

The synthesization of Fe₃O₄ magnetic nanoparticles based on natural iron sand by co-precipitation method for the used of the adsorption of Cu and Pb ions

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Abstract. Magnetic nanoparticles of Fe₃O₄ (magnetite) have been synthesized from natural sand iron by co-precipitation method. The nanoparticles were synthesized using HCl as solvent and NH₃ as co-precipitate. The nanoparticles synthesized at 70°C in two different treatments. Sample without Polyethylene Glycol (PEG) 6000 noted by A and sample with PEG 6000 noted by B symbol. The measurement that have been done for both samples were XRD (X-ray diffraction), FTIR (Fourier Transform Infrared) Spectrometry, SEM (Scanning electron microscopy), VSM (Vibrating sample magnetometer) and SAA (Surface area analyzer). The results showed that both samples were having Fe₃O₄ phases. Particle size, coercivity and magnetic saturation of B samples were smaller than A samples. But the surface area of B sample was larger than A sample. Both samples were then used to adsorb Cu and Pb ions using shaker method. Adsorption analysis from Atomic Adsorption Spectroscopy (AAS) showed that B was more effective in adsorbing metal ions than A. The adsorption value of Cu and Pb ions were 79 and 91% respectively.

1. Introduction

Magnetic nanoparticles have been widely studied since this material has unique properties. For examples it's super-paramagnetic properties, which is not exist on bulk material. Super-paramagnetic properties of materials have a high saturation magnetization, and the average coercivity equal to zero when those material are not influenced by an external magnetic field [1]. These properties appear only when a ferromagnetic or ferrimagnetic material is in a very small size (in order of nanometer), so this phenomenon had been attracted to many of researchers in using this material in various applications, such as drugs delivery, hyperthermia treatment, magnetic resonant imaging [2], enhancement agent, manipulating cell membranes, biosensors, bio-labelling [3] and adsorption of metal ions [4]. The materials which have these kind of properties are Fe₃O₄, CoFe₂O₄, NiFe₂O₄ and others. The use of nanoparticles materials as an adsorbent for heavy metal ions should have some properties, such as high saturation value, small coercivity and large surface area per unit mass. Larazza *et al* [4] have been used Fe₃O₄ mixed with polyethylenimine and montmorillonite as magnetic adsorbents for Cr (VI) water treatment. They founded that the surface area of material will be larger if the particle size is smaller.



The natural iron sand contains abundant of ferrite materials. Synthesis of nanoparticle can be used with various methods, such as hydrothermal synthesis, thermal decomposition, microwave plasma synthesis [5], sol gel, sono-chemical, thermal hydrolysis, and co-precipitation [1]. The synthesis of nanoparticles based on iron sand has been developed for the last few years. Sunaryono *et al* reported that the average diameter of nanoparticles from iron sand strongly depends on the stirring rate of co-precipitation reaction [6]. Mashuri *et al* substituted Ni and Zn ions in order to improve their sample's magnetic properties [7]. While Bukit *et al* has been used PEG 6000 as nanoparticles template to control the particles size, surface modification and to control the interaction among particles [8]. In this paper will be discussed the synthesis of Fe₃O₄ nanoparticles from nature iron sands by co-precipitation method. This method was chosen because the procedure is quite simple and easy to perform in relatively low temperature [9]. Two different treatments will be applied to the synthesized nanoparticles. Samples A were treated without Polyethylene Glycol (PEG 6000 modification) and samples B with PEG 6000 modification. PEG 6000 modification was applied to control the particle size, and improving biocompatibility and chemical stability [1]. Synthesized nanoparticles then analyzed their ability to adsorb Cu and Pb ions which were classified as heavy metal ions.

2. Experimental Method

Natural sands iron that was used in this research was taken from Buaya River in Deli Serdang, North Sumatera. The iron sands was then synthesized by co-precipitation method using 400 ml 12 M HCl (Merck 37%,) as a solvent, stirred for 90 minutes at 300 rpm using a magnetic stirrer, then filtered using paper filter with 8 µm pore sizes. Two glasses of 50 ml 6.5 M NH₃ solution (Merck 32%) was prepared by stirring with 300 rpm at 70°C. The first glass without any addition and the second glass was added 1 mmol of polyethylene glycol (PEG 6000). Then the filtered iron sands was added into both glasses while stirred for 90 minutes until precipitation appeared at the bottom of both glasses. The precipitate material then was separated from the solution, washed with aquades until its pH has reached 7, dried it at 100°C for 5 hours, until Fe₃O₄ nanoparticles powder were obtained.

The nanoparticles powder resulted from the first glass (without PEG 6000) was noted as "A" samples and that from the second glass was noted as "B" samples. Both samples, A and B, were characterized using X-ray Diffraction (XRD - Rigaku SmartLab) at wavelength $\lambda_{\text{CuK}\alpha} = 1.5418 \text{ \AA}$, Scanning Electron Microscopy (SEM - Hitachi SU 3500), vibrating sample magnetometer (VSM - Electromagnetic VSM250), IR Spectroscopy (FTIR - Quanta Crome Instrument) and Surface area analyzer (SAA - Nova 4200e) to analyze their phase, particle size distributions, functional groups, magnetic properties, and surface area.

Analysis of their ability to adsorb heavy metal ions was done by setting up artificial wastewater containing Pb and Cu metals of 706 and 277 ppm, respectively. Nanoparticles powder (50 mg) was poured into the wastewater (25 ml), then mixed using shaker mill for 30 minutes. Atomic Adsorption Microscopy (AAS - Shimadzu AA6800) was used in examining the residual waste. The analysis were performed on both samples, A and B.

3. Results and Discussion

The synthesized nanoparticles from natural iron sand that we obtained are black in color and responsive to external magnetic field. XRD characterization are shown in Figure 1. It shows that both samples have single phase of Fe₃O₄ with cubic spinel structures, and with lattice parameter of 8.393 Å [10]. The average particles size were estimated using Scherrer equation,

$$d = \frac{k\lambda}{B \cos \theta} \quad (1)$$

Where d is crystalline size, k is a Scherrer constant, λ is wavelength of the x-ray and B is full width at half maximum (FWHM).

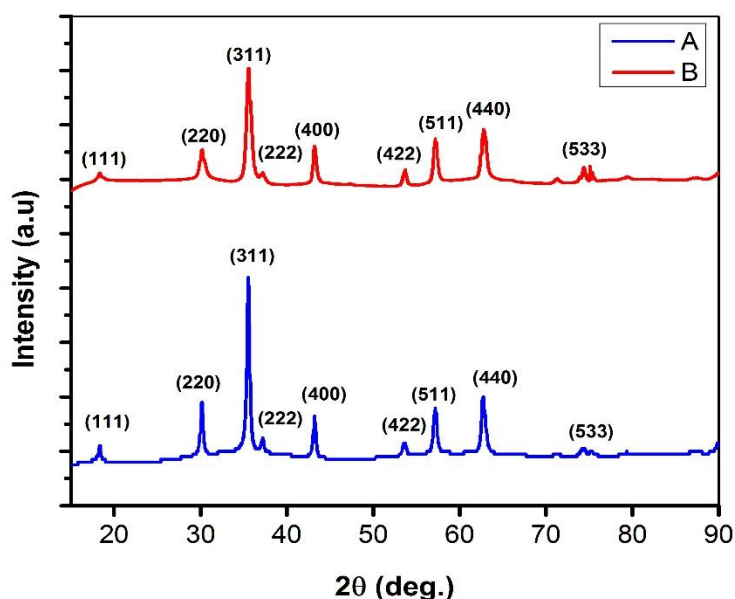


Figure 1. XRD pattern of Fe_3O_4 (a) sample A without PEG 6000 and (b) sample B with PEG 6000

The particles size calculated using Scherrer equation were 32.3 nm and 14.4 nm for A and B samples respectively. Based on these results, it is clearly that the nanoparticles had been successfully synthesized from natural iron sands using this technique.

Figure 2 shows morphological properties of nanoparticles for both samples (A and B). The nanoparticles tends to form rough spherical in shape. It has been reported that spherical shape is formed because the nucleation rate per unit area is isotropic at the interface between the Fe_3O_4 magnetic nanoparticles [3]. Particle size distribution of A sample varied around 25-50 nm, while B sample varied around 12-30 nm.

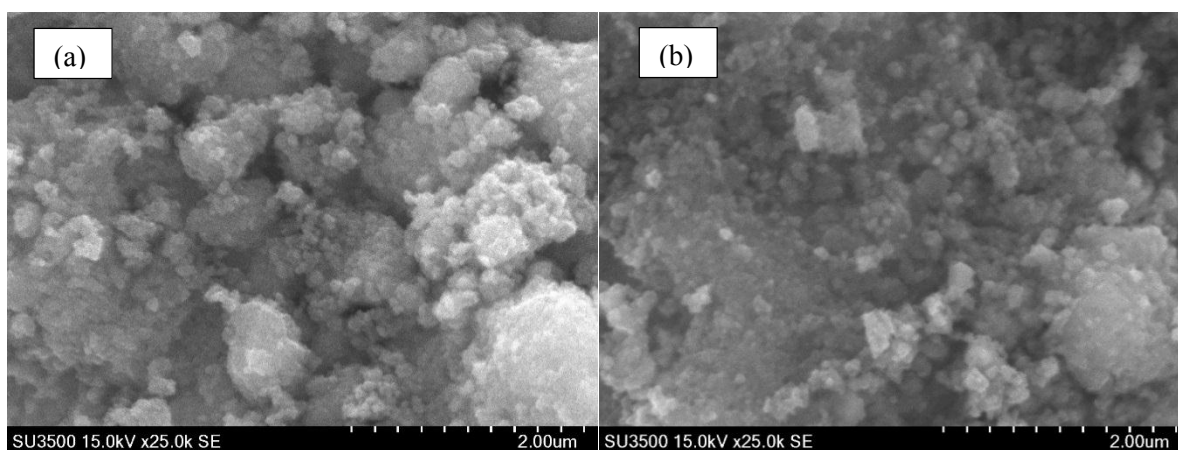


Figure 2. SEM imaging of Fe_3O_4 (a) sample A without PEG 6000 and (b) sample B with PEG 6000

These values are consistent with the particle size that we calculated using Scherrer equation. Average particle size of A sample is larger than the B sample. This is due to the addition of PEG 6000 on sample B. The addition of PEG 6000 can contribute as the coating and reducing agents on nanoparticles, thus decrease the agglomeration of nanoparticles. It has been explained also that the use of polymers such as

PEG in nanoparticles materials is to reduce the agglomeration and to prevent further aggregation, so that the size of nanoparticles will be well controlled [2].

From Figure 3, it can be seen that at wave number of 401.19 and 570.93 cm^{-1} for both samples show characteristic of Fe-O stretching, tetrahedral and octahedral of Fe_3O_4 . At wavenumber of 1627.9 and 3402.43 cm^{-1} are O-H bending and stretching of water groups. On B sample, there are C-O-C stretching and C-H stretching bond at 1072.42 and 2368.59 cm^{-1} wavenumbers, which belongs to the functional groups of PEG 6000. The presence of those two wavenumbers indicate that the nanoparticles of B sample have coated by PEG 6000 [11]–[13]. The PEG coating improves chemical stability, biocompatibility and particle size control from agglomeration effects [11].

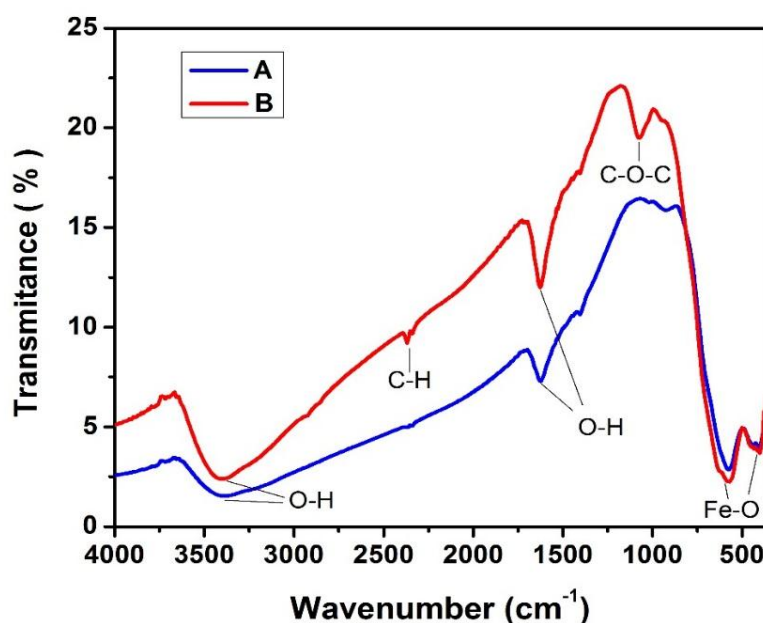


Figure 3. FTIR pattern of Fe_3O_4 (a) sample A without PEG 6000 and (b) sample B with PEG 6000

In Figure 4 is showing the hysteresis curve of the VSM measurement. Based on the hysteresis curve, the coercivity, magnetic saturation, and magnetic remanent of A samples are 92.80 Oe , 1.95 kG and 0.27 kG consecutively. Meanwhile for B sample are 85.65 Oe , 1.41 kG and 0.20 kG , respectively. Based on that value, magnetic saturation and remanence of B sample is smaller than A sample. This is due to the effect of the addition of PEG 6000 which acting as paramagnetic polymer. Hence, when an external magnetic field is applied to the nanoparticles, the magnetic net on B sample will be smaller than on A sample [1]. While the coercivity of B is smaller than A, is because the particle size of B sample is smaller than A sample. When particle size of materials is quite small (nano size), they tend to have a single domain wall, so that the magnetic moments will be easier to switch when an external magnetic field is applied, and also easier to turn back into previous condition when the external magnetic field is removed [1]. The small value of coercivity is one of the characteristic of superparamagnetic material. Then, based on the coercivities values ($<132\text{ Oe}$), both samples are classified as soft magnets [14].

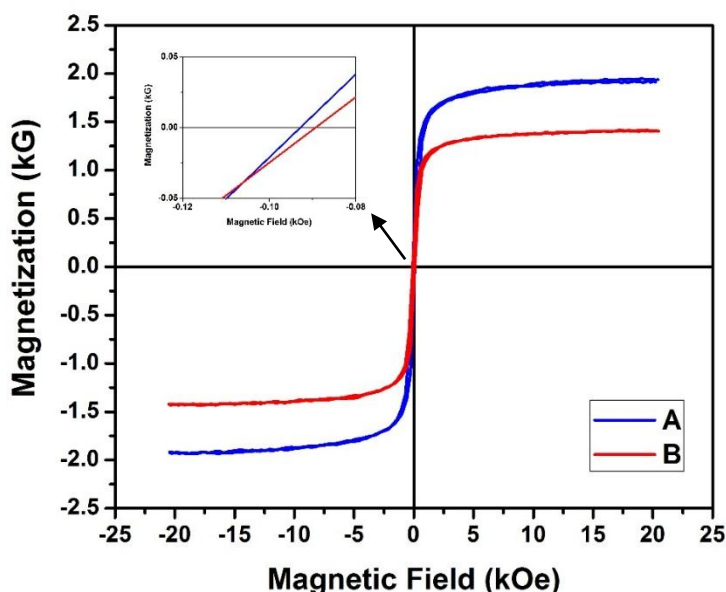


Figure 4. Hysteresis curves of Fe_3O_4 (a) sample A without PEG 6000 and (b) sample B with PEG 6000

In order to know the ability of the obtained synthesized nanoparticles in adsorbing heavy metal ions, it was conducted an experiment using an artificial wastewater containing Pb and Cu metal ions. The 50 mg Fe_3O_4 nanoparticles was poured into 25 ml wastewater contained 706 and 277 ppm of Pb and Cu ions respectively, then mixed with a shaker mill for 30 minutes. It was observed that the surface area of samples are affecting the adsorption process. The SAA measurement shows the surface area of A sample was $129.82\text{m}^2/\text{g}$ while B sample was $140.49\text{m}^2/\text{g}$. The residual wastewater then was analyzed using AAS to determine the adsorption value, that is shown in Table 1.

Table 1. The Adsorption of Cu and Pb ions by Fe_3O_4 samples

Indicator	Initial Concentration (ppm)	After Adsorption by			
		Sample A		Sample B	
		Concentration (ppm)	Percentage of Adsorption (%)	Concentration (ppm)	Percentage of Adsorption (%)
Cu	277	46.3	83	24.3	79
Pb	706	509	28	151	91

From Table 1 can be seen that the B sample is more effective in adsorbing Pb and Cu metal ions, compared with A sample. The concentration of Pb and Cu on wastewater residu on sample A, reduced around 28% and 83% respectively. While the concentration of Pb and Cu wastewater residu on sample B, reduced around 79% and 91% respectively. It is clearly seen that B sample adsorb more metal ions than A sample. This is due to B sample has a smaller particle size than A Sample. Since the smaller the particle size, the larger the surface area is. So the larger the surface area, then more ions will be adsorbed on the surface. Beside, the existence of PEG 6000 coating on nanoparticles surface will also increase its stability and prevent it from oxidation [3].

4. Conclusion

The Fe₃O₄ nanoparticles have been successfully synthesized from natural iron sand of Buaya River in Deli Serdang, North Sumatera by co-precipitation method. Two different treatments were done to get two different samples, such as with and without PEG 6000. XRD results showed that both samples had a single phase Fe₃O₄. Fe₃O₄ with PEG 6000 had smaller particle size and greater surface area than sample without PEG 6000. Fe₃O₄ with PEG 6000 has smaller coercivity and saturation magnetization than Fe₃O₄ without PEG 6000. While the Fe₃O₄ with PEG 6000 was more effective to absorb Cu and Pb metal ions (79% and 91%) compared to Fe₃O₄ without PEG 6000 (28% and 83%).

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