The effect of NH4OH pH on the synthesis of MnFe2O4 as heavy metal adsorbent by using co-precipitation method

E A Setiadi1,*, I Priyadi1, E M Siregar2, A P Tetuko1, C Kurniawan1, Achiruddin2 and P Sebayang1

1 Research Center for Physics, Indonesian Institute of Sciences (LIPI), Puspiptek Office Area, Tangerang Selatan, Indonesia 15314
2 Department of Physics, Faculty of Mathematics and Natural Science, University of North Sumatera (USU) 1st, Bioteknologi St. USU, Medan, Indonesia 20155

*E-mail: eko.ariel.setiadi@lipi.go.id

Abstract. The Fabrications of MnFe2O4 have been completed using co-precipitation method with NH4OH pH variations of 11.7; 12.0; and 12.7. The iron sand and the MnCl2.4H2O powder were mixed using HCl as solvent and NH4OH as setting solution. Then the samples were dried and characterized including: morphology analysis (FE-SEM), powder density, crystal size and structure (XRD), magnetic properties (VSM) and the absorption of Pb and Cu using Atomic Absorption Spectroscopy (AAS). The result of FE-SEM showed that the MnFe2O4 particles were agglomerated. On the other hand, the results of XRD characterization indicated that there is a dominant phase of MnFe2O4. The density powder characterization using a pycnometer suggested that the crystal grain size tends to decrease and the true density tends to increase with the increasing of NH4OH concentrations. The result of VSM showed that the optimum condition was achieved with the addition of NH4OH (pH of 12.7) where the magnetic properties characterizations indicate that the coercivity value, the magnetic saturation and the magnetic remanence of 1.96 emu/g are 43.82 Oe, 62.78 emu/g, and 1.96 emu/g, respectively. The AAS characterization suggested that the nanoparticles of MnFe2O4 were able to adsorb heavy metals, (Pb and Cu up to 197 mg/g).

1. Introduction
The rapid development of electronic industries produces both advantages and disadvantages, particularly in the disposal of heavy metals [1, 2]. Moreover, heavy metal pollutants in aquatic environment pose severe threat to public health and ecological systems as a result of complex interaction between ions and aquatic elements [3]. Significant efforts have been taken to obtain effective treatment techniques for removing heavy metal ions from water, such as: chemical precipitation, ion exchange, membrane separation, electrodialysis, and adsorption methods [4-6]. The adsorption method is the most usual in practical use compared to other methods mentioned earlier [7]. Currently, the development of adsorbent materials with high capacity, fast kinetics process, and effortless separation and regeneration is in high demand as a solution to reduce the heavy metals pollution.

Indonesia has a vast amount of natural magnetic material, particularly iron sand. Natural iron sand contains magnetic minerals such as magnetite (Fe3O4), hematite (α-Fe2O3) and maghemite (γ-Fe2O3)
which potentially becomes a precursor of magnetic nanoparticles [8]. This nanoparticle is commonly used as potential heavy metals adsorbent due to their wide surface area and its advantage of easy separation under the external magnetic field [9-11].

In this work, manganese ferrite (MnFe$_2$O$_4$) was fabricated through a co-precipitation method which is considered more effective and able to be processed at a low temperature ($\leq$ 200°C). The particle size can be controlled to evaluate the correlation with its magnetic properties [12]. Furthermore, crystal structures and magnetic properties can be optimized by adjusting the synthesis parameters, such as the co-precipitant pH, the frequency, the duration of stirring, and the co-precipitant concentrations [13]. However previous work on synthesizing ferrites nanoparticles showed that the powders fabricated using co-precipitation method might have tendency to be agglomerated, even for the non-ferrite powders such as yttrium aluminium garnet (YAG) powders [14, 15].

The intriguing facts about manganese ferrite nanoparticles of are related to its properties, such as high magnetic permeability (compared to CoFe$_2$O$_4$), high biocompatibility, and magnetic susceptibility compared to other ferrite types [16]. Previous work on the fabrication of MnFe$_2$O$_4$ suggested that a lower temperature condition ($\leq$ 200°C) affect increase the magnetization saturation [17]. In this research, the pHs of co-precipitant solution were varied to achieve optimum nanoparticles size and magnetic properties.

2. Experimental Methods
The natural iron sand from Kata Beach of West Sumatera was used as raw material. The synthesis of nano-MnFe$_2$O$_4$ was started by mixing 8 gram of iron sand as source of Fe$^{3+}$ ions with 25 ml of HCl 12M. The manganese chloride tetra hydrate (4.18 gram) as a source of Mn$^{2+}$ ions was added into the mixture, and then the solution was stirred until homogenous condition obtained. The precursor solution was added (dropwise) into 99 ml of NH$_4$OH 2M solution at pH variations of 11.7, 12.0, 12.7 and designated as samples A, B, and C, and the samples were simultaneously stirred for 120 minutes at 500 rpm and 100°C to form dark precipitate. The precipitate was placed on permanent magnet to separate from its solution and then the solution was cleaned using distilled water to reach neutral pH and decontaminated from its impurities. The purified samples were dried at a temperature of 50°C, and then powdered to acquire nanoparticles of MnFe$_2$O$_4$. The samples were characterized using pycnometer, X-Ray diffraction (XRD – Rigaku wavelength $\lambda$ = 1.5418 Å), field emission scanning electron microscope (FE-SEM – JEOL JIB 4610F), and vibrating sample magnetometer (VSM – Electromagnetic VSM250) to obtain powder density, crystal phase, microstructure, and magnetic properties, respectively. The heavy metal adsorption test was carried out by mixing 50 mg of MnFe$_2$O$_4$ powder into each of 25 ml of Pb and Cu ions solution in water. The mixture was then vibrated using a shaker mill for 30 minutes. Finally, the heavy metal ions content (before and after the adsorption process) were tested using an atomic absorption spectroscopy (AAS – Shimadzu AA6800).

3. Results and Discussion
Figure 1 depicts diffraction patterns of the MnFe$_2$O$_4$ nanoparticles synthesized using three variations of NH$_4$OH pH. The patterns indicate that the highest peak occurred at $2\theta = \pm 35^\circ$ which is (311) plane of MnFe$_2$O$_4$. The XRD results were compared to JCPDS (PDF card No. 74-2403) and suggested that the dominant phase is manganese ferrite (MnFe$_2$O$_4$) with cubic crystal structures sample A also indicates a hematite phase($\alpha$-Fe$_2$O$_3$) which occurs as an impurity. This observation can be used to calculate the lattice parameter and the crystallite diameter of MnFe$_2$O$_4$ through Scherrer equation:

$$\alpha^2 = \frac{\lambda^2}{4\sin^2 \theta} (h^2 + k^2 + l^2)$$  

$$D = \frac{K\lambda}{B \cos \theta}$$
Where $D$ is the crystallite diameter, $\alpha$ is the lattice parameter, $\theta$ is the diffraction angle, $h$, $k$, and $l$ are the Miller indexes, $K$ is the Scherrer constant, $\lambda$ is the X-ray wavelength, and $B$ is the full width at half maximum (FWHM). The lattice parameter and the crystallite diameter are shown in table 1.

Based on table 1, it can be concluded that the lattice parameter tends to increase when the pH of NH$_4$OH increased with a maximum value of 8.47 Å for sample C. The result has a good agreement with the reference value (8.40 Å) for a cubic spinel [17]. This result confirmed that the synthesized powder is MnFe$_2$O$_4$ with a crystalline structure. Based on the calculation result, the smallest crystallite size of 10.57 nm was obtained with NH$_4$OH pH of 12.7. On the other hand, the increase on pH of NH$_4$OH decreases the powder density where the highest value acquired at sample C. This measurement corresponds to the XRD analysis that implied that the smaller powder was obtained when higher pH of NH$_4$OH was used.

Based on magnetic properties, cubic ferrite is classified as a better heavy metal adsorbent compared to hexaferrites as it has high magnetic saturation, low coercivity value and low magnetic remanence [18]. In this work, sample C exhibits the optimum magnetic properties as metal adsorbent (coercivity of 43.82 Oe, magnetic saturation of 62.78 emu/g of, and magnetic remanence of 1.96 emu/g). In general, the adsorption of material firmly depends on the particle size where the decreasing in the particle size affects the increasing size of the surface absorption area. As we can see in table 2,
the coercivity value of MnFe$_2$O$_4$ and the crystallite size decreased proportionally as a result of its tendency to form a single domain. The energy barrier of materials drops when a single domain forms, hence MnFe$_2$O$_4$ is getting easier to be magnetized by the presence of an external magnetic field. However, the magnetic remanence of sample C did not decrease due to the agglomeration. As a result of the impurities that presence in sample A, the saturation become lower compared to other samples. Magnetic properties of MnFe$_2$O$_4$ tend to be superparamagnetic and its properties emerged when ferromagnetic material reaches nanoscale size. [17, 18].

FE-SEM characterization of sample C is presented in figure 3 which shows the particles have spherical shape. Based on figure 3, it can be observed that the average particle size is lower than 100 nm and the agglomeration occurred due to the Van der Walls force [19]. EDX analysis suggested that sample C contains 6.32% of Mn, 34.08% of Fe, and 59.60% of O. Table 4 indicated that sample C is the optimum material to be used as heavy metal adsorbent with 197 mg/g of adsorption capacity. This result is well correlated with other characterizations for example particles size and magnetic properties. As we have mentioned, the smaller particles becomes the bigger its surface area becomes the bigger its ratio of surface area to mass becomes, therefore its capability to adsorb increase. As a result of a decrease in particles size, the magnetic properties of MnFe$_2$O$_4$ shifted to higher magnetic saturation and lower coercivity value. The presence of non-magnetic impurities also has contribution to decrease the adsorption capability of the material. For the sake of clarity, the results suggested that the adsorption of heavy metal ion increased as the pH of NH$_4$OH increased.

| Element | Weight% | Atomic% |
|---------|---------|---------|
| O       | 29.76   | 59.60   |
| Mn      | 10.84   | 6.32    |
| Fe      | 59.40   | 34.08   |
| Total   | 100     | 100     |

Table 3. EDX of MnFe$_2$O$_4$ using pH 12.7 of NH$_4$OH

Figure 3. FE-SEM image of MnFe$_2$O$_4$ using pH 12.7 of NH$_4$OH.

| MnFe$_2$O$_4$ sample | pH of NH$_4$OH | Pb and Cu ions concentration (mg/L) | Adsorption capacity (mg/g) |
|----------------------|---------------|------------------------------------|---------------------------|
|                      |               | Before                     | After                     |                           |
| A                    | 11.7          | 1092                       | 858                       | 117                       |
| B                    | 12.0          | 1092                       | 757                       | 168                       |
| C                    | 12.7          | 1092                       | 699                       | 197                       |

Table 4. Adsorption properties of MnFe$_2$O$_4$
4. Conclusions
The fabrications of MnFe$_2$O$_4$ from iron sand using variations of NH$_4$OH pH have been successfully completed through a co-precipitation method. The lattice parameters were determined by analyzing the XRD patterns of MnFe$_2$O$_4$ nanoparticles which resulted in 8.37 Å, 8.43 Å, and 8.47 Å for sample A, B and C, respectively. The crystallite sizes of the samples tend to be smaller when the pH variations of NH$_4$OH increased, whilst the powder density have the similar trend with the pH variations. The FE-SEM image of sample C (pH = 12.7) exhibited the particles were agglomerated. The result of VSM investigation indicated that the magnetic saturation and the magnetic moment were increased correspondently with the pH of NH$_4$OH. Moreover, sample C became the optimum MnFe$_2$O$_4$ as heavy metal absorbent considered by its magnetic properties: the magnetic coercivity of 43.82 Oe, the magnetic saturation of 62.78 emu/g, and the magnetic remanence of 1.96 emu/g. The result of VSM characterization, and AAS investigation suggested that the sample with 12.7 pH of NH$_4$OH resulting an optimum adsorption property of 197 mg/g, for adsorption capacity of Pb and Cu ions.

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