 3 hours at a temperature of 50°C, then characterized using FTIR and XRD.

The average crystal size of magnetite was calculated based on the XRD, using the Debye-Scherrer equation as presented in equation 5.

$$L = \frac{0,94 \lambda}{\beta \cos \theta} \quad (5)$$

where L was the crystal size (nm), λ was the x-ray wavelength (nm), β was the Full Width at Half Maximum (FWHM) of the reflection peak (rad) and θ was the diffraction angle (rad).

Ten mg of magnetite was added to the aquabidest whose pH had been adjusted with pH variations 1-10. Then the mixture was shaken for 1 hour and filtered using a buchner filter. The filtrate was taken to measure its absorbance using AAS. (4)

RESULT AND DISCUSSION

The process of solution oxidation depends on many factors, including pH, temperature and dissolved oxygen in the system. If the initial pH of the system was low, then the chances of the solution being oxidized will be even greater, because it takes a longer time to reach a media pH above 9. In this study, the coprecipitation method was carried out in reverse, namely by adding a mixture of solutions FeSO₄·7H₂O and FeCl₃·6H₂O gradually with constant velocity into NH₄OH solution with pH > 9. In the hope that the system pH condition was maintained in the range 9 - 13. The initial pH of this study was 13 and the final pH was 9.

Based on the FTIR spectra of the synthesized material presented in Figure 1, it can be seen that the absorption in the area of 578 cm⁻¹ with a strong intensity was given by the synthesized material with a mole ratio of Fe(III) and Fe(II) = 1.5:1. The absorption that appears at 578 cm⁻¹ area indicates the presence of Fe-O bonds in the synthesized material. When viewed from the absorption that appears at 3600-3200 cm⁻¹ area, it is possible that the synthesized compounds obtained in this condition were still mixed with Fe(OH)₂. However, from the XRD results, it appears that the

synthesized compound does not mix with Fe(OH)₂. It was suspected that the absorption that appears at 3600-3200 cm⁻¹ area comes from water contained in the synthesized solids. Synthesized material with a ratio = 2:1; 1,75:1 and 1,1:1 do not provide absorption at 3600-3200 cm⁻¹ area so that it can be said that the resulting magnetite does not mix with Fe(OH)₂. The absorption that appears for the synthesized material with a variation of the mole ratio = 2:1; 1,75:1 and 1,1:1 did not show a significant difference both from the emergent absorption area and the absorption intensity. Yield

of synthesis results in various comparisons of Fe(III) and Fe(II) are presented in Table 1. Based on table 1, it can be seen that the highest yield of synthesized material was obtained under synthesis conditions with the mole ratio of Fe (III) and Fe(II) = 1.5: 1. The obtained yield was 81%. From this study it can be seen that reducing the initial mole ratio of Fe(III) and Fe(II) < 2:1 produces magnetite with better characteristics, so it can be said that during the reaction process, it is possible to have an oxidation reaction of Fe(II) to Fe(III).

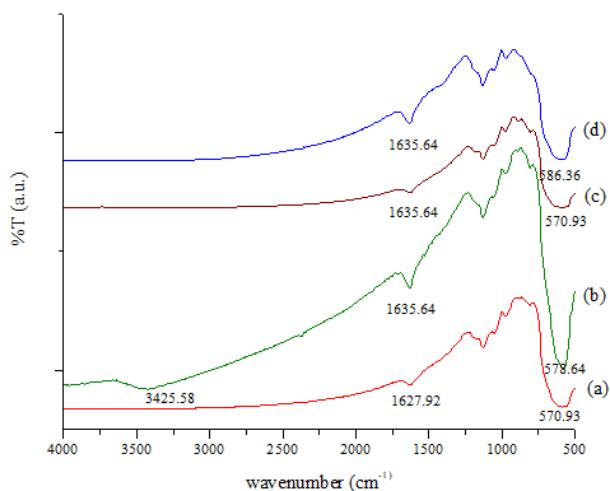


Fig 1. FTIR spectra of the synthesized material at various variations of the mole ratio of Fe(III) and Fe(II) (a) 1,1:1 (b) 1,5:1 (c) 1,75:1 (d) 2:1 (with a concentration of NH₄OH = 3.5 M, reaction time of 60 minutes and reaction temperature = 60°C)

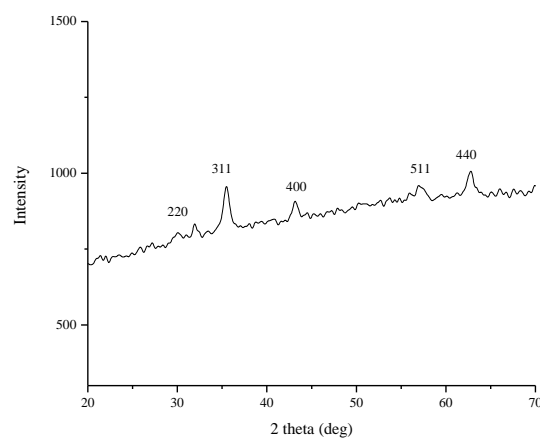


Fig 2. XRD diffractogram of the synthesized material at the mole ratio of Fe (III) and Fe (II) = 1.5 : 1 with a concentration of NH₄OH = 3.5 M, reaction time of 60 minutes and reaction temperature = 60°C

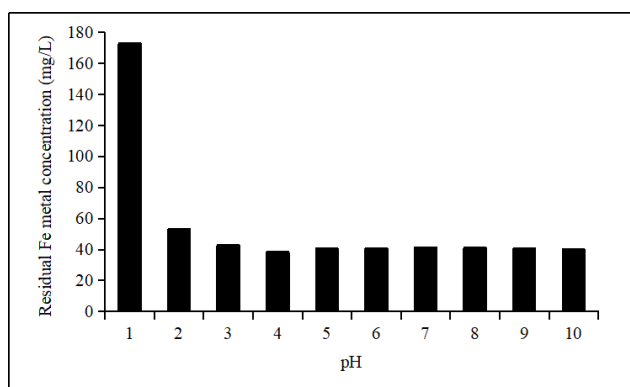


Fig 3. Stability of Magnetite

The XRD diffractogram of the synthesized material at the mole ratio of Fe(III) and Fe(II) = 1,5:1 was presented in Figure 2. The peaks that appear for each variation in the mole ratio are characteristic peaks for magnetite such as peaks that appear at a diffraction angle of about 30, 35, 43, 57 and 62 ° with the Miller indexes

[220], [311], [400], [511], and [440], respectively. There were no other peaks indicating the presence of Fe(OH)₂ or hematite compounds (Liu *et al.*, 2018; Azadi *et al.* 2018; Mahdavi *et al.*, 2013; Rahmayanti, 2020). The intensity of the diffractogram peaks obtained in this study is quite high.

The average crystal size of the synthesized magnetite was presented in Table 2. Based on Table 2, the size of the magnetite crystals obtained in this study was smaller than the size of the magnetite crystals obtained by Rahmayanti et al. (2016). The small crystal size will result in a large material surface area. Thus, the magnetite synthesized in this study has the opportunity to be applied as an adsorbent.

The stability test of magnetite at various pH was carried out to obtain the proper pH conditions if magnetite was used as an adsorbent. The magnetite stability tests at various pH ranges were presented in Figure 3. Based on this figure, magnetite was stable at pH 2-10. The results of this study confirm the reasons why magnetite was heavily modified with organic and inorganic compounds. Modification of organic and inorganic compounds can increase their stability over various pH ranges (Fauzi et al., 2020).

Table 1. Yield of Synthesis Results in Various Comparisons of Fe(III) and Fe(II)

Reaction Time (minute)	Temperature (°C)	Concentration NH ₄ OH (M)	Mole ratio Fe ³⁺ /Fe ²⁺	Yield (%)
60	60	3,5	2 : 1	75
60	60	3,5	1.75 : 1	78
60	60	3,5	1.5 : 1	81
60	60	3,5	1.1 : 1	70

Table 2. Distribution of The Average Crystal Size Of The Synthesized Material

Precipitating Agent	Temperature (°C)	Mole ratio Fe ³⁺ /Fe ²⁺	The average crystal size (nm)
NH ₄ OH 3.5 M (this research)	60	1.5 : 1	9.0
NaOH 0.1 M (Rahmayanti et al., 2016)	60	2 : 1	15.0
NaOH 0.5 M (Rahmayanti et al., 2016)	60	1.5 : 1	8.7

CONCLUSION

Magnetite has been successfully synthesized using the reverse coprecipitation method with the precipitating agent NH₄OH. The mole ratio of Fe(III) and Fe(II) affects the yield and characteristics of the resulting magnetite. The mole ratio of Fe(III) and Fe(II) which produced the largest yield and the best characteristics of magnetite was = 1.5: 1. The yield produced = 81%. Based on the stability test, magnetite was stable at pH 2-10.

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