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Synthesis, Properties and Application of Glucose Coated Fe_3O_4 Nanoparticles Prepared by Co-precipitation Method

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Abstract. Synthesis of glucose coated Fe_3O_4 magnetic nanoparticles have been successfully prepared with co-precipitation method. Raw material of natural iron-sand was obtained from Buaya River, Deliserdang, Indonesia. The milled iron-sand was dissolved in HCl (37 mole %), and stirred in 300 rpm at 70^{o}C for 90 minutes. Glucose was added to the filtered powder with varied content of 0.01, 0.02, and 0.03 mole, and precipitated by NH_3 (25 mole%). After drying process, the final product subsequently was glucose coated magnetite (Fe_3O_4) nanoparticles. The characterizations performed were true density measurement, FTIR, VSM, XRD, BET, and adsorbent performance by AAS. The FTIR analysis showed that M-O (bending) with M=Fe (stretching vibration) with υ = 570.92 and 401.19 cm^{-1}. While glucose coated well on nanoparticle Fe_3O_4, proved by functional groups C=O (stretching), M-O (stretching) and C-H (bending) with υ = 1404.17, 570.92, and 2368.58 cm^{-1}, respectively. Single phase of magnetite (Fe_3O_4) structure was determined from XRD analysis with cubic spinel structure and lattice parameter of 8.396 Å. The optimum conditions, obtained on the Fe_3O_4 nanoparticles with 0.01 mole of glucose addition, which has true density value of 4.57 g/cm^3, magnetic saturation, M_s = 35,41 emu/g, coercivity, H_{cJ} = 83.58 Oe, average particle size = 12.3 nm and surface area = 124.88 m^2/g. This type magnetic nanoparticles of glucose-coated Fe_3O_4 was capable to adsorbed 93.78 % of ion Pb. Therefore, the glucose-coated Fe_3O_4 nanoparticle is a potential candidate to be used as heavy metal removal from wastewater.

1. Introduction

Nanoparticle is a particle with nanometer size (1-100 nm), and having different properties from the original [1]. Nanoparticle, such as nano magnetic, can be prepared from the natural resource iron-sand. Iron-sand is abundant in Indonesia and it is needed to be added-value for the competitiveness of economy. Iron-sand has four phases: maghemite (γ-Fe_2O_3), hematite (α-Fe_2O_3), goethite (FeO.OH) and magnetite (Fe_3O_4). Among them, only maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) phases have a good magnetic properties. In addition, magnetite (Fe_3O_4) is also amphoteric and has high absorption. Magnetite contains one ion of Fe^{2+} and two ions of Fe^{3+} in spinel structure, and has a black color [2]. There are several methods to treatment iron-sand, such as co-precipitation, to obtain Fe_3O_4 products. The interests of this mechanism are low temperatures required, easily control the particle size, and short time needed[3].

There are some applications of Fe_3O_4 magnetic nanoparticle, such as : ferrofluid [4], Radar Absorber Material (RAM), biosensors, biotechnology, biomedicine [5], catalyst [6], magnetic resonance imaging (MRI) [7], magnetic gel, and data storage [8]. In addition, magnetite is a promising materials as magnetic adsorbents due to its capability of adsorption in aqueous solutions [4]. Furthermore, to avoid corrosion and coagulation mass, the modification of Fe_3O_4 require a coating substance from polymer and organic material[9]. One of organic coating material for Fe_3O_4 is glucose and it can be used as a particle size reduction agent [10]. However, there are limited study of glucose coated Fe_3O_4 especially in the application as adsorbent material to remove heavy metal elements. Therefore, in this study we investigated the effects of glucose addition as a coating agent. The synthesis of Fe_3O_4 magnetic nanoparticles from iron-sand Sungai Buaya – Deliserdang then coated with glucose, are conducted by co-precipitation method.

2. Experimental Method

Iron-sand from sungai Buaya - Deliserdang was used as raw material in the manufacture of Fe_3O_4 magnetic nanoparticles. The process were performed from iron-sand milling with a planetary ball mill (PBM) for 15 hours. Then, a milled powder was dissolved using HCl (Merck 37%, 12M) and stirred using a magnetic stirrer (300 rpm) at temperature 70 °C for 90 minutes. The solution was then filtered using Whatman filter paper 40 (d = 110 mm and size of pore = 8 μm). The varied of glucose, 0.01, 0.02, and 0.03 mole, was combined into filtered powder. Then, the mixtures were precipitated by NH_3 solution (Merck 6.5 M). Furthermore, the solutions are heated at temperature 70°C for 90 minutes and stirred at 300 rpm speed using a magnetic stirrer, resulting a blackish brown sediment. Moreover, the sediment was washed repeatedly with distilled water until normal pH solution is obtained, and then dried at 100 °C (for 5 hours) and resulting a coated Fe_3O_4 nanoparticles.

Characterizations were carried out by true density (ASTM D. 1217-15), analysis of functional groups using the FTIR, magnetic properties using the VSM, microstructures using the XRD, surface area and particle size using the BET, and adsorption of heavy metal ions Cu and Pb using the AAS.

3. Results and Discussion

The true density value of Fe_3O_4 magnetic nanoparticle with variation of glucose composition (0, 0.01, 0.02 and 0.03 mole) as a coated are shown in Figure 1. From the result show that the highest true density, about 4.57 g/cm3, is obtained by the addition of 0.01 mole of glucose. It is indicated that the densification reach 88.4%, and from literature, the theoretical value of density is 5.17 [11]. The decrease in density in other samples occurs due to the existence of the cavity and the non-homogenous size of grains produced.

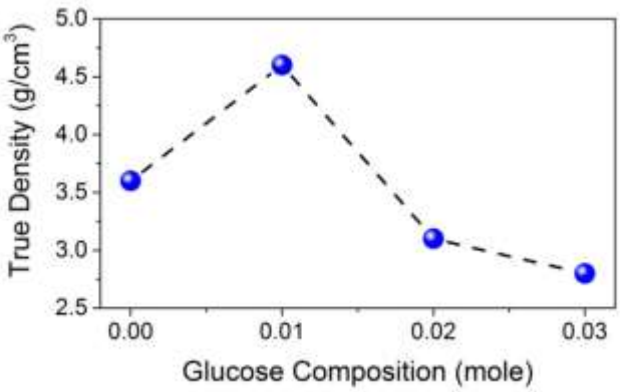

Figure 1. Measurement of True Density with Variation of Glucose Composition.

The analysis results of the FTIR spectroscopy from the samples are shown in Figure 2 and Table 1. The Fe_3O_4 measurement give only M-O and C-H bond. For M-O bond has wave number (υ) = 570.92 and 401.19 cm^{-1} with the stretching vibration, where M is the identification of Fe. While the O-H bond, with the bending and stretching vibration, occurs at υ = 1627.9 and 3387.0 cm^{-1} and it describe the presence of water content. On the other hand, Fe_3O_4 magnetic nanoparticle with variation of glucose coated give a M-O, C-O, C=O, O-H and C-H bonds. In addition, M-O, C=O and C-H bond are indicating of glucose existence. For Fe_3O_4 with 0.01 mol glucose has υ = 1026.1 and 1404.2 cm^{-1} as C-O bond and C = O , respectively with the stretching vibration. And as C-H bond give at υ = 2368.6, and 2931.8 cm^{-1} with bending vibration. The stretching vibration is only change the interatomic distance along bond axis, while bending vibration can change the angle between two bonds.

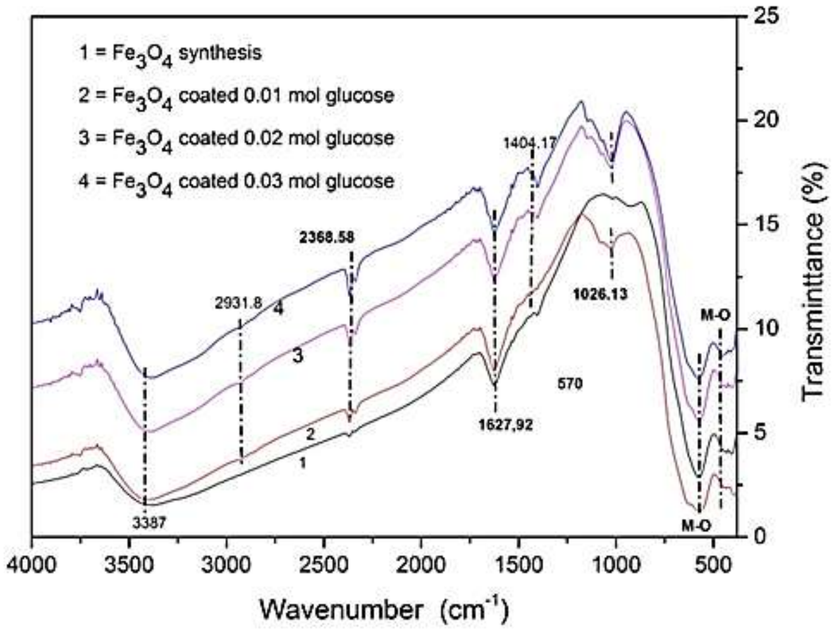

Figure 2. Results of the FTIR Spectroscopy of Magnetic Nanoparticles 1). Sample A, 2). Sample B, 3). Sample C, and 4). Sample D.

Table 1. Bond, Wave Number and Vibration of Fe_3O_4 and Fe_3O_4 Coating Glucose

NO	Bond	Wave number, cm^{-1}				Vibration
		A	B	C	D	
1	M-O	401,2	393,5	455,2	401,2	Stretching
2	M-O	570,9	570,9	578,6	570,9	Stretching
3	C-O		1026,1	1026,1	1026,1	Stretching
4	C=O	-	1404,2	1404,2	1404,2	Stretching
5	O-H	1627,9	1627,9	1620,2	1620,2	Bending
6	C-H	-	2368,6	2368,6	2368,6	Bending
7	C-H	-	2931,8	2931,8	2931,8	Bending
8	O-H	3387,0	3387,0	3387,0	3387,0	Stretching

A = Fe_3O_4, C = Fe_3O_4 + 0.02 mol glucose and
B = Fe_3O_4 + 0.01 mol glucose, D = Fe_3O_4 + 0.03 mol glucose.

The magnetic properties of samples A (Fe_3O_4), B (Fe_3O_4 + 0.01 mole of glucose), C (Fe_3O_4 + 0.02 mole of glucose) and D (Fe_3O_4 + 0.03 mole of glucose) were measured using the VSM, the results are shown in Figure 3 and Table 2.

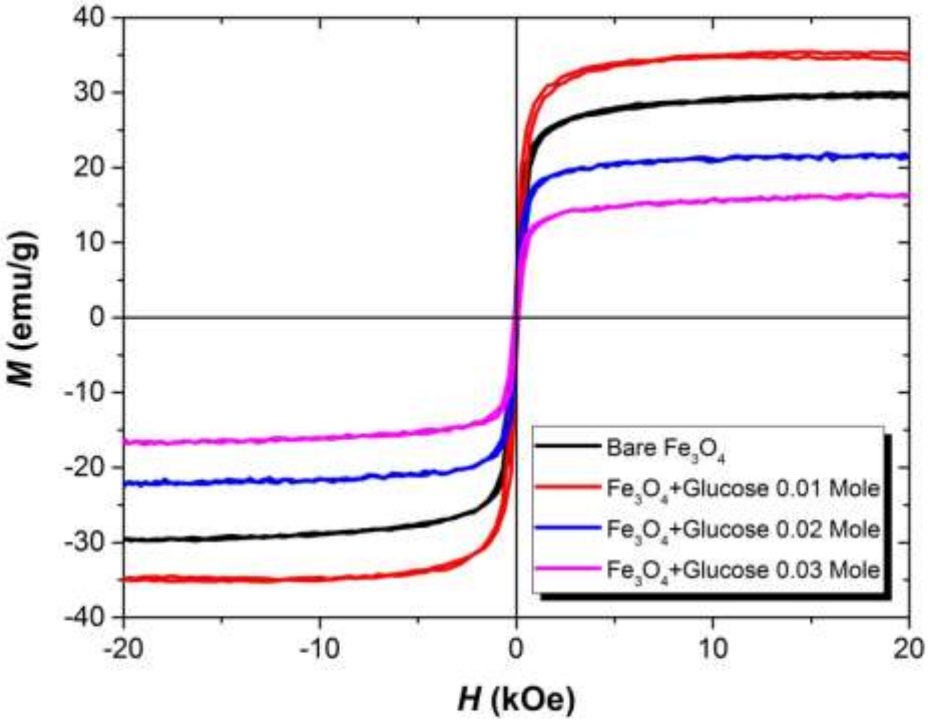

Figure 3. Hysteresis Curve of Sample A, B, C and D.

From Figure 3, it can be seen that all samples show a soft magnetic behaviour since the coercivity (H_{CJ}) is smaller than 126 Oe (the boundary conditions of soft magnetic). The lowest coercivity (H_{CJ}) was obtained in sample B, about 83.58 Oe. It also has a high saturation magnetization (σs), around 35.41 emu/g, resulting a superparamagnetic properties. According to the reference, saturation magnetization (σs) value for Fe_3O_4 coated with glucose is 29.55 emu/g [10].

Table 2. H_{CJ}, M_s and M_r Values of Nanoparticle Magnetic Fe_3O_4 and Fe_3O_4 Glucose Coated

Sample	Magnetic Nanoparticle	H_{CJ} (Oe)	σ_s(emu/g)	σ_r (emu/g)
A	Fe_3O_4	92.80	30.01	4.20
B	Fe_3O_4 + 0.01 mol glukosa	83.58	35.41	4.62
C	Fe_3O_4 + 0.02 mol glukosa	92.05	16.48	2.47
D	Fe_3O_4 + 0.03 mol glukosa	88.24	21.88	3.19

Analysis of XRD pattern for sample A and B are depicted in Figure 4. From the Figure 4, it can be seen that both samples only have a single phase magnetite (Fe_3O_4) with a cubic spinel structure and the lattice parameter is 8.123 Å. A cubic spinel structure can be determined by planes (hkl) for each peaks in XRD pattern, which are (111), (202), (311), (222), (400), (422), (333) and (404) [12]. Within the main peak 2θ = 35.56 ° and hkl (311), the crystal size of sample B =14.7 nm and sample A = 32.3 nm were obtained using scherrer equation [7].

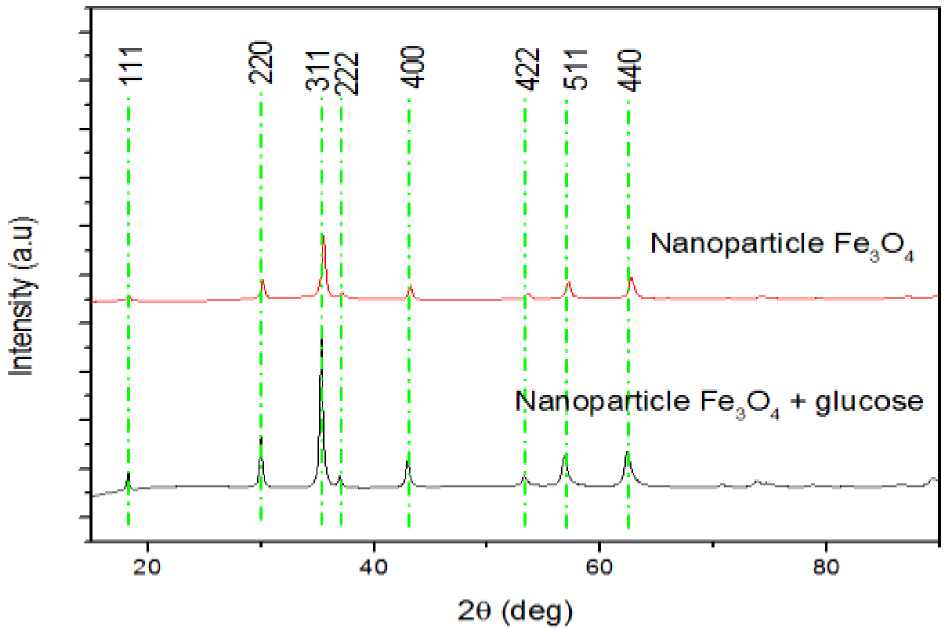

Figure 4. XRD Result of Nanoparticle Magnetic, a). Sample A, and b).Sample B.

From the measurement of surface area and pore size of Fe_3O_4 magnetic nanoparticles + 0.01 mole of glucose (sample B) conducted using the BET, 124.88 m^2/g and 4.8 nm were obtained. The average particle diameter given value 12.3 nm, which the calculation can be obtained from BET data measurement. While the surface area and pore size from reffrence [13] using glucose-coated Fe_3O_4 (Aldrich) are 35.7 m^2/g and 13.4 nm.

The sample B compound has been attempted for the adsorbent of heavy metal ions Cu and Pb using the AAS and the results are shown in Table 3. Apparently, Fe_3O_4 magnetic nanoparticles with 0.01 mole of glucose was capable of adsorbing heavy metal ions Pb in the amount of 93.78%.

Table 3. Analysis Measurement of AAS on sample B, for ion Cu and Pb

Heavy Metal	Concentration (ppm)		Adsorption (%)
	Initial	Final	
Cu	277	32.2	88.37
Pb	706	43.9	93.78

4. Conclusion

Fe3O4 magnetic nanoparticles and glucose coated Fe_3O_4 have successfully been synthesized using the co-precipitation method from iron-sand sungai Buaya - Deliserdang as a raw material. Fe_3O_4 are well coated by glucose, with presence of glucose functional group in the C=O, M-O and C-H bonds with stretching, stretching and bending vibration. The results of the XRD analysis show that there is only single phase magnetite (Fe_3O_4) with a cubic spinel structure and the lattice parameter of 8.123 A. The optimum condition was obtained in the composition of Fe_3O_4 coated with 0.01 mole of glucose. This composition resulting value of true density = 4.57 g/cm3, Ms = 35.41 emu/g, HCJ = 83.58 Oe, average particle size = 12.3 nm and surface area = 124.88 m^2/g. Fe_3O_4 magnetic nanoparticles coated with 0.01 mole of glucose is capable of adsorbing metal ion Pb up to 93.78%.

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