Synthesized and characterization nanosized synthesis Fe$_3$O$_4$ powder from natural iron sand

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Abstract. This study aims to synthesize Fe$_3$O$_4$ nanoparticles from natural iron sand as a starting material. The synthesis process was carried out by the coprecipitation method at a synthesis stirring rate of 270 rpm. Fe$_3$O$_4$ nanoparticle samples' characterization process was carried out using scanning electron microscopy - energy dispersive X-ray (SEM-EDX), which produced a particle size of 10.76nm, and the Fe content of the sample was 60.96%. Characterization using X-ray diffraction resulted in a crystal size of 12.49 nm and a magnetite phase (Fe$_3$O$_4$) content of 48%. XRD characterization also showed the presence of another phase peak of NH$_4$Cl. NH$_4$Cl contaminants can be degraded by repeated washing using distilled water. This study proves that this synthesis can degrade other elements in natural iron sand to produce Fe$_3$O$_4$ nanoparticles.

1. Introduction
Over the last few years, research about magnetite nanoparticles has rapidly increased because of their unique properties such as high saturation of magnetization, high coercivity, lowest toxicity, biocompatible, and low Currie temperature (Tc) [1]. The utilization of natural iron sand in Kulon Progo is still very low due to the ignorance of the public on how to use the abundant iron sand. This research is about optimizing the utilization of natural iron sand from Kulon Progo beach. Magnetite (Fe$_3$O$_4$) nanoparticle has been applied in many application for the environment, biomedical and biological such as drug delivery [2], photothermal therapy for cancer diagnosis [3], magnetic hyperthermia therapy [4], targeted medical imaging by magnetic resonance imaging (MRI) [5], tissue contrast [6], targeting-carriers for treatment of cancer [7], and many more for further application.

Fe$_3$O$_4$ nanoparticles synthesized by several chemical or physical methods include microwave-solvothermal method, hydrothermal method, co-precipitation [8], sonochemical method, microemulsion method, electrodeposition, polylol [9], and mechanical high energy milling. As one of many preparation methods, co-precipitation has a simple method because it requires low temperatures for preparing samples. However, this method’s result does not have a homogeneous nano-scale particle size directly without further treatment, such as using ultrasonic waves for uniform yield particle size [10]. Therefore, Fe$_3$O$_4$ nanoparticles required surface modification by added organic or inorganic materials. Surface modification forms a barrier for magnetite that does not oxidation by interaction with oxygen. Magnetite nanoparticles commonly need nano-scale size and uniform average particle size.
The major required from magnetic nanoparticles was to obtain uniform sized nanocrystals with restricted nano-scale sized [11]. The nanosize magnetite is essential for biomedical applications that require high magnetization values, this can be discovered by nano-scaled distribution with uniform size particles. On the other hand, the uniform particle size can be determined by various outside factors such as physical interaction or chemical reaction.

Although the modification of particle size to obtain uniform nanocrystals Fe$_3$O$_4$ using stirring rate have been published [12], they barely operated the stirring rate machine with a higher stirring rate upper 500 rpm [13]. Therefore, this paper aims to analyse the synthesized of magnetite nanoparticles at 270 rpm stirring rate from raw material natural iron sands by co-precipitation chemical methods. The researchers use this method because it is the simplest experiment to operate in relatively low temperature synthesis. These treatments were required to obtain nanoparticle magnetite for further biomedical applications.

2. Experimental

2.1. Materials

The raw material for obtaining Fe$_3$O$_4$ nanoparticles is natural iron sand from Kulon Progo beach. Extraction of iron sand was separated using a permanent magnetic bar. Accordingly, the iron sand obtained has a purify metal element. The materials are chloride acid 37% (HCL), ammonium hydroxide (NH$_4$OH) solution, and distilled water.

The instrument for characterization using X-ray diffraction (XRD) (Shimadzu XRD-7000) by Cu $K_{\alpha}$ radiation at 1.54056Å wavelengths for obtaining the XRD pattern and analytical Scanning Electron Microscope (SEM-EDX JED-2300 JEOL) at the center of research and services-Diponegoro University (CORES-DU) to obtain the morphology structure of Fe$_3$O$_4$ powder. The Profex 4.2.0 is used to measure the crystallite size from broadening peak and obtain the fraction of all phases in XRD pattern using refinement.

2.2. Synthesis

Synthesis of Fe3O4 nanoparticles using the co-precipitation method with chemical reactions. The purified iron sand was dissolved by chloride acid at 270 rpm stirring rate for 6 hours. The paper filter has filtered the FeCl$_3$ solution with small pores for 12 hours until the solution was separated from rough iron sand sediment. Secondly, the solution of FeCl$_3$ was added by ammonium hydroxide (NH$_4$OH). FeCl$_3$ reacts chemically with NH$_4$OH to form salts NH$_4$Cl, thus leaving Fe and H$_2$O that will evaporate when drying by the furnace. After adding ammonium hydroxide, the solution was washed with distilled water until it reached the normal PH. The solution was dried by a furnace for 2 hours, then the Fe$_3$O$_4$ lump reduced using mortar until Fe$_3$O$_4$ nanoparticles powder were obtained.

3. Result and discussion

Fe$_3$O$_4$ synthesis using natural iron sand as a raw material by the co-precipitation method generates the nanoparticles Fe$_3$O$_4$. The synthesis result is black color powder Fe$_3$O$_4$. The sample powder is very responsive in collision with external magnetic permanent. The XRD pattern are shown in Figure 1. It shows the sample has a phase of Fe$_3$O$_4$ and the phase of salammoniac (NH$_4$Cl) contains the Fe$_3$O$_4$ powder. XRD patterns represented the characteristic peaks of Fe$_3$O$_4$ at $2\theta$ of 30.22°, 35.59°, 37.23°, 43.26°, 47.37°, 53.67°, 57.22°, 62.84°, and 67.14° correlated from $2\theta$ we gain the Miller index of Fe$_3$O$_4$ are (220), (311), (222), (331), (422), (511), (440) and (442) from Profex 4.2.0 and this is match with Joint Committee on Powder Diffraction Standard (JCPDS) 19-0629 Fe$_3$O$_4$ crystallize. The refinement detected new peak from XRD pattern using profex 4.2.0, we obtain that is NH$_4$Cl phase at $2\theta$ of 22.92°, 32.63°, and 40.25° and measure the index Miller using profex, the results are (100), (110), and (111), it was correlated with JCPDS 07-0007 NH$_4$Cl peak position. The peak broadening corresponding to XRD pattern can be used to measure the crystallize size of Fe$_3$O$_4$ nanoparticles using the Debye-Scherrer equation:
\[ d = \frac{k\lambda}{\beta \cos \cos \theta} \]  

(1)

Where \(d\) is crystallite size in nano-meter, \(k\) is a grain size constant (0.89 for the spherical shape of crystallite), \(\lambda\) is the wavelength of the XRD radiation (Cu K\(\alpha = 1.54056\) Å), \(\beta\) is full width at half maximum (FWHM) in radians, and \(\theta\) is the Bragg’s angle [14].

The lattice parameter values obtained using Profex 4.2.0 (\(d = 2.503\) Å and \(a = 8.359\) Å) were slightly lower than the values found in the JCPDS 19-0629 for Fe\(_3\)O\(_4\) (\(d = 2.532\) Å and \(a = 8.396\) Å). Reported by Lemine et al. [15], this difference occurs due to the influence of different crystal size variants on the crystal lattice.

The results of crystallite size using profex 4.2.0, that is measure using Lorentzian approach with refine the XRD pattern and add the phase from crystallography database Fe\(_3\)O\(_4\) and salammoniac (NH\(_4\)OH) Figure 1. (a) it shows the result from refining XRD pattern, from profex 4.2.0 we obtain the grainsize from each phase and chemical composition (wt-%). The chemical composition is presented at Table 1. It represents the composition from each atom at each phase.

![Figure 1](image-url)

**Figure 1.** (a) The X-ray diffraction pattern of Fe\(_3\)O\(_4\) (b) analytical scanning electron microscopy (SEM) with 1000 times amplification.

The formation of the salammoniac phase occurs because of the reaction between the synthesized FeCl\(_3\) solution and the addition of NH\(_3\)OH. The formed NH\(_4\)Cl will be dispersed with Fe\(_3\)O\(_4\) solution. According to their properties, the Fe\(_3\)O\(_4\) nanomaterial has a large surface area [16] so that the remaining distance between the particles can cause the NH\(_4\)Cl compound to be evenly dispersed. NH\(_4\)Cl can be trapped among the Fe\(_3\)O\(_4\) nanoparticle sediments even though the sample has been washed with distilled water. When heating the solution with a furnace, the H\(_2\)O contained in the solution will evaporate and leave NH\(_4\)Cl and Fe\(_3\)O\(_4\) crystals. As a result, during the mortar grinding process, the Fe\(_3\)O\(_4\) powder was contaminated by NH\(_4\)Cl. It can be seen from the XRD results that the peak formation at 32.63° is the peak of the NH\(_4\)Cl phase.

| Quantity Goal | Chemical formula | Phase quantity (wt-%) | N (wt-%) | O (wt-%) | Cl (wt-%) | Fe (wt-%) |
|---------------|------------------|-----------------------|---------|---------|----------|----------|
| Magnetite     | Fe\(_3\)O\(_4\)  | 48.00                 | 0.00    | 27.64   | 0.00     | 72.36    |
| Salammoniac   | NH\(_4\)OH       | 52.00                 | 28.32   | 0.00    | 71.68    | 0.00     |
The fraction formed is pure Fe$_3$O$_4$ and NH$_4$Cl. This proves that the other metal phases found in natural iron sand can be degraded. This is in accordance with the objectives of this study to produce Fe$_3$O$_4$ from iron sand starting materials. Through the XRD graph generated using the Profex software and the calculation of the crystal size with the Debye-Scherrer equation, the crystal size can be seen in Table 2. The difference in crystal size obtained by the Debye-Scherrer equation has a high error rate, while the calculation using the Profex 4.2.0 is more conscientious because it is done by refinement so that it goes through several iterations that result in a small value of chi ($X^2$). However, evidence of crystal size can also use scanning electron microscopy (SEM) [17].

| Calculation            | Crystallite size (nm) |
|------------------------|----------------------|
| Debye-Scherrer eq.     | 24.38                |
| Profex 4.2.0           | 12.49                |
| SEM with imageJ        | 10.76                |

Investigation of surface morphology and particle distribution of Fe$_3$O$_4$ powder produced using SEM at Figure 1 (b). It shows that the crystals formed are mostly uniform polyhedral. Figure 2. (b) crystal grain calculations with SEM images using image J 1.52V software through particle distribution by assuming the particles are roughly spherical. The results obtained the average size of crystal grains 10.76 nm. SEM images show the occurrence of agglomeration between nanoparticles. Rani et al. [18] reported, the agglomeration process because iron oxide nanoparticles have a tendency to agglomerate between particles due to magnetic interactions. This statement is supported by Khatamian et al. [19], that the nature of Fe$_3$O$_4$ in bulk form has a tendency to agglomerate. Analyze the constituent elements contained in Fe$_3$O$_4$ powder using EDX [20].

![EDX spectra of Fe$_3$O$_4$ nanoparticles](image)

Figure 2. EDX spectra of Fe$_3$O$_4$ nanoparticles

Figure 2. shows the resulting EDX spectra, this analysis confirms the presence of the elements Fe, O, and Cl seen at energies of 6.398 keV, 0.525 keV, and 2.621 keV, respectively. Total percent wt. Fe elements contained as much as 60.96% and O 39.04%, this indicates that this research succeeded in producing Fe$_3$O$_4$ nanoparticles from natural iron sand as the starting material. The Cl content indicates that there is contamination due to the precipitation method, which involves an acid-base reaction. Washing is necessary to remove NH$_4$Cl. according to Rashka et al.[21], NH$_4$Cl is a compound that is...
easily soluble in polar solvents. Furthermore, remove the contaminant salt during the acid-base reaction will be able to wash with distilled water.

4. Conclusion
Fe₃O₄ nanoparticles samples have been successfully synthesized from natural iron sand, which produces Fe₃O₄ nanoparticles with a crystal size of 12.48 nm, and 48% Fe phase fraction was generated through XRD data analysis. The SEM-EDX characterization results showed a particle size of 10.76 nm with an elemental composition of 60.96% Fe. Through characterization, the NH₄Cl phase is a contaminant, and it can be removed by washing with distilled water.

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