Synthesis and characterization of magnetite (Fe$_3$O$_4$) via radiolytic reduction method

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Abstract. The radiolytic reduction method has been used in the synthesis of magnetite, which applied solvated electrons (e$_{-a}$) as a reductor. The aqueous solution containing iron chloride salt and iso-propanol as scavenger agents were irradiated in the gamma-irradiated chamber at Gamma Irradiator Laboratorium Dr. Mirzan T. Razzak, M.Eng., STTN-BATAN, Indonesia. The purpose of this research is to study the formation of Fe$_3$O$_4$ particles via radiolytic reduction by varying the irradiation dose (25, 50, 75, and 100 kGy). The analysis result using X-Ray Diffractometer (XRD) shows the Fe$_3$O$_4$ phases were formed since irradiation dose 25 kGy. As the irradiation dose increase caused the increasing of saturation magnetization of Fe$_3$O$_4$ with Ms value 5.24; 8.00; 14.2; 21.1emu/g for irradiation dose 25, 50, 75, 100 kGy respectively. Particle size analysis of Fe$_3$O$_4$ that irradiated at 100 kGy has an average size of 331 nm. Functional group identification was confirmed using Fourier Transform Infra-Red (FTIR) Spectrophotometer to show the formation of Fe-O bonds. Based on the characterization results, the radiolytic reduction method has been successfully used in the synthesis of Fe$_3$O$_4$ since radiation dose 25 kGy.

1. Introduction
Synthesis of nano-sized metal oxides currently become the focus of considerable research due to the many technological applications. Nanoparticles containing magnetic materials (such as iron, nickel and cobalt oxides) have potential applications in medical biotechnology, drug delivery, and hyperthermia cancer treatment [1]. The magnetic, catalytic, optical, and electronic properties of these metal oxides are determined by the size, structure and shape of the particles when they form that play a role in the application.

Fe$_3$O$_4$ nanoparticle is iron oxide that has been intensively investigated because of their superparamagnetic, high coercivity, low Curie temperature, non-toxic, and biocompatible [2]. It has been synthesized by different techniques including co-precipitation [3], wet chemical
reduction [4], hydrothermal synthesis [5], thermal decomposition [6], and microemulsion [7]. Those methods are either complicated or required high temperature and pressure conditions, also need the addition of other chemical compounds in the synthesis process. The radiolytic reduction method is another promising technique that avoids the use of reducing agents which could contaminate the product and lead the associated side reactions[8,9]. At gamma-ray generator as the radiation source, a large number of solvated electrons are produced during irradiation in an aqueous solution to reduce Fe³⁺ ions become Fe²⁺ ions [10]. In the radiolytic reduction method, the average size of the nanoparticles is influenced by the concentration of reducing species released during irradiation [11]. Control of this concentration can be done through the irradiation dose that used.

In some previous researches, the radiolytic reduction method has been employed to synthesize nanocrystalline Fe₃O₄, but the absorbed doses of irradiation used in the preparation of this material were high, in the range of 102 kGy and 360 kGy [12,13]. In this present work, the synthesis of Fe₃O₄ nanoparticles in alkaline medium has been studied via the irradiation dose from 25-100 kGy. The alkaline condition has been adjusted using sodium hydroxide which dripped into the iron salt solution. The synthesis products have been characterized using XRD, FTIR, VSM, and PSA.

2. Materials and Method
2.1 Materials
Ferric chloride hexahydrate (FeCl₃.6H₂O) from Sigma Aldrich was used as the precursor material. Isopropanol (Merck) was used as a radical scavenger of hydroxyl radicals, sodium hydroxide (NaOH) from Merck as a pH adjuster, and deionized water 18.2 MΩ-cm as the solvent. All the chemical reagents were research-grade and used without further purification.

2.2 Synthesis of Samples
The 4 mmol of iron (III) was dissolved in deionized water then mixed with the ultrasonic probe for 3 minutes. The aqueous salt solution of Fe(III) was adjusted to pH 12 by adding NaOH 1 M. The final solutions were added with 2 mL of Isopropanol before irradiated. The samples were stored in polyethylene bottles then irradiated with gamma-rays in various irradiation doses 25, 50, 75, and 100 kGy at Gamma Irradiator Laboratorium, STTN-BATAN, Indonesia.

2.3 Characterization of Samples
The identification of compounds formed before and after irradiation was carried out by analyzing X-ray diffraction patterns of powder samples as measured by X-Ray Diffractometer (XRD). Measurement was made with a source of Cu Kα (λ=1.54056Å) continuously in the angle range 10° to 80°. The effect of the irradiation dose variations on magnetite nanoparticles (Fe₃O₄) is known by reviewing the functional groups in the characterization samples using the Fourier Transform InfraRed (FTIR) Spectrophotometer. The analysis was conducted from wavenumbers 500 cm⁻¹ to 4000 cm⁻¹. The magnetic properties of Fe₃O₄ nanoparticles formed were characterized using Vibrating Sample Magnetometer (VSM) with a range of external magnetic field ± 1 Tesla at room temperature. The size and size distribution of Fe₃O₄ nanoparticles was characterized using Particle Size Analyzer (PSA). These measurements used the Dynamic Light Scattering (DLS) method to determine the size, size distribution, and properties of particle agglomeration.
3. Result and Discussion
The process of Fe₃O₄ synthesis by radiolytic reduction method uses solvated electrons (eₐq⁻) produced by radiolysis of water. The solvated electrons will reduce Fe³⁺ ions from Fe(OH)₃ in an alkaline condition to form Fe₃O₄ particles. The reaction that occurs as follows:

$$\text{Fe}^{3+} + e_{aq}^{-} \rightarrow \text{Fe}^{2+}$$

$$\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^{-} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} \quad (11)$$

![Fig 1. (a) sample before irradiation, (b,c,d,e) after irradiation 25, 50, 75, 100 kGy respectively.](image)

Figure 1 shows the colors changing in the sample before and after irradiation at various doses. The resulting color tends to be black at 100 kGy which indicates that magnetite particles have been formed [14].

4. XRD
The synthesis of Fe₃O₄ nanoparticles via radiolytic reduction method utilizes eₐq⁻ to reduce Fe(OH)₃ to Fe₃O₄. Samples prepared before and after irradiation at doses of 25 kGy and 100 kGy were characterized by XRD.

![Figure 2. Diffractogram of iron oxide samples before and after irradiation](image)

In figure 2, the analysis results of the sample before irradiation only showed the α-FeOOH phase with peaks at the diffraction angle of 21.1°(110), 26.3°(120), 33.2°(130), 45°(131), 56.3°(231), 66.5°(112), and 75.5°(312) in accordance with JCPDS PDF no.01-081-0463. An α-FeOOH phase can be formed in a large pH range that is in an acidic or alkaline state [15]. Because the formation of Fe(OH)₃ precipitation is very fast in the alkaline medium, it will cause the formation of α-FeOOH [16].
Samples that have been irradiated at doses of 25 kGy and 100 kGy have 3 phases, namely FeO, α-FeOOH and γ-FeOOH. Phase γ-FeOOH is a phase of FeOOH which can be produced from the oxidation of Fe\(^{2+}\) in a solution with pH 6. In the formation of FeO, there are Fe\(^{2+}\) and Fe\(^{3+}\) ions in an alkaline solution (pH = 12). Before the characterization process, the solution was washed to pH 6. This treatment purpose is to eliminate NaCl compounds as by-products of FeO synthesis. Because the solution has pH 6 and in the solution there are still Fe\(^{2+}\) ions made the γ-FeOOH phase might be formed. Phase γ-FeOOH is showed at diffraction angles of 27.2°(120), 36.5°(031), and 52.3°(151) in accordance with JCPDS No. 08-0098.

The FeO phase is showed at diffraction angles of 21°(111), 35.5°(220), 43.38°(311), 53.39°(422), and 57.13°(511) in accordance with JCPDS PDF no. 00-019-0629. Each diffraction peak produced in Fe(OH)\(_3\) samples before irradiation contained α-FeOOH compounds and didn’t show any FeO\(_2\) compounds. However, in the Fe(OH)\(_3\) sample which was irradiated there was a diffraction peak of FeO, α-FeOOH and γ-FeOOH. This shows that after the irradiated sample there was a reduction process of Fe(OH)_3 with e\(^-\) to produce FeO compounds. At irradiation dose of 25 kGy the formation of FeO compounds has been already begun.

5. FTIR

![Figure 3. Functional groups of the samples before and after irradiation.](image)

The increasing of the irradiation dose will affect the formation of FeO nanoparticles that can be determined by identifying functional groups in the samples at various irradiation doses using FTIR. Figure 3 shows the FTIR spectra of Fe(OH)\(_3\) at various irradiation doses. Stretching vibration of the functional group O-H is showed at wave number 3420 cm\(^{-1}\) from the Fe(OH)\(_3\) chain before irradiation. At the irradiation dose, 25 kGy, causes peak shifting to lower wavenumber at 3140 cm\(^{-1}\). This shifting is caused by the intramolecular interaction of hydrogen bonds form Fe(OH)\(_3\) have been affected by FeO formation that also has O-H groups on their surface (Fe-OH)[17,18]. The number of FeO nanoparticles increases along with the increasing radiation dose leads to the higher potential for collision between the O-H group from the surface of FeO (Fe-OH). The peaks at 900 cm\(^{-1}\), 800 cm\(^{-1}\), and 650 cm\(^{-1}\) indicate the presence of stretching vibrations of the Fe-O group from FeO [19]. These peaks only appear at the samples
treated with irradiation. This is due to the electrons produced by gamma irradiation reduced Fe(OH) to become Fe$_3$O$_4$.

6. VSM

The magnetic properties of Fe$_3$O$_4$ nanoparticles were analyzed using VSM. Magnetic properties of the samples are presented in a hysteresis curve which states the relationship between H (Tesla) and Saturation Magnetization (Ms) (emu/gram). The hysteresis curve of the samples that got irradiation treatment shows the shape of the superparamagnetic curve [20].

![Hysteresis curve of iron oxide irradiated at various doses.](image)

Figure 4. Hysteresis curve of iron oxide irradiated at various doses.

Figure 4 informs that there was an enhancement in the saturation magnetization value along with the increase in irradiation dose. The higher irradiation dose causes the more solvated electrons (e$_{aq}$) that produced. The solvated electrons reduce Fe(OH)$_2$ to obtain Fe$_3$O$_4$ that confirmed by XRD results (Figure 2). The highest saturation magnetization value is produced at samples 100 kGy with Ms value 21.1 emu/g. However, this value is lower than the bulk material Fe$_3$O$_4$ which is 92 emu/g [21], this is because in the sample still present other phases such as α-FeOOH and γ-FeOOH. This indicates that not all of the FeOOH in the sample at 100 kGy has been reduced.

7. PSA

The particle size distribution in a solution can be measured using a PSA. Measurements using PSA are more likely to measure the largest particles or agglomerates than the smallest ones [22]. This is because the principle of PSA is to measure particle size hydrodynamic or whole particles in solution [23].
Figure 5 shows the measurement results of Fe$_3$O$_4$ at 100 kGy. The measurement result shows that the distribution of Fe$_3$O$_4$ at 100 kGy is polydisperse and tend to agglomerate with average particle size 331 nm. The agglomeration of Fe$_3$O$_4$ is caused by van der Waals force in particle surfaces [24]. Furthermore, based on the XRD results, the agglomeration also caused by the presence of other iron oxide phases and FeOOH that has not reduced.

8. Conclusion
This study of synthesis of Fe$_3$O$_4$ via radiolytic reduction at various doses informs that magnetite has been formed since irradiation at 25 kGy. This study has proven that gamma irradiation quite efficient as a method in synthesis Fe$_3$O$_4$.

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